Sasan Moradi

A study of epoxy composites for high thermal conductivity applications

Doctoral thesis

Thesis by a compendium of publications

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Hereby,

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Si crees en ti mismo continúa tu camino, tarde o temprano todos te admirarán

اگر خودت رو باور داری به راهت ادامه بده، دیر یا زود همه ستایشت خواهند کرد

If you believe in yourself continue your way, late or soon everybody will admire you

Sasan

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1. Remarkable thermal conductivity of epoxy composites filled with boron nitride and cured under pressure.

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2. Densification: a route towards enhanced thermal conductivity of epoxy composites.

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3. Thermal conductivity and cure kinetics of epoxy-boron nitride composites—a review.

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4. Epoxy composites filled with boron nitride: cure kinetics and the effect of particle shape on the thermal conductivity.

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5. Achieving high thermal conductivity in epoxy composites: effect of boron nitride particle size and matrix-filler interface.

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3. The effect of cross-linking agent and initiator on the thermal conductivity and cure kinetics of epoxy-boron nitride composites. 2nd Journal of Thermal Analysis and Calorimetry Conference (2nd JTACC+V4 2019), June 18–21, 2019 Budapest, Hungary

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   S. Moradi, Y. Calventus, F. Román, J. M. Hutchinson.

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   S. Moradi, Y. Calventus, F. Román, J. M. Hutchinson.

Summary

Nowadays, both electronic and microelectronic circuits have great relevance and wide application in our daily lives and are increasingly being used with higher powers and frequencies. One of the main problems faced by their manufacturers is the dissipation of heat generated during their operation, since it reduces the useful life of these devices. One of the useful options that can help dissipate the generated heat is the Insulated Metal Substrate (IMS). The IMS consists of three layers: copper foil, a dielectric layer, and a metallic substrate. The thermal conductivity of the material that constitutes the dielectric layer will be of vital importance when it comes to dissipating the heat generated. The most widely used system as a dielectric layer for IMS is an epoxy resin matrix with a crosslinking agent and a filler. As the thermal conductivity of the epoxy resin is low, it is essential to use a filler with high thermal conductivity that allows efficient dissipation of the generated heat. Therefore, in this thesis, the preparation of samples based on epoxy resins with boron nitride (BN) charges is studied. The effect of the BN particle size, the effect of the crosslinking agent used, the curing kinetics, the shape of the BN particles, the application of pressure on the material during the curing process, and the role of densification are analyzed. It is found that the thermal conductivity of epoxy-BN composites increases with increasing BN particle size for a given content of filler, and that BN agglomerates provide a higher thermal conductivity in comparison with the same size platelets, which is attributed to there being fewer interfaces with the epoxy matrix for the agglomerates. The epoxy-thiol system provides a higher thermal conductivity than the epoxy-Jeffamine system, which is attributed to a Lewis acid-base interaction. In the cure kinetics experiments, it was observed that the cure reaction of the epoxy-thiol composites was retarded with increasing the BN content for all particles (platelets or agglomerates). For the epoxy-Jeffamine system, it was observed that the cure reaction is independent of BN particle content, which is also correlated with the thermal conductivity measurements. The heat of reaction (ΔH_{ee}) and the glass transition temperature of the fully cured system, $T_{g\infty}$, are independent of BN particle content, size and shape for both epoxy-thiol and epoxy-Jeffamine. On the other hand, the thermal conductivity increases by applying pressure for both epoxy-thiol and epoxy-Jeffamine systems in comparison with the composites cured at ambient pressure; the enhancement for the epoxy-Jeffamine system is greater. It is revealed that the mechanisms of the enhancement of the thermal conductivity by application of pressure for each system are different. And finally, densification is shown to be a way of increasing the thermal conductivity; it is also shown to be a reversible effect.

Resumen

En la actualidad, tanto los circuitos electrónicos como los microelectrónicos tienen una gran relevancia y una amplia aplicación en nuestra vida diaria y cada vez se utilizan mayores potencias y frecuencias. Uno de los principales retos que encaran sus fabricantes es la disipación del calor generado durante su funcionamiento, ya que reduce la vida útil de estos dispositivos. Una de las opciones útiles que pueden ayudar a disipar el calor generado es el denominado sustrato metálico aislado (IMS). El IMS consta de tres capas: una lámina de cobre, una capa dieléctrica y un sustrato metálico. La conductividad térmica del material que constituye la capa dieléctrica será de vital importancia a la hora de disipar el calor generado. El sistema más utilizado como capa dieléctrica para IMS es una matriz de resina epoxi con un agente reticulante y un relleno (filler). Dado que la conductividad térmica de la resina epoxi es baja, es fundamental utilizar un relleno con alta conductividad térmica que permita una eficiente disipación del calor generado. Por tanto, en esta tesis se estudia la preparación de muestras a base de resinas epoxi con cargas de nitruro de boro (BN). Se analiza el efecto del tamaño de partícula de BN, el efecto del reticulante utilizado, la cinética de curado, la forma de las partículas de BN, la aplicación de presión sobre el material durante el proceso de curado y el papel de la densificación. Se encuentra que la conductividad térmica de los compuestos epoxi-BN aumenta con el aumento del tamaño de partícula de BN para un contenido dado de relleno, y que los aglomerados de BN proporcionan una conductividad térmica más alta en comparación con los platillos (platelets) del mismo tamaño, lo que se atribuye a que hay menos interfaces con la matriz epoxi para los aglomerados. El sistema epoxi-tiol proporciona una conductividad térmica más alta que el sistema epoxi-Jeffamine, que se atribuye a una interacción ácido-base de Lewis. En los experimentos de cinética de curado, se observó que la reacción de curado de los compuestos de epoxi-tiol se retrasó al aumentar el contenido de BN para todas las partículas (platillos o aglomerados). Para el sistema epoxi-Jeffamine, se observó que la reacción de curado es independiente del contenido de partículas BN, que también se correlaciona con las medidas de conductividad térmica. El calor de reacción (ΔH_{ee}) y la temperatura de transición vítrea del sistema completamente curado, $T_{g\infty}$, son independientes del contenido, tamaño y forma de partículas de BN tanto para el epoxi-tiol como para la epoxi-Jeffamina. Por otro lado, la conductividad térmica aumenta aplicando presión para los sistemas epoxi-tiol y epoxi-Jeffamine en comparación con los compuestos curados a presión atmosférica; remarcar que la mejora del sistema epoxi-Jeffamine resulta mayor. Se hace evidente que los mecanismos de mejora de la conductividad térmica

mediante la aplicación de presión para cada sistema son diferentes. Y finalmente, se demuestra que la densificación es una forma de incrementar la conductividad térmica; que también se muestra como un efecto reversible.

Chapter 1. Introduction

1.1. Overview of polymers

1.1.1. Epoxy resins

1.2. Importance of thermal conductivity

1.3. Various properties in the enhancement of epoxy composites thermal conductivity

1.3.1. The effect of BN content

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1. Introduction

1.1. Overview of polymers

The simplest definition of a polymer is the expression of an efficient chemical substance consisting of repeating units. The polymer can be in the form of a three-dimensional network in which the repeating units are connected from the right and left, front and back and up and down, or a two-dimensional network in which the repeating units from top and bottom and right and left are connected on a page or a one-dimensional grid in which duplicate units from the right and left are connected like a chain. Each repeating unit is a "mer" and the combination of "poly" (meaning several) and "mer" forms the word "polymer", which means a large number of repeating units. Duplicate units are generally made of carbon and hydrogen and sometimes of oxygen, nitrogen, sulfur, chlorine, fluorine, phosphorus, and silicon. To form a chain of these units, the "mers" are chemically bonded together or so-called polymerized.

Binding countless pieces of coloured paper together to create paper loops, or hooking hundreds of pieces of paper together into a chain or strand of beads can all help to better understand polymers. Polymers are used widely as the material for electronic packaging, concerning their several merits, such as lightweight, electrical insulation, low cost, and ease of processing [1]. Pure polymers have very low thermal conductivity, so for use in applications that require a high thermal conductivity, they should be used in combination with other materials.

Polymers can be categorised by different methods. The simplest method is to classify polymers according to their source, where they fall into natural or biopolymers, synthetic and semi-synthetic polymers. Natural polymers are found in nature and exist in natural resources such as plants and animals. Examples of natural polymers are proteins, polysaccharides, polypeptides, lignin, nucleic acids, etc. which are derived from plants and animals. Cellulose and starch are usually derived from the roots of tropical plants that also fall into this category. Polymers such as proteins and DNA that control various processes in our bodies are called “biopolymers”.

They also can be categorised based on polymerization such as polycondensation and polyaddition, shown in Figures 1.1 and 1.2 respectively.

$$n\left(HO-R-OH\right)+n\left(HOOC-R^1-COOH\right)$$

$$\downarrow$$

$$HO-\left[RCOO-R^1-COO\right]_n-H + 2n\text{-}1\ H_2O$$

Figure 1.1. Preparation of polyesters by condensation method.

$$nCH_2=CHCl \rightarrow \left[CH_2-CHCl\right]_n$$

Figure 1.2. Polymerization of vinyl chloride.

One of the most important classifications of polymers is based on their thermal behaviour, in which polymers fall into the categories of thermosets and thermoplastics. The produced polymers that appear in the form of 3D grids and are not able to be re-melted after formation are called "thermoset polymers". Manufactured polymers can also appear as one-dimensional chains with the ability to re-melt. These chains are known as thermoplastic polymers as well as "linear polymers". Bottles, films, cups, and plastic fibres are all considered thermoplastic plastics. Epoxy resin, which is used in all sections of this dissertation, is one of the thermosets.

Rubber and cellulose are used as raw materials for the production of rubber and polymer plastics. The first plastic produced was Bakelite, dating back to 1909, when it was used to make the body of telephones and electronic components. The first polymer fibre produced named Rayon was obtained in 1910 from cellulose. Nylon also emerged in 1935, in an attempt to produce artificial spider silk.

Another categorization of polymers is based on monomer composition which is divided into homopolymers and copolymers. This classification takes place depending on whether the repeating units in the polymers are one or more. For the homopolymers, there is only one type of repeating unit. Polyvinylchloride, (PVC), polypropylene (PP), polyethylene (PE) and polystyrene (PS) are some examples of homopolymers whose properties are essentially determined by their nature of monomers. A general classification of polymers can be seen in Figure 1.3.

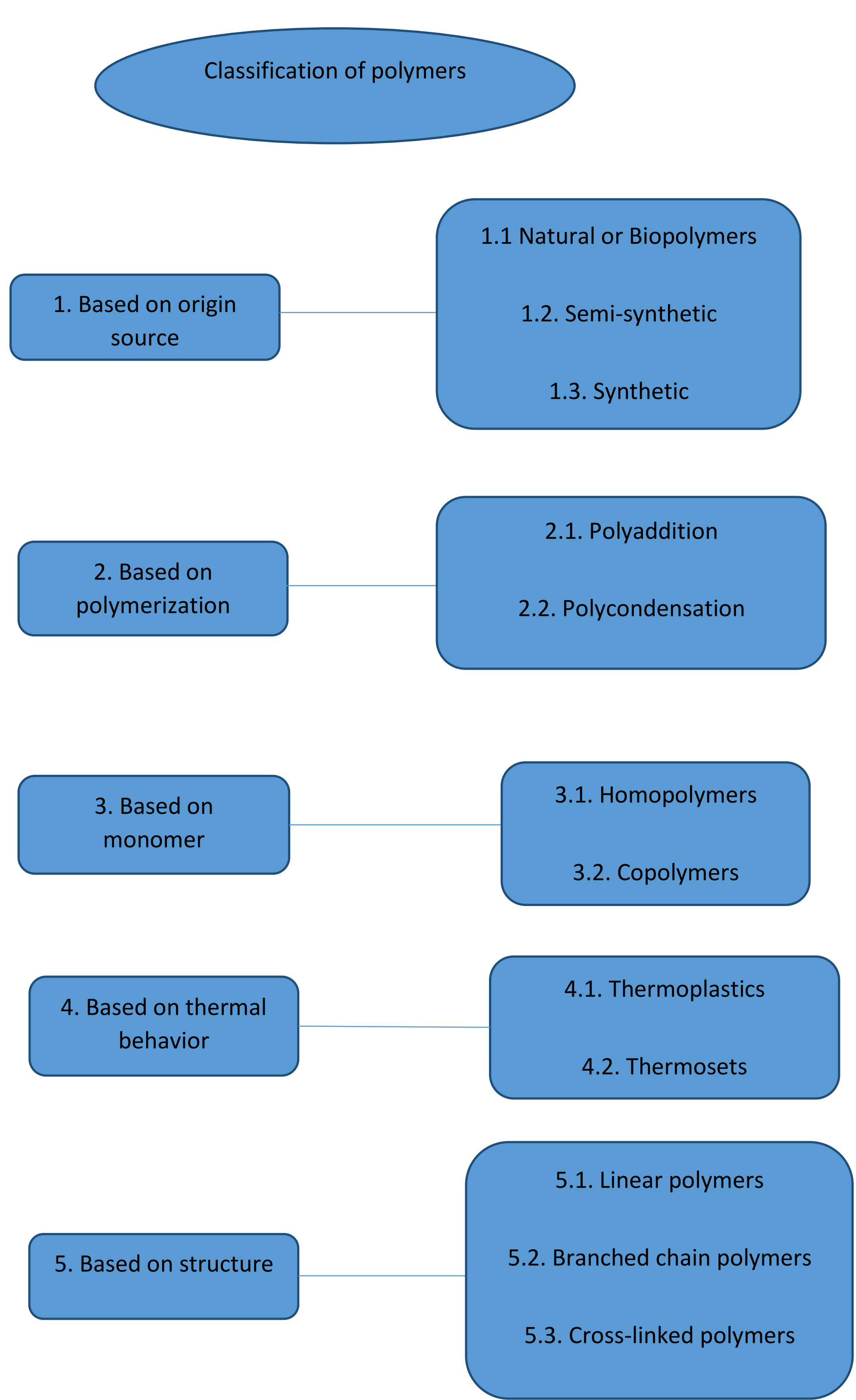


Figure 1.3. The general classification of polymers.

Polymers are also classified in terms of their structure, which can be linear, branched-chain, cross-linked, or other topologies. Some different topologies of polymers are shown in Figure 1.4.

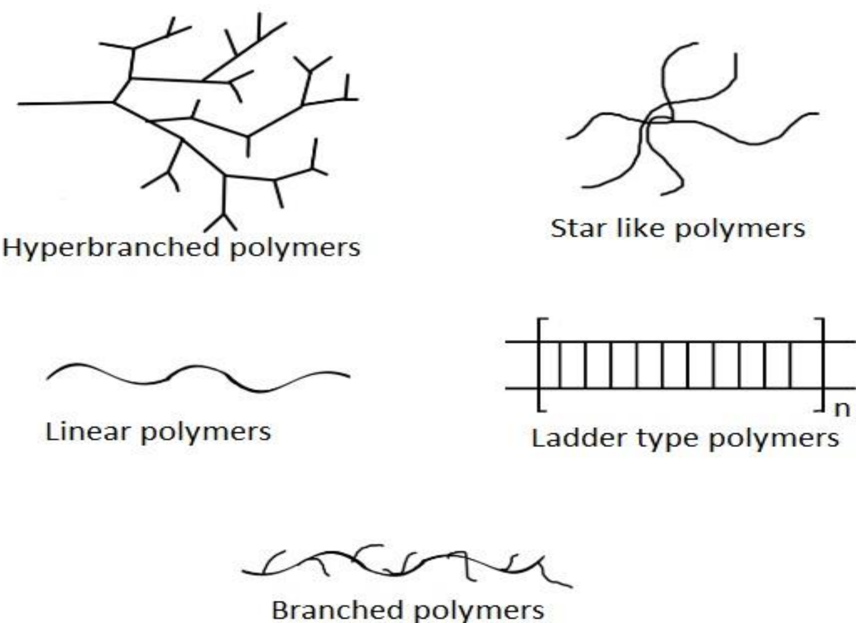


Figure 1.4. Some topologies of polymers.

1.1.1. Epoxy resins

Epoxy resins, which have different merits such as electrical insulation, high abrasion resistance and appropriate adhesion (before curing), can be used for different purposes. There is a wide range of epoxy resins regarding having a different duration of the curing process, the hardness, the viscosity, etc. The majority of the epoxy market production is used in coatings and electronics [2]. The word “epoxy” represents a reactive functional group in all epoxy resins. It is also known as a three-membered ring in which an oxygen atom is attached to two carbon atoms and is called the oxirane group. An example of the oxirane group is shown in Figure 1.5. Another example of the epoxy resins is diglycydl ether of bisphenol A (DGEBA), which is one of the most commercialised epoxy resins. As is shown in Figure 1.6, DGEBA is a bifunctional epoxy resin and also it can be understood that the repeating units can be aliphatic, aromatic, or cycloaliphatic, which are in fact the non-epoxy part of the molecule. The number of repeating units in DGEBA can change its molecular weight. Likewise, the viscosity changes with the number of repeating units, so that the more repeating units, the higher the viscosity.

Figure 1.5. Structure of epoxide group

Figure 1.6. Structure of diglycidyl ether of bisphenol A (DGEBA)

Epoxy resins can be cured by mixing with an agent called the curing agent. Using the sufficient stoichiometric ratio of the curing agent to epoxy, provides a fully cured state in which the mixture converts to a solid. The curing process duration depends on the cure temperature as well as the type of curing agent used. The curing procedure is an exothermic reaction between the curing agent and epoxy. A curing agent is considered to be a chemical that has reactive hydrogens such as photosensitive chemicals, anhydrides, amines, acids, acids anhydrides, alcohols, phenols, thiols, etc. which are also called the hardener. This type of curing process for epoxy resins in which curing agents are used is an example of co-polymerization. Epoxy resins can be fully or partially cured, depending on whether the amount of curing agent used is equal to the stoichiometric ratio or not. The curing process can also occur by reacting an epoxy with itself which is a type of homopolymerization reaction.

1.2. Importance of thermal conductivity

As in today's life, electronic and microelectronic devices are increasingly integrated and used at higher powers and frequencies, one of the serious concerns is how the generated heat can be removed while these devices are working. Several reports prove this generated heat reduces the service life; a rule of thumb is that with an increase of 10% in the temperature the service life will reduce to half [3]. One of the useful options that can help to dissipate the generated heat is the Insulated Metal Substrate (IMS). Normally an IMS consists of three layers: copper foil, a dielectric layer, and a metal part which is usually aluminium. The average thickness of these three different parts is 50 μm, 0.1 mm and 1.5 mm, respectively. Depending on what the dielectric layer is made of, this layer can help dissipate the heat generated.

There are many commercial IMS systems available with thermal conductivity of about 3 $Wm^{-1}K^{-1}$, from companies such as Bergquist [4], AI Technology [5], and Technoboards Kronach [6]. Using thermally conductive fillers, which are not electrically conducting, in the electrically insulating matrix is one the most useful methods that can lead to higher thermal conductivity. Fabricating such a dielectric layer in an IMS provides the thermal conductivity values much higher than the standard FR-4 in which generally consists of fiber glass and epoxy resin giving a thermal conductivity value of about 0.3 $Wm^{-1}K^{-1}$. LED technologies, the automotive industry, power electronics, switches and semiconductors are some examples of IMS applications. An example of an IMS is shown in Figure 1.7.

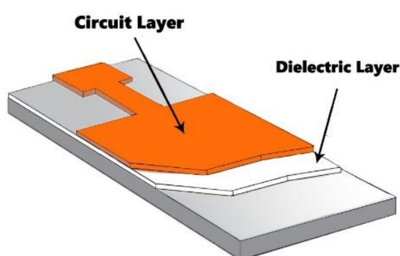


Figure 1.7. IMS structure including a circuit layer, a dielectric layer, and metal support (modified from reference number 4).

Epoxy resin cured with a hardener as a matrix is the most widely used system in the dielectric layer of IMS. Since pure epoxy has a very low thermal conductivity, around 0.2 $Wm^{-1}K^{-1}$ [7], the presence of a thermally conductive filler is essential. The main focus of this dissertation is to investigate and create possible ways to fabricate epoxy-based composites that can help to improve the mentioned issues. Many efforts have been made to increase the values of thermal conductivity of epoxy-based composites, but having various requirements together at the same time such as electrical insulation, ease of processing, having acceptable values of thermal conductivity and a desirable composite thickness will significantly limit favorable results. Some examples of the most commonly used fillers that provide high thermal conductivity while being electrically insulating are Al_2O_3, AlN, SiC and BN [7]–[15].

1.3. Various properties in the enhancement of epoxy composites thermal conductivity

Among the mentioned fillers, hexagonal BN (*h*-BN) is one of the best options due to having electrical insulation as well as having a very high thermal conductivity, with values

up to 30 $Wm^{-1}K^{-1}$ perpendicular to the hexagonal plane and up to 600 $Wm^{-1}K^{-1}$ parallel to these planes [16]. *h*-BN also exhibits excellent oxidation resistance, performs exceptionally well at high temperatures (up to 3000 °C), and has resistance to corrosive attack. Besides, the surface of BN particles can be treated using coupling agents to provide higher thermal conductivity and also they have an advantage in the form of platelets that make it possible to achieve high thermal conductivity through the orientation effect in the in-plane direction.

Many factors play a role in the values of thermal conductivity of the epoxy-BN composites such as filler content, size and shape, using hybrid fillers, surface treatments, the effect of pressure before and during cure, using a coupling agent, the effect of densification, etc.

1.3.1. The effect of BN content

The most important effect of BN content on the epoxy composites that is almost universally accepted is that the thermal conductivity increases with the BN content [17]–[26]. For the way in which the thermal conductivity increases with BN content, there are two principal aspects: the first one is that this enhancement is non-linearly with an upward curve; the second one is that there is a limiting amount of BN that can be introduced. Noting that if too much BN is tried to be introduced, lots of voids will appear in the mixture, which cannot be removed later by vacuum because of the very high viscosity of the mixture. This leads to a reduction in the thermal conductivity from its "ideal" value (the value that can be drawn by the trend line). So, in general, increasing thermal conductivity with increasing BN is expected, but the questions are: by how much can the thermal conductivity be increased for a given content, and how high a content can be achieved?

The viscosity of uncured epoxy composites during fabrication increases with BN content. Depending on the specific surface area (SSA) of BN particles there are limitations for the loading especially without application of pressure or using hybrid fillers, due to the increasing stiffness of the mixture. Also, the viscosity of other components involved in sample fabrication could affect the amount of loading, but the presence of BN has a far higher effect on increasing the viscosity of the mixture. The stiffness of the epoxy-BN mixture increases the likelihood of multiple voids, which can reduce the thermal conductivity.

Isarn et al. [18] reported a systematic enhancement in thermal conductivity for the epoxy composites filled with 6 μm BN agglomerates and cured with thiol. These authors observed that the value of around 0.3 $Wm^{-1}K^{-1}$ for 10 wt.% filler loading was increased

to 0.97 $Wm^{-1}K^{-1}$ for 40 wt.% filler loading. Elsewhere Isarn et al. [19] reported a systematic enhancement in thermal conductivity for cycloaliphatic epoxy composites obtained by cationic curing and filled with 6 μm BN particles. These authors found that the value of thermal conductivity 0.2 $Wm^{-1}K^{-1}$ for 10 wt.% of filler loading improved to 1.1 $Wm^{-1}K^{-1}$ for 40 wt.% filler content. In another work, Hutchinson et al. [21] reported that the thermal conductivity value increases from 0.2 $Wm^{-1}K^{-1}$ with no filler to more than 2.0 $Wm^{-1}K^{-1}$ for an epoxy composite cured with thiol and filled with 44.7 vol.% of 6 μm BN.

Feng et al. [26], in a similar report, showed that for their epoxy composites which were cured with 2-ethyl-4-methylimidazole and filled with *h*-BN particles of around 10 μm, the thermal conductivity value of 0.4 $Wm^{-1}K^{-1}$ for 10 wt.% BN increased to the value of 1.4 $Wm^{-1}K^{-1}$ for 40 wt.% BN content.

In another work, Chen et al. [22] for epoxy composites filled with boron nitride nanosheets (BNNS) at very low filler contents, found an enhancement in the thermal conductivity whether for a single filler (BNNS) or using hybrid fillers (3D cellulose/BNNS). For the composites filled with hybrid, a 3D BNNS network was fabricated by self-assembly of BNNSs on a 3D cellulose skeleton via sol-gel and freeze-drying, and then impregnating epoxy resin into the 3D BNNS aerogel. The samples were prepared from 1 vol.% up to 10 vol.% filler. It was observed that the thermal conductivity of the composites filled only with BNNS increased from 0.25 $Wm^{-1}K^{-1}$ to 0.35 $Wm^{-1}K^{-1}$ and for the fabricated composite using hybrid filler the thermal conductivity increased from 0.3 $Wm^{-1}K^{-1}$ to 3.2 $Wm^{-1}K^{-1}$ for 10 vol.% BNNS. Both composites show the effect of BN content in the enhancement of thermal conductivity, noting that for the hybrid samples the authors reported the content of BNNS is increasing while the cellulose content remains invariant with increasing the filler content. The other point is that in such a 3-dimensional structured aerogel there is a structural effect on the enhancement of thermal conductivity due to the reduction of the total interfacial area with the increase of filler dimensions [22].

The discussions above show that thermal conductivity increases with BN content. Since various ranges of thermal conductivity are obtained for a given BN content, thus, it would be interesting to do a systematic study with different BN particles to understand why there are such large variations in the thermal conductivity as a function of BN content and also to understand the limiting factor for filling the epoxy matrices.

1.3.2. Effect of BN particle size

The interface between the epoxy matrix and BN particles is considered to be an important factor because these interfaces make a barrier for heat conduction in epoxy

composites. Therefore, on the one hand, surface treatment by improving these interfaces and, on the other hand, using larger BN particles in order to provide fewer interfaces, can be considered two effective ways in which to enhance the thermal conductivity of the epoxy composites. The majority of reports show the thermal conductivity of the epoxy-BN composites increased with increasing BN particle size [15], [18], [24], [27]–[30]. Chung and Lin [24] reported an increase in thermal conductivity from 2.3 $Wm^{-1}K^{-1}$ to 7.0 $Wm^{-1}K^{-1}$ without using a coupling agent, and from 2.8 $Wm^{-1}K^{-1}$ to 7.5 $Wm^{-1}K^{-1}$ with a coupling agent at 60 vol.% of filler when they changed the BN particle size from 3.6 µm to 10.6 µm. They stated that, increasing the particle size increases the thermal conductivity, for the same BN content, and this is true whether or not a coupling agent is used.

Hong et al. [29] studied the effect of hybrids of polygonal aluminium nitride particles and micro BN platelets to enhance thermal conductivity, and studied the effect of particle size, the effect of coupling agent, packing efficiency and maximum filler content. They observed an increase in the values of thermal conductivity from 1.4 to 3.5 $Wm^{-1}K^{-1}$ by increasing the average size of BN platelets from 6 to 18 µm at 88 wt.% loading.

Kim et al. [30] studied the effect of BN particle size in epoxy composites filled with different BN particle sizes of 1, 8 and 12 µm for three different filler contents of 50, 60 and 70 wt.%. The authors found a systematic increase in the thermal conductivity of epoxy composites by increasing the BN particle size. The obtained values of thermal conductivity at 70 wt.% of filler without any treatment were 2.15, 2.77 and 2.92 $Wm^{-1}K^{-1}$ for 1, 8 and 12 µm BN particles respectively.

Isarn et al. [18] also reported an increase in thermal conductivity from 1.0 $Wm^{-1}K^{-1}$ to 1.7 $Wm^{-1}K^{-1}$ at 40 wt.% BN loading for their cycloaliphatic epoxy composites cured with a thiol when they increased the particle size from 6 µm to 80 µm.

In another study, Tang et al. [27] observed a thermal conductivity of 0.6 $Wm^{-1}K^{-1}$ for their epoxy composite filled with 30 wt.% loading of 1.5 µm BN. This value of thermal conductivity was enhanced more than 100% to the value of 1.4 $Wm^{-1}K^{-1}$ for a 30 wt.% loading of 30 µm BN. Likewise, a similar result was reported by Yung et al. [28] showing the thermal conductivity increases by increasing the BN particle size from 53 nm to 4 µm. These authors also used a coupling agent to fabricate the epoxy composites. At 43 wt.% BN the highest value achieved was greater than 1 $Wm^{-1}K^{-1}$, corresponding to 4 µm BN while the value obtained from the composite filled with 53 nm BN was 0.85 $Wm^{-1}K^{-1}$. Another group that reported an increase in the thermal conductivity by increasing the BN particle size is Zhu et al. [15]. These authors in their study observed that the thermal

conductivity increased from 0.73 $Wm^{-1}K^{-1}$ to 1.19 $Wm^{-1}K^{-1}$ by changing the BN filler from 70 nm to 7 µm at 34 wt.% BN.

On the other hand, among almost all reports related to the effect of BN particle size on the thermal conductivity of epoxy-BN composites, three reports seem strange. Pawelski et al. [31] for their epoxy composites cured with diethylmethyl benzenediamine at 45 wt.% BN platelets of 2, 12 and 45 µm size, found the thermal conductivity values of 0.53, 0.59 and 0.66 $Wm^{-1}K^{-1}$, respectively, which represent a very slight increase in thermal conductivity with respect to BN particle size. These values of thermal conductivity for such filler loadings seem very low, which probably indicates the presence of voids in the fabricated composites. Similarly, Permal et al. [32] observed the thermal conductivity of their fabricated composites are independent of BN particle size for the mixture of three different epoxies (DGEBA, Novolac and cycloaliphatic epoxy) cured with anhydride. Their study was performed at a content of 30 wt.% BN in the sizes of 1 and 5 µm. As discussed at the beginning of this section, the interfaces decrease by increasing the particle size for a given content of the same BN shape and consequently the thermal conductivity is expected to increase; the results reported by Permal et al. and Pawelski et al. are not in line with this concept.

Yung et al. [33], for bisphenol-A epoxy composites cured with anhydride and filled with BN platelets from 3 to 10 vol.% in the ranges of 1.5 to 15 µm, observed that, although using a coupling agent increases the thermal conductivity, the thermal conductivity values decreased by increasing BN particle size, whether or not the coupling agent was used. The authors found the thermal conductivity for 3, 5, 8, and 10 vol.% decreases by increasing BN particle size from 1.5 to 15 µm. This decrease at 10 vol.% of loading was from 2.71 to 1.92 $Wm^{-1}K^{-1}$ by increasing the BN size from 1.5 to 15 µm. As a summary of these last three reports [31]–[33], it should be noted that the first reports [31] only a very small increase in thermal conductivity with particle size, the second reports [32] that it is independent of particle size, and the third reports [33] a decrease in thermal conductivity with increasing the BN particle size. These results are all, in their own ways, different from the observations of other workers.

Some authors [35]–[37] also reported higher thermal conductivity for epoxy composites filled with larger particles in which the fillers are not in the same shape. For example, Gaska et al. [35] reported a thermal conductivity of 2.75 $Wm^{-1}K^{-1}$ for composites filled with the 25 µm BN agglomerates in comparison with the value of 2.32 $Wm^{-1}K^{-1}$ for 13 µm BN platelets, both with the same filler content of 39 wt.%. However, the reason for this

enhancement in thermal conductivity is not clear, because it could be due to either the particle size or the shape of the particles.

Huang et al. [36] used spherical BN particles in the ranges of 200 to 400 nm as well as flakes in the ranges of 3 to 6 μm. For loadings up to 30 wt.%, the thermal conductivity measurements showed a value of 0.95 $Wm^{-1}K^{-1}$ for the composites filled with flakes and a value of 0.45 $Wm^{-1}K^{-1}$ for the composites filled with spherical particles. In this report, although the larger particles provided the higher thermal conductivity, contrary to reports of Gaska et al. the platelet particles gave higher thermal conductivity, contrary to the results of Gaska et al.

Likewise, Sun et al. [37] found values of 1.03 $Wm^{-1}K^{-1}$ and 0.86 $Wm^{-1}K^{-1}$ using a hot-pressing method for epoxy composites filled with 40 wt.% of 30 μm BN agglomerates and 18 μm BN platelets, respectively, so again it is not possible to distinguish whether the enhancement is because of the particle size or because of particle shape. Besides, the hot-pressing induces a certain amount of in-plane orientation for the platelets, which does not occur for the agglomerate particles.

In summary, according to the studies discussed above, although generally it is observed that the thermal conductivity increases with particle size, there are some “curious” results [31]–[33] that create some doubt about the effect of particle size on the thermal conductivity, which means that no firm conclusions can be drawn. Consequently, a systematic study of the effect of BN particle size is required.

1.3.3. Effect of BN particle shape

The heat conduction through the materials depends on the transport of phonons. Since at the interfaces there is interfacial thermal resistance (ITR), the shape of BN particles can be an important factor in how the heat can be conducted. Looking at various studies, it became clear that the shape effect of BN particles was never systematically studied. Although there are some papers in which the thermal conductivity of different epoxy composites filled with different types of BN particles are compared, this comparison is somehow confusing [35], [37], because higher thermal conductivity values belong to epoxy composites filled with agglomerate particles that are larger than platelet particles.

As is mentioned in the earlier section, Huang et al. [36] compared two different epoxy composites: one filled with the BN flakes in the form of platelets and the other one filled with BN particles in the form of spherical agglomerates in which the flake-BN particles are 16 times larger than the spherical agglomerates. Although the authors highlighted

the effect of content on the enhancement of thermal conductivity, with such a difference in the size of particles it would not be possible to compare the effect of the particle shape.

For the results of Sun et al. [37] again the same situation as for Huang et al. applies, but with this difference: that here the agglomerates are almost 1.6 times larger than BN platelets. Once again, a reliable conclusion cannot be drawn about the shape effect of these BN particles on thermal conductivity.

Since none of the published articles investigated specifically the effect of BN shape on the thermal conductivity of epoxy composites, it will be interesting to know how the shape of BN particles can play a role in thermal conductivity enhancement.

1.3.4. Effect of applying pressure and effect of orientation

There are very few systematic studies of the effect of applying pressure on the thermal conductivity of epoxy composites. The pressure can be applied in several ways. In some reports, the pressure was applied to the mixture before curing at ambient pressure [44], [75], [79]. Lewis et al. [79] used approximately 1.6 MPa pressure to consolidate the mixture and also Isarn et al. [75] to "compact and shape" cylindrical samples before cure used approximately 74 MPa and they made no mention of the effect of this pressure on the increase in thermal conductivity of their epoxy composites.

As the BN platelets have a much higher thermal conductivity in the in-plane direction in comparison with the through-plane direction, many studies have been performed to achieve the in-plane alignment of BN particles in their epoxy composites, which would result in a highly anisotropic material and an enhancement in the thermal conductivity.

There are several ways to achieve the orientation of the BN particles. Kim and Kim [38] used the sedimentation of the particles in a low viscosity mixture using ethanol as a solvent for an epoxy-terminated dimethyl siloxane matrix cured with diaminodiphenylmethane filled with 12 μm *h*-BN and exfoliated BN nanosheets (BNNS). During solvent removal by filtration, 12 μm *h*-BN particles were oriented much more than BNNS, which led to an anisotropic thermal conductivity, with greater values of anisotropy for the *h*-BN. At 68 wt.% of *h*-BN, the thermal conductivity in the in-plane direction was 4.7 $Wm^{-1}K^{-1}$, which is much higher than the value obtained in the through-plane direction (2.5 $Wm^{-1}K^{-1}$).

In another study, orientation was induced by gravity alignment of 10 to 30 μm size *h*-BN platelets by Yu et al. [39]. The *h*-BN particles were mixed with ethanol solution by sonication, followed by vacuum filtration. A "*h*-BN cake" with a diameter of 4 cm and a height of 3 cm was obtained and cut up in lengthways into very fine slices. Then epoxy

resin and hexahydro-4-methylphthalic anhydride (HMPA) as a curing agent and DMP-30 initiator diluted with acetone and after evaporating about 10 hours, were infiltrated into the *h*-BN slices. The composites were obtained by curing at 100 °C for 2h. The value obtained for through-plane (9.0 $Wm^{-1}K^{-1}$) was much higher than the value obtained for a random dispersion of BN particles in the epoxy composite (3.5 $Wm^{-1}K^{-1}$).

In another report, Lee et al. [40] fabricated a composite consisting of diglycidyl ether of bisphenol-A cured with diethyltoluenediamine and filled with *h*-BN nanoparticles. These authors applied an orientation effect to their samples. At 10 wt.% of filler, they observed that the value of thermal conductivity in the through-plane direction is 0.6 $Wm^{-1}K^{-1}$, while the value for the in-plane direction was 1.7 $Wm^{-1}K^{-1}$.

Perhaps the most common method which provides a desirable result in thermal conductivity is hot-pressing using a dual-cure technique. Hu et al. [41] fabricated epoxy-anhydride composites filled with various sizes (5, 18, 25 μm *h*-BN) at different loading from 10 to 60 wt.%. The mixture was obtained using a planetary mixer at 200 $r.min^{-1}$ for 15 minutes at 25 °C in a vacuum atmosphere. In the next step, the mixture then was pre-cured at 120 °C for about 10 minutes on a copper film in an electrothermal blowing dryer to increase the viscosity especially for the composites filled with less than 30 wt.% loading. In the next stage, the mixture was encapsulated by copper foil and then was hot-pressed under the environment of 130, 150, 170 °C and 7, 10, 13 MPa pressure for 10 hours. Without using the hot-pressing method the maximum filler content achieved was 50 wt.% while this method helped to obtain 60 wt.% loading. For the non-oriented sample filled with 18 μm *h*-BN at 50 wt.%, the value of 2.44 $Wm^{-1}K^{-1}$ was obtained which is much lower than the oriented sample (6.09 $Wm^{-1}K^{-1}$) under 10 MPa pressure at the same 50 wt.% of filler. Also, at 60 wt.% the values of around 8.5, 11 and 12 $Wm^{-1}K^{-1}$ were obtained for the oriented composites cured under 5, 10 and 13 MPa respectively, which indicates that the greater the pressure the greater is the orientation of the sample, and consequently the higher is the thermal conductivity.

Liu et al. [42] used a low viscosity epoxy-amine system filled with exfoliated BNNS or either 1 to 2 μm *h*-BN platelets using isopropanol as a solvent. A spin-coating method was used for the fabrication of composites and then the solvent evaporated. In order to achieve a desirable viscosity, the mixture was partially cured at room temperature for 5 hours. In the next stage, a magnitude of 5 MPa was applied at 80 °C for 30 min before completing the cure at 60 °C for 5 hours. Significant anisotropy was observed at 40 wt.% loading for both fillers, but this value was higher for BNNS than for the *h*-BN platelets. In the through-plane direction, the thermal conductivities obtained were 1.9 $Wm^{-1}K^{-1}$ for the

BNNS composite and 1.3 $Wm^{-1}K^{-1}$ for the *h*-BN platelet composite, which are lower than the values of 6.0 $Wm^{-1}K^{-1}$ and 3.0 $Wm^{-1}K^{-1}$ in the in-plane direction, respectively.

In another work, Zhang et al. [43] for their epoxy composites cured with anhydride and filled with 18 μm BN platelets, used a hot-pressing process to obtain an orientated composite (hot-pressed epoxy/BN platelets) and compared them with non-oriented composites (random epoxy/BN platelets). For the former they used a pressure of around 200 kPa at 100 °C for 10 min followed by a fully cured stage at the required time for the composite filled with 62 wt.% BN. The results showed the random epoxy/BN platelets had the value of 2.1 $Wm^{-1}K^{-1}$ and the hot-pressed epoxy/BN platelets had 9.5 $Wm^{-1}K^{-1}$ and 2.6 $Wm^{-1}K^{-1}$ for the in-plane and the through-plane directions, respectively.

Zhu et al. [44] used an epoxy-amine system filled with BN platelets using tetrahydrofuran as solvent. Before curing, they compressed their composite in a mould at 43, 108 and 215 MPa for 5 min and then the samples were put in an oven at 80 °C for 30 min and again at 120°C for 60 min. In the thermal conductivity measurements, the values of 8.63 $Wm^{-1}K^{-1}$ for the in-plane direction, 7.95 $Wm^{-1}K^{-1}$ for the through-plane direction and 3.3 $Wm^{-1}K^{-1}$ for the cured composite without pressure were obtained at 84 wt.% BN. Although the effect of orientation was observed in the work of these authors, it is due to the use of a very high magnitude of pressure before the curing stage in the mould, which is significantly different from the hot-pressing method. In the hot-pressing method, a significant difference was observed between the thermal conductivity values of in-plane and through-plane direction using a far lower magnitude of the pressure.

At this point it should be taken into account that a composite can be either partially cured under pressure [29], [41]–[43] and subsequently post-cured without pressure, or directly cured [11], [55], [80] in which all of them are under specified conditions of temperature, pressure and cure time. Another important point is that there is a difference in the way in which the pressure can be applied: (i) the pressure is applied by the hot-pressing [41]–[43] method in order to introduce the effect of orientation, for which, with relatively low-pressure values, large differences in thermal conductivity are obtained between the in-plane and the through-plane direction; (ii) the composites are fabricated by applying pressure in a mould [11], [24], [29], [80]–[82], therefore indicating hydrostatic pressure without any significant effect of orientation.

Using the hydrostatic pressure (applying pressure in moulds) during cure, is expected to improve the thermal conductivity of epoxy-BN composites in a way other than the orientation effect, which is worthy to be performed on different epoxy systems such as 1) epoxy composites cured with different cross-linking agents filled with the same BN

particles; 2) epoxy composites cured with the same curing agent filled with different BN particle sizes but all in the same shape; 3) epoxy composites cured with the same curing agent filled with different BN particle shape. By using the SEM technique, the mechanism of the enhancement for each epoxy system will be understood.

1.3.5. Effect of coupling agent or effect of surface treatments

It has been repeatedly pointed out that the interfaces between the filler particles and the epoxy matrix are barriers to thermal conductivity, however, there are several functional groups to improve interfaces between filler particles and epoxy matrix as well as between the fillers. Amino groups and hydroxyl groups are two of the most common groups to improve these interfaces. The functionalization of BN can be used directly in the epoxy-BN composites [25], [40], [42], [45]–[48] and also can be used with a coupling agent. The most commonly used coupling agents are silanes such as (3-aminopropyl) triethoxysilane, APTES [11], [49], [50], epoxy-terminated dimethyl siloxane, ETDMS [51], and (3-glycidyloxypropyl) trimethoxysilane, GPTMS [24], [52]–[56]. In order to improve the thermal conductivity, many researchers reported the addition of coupling agents such as APTES [11], [42], [49], [50], GPTMS [24], [52]–[56] or N-(β-aminoethyl)-γ-aminopropyl trimethoxysilane [34] which has been added directly to the BN composites. This addition of coupling agents is usually done with the help of solvents such as acetone or ethyl alcohol. The sol-gel treatment [30], [57] using hydroxylate or aminate also is a common treatment to functionalise the edge of BN particles in the shape of platelets.

In one study, Jiang et al. [20] found an increase in thermal conductivity for an epoxy composite using the surface modification of BN. These authors used silane materials with different carbon chain lenghts (C3 and C16) which were introduced on the BN surface through sol-gel reaction with NH_4OH in order to provide a better interface between BN and epoxy matrix. The values of 3.37 $Wm^{-1}K^{-1}$ and 3.49 $Wm^{-1}K^{-1}$ were obtained for the treated composite by C3 and C16 silane materials, respectively, which were higher than the untreated composites (2.40 $Wm^{-1}K^{-1}$). These authors stated that dispersion increases by increasing the carbon chain length of silane materials and resulting in a better interface between BN and epoxy matrix.

Wattankul et al. [11] similarly observed an increase in the thermal conductivity of epoxy composites by increasing the chain length of cationic surfactants of trimethyl ammonium bromide which adsorbed onto the surface of BN particles.

Kim et al. [30] compared the effect of GPTMS and 3-chloropropyl trimethoxysilane (CPTMS) coupling agents for their epoxy-BN composites. They found the thermal conductivity of epoxy-BN fabricated with GPTMS is higher than the epoxy-BN fabricated

with CPTMS for 70 wt.% BN, indicating that the GPTMS is more effective than CPTMS. Also, they found both of the epoxy-BN composites fabricated with coupling agents showed values of thermal conductivity higher than the epoxy-BN composite with no coupling agent.

Although an increase in thermal conductivity for epoxy composites is almost always observed regarding surface treatments or using coupling agents, one report [52] indicates a decrease in the thermal conductivity values for almost all epoxy/agglomerates BN composites made after the application of the coupling agent. These authors believed that proper surface treatment occurs when the fillers are in the form of platelets, rather than agglomerates, because the platelets present edges that are active for functionalization.

Sometimes the effect of enhancement in thermal conductivity is very small [49], [50], but when an untreated epoxy composite has a very small value of thermal conductivity, a small increase in the unit of thermal conductivity ($Wm^{-1}K^{-1}$) could appear large when expressed as a percentage. Lee et al. [49] for their epoxy composite filled with 1 μm BN platelets and functionalized by silane coupling agent using ethanol as a solvent, observed a thermal conductivity of 0.36 $Wm^{-1}K^{-1}$ at 10 wt.% BN. The thermal conductivity of the untreated BN composite for the same filler loading was 0.27 $Wm^{-1}K^{-1}$, which shows a 35% enhancement for the epoxy composites with treated BN.

Zhang et al. [50] for their epoxy composite filled with 10 vol.% treated BN by silane coupling agent KH-550 with using ethanol as a solvent, observed a thermal conductivity of 0.45 $Wm^{-1}K^{-1}$ which was almost 30% higher than the thermal conductivity of the fabricated composite with untreated BN at same filler content.

In another study, Yung and Liem [34], fabricated an anhydride-cured bisphenol-A phenolic resin, filled with BN particles of sizes 1.5, 5, 10 and 15 μm, which were treated with a silane coupling agent. The important aspect to note in the result of these authors is that the dependence of thermal conductivity is different from the usual upward curvature where it seems that the thermal conductivity of the samples reaches a limiting value as the boron nitride content increases. The results of these authors, which are quite contrary to the usual dependence of thermal conductivity on BN content, suggest that these authors may not be doing their experiments correctly.

Although using a coupling agent is considered to be an effective factor in the enhancement of thermal conductivity in epoxy composites, there are reports of significant enhancements in thermal conductivity without the use of any coupling agent. For example, Gaska et al. [35] achieved a value of 2.75 $Wm^{-1}K^{-1}$ with only simple mixing at

a filler content of 25 vol% and, in another report, Kargar et al. [58] achieved a thermal conductivity of 5.55 $Wm^{-1}K^{-1}$ at 59 wt.% BN. Nevertheless, a systematic study of the effect of surface treatments on epoxy composites filled with different types of BN fillers (agglomerates or platelets) would be useful to understand which type of fillers can be affected by the coupling agent in order to improve the thermal conductivity.

1.3.6. Effect of hybrid fillers

Looking at the many reports about the effect of hybrids including BN on the thermal conductivity of epoxy composites shows that, for the majority of them, the thermal conductivity increases [14], [22], [25], [26], [29], [59], [70] but the important point here is that the presence of hybrid filler may increase the thermal conductivity in two different ways. The first way is that using the hybrid fillers in different sizes allow that the gap between larger filler be filled with the smaller ones and this provides the possibility of higher loading. Even if at the same filler loading, the hybrid composite has a lower thermal conductivity than the epoxy composite filled with a single BN [17] [59], this higher loading can help to increase the thermal conductivity. The second way is that the use of hybrid fillers for the same loading content provides higher thermal conductivity than the epoxy composite filled with a single BN filler [14], whether using hybrid allows higher loading or not.

Sanchez et al. [59] reported a value of around 1.25 $Wm^{-1}K^{-1}$ for an epoxy composite filled with 40 wt.% of 2.5 µm BN flake. Because of the stiffness of the mixture, higher filler loading was impossible. A loading content of up to 80 wt.% filler was achieved using a micro AlN-BN (the same type of BN) hybrid. By using this hybrid with such a loading, a value of 1.75 $Wm^{-1}K^{-1}$ was obtained, while even the composite filled with 50 wt.% hybrid showed a lower thermal conductivity value (0.9 $Wm^{-1}K^{-1}$) than the epoxy composite filled with 40 wt.% BN flake (1.25 $Wm^{-1}K^{-1}$). It is understood that for the systems studied by this group, BN particles as a single filler provide higher thermal conductivity than their hybrid at the same loading content and the hybrid filler leads to an increase in the thermal conductivity only as a consequence of higher loading.

Liang et al. [14] stated, "Synergetic enhancement of thermal conductivity was observed between BN and AlN fillers owing to the better dispersion of hybrid fillers". The authors reported a value of 2.4 $Wm^{-1}K^{-1}$ for the epoxy composite filled with AlN/BN hybrid and values of 1.25 $Wm^{-1}K^{-1}$ and 1.40 $Wm^{-1}K^{-1}$ for the epoxy composite filled with only BN and AlN respectively, all at 40 vol.% filler loading. Thus, the results of this group show that the hybrid fillers provide more pathways for phonon transport in comparison with using a single BN filler for a given content of filler.

After discussing above, it is worthy to do a systematic study in order to understand the effect of hybrid fillers in various conditions such as changing the proportion of hybrid, changing the shape of BN particles used in hybrid and using different BN particles in terms of size to fill the gaps between the larger BN particles.

1.4. Cure reaction kinetics of epoxy composites

Since one of the most important factors in the thermal conductivity of the epoxy-BN composites depends on the interfaces between the BN particles and epoxy matrix, possible interactions between the epoxy matrix and the filler particles can affect these interfaces. Cure kinetics study is an appropriate technique to show the quality of these possible interactions between the epoxy matrix and BN filler. Therefore, It would be interesting to investigate whether or not the filler particles have an effect on the cured epoxy network structure as well as on the cure reaction of epoxy composites.

The peak temperature (T_p), in non-isothermal DSC, and the peak time (t_p) in isothermal DSC, are two factors that can reveal whether a filler addition can influence the curing reaction kinetics or not. Although it is assumed that most of the fillers in these epoxy composites are inert, in practice the reaction could be influenced by different chemical species that can be present on the surface of fillers. Therefore, the type of fillers could play a role in accelerating or retarding a reaction for systems with a given curing agent and/ or initiator.

Many authors have reported that the reaction is accelerated by the addition of fillers [13], [60]–[66]. Some of these authors used anhydride [13], [63] and some others used amine [60]–[62] in the curing process. Olivier et al. [64] for their polyepoxy system that was filled either with polyamide-12 or ceramic and cured with polyamineaniline, reported a clear reduction in T_p, indicating an acceleration in the cure reaction. In another work, Sanctuary et al. [65] observed an acceleration in the isothermal cure of epoxy/nano-alumina composites but not for the non-isothermal cure. They attributed this acceleration to the surface catalytic action of –OH groups. Also, the lack of any acceleration effect in non-isothermal cure was attributed as a consequence of the reduction of the molecular mobility by the “interphases” for the DGEBA epoxy cured by triamine. Harsch et al. [66] for their cycloalyphatic epoxy cured with anhydride and filled with different fillers found that the addition of the surface-treated filler accelerates the reaction. However, they did not offer any explanation for this observation.

On the other hand, there are a few reports of the reaction being retarded by the addition of fillers. Omrani et al. [67] used a DGEBA epoxy and filled it with up to 15 parts per hundred (phr) of barium carbonate and in non-isothermal DSC observed that T_p increased by 10 °C for the highest filler content. Zabihi et al. [68] fabricated a DGEBA epoxy cured with anhydride and filled with only 1 vol.% of BN nanoparticles; the result showed an increase of 10 to 15 °C in T_p for the non-isothermal experiment. Another increase in T_p was reported by Haman et al. [69]; here the particles were surface treated by zirconium tungstate, and the retardation which was found in the cure reaction was attributed to the shielding of –OH groups by silane.

A non-isothermal study was performed by Isarn et al. [12] in which they used DGEBA epoxy initiated by an antimonite cationic initiator and filled with up to 20 wt.% of 6 μm BN. They found a slight increase in T_p from 120 to 123 °C and attributed this to “the hindrance produced by BN particles” or “the increased viscosity of the formulation”. Elsewhere they reported [70] a larger increase in T_p, from 120 to 133 °C, for a BN content of 40 wt.% loaded in the same epoxy/initiator.

Tarrío-Saavedra et al. [71] in a DSC non-isothermal study for an epoxy-amine system filled with up to 50 wt.% of fumed silica, reported that the peak temperature is independent of filler content. This independence of T_p from the filler content may be due to the weak interaction between the curing agent or the epoxy and the filler particle. These authors also found that the values of ΔH were changed non-systematically by the addition of filler particles, which were interpreted by them as resulting from the agglomeration of the nanoparticles and a possible loss of stoichiometry in the reaction.

There is a general belief about T_g in epoxy composites that the value of T_g increases due to the inhibition of molecular mobility by the addition of filler. On the other hand, one author reported a reduction in T_g [72] and stated “adsorptive-adhesional interaction between resin components and the filler surface” is the reason for this reduction. In one study Sanchez et al. [59] for the epoxy composites filled with a hybrid of Al_2O_3/BN observed at low wt.% BN the T_g increases and then at high wt.% BN loading decreases.

Consideration of the related publications in the theme of the effect of fillers on the cure kinetics of epoxy composites shows that many results suggest that there is no significant effect of fillers on T_g [12], [19], [70], [73]–[75].

Isarn et al. also in almost all [12], [18], [19], [70] of their non-isothermal DSC studies, found the heat of reaction per epoxy equivalent (ΔH_{ee}) and $T_{g\infty}$ (glass transition of the fully cured system) were essentially independent of filler content. They also stated that

the BN particles are inert concerning epoxy structure whether it is cured with thiol or cationic epoxy homopolymerization.

The study of cure kinetics can help to reveal the effect of filler content, size and shape, the effect of initiator, and the effect of curing agent on the cure reaction kinetics of epoxy composites (by evaluation of the T_p of the non-isothermal cure reaction and the t_p of the isothermal cure reaction) as well as on the final structure of the fully cured epoxy composites (by observation of the values of $T_{g\infty}$ and ΔH_{ee}).

1.5. Advantages of the epoxy-thiol system

Looking at the majority of published papers in the field of epoxy-based composites, it will be understood that the most common curing agents for the curing procedure of epoxy resins are dianiline [76], [77], anhydrides [13], [63] or amines [60]–[62]. Although using thiol as a curing agent has received very little attention on the epoxy-BN composites, two reports [17], [21] show very promising results in thermal conductivity of epoxy composite cured with thiol. In one of these works [17] for the epoxy-thiol system filled with 80 μm agglomerates BN as well as hybrid filler of 80/6 μm agglomerates BN, the values of 3.4 $Wm^{-1}K^{-1}$ for 34.2 vol.% BN and 4.17 $Wm^{-1}K^{-1}$ for 40.9 vol.% hybrids of 80/6 μm were obtained. In the other one [21] for the epoxy-thiol system, the value of 2.2 $Wm^{-1}K^{-1}$ was obtained for 34.2 vol.% BN of 6 μm platelets, while the epoxy-diamine system filled with the same BN filler for 37.2 vol.% loading shows a value of 1.8 $Wm^{-1}K^{-1}$.

In both studies, it was found that the T_g and ΔH_{ee} of the cured composites are independent of BN particles which shows the structure of the epoxy matrix remained invariant. Also in both studies for the epoxy-thiol system, there is an initial acceleration of the reaction, which diminishes with increasing BN content, and the reaction is even significantly retarded at high contents for BN, while for the epoxy-diamine system T_p, remained almost invariant. There must therefore be some physical interaction between the BN particles and the thiol in the matrix that influences the kinetics in this system. This interaction was attributed to the Lewis acid-base interaction by the authors, which was also evident in the thermal conductivity results, which confirmed the better interaction for the epoxy-thiol system compared with the epoxy-diamine system by higher values of the epoxy-thiol system. In fact, comparing these values with many other reports shows that the epoxy-thiol system is very promising for achieving high thermal conductivity.

1.6. Objectives

As can be understood from the introduction, polymers play a very important role in the life of today. Among these polymers and the range of their properties, this doctoral dissertation is focused on epoxy resins. This doctoral thesis, on the one hand, intends to find ways to fabricate epoxy composites with high thermal conductivity while being electrically insulating. On the other hand, in order to better understand and also provide ideas for other researchers in the same field, this thesis tries to identify the mechanisms of these enhancements in thermal conductivity values.

The outlines of this doctoral thesis are listed below:

- Clarifying the effect of BN particle content and size on the thermal conductivity of the epoxy-thiol system.
- Demonstrating the effect of BN shape on the thermal conductivity of the epoxy-thiol system.
- Revealing the effect of BN content, size and shape on the cure reaction kinetics of epoxy composites as well as on the final structure of the cured epoxy composite
- Understanding the effect of the cross-linking agent on the thermal conductivity and cure kinetics of epoxy composites.
- Revealing the effect of pressure during cure on the enhancement of thermal conductivity for different epoxy systems (cured with different curing agents) as well as on the epoxy-thiol composites filled with different BN particles, with the approach to clarifying the mechanism of the enhancements for each epoxy composite systems.
- Showing the role of densification on the promotion of thermal conductivity in epoxy composite systems.

Chapter 2. Experimental section

2.1. Materials

2.2. The proportion of the components for fabrication of samples

2.3. List of instruments used in different sections

2. Experimental section

2.1. Materials

All materials used in different sections are listed below:

Epoxy resin: Diglycidyl ether of Bisphenol-A, DGEBA (Araldite GY-240) provided by Huntsman Advanced Materials (182 g.eq^{-1}, density 1.17 g.cm^{-3}).

Curing agents: 1. Thiol pentaerythritol tetrakis(3-mercaptopropionate) (488.66 g.mol^{-1}, density 1.28 g.cm^{-3}) provided by Sigma-Aldrich, Saint Louis, MO, USA.

2. Jeffamine® D-230 amine (230 g.mol^{-1}, density 0.948 g.cm^{-3}) provided by Huntsman Advanced Materials.

Accelerators: Encapsulated imidazole (Technicure® LC-80,) and N,N-Dimethyl Phenyl Urea (Technicure® PDU-250)

BN filler particles: PCTP2, 2 μm, 10 m^2 g^{-1}; PCTP30, 30 μm, 1 m^2 g^{-1}; PCTP30D, 180 μm, 1m^2 g^{-1}; CTS7M, 120 μm, 3.5 m^2 g^{-1}. All were denominated with the average particle size and specific surface area (SSA). The SEM micrographs of each particle are shown in Figure 2.1.

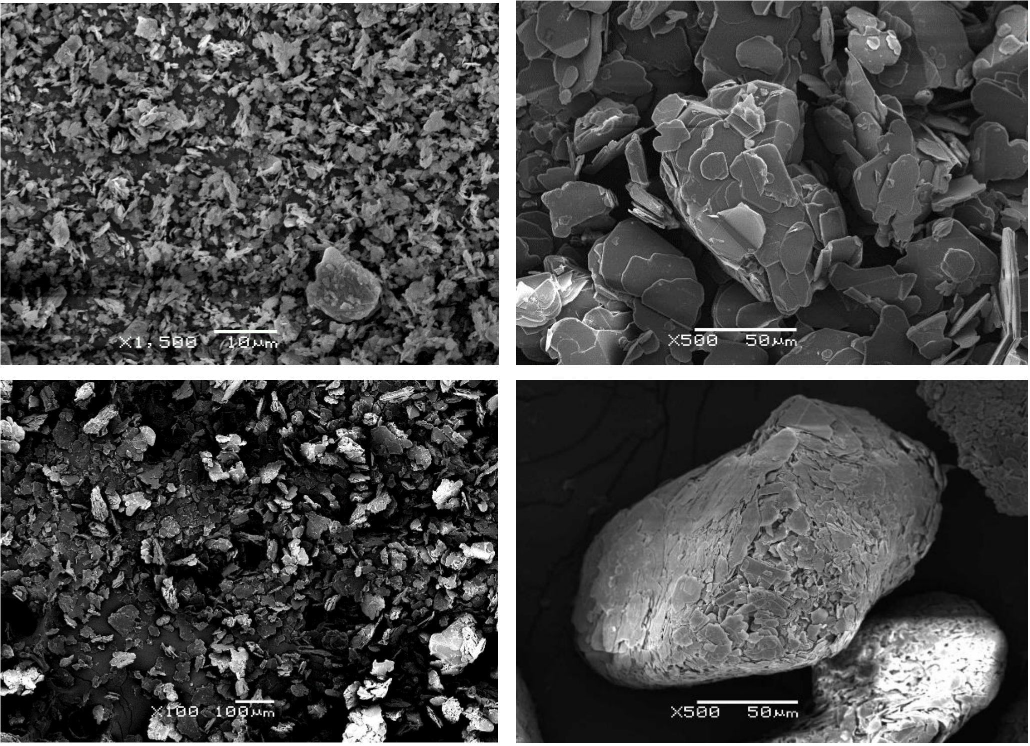


Figure 2.1. SEM micrographs of boron nitride (BN) particles from Saint-Gobain [78]: top left, 2 μm platelets, PCTP2; top right, 30 μm platelets, PCTP30; bottom left, 180 μm platelets, PCTP30D; bottom right, 120 μm spherical agglomerates, PCTL7MHF.

2.2. The proportion of the components for fabrication of samples

A complete description of all the compositions used is given in Tables 2.1 and 2.2. The nomenclature of epoxy-thiol-LC80 samples filled with BN is ETLBN*x*-*y* in which "*x*" shows the BN particle size and "*y*" is the proportion required of BN, to give wanted contents with respect to the combined weight of epoxy and BN. The epoxy-Jeffamine is also named EJ.

Table 2.1. Composition of samples: parts by mass, wt% BN and approximate vol% BN. Filled with BN particles with size *x* (= 2, 30, 100, 120, and 180 µm)

samples	parts by mass				wt.% of BN	vol.% of BN
	Epoxy	BN	Thiol	LC-80		
ETL	100	0.0	67	2.0	0.0	0.0
ETLBN*x*-10	90	10	60.3	1.8	6.2	3.7
ETLBN*x*-30	70	30	47	1.4	20.3	12.9
ETLBN*x*-50	50	50	33.5	1.0	37.2	25.7
ETLBN*x*-60	40	60	27	0.8	47.1	34.1
ETLBN*x*-70	30	70	20	0.6	58.0	45.0

For the epoxy-Jeffamine system, the same epoxy-thiol mixing method was followed; the epoxy:Jeffamine stoichiometry ratio is approximately 75:25 by mass (it comes from the equivalent weight of epoxy and molecular weight of Jeffamine relates to their functional group).

Table 2.2. Composition by mass of epoxy-Jeffamine samples filled with 30 µm BN particles.

samples	parts by mass			wt.% of BN	vol.% of BN
	Epoxy	BN	Jeffamine		
ETL	100	0.0	33.0	0.0	0.0
EJBN*x*-10	90	10	29.7	7.7	4.2
EJBN*x*-30	70	30	23.1	24.4	14.5
EJBN*x*-50	50	50	16.5	42.9	28.4
EJBN*x*-60	40	60	13.2	53.0	38.1
EJBN*x*-65	35	65	11.6	58.2	43.1

2.3. List of instruments used in different sections

- The differential scanning calorimetry (DSC) studies were done using the Mettler-Toledo DCS821e, Greifensee, Switzerland accompanied by intracooler provided by Haake EK90/MT, Vreden, Germany. The photographs of both instruments are shown in Figure 2.2.

Figure 2.2. Top left, DSC machine; top right, the sample handler of DSC machine; bottom, intracooler.

- The thermogravimetric analysis (TGA) studies were performed by a combined TGA/DSC provided by Mettler-Toledo TGA/DSC1, Greifensee, Switzerland. The mentioned TGA machine is shown in Figure 2.3.

Figure 2.3. Thermogravimetric analysis machine.

- The thermal conductivity measurements were performed using the Transient Hot Bridge method and the instrument was provided by Linseis GmbH, THB-100, Selb, Germany. In Figure 2.4 a view of the thermal conductivity meter and its sensor is shown.

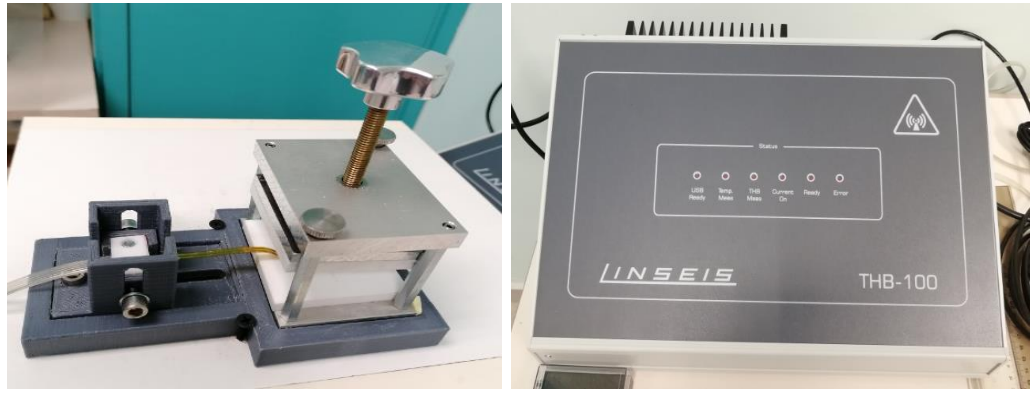


Figure 2.4. Linseis THB-100, on the right; the sensor with the grip of the samples, on the left.

- SEM studies were performed using Baltec SC-005, Leica Biosystems, Wetzlar, Germany for the gold sputter-coating and JEOL JSM-5610, Tokyo, Japan for examination in a Scanning Electron Microscope.

Chapter 3. Global discussion of results and conclusions

3.1. Effect of various parameters on the thermal conductivity of epoxy-BN composites

3.2. Effect of BN particle size on the epoxy-thiol composites

3.2.1. Effect of BN particle size on the cure kinetics of the epoxy-thiol composites

3.2.2. Effect of BN particle size on the thermal conductivity of the epoxy-thiol composites

3.3. Effect of the curing agent on the epoxy-BN composites

3.3.1. Effect of the curing agent on the cure kinetics of the epoxy-BN composites

3.3.2. Effect of curing agent on the thermal conductivity of the epoxy-BN composites

3.4. Effect of BN particle shape on the epoxy-thiol composites

3.4.1. Effect of the particle shape on the cure kinetics of the epoxy-thiol composites

3.4.2. Effect of the particle shape on the thermal conductivity of the epoxy-thiol composites

3.5. Effect of applying pressure during cure on the epoxy-BN composites

3.5.1. Effect of applying pressure on the thermal conductivity of epoxy-BN composites

3.5.2. Correlation of applying pressure with the density

3.6. Effect of densification on the epoxy-BN composites

3.6.1. A view of densification

3.6.2. Effect of densification on enthalpy

3.6.3. Effect of densification on the thermal conductivity of the epoxy composites

3. Global discussion of results and conclusions

3.1. Effect of various parameters on the thermal conductivity of epoxy-BN composites

The diagram of thermal conductivity as a function of BN content is shown in Figure 3.1, in which three different trend lines [Paper IV] obtained from a large number of epoxy-BN composites reported in the literature are drawn to indicate the large variation on values of thermal conductivity, and to simplify in some way their representation. Locating our reported values of thermal conductivity concerning these trend lines it is possible to discuss the various effects involved. The upper trend line represents the estimated limit below which 95% of the reported values lie. The intermediate trend line is an approximation to the upper limit for isotropic samples. The lower trend line indicates the approximate limit below which very few results lie; the majority of values of thermal conductivity reported for composites prepared without special processes or orientation of the BN platelets lie between the lower and intermediate trend lines. These large variations could be concerning different parameters for which this dissertation is intended to clarify. The obtained results of this study are compared with these trend lines. This comparison is made in different subsections according to our published papers. The primary objective of this dissertation is to improve the thermal conductivity of epoxy composites using different ways such as the effect of BN content, size [Paper I] and shape [Paper II], the effect of the cross-linking agent [Paper I], the effect of applying pressure [Paper V] and the effect of densification [Paper III]. Other promising ways such as the effect of BN orientation and using coupling agents were not investigated because of time constraints. Each parameter was investigated systematically, and independently of the other parameters, concentrating particularly on the epoxy-thiol system.

As discussed in the section of Introduction, an investigation on the cure kinetics of epoxy composites might help to reveal a possible correlation with the thermal conductivity, so in parallel with thermal conductivity studies, the cure kinetics were investigated as well [Paper I], [Paper II], [Paper IV]. The cure kinetics is characterised by T_p or t_p in non-isothermal and isothermal DSC cure, respectively, as well as by $T_{g\infty}$ and ΔH.

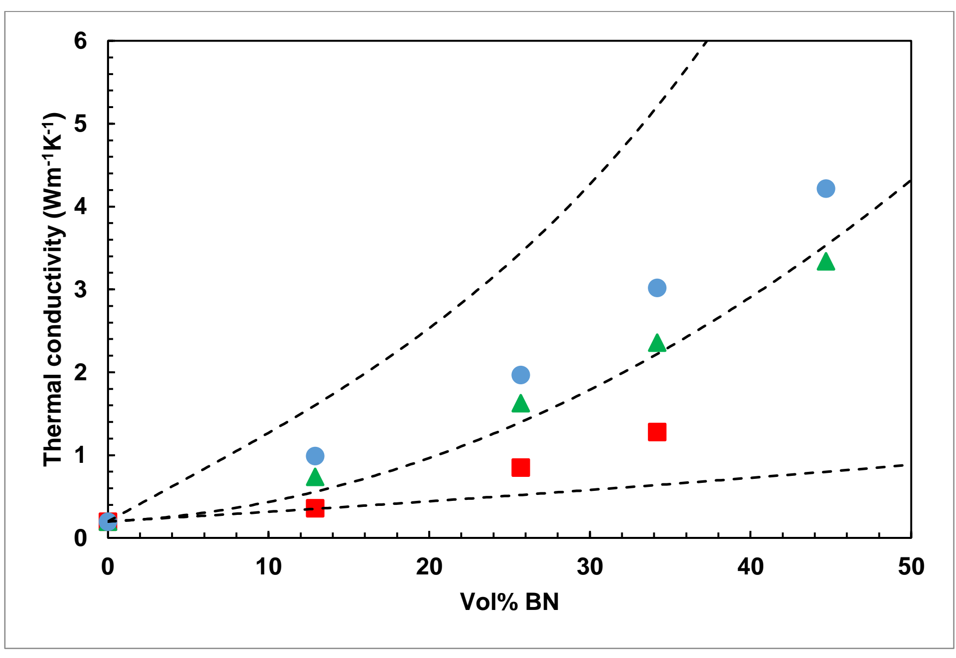


Figure 3.1. Thermal conductivity as a function of BN content for epoxy-BN composites. ETLBN2, squares; ETLBN30, triangles; ETLBN180, circles.

3.2. Effect of BN particle size on the epoxy-thiol composites

3.2.1. Effect of BN particle size on the cure kinetics of the epoxy-thiol composites

In the DSC experiments, it was observed that for the epoxy-thiol system filled with BN particles the T_p shifts to a higher temperature by increasing the BN content up to about 45 vol.% and t_p shifts to longer times [Paper I]. This trend was observed for all three BN platelets (2, 30 and 180 µm), and implies a significant retardation in the cure reaction on the addition of BN, contrary to most other reports [Paper IV]. In Figure 3.2 the diagram of peak temperature during non-isothermal cure relative to that for the unfilled system, $T_p - T_{p0}$, as a function of BN content for epoxy composite cured with thiol and filled with 30 µm BN platelets is shown. The $T_{g\infty}$ and ΔH_{ee} were independent of BN content, heating rates (non-isothermal) and cure temperature (isothermal), which means the network structure of the epoxy composite is independent of BN content. The samples filled with the smallest particles, 2 µm BN, showed the highest shift for the T_p and t_p, which is attributed to the effect of very high SSA of this particle that resulted in a larger matrix/filler interface. A small initial acceleration was observed in some of the samples at small BN loading which shows a definite effect of BN particles on the epoxy cure reaction.

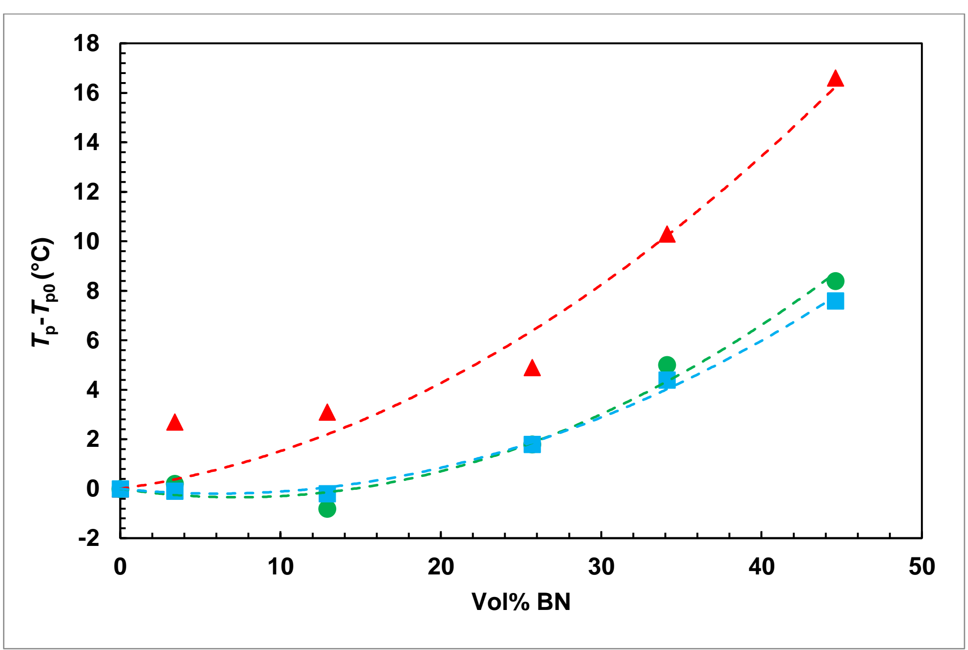


Figure 3.2. Peak temperature during non-isothermal cure relative to that for the unfilled system, $T_p - T_{p0}$, as a function of BN content for epoxy composite cured with thiol and filled with 30 µm BN platelets, as indicated, and for different heating rates: 10 K.min^{-1}, red triangles; 5 K.min^{-1}, green circles; 2 K.min^{-1}, blue squares.

3.2.2. Effect of BN particle size on the thermal conductivity of the epoxy-thiol composites

Thermal conductivity measurements showed that the values of thermal conductivity (λ) were increased for the epoxy-thiol system with increasing BN content in the usual way. For the same geometry of BN particles (here platelets) for given BN contents, as is shown in Figure 3.1, λ increases with increasing platelet size because larger particles imply a smaller interfacial area between particles and matrix. As it can be seen in Figure 3.1, the obtained values for 30 µm samples are as large as almost all others in the literature and for the 180 µm samples without any surface treatment are significantly higher than almost all others reported in the literature who has not used specific procedures.

3.3. Effect of the curing agent on the epoxy-BN composites

3.3.1. Effect of the curing agent on the cure kinetics of the epoxy-BN composites

A curing agent can affect the cure kinetics reaction of the epoxy-BN composites due to a strong interaction with the BN particles. The effect of changing the curing agent is shown in Figure 3.3 in which the dependence of peak temperature during non-isothermal

cure relative to that for the unfilled system, $T_p - T_{p0}$, is shown as a function of BN content. As can be seen, for the epoxy-Jeffamine system T_p remained almost invariant [Paper I] while T_p for the epoxy-thiol system increases with increasing BN content; this is interpreted as a consequence of a better interface between thiol and BN particles, which can be attributed to the Lewis acid-base interaction.

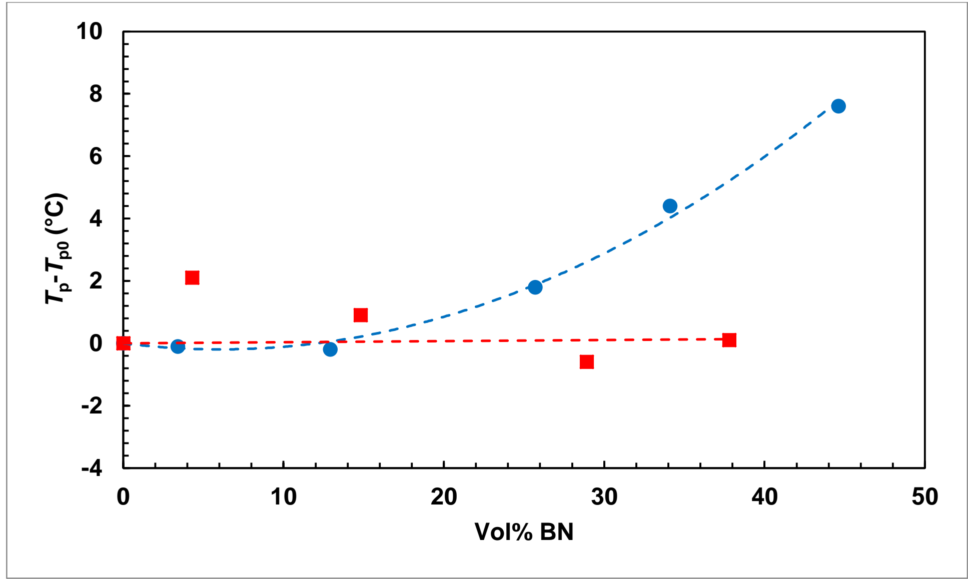


Figure 3.3. Peak temperature during non-isothermal cure relative to that for the unfilled system, $T_p - T_{p0}$, as a function of BN content for the heating rate of 2 K.min^{-1}: epoxy-Jeffamine system, red squares; epoxy-thiol system, blue circles.

3.3.2. Effect of curing agent on the thermal conductivity of the epoxy-BN composites

The thermal conductivity for both epoxy-thiol and epoxy-Jeffamine systems increases with BN content in the usual way. In correspondence with the DSC results, the values of λ for the epoxy-thiol system, as can be seen in Figure 3.4, are much higher than the values of the epoxy-Jeffamine system, which supports the idea of an improved interface between matrix and filler as a consequence of Lewis acid-base interaction.

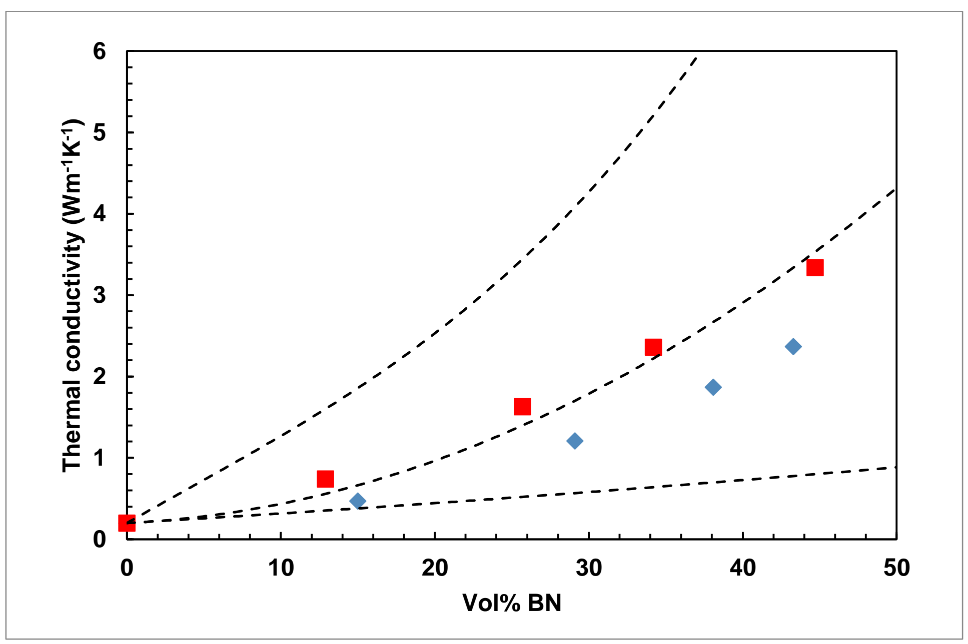


Figure 3.4. Thermal conductivity as a function of BN content for epoxy-BN composites. ETLBN30, red squares; EJBN30, blue diamonds.

3.4. Effect of BN particle shape on the epoxy-thiol composites

3.4.1. Effect of BN particle shape on the cure kinetics of the epoxy-thiol composites

The effect of BN particle shape was studied [Paper II] using a comparison between 120 µm BN agglomerates and three different BN platelets in DSC experiments. These showed that for all samples (platelets and agglomerates) T_p and t_p shift to higher temperatures and longer times respectively, indicating retardation of the cure reaction. This shift for agglomerates due to the larger SSA is greater than 30 and 180 µm platelets and smaller than the 2 µm platelets which have the highest SSA. In some cases, a small acceleration [Paper I], [Paper II] was observed for the small addition of BN particles. As it can be seen in Figure 3.5 the kinetics of the cure reaction clearly is influenced by the BN filler. The addition of BN particles results in a shift of the curves to higher temperatures. This shift to higher temperatures is most dramatic for the smallest particle size of 2 µm, for which the exothermic peak is shifted by as much as 35 °C. This observation probably can be explained by the relationship between surface area and volume of the BN platelets. The surface area to volume ratio of filler particles have an important influence on the interaction between epoxy-thiol and BN particles and this value for the 2 µm particle (10 m^2g^{-1}) is much larger than other ones. The other reason that can play a role for such a large shift of exothermic peaks to higher temperatures is

that the edge surfaces of the platelets are involved in this interaction, for which the area to volume ratio is inversely proportional to the particle size and this ratio for the 2 μm platelets is an order of magnitude larger. The presence of the LC-80 initiator, which is an encapsulated imidazole also may have an effect on this shift. This encapsulation means that, in principle, the start of the epoxy-thiol reaction by the LC-80 occurs when the temperature of 70 to 80 °C is attained during non-isothermal cure. In addition, though, the reaction kinetics is influenced also by the presence of the BN platelets, and in a different way depending on the particle size, as discussed above. This combination results in different displacements for the 2 μm platelets in comparison with that of other particles.

$T_{g\infty}$ and ΔH_{ee} for the epoxy composite filled with 120 μm BN agglomerates are also independent of BN content, heating rates (non-isothermal) and cure temperature (isothermal), which means the network structure of the epoxy composite is independent of BN content.

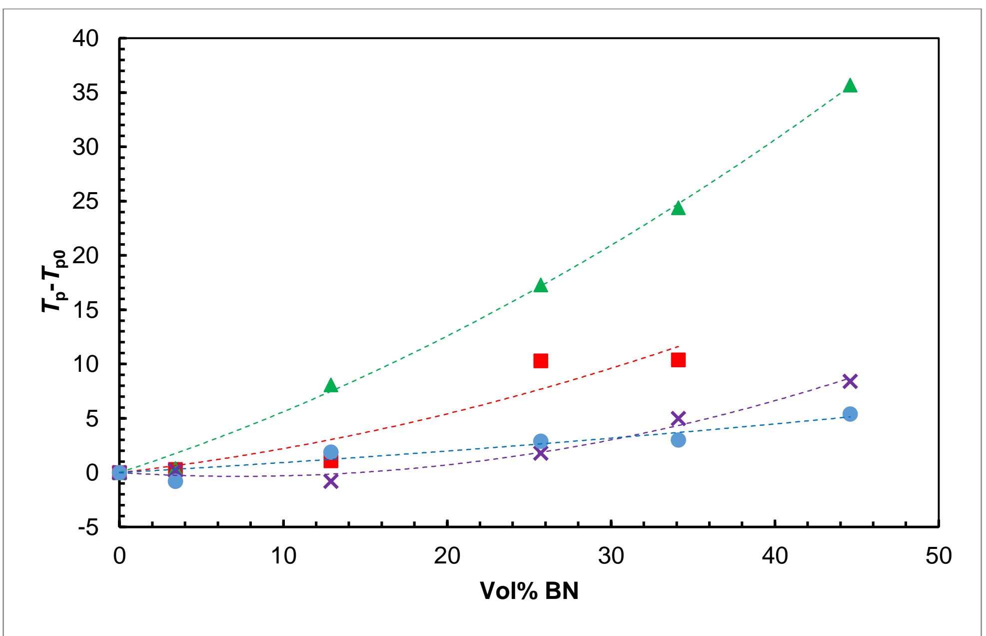


Figure 3.5. Peak temperature during non-isothermal cure relative to that for the unfilled system, $T_p - T_{p0}$, as a function of BN content for different particle sizes at 5 K.min^{-1} heating rate: 2 μm, green triangles; 30 μm, blue circles; 180 μm, purple crosses; 120 μm agglomerates, red squares.

3.4.2. Effect of BN particle shape on the thermal conductivity of the epoxy-thiol composites

In the thermal conductivity measurements, as is shown in Figure 3.6, the λ values for 120 μm agglomerates are even higher than for 180 μm platelets for a given BN content which results from fewer interfaces between agglomerates and epoxy matrix rather than platelets. Another point that can be taken into account is that, for the composite filled with 34.2 vol.% of 120 μm agglomerates, the thermal conductivity is less than the expected value presumably due to the limited area of contact with their neighbouring particles. The obtained value from one of the earlier works in our group [21] shows that the λ value for the epoxy composite cured with thiol and filled with 80 μm agglomerates for the same filler content, is almost equal (3.40 $Wm^{-1}K^{-1}$) with the 120 μm agglomerates value (3.42 $Wm^{-1}K^{-1}$). SSA of the 80 μm agglomerates (3.2 m^2g^{-1}) is slightly lower than the 120 μm agglomerates (3.5 m^2g^{-1}) which directly affects the composite mixture procedure in terms of having a good area of contact with their neighbouring particles so that the higher SSA the more stiffness of mixture and consequently less area of contact. However, the obtained values, are significantly higher than almost all others reported in the literature who obtained without any surface treatment, and even higher than many reports that belong to composites prepared with surface-treated fillers. Using surface treatments would be expected to give higher values, possibly even higher than the upper trend line.

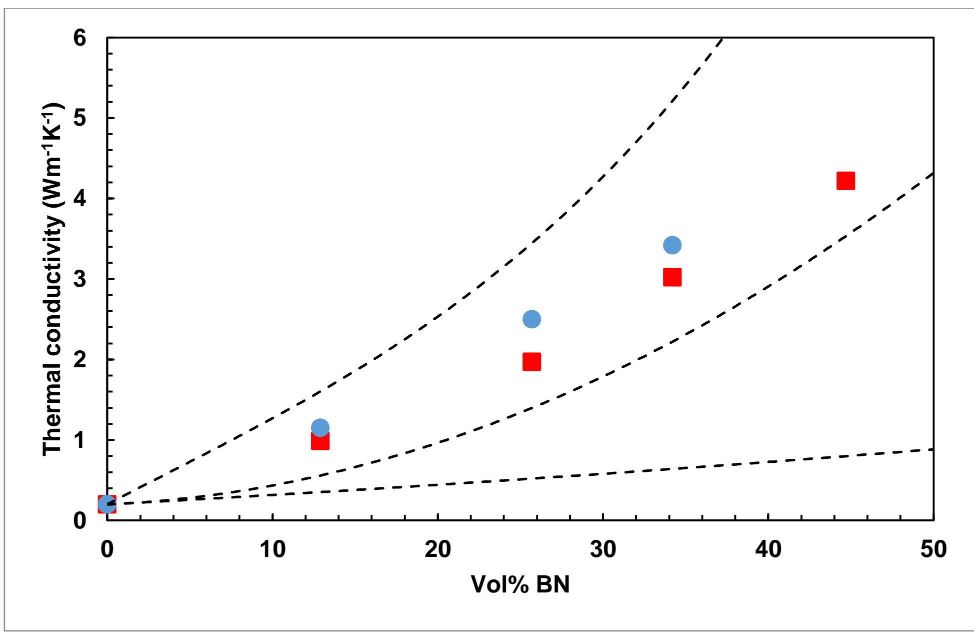


Figure 3.6. Thermal conductivity as a function of BN content for epoxy-BN composites. ETLBN180, red squares; ETLBN120 (agglomerates), blue circles.

3.5. Effect of applying pressure during cure on the epoxy-BN composites

3.5.1. Effect of applying pressure on the thermal conductivity of epoxy-BN composites

In our studies, before applying pressure, the highest values were obtained for the composite filled with 180 μm BN platelets at 44.7 vol.% with 4.22 $Wm^{-1}K^{-1}$,and also the composite filled with 120 μm BN agglomerates with 3.42 $Wm^{-1}K^{-1}$ at 34.2 vol.%. Due to the spherical shape of 120 μm BN, as well as the rather high SSA of these particles, it was impossible to reach 44.7 vol% at ambient pressure. In order to further increase the thermal conductivity, a study was performed at two different magnitudes (175 kPa and 2 MPa) of pressure during cure and then cooled down under the same applied pressure to room temperature. Hydrostatic pressure was applied to the samples in a cylindrical mould and then the samples were cured while maintaining the pressure.

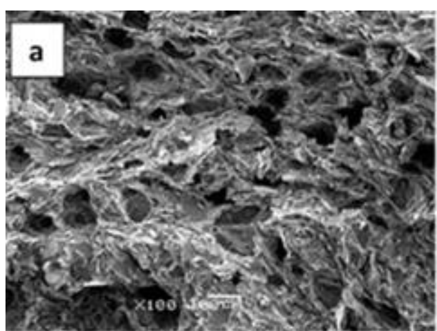
As can be seen in Table 3.1 the thermal conductivity increased for both epoxy-thiol and epoxy-Jeffamine systems at 175 kPa and this enhancement for epoxy-Jeffamine is greater than for epoxy-thiol. This dramatic increase for the epoxy-Jeffamine samples at 175 kPa, is because of removing a large number of voids. The viscosity of Jeffamine (9000 mPa.s) is much larger than the viscosity of thiol (500 mPa.s) in which is the cause of such voids in the epoxy-Jeffamine samples cured at ambient pressure. Figure 3.7 shows that the number of voids in the EJBN30-60 composites cured at 175 kPa is significantly reduced compared to the EJBN30-60 cured at ambient pressure. Also, as is shown in Table 3.1, increasing the magnitude of pressure to 2 MPa at 44.7 vol.%, resulted in remarkable values of thermal conductivity. The highest value obtained was 10.49 $Wm^{-1}K^{-1}$ at 2 MPa for the composite filled with 120 μm BN agglomerates that, in comparison with the values obtained from the literature as can be seen in Figure 3.8, is even higher than the upper trend line. Noting that those 5% values above the upper trend line are surface-treated or oriented whereas the values obtained from this study come from untreated samples. This point should be taken into account that the thermal conductivity of the sample filled with 44.7 vol.% of 120 μm BN agglomerates at 175 kPa (5.55 $Wm^{-1}K^{-1}$) is not very different from the thermal conductivity of the sample filled with 34.2 vol.% of 120 μm BN agglomerates (5.34 $Wm^{-1}K^{-1}$). This value of ETLBN120-70 can be explained due to the stiffness of the mixture of this sample for which the amount of pressure (175 kPa) is not enough to create a great contact area between the particles. However, the thermal conductivity value obtained for ETLBN120-60 cured at 175 kPa, as is shown in Figure 3.8 is on the upper trend line. Except for the ETLBN2 which falls below the intermediate trend line, the other values fall close to the upper trend line or

between the intermediate and upper trendlines. Looking at Figure 3.8, after the value of ETLBN120-70 cured at 2 MPa which is the highest, the values of ETLBN180-70 and ETLBN30-70 samples both cured under 2 MPa pressure, are located higher than the other samples fabricated in this study. These values are still even higher than the majority of reports obtained from the literature in which are mostly fabricated with special procedures.

It is also observed that the mechanisms of enhancement for each system are different [Paper V]. For the epoxy-Jeffamine system, the thermal conductivity increases concerning reducing the void contents. On the other hand, for the epoxy-thiol system which is filled with platelets, the enhancement of λ, results from an improvement in the matrix-filler interface [Paper V], and the closer proximity of the particles. In contrast, for the epoxy-thiol system filled with agglomerates BN particles, the agglomerates were deformed due to the effect of pressure, which resulted in a significantly increased area of contact between the particles and consequently these composites reach a remarkable thermal conductivity [Paper V].

Table 3.1. Thermal conductivity (λ) values of composites, ETLBN*x*-*y* and EJBN*x*-*y*, cured at ambient pressure, P_{amb}, and those with 175 kPa and 2 MPa, where *x* refers to the particle size and *y* refers to the BN content.

samples	vol.%	λ (P_{amb})	λ (175 kPa)	λ(2 MPa)
ETLBN2-60	34.2	1.28	1.49	-
ETLBN30-60	34.2	2.36	4.44	-
ETLBN30-70	44.7	3.34	4.77	7.67
ETLBN180-60	34.2	3.02	-	-
ETLBN180-70	44.7	4.22	5.38	8.52
ETLBN120-60	34.2	3.42	5.34	-
ETLBN120-70	44.7	-	5.55	10.49
EJBN30-60	38.1	1.87	4.19	-
EJBN30-65	43.3	2.37	4.32	-



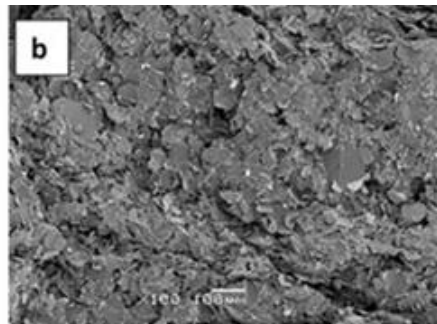


Figure 3.7. SEM micrographs of epoxy–Jeffamine samples [Paper V]: (a) EJBN30-60 and (b) EJBN30-60 cured under 175 kPa pressure. Magnification 100×, scale bar 100 µm.

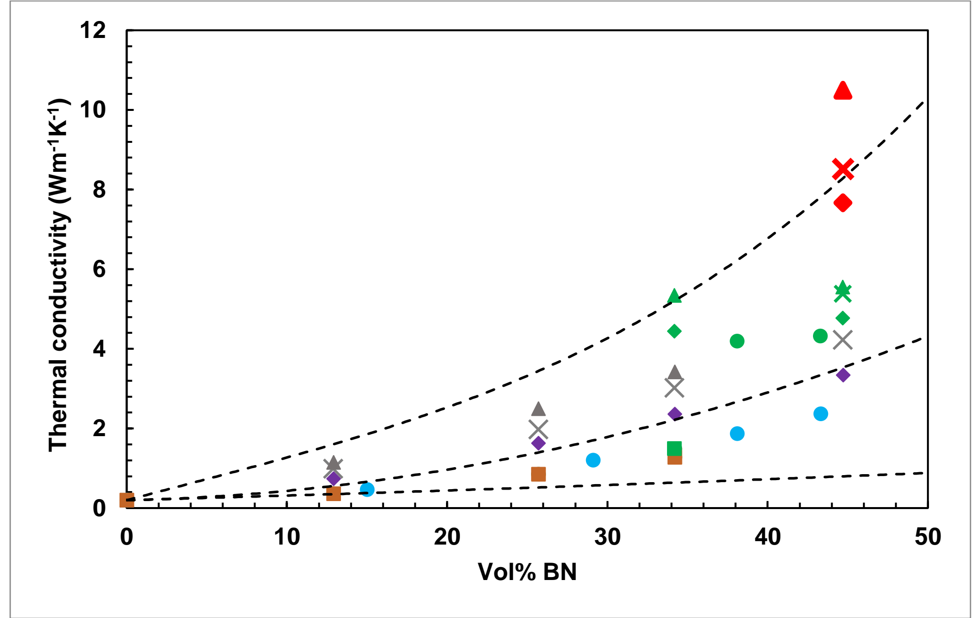


Figure 3.8. Thermal conductivity as a function of BN content for epoxy-BN composites. ETLBN2, squares; ETLBN30, diamonds; ETLBN180, crosses; EJBN30, circles; ETLBN120 (agglomerates), triangles. Red symbols, cured under 2 MPa; green symbols, cured under 175 kPa pressure.

3.5.2. Correlation of applying pressure with the density

Density measurements for samples cured at ambient pressure showed that the density increases with BN content up to 34.2 vol%; for the higher contents due to the stiffness of mixtures and consequently the presence of voids, there is a significant deviation from their ascending trend line [Paper I]. Those composites that were cured with thiol and filled with BN platelets of different sizes showed almost the same values of density for a given content, indicating the density is independent of BN platelet size. But for the epoxy composites cured with Jeffamine and filled with 30 μm BN platelets the density was much lower than the composite cured with thiol. The density of the EJBN30-60 and EJBN30-65 cured at 175 kPa shows a dramatic increase [Paper V] compared to the EJBN30-60 and EJBN30-65 cured at ambient pressure which is due to the elimination of a large

number of voids in the compressed samples as is shown in Figure 3.7. For the epoxy-thiol composites filled with 34.2 and 44.7 vol.% platelets, there is very little density change at 175 kPa, but a large increase at 2 MPa was observed. In contrast, no increase of density was observed for composites with 120 μm agglomerates, which again may be explained on the basis of different mechanisms.

A correlation was observed between the thermal conductivity values and the density for the samples filled with BN platelets that can raise the question of whether or not these two properties are inter-related in respect of the effect of pressure. In Figure 3.9 the thermal conductivity is plotted as a function of the density for all the epoxy-BN composites studied. As can be seen for the epoxy composites filled with 30 and 180 μm platelets the drawn trend lines show a correlation between density and thermal conductivity which the apparent correlation can be attributed as follows. Both increased BN content and the application of pressure during cure can increase the thermal conductivity. The former increases the number of heat conduction pathways and consequently, the density increases due to the higher density of BN particles in comparison with the epoxy matrix. The latter improves the matrix-filler interface as a consequence of the density increase (as observed for the epoxy composites filled with platelets). For the epoxy composites filled with 120 μm agglomerates, as can be seen in Figure 3.9 the density in the opposite with the thermal conductivity was not increased by applying pressure.

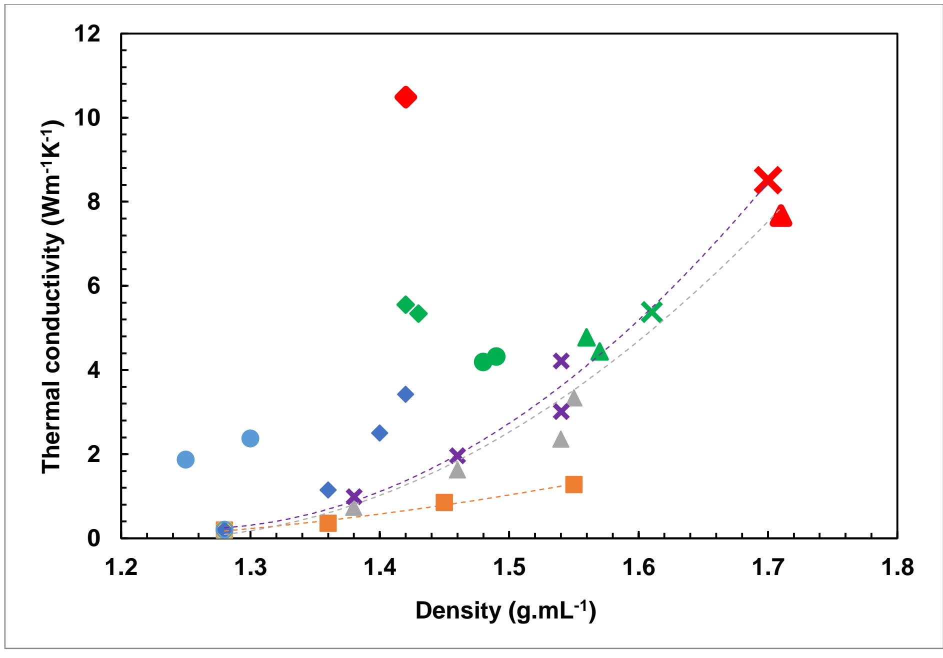


Figure 3.9. Thermal conductivity as a function of the density for the epoxy-BN composites. Large red symbols, cured under 2 MPa; green symbols, cured under 175 kPa pressure. ETLBN2, squares; ETLBN30, triangles; ETLBN180, crosses; EJBN30, circles; ETLBN120s, diamonds.

3.6. Effect of densification on the epoxy-BN composites

3.6.1. A view of densification

When a glassy polymer such as an epoxy is cooled at ambient pressure from above to below its glass transition temperature, this process leads to a glassy state which is one of non-equilibrium. A diagram of the volume-temperature (V-T) or enthalpy-temperature (H-T) is illustrated schematically in Figure 3.10: there is the liquid-like region (AC) which is converted to the glassy region (CB) at the transition point (C) during cooling that also defines the glass transition temperature, T_g. Leaving the sample at room temperature will display physical aging [83], which leads to a decrease in both volume and enthalpy and approach the equilibrium state at that temperature, indicated in Figure 3.10 by the dashed line extrapolation of the equilibrium liquid-like region. This physical aging shows many changes in mechanical and physical properties due to the structural (volume, enthalpy) changes in the glass.

If an epoxy composite system is cured at ambient pressure above its $T_{g\infty}$ which is equivalent to point (A) in Figure 3.10, then is cooled to room temperature it will transform to a glass and reach state B. If, on the other hand, the epoxy composite system is cured under pressure and at the same temperature as before, it will reach the state D in Figure 3.10, which is supposed to be above its $T_{g\infty}$, state F in Figure 3.10; this point should be taken into account that the increase in T_g with pressure is much less than 1 °C per MPa [84]. When this sample is cooled to room temperature while maintaining pressure, it will reach state E. If the pressure is now released, this gives a densified sample, point G in Figure 3.10.

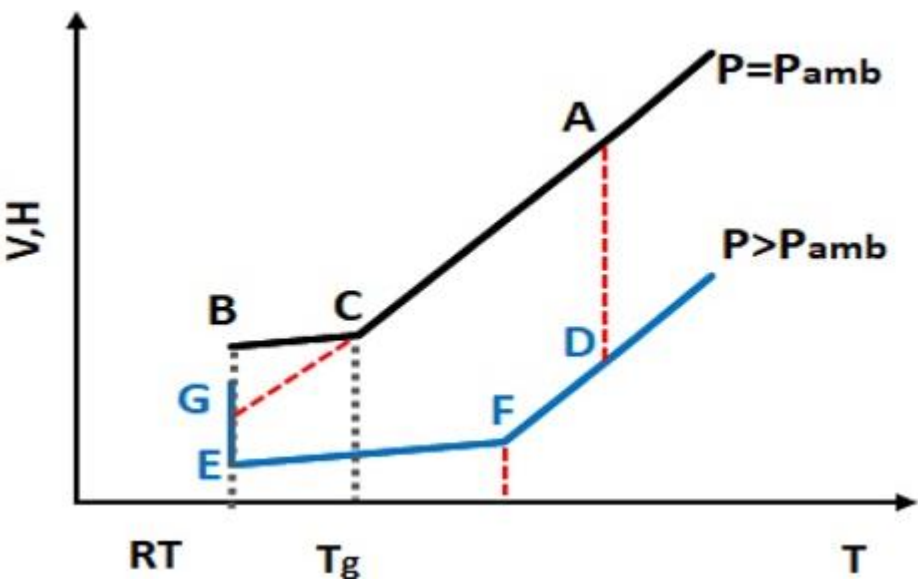


Figure 3.10. Schematic diagram of the glass transition region and the effect of pressure.

3.6.2. Effect of densification on enthalpy

An epoxy composite filled with 44.7 vol.% of 30 µm BN platelets (named sample 1) was fabricated by curing under 2 MPa pressure above its $T_{g\infty}$, then it was cooled to room temperature whilst maintaining the pressure. The DSC scan of this sample, together with the second scan, are shown in Figure 3.11. There is an enthalpy difference between the two scans; the greater area under the first scan, by 0.50 Jg^{-1} with respect to the second scan, shows the enthalpy difference between states B and G in Figure 3.10, this lower amount of enthalpy for state G was recovered by heating to above the $T_{g\infty}$.

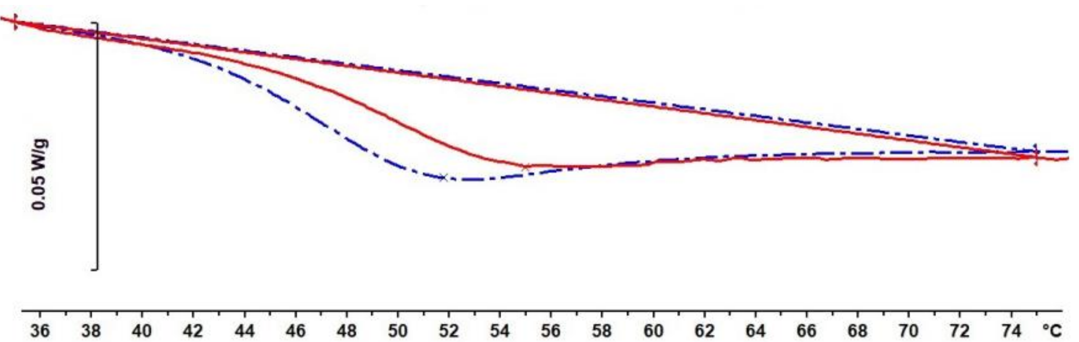


Figure 3.11. Differential Scanning Calorimetry (DSC) scan at 10 $K.min^{-1}$ of sample 1 (dash-dotted blue curve), densified at 2.0 MPa, followed by second scan (full red curve). Baselines for the determination of the areas are constructed from 35 °C to 75°C. Endothermic direction is downward.

3.6.3. Effect of densification on the thermal conductivity of the epoxy composites

Consider the densified sample (sample 1) in state G in Figure 3.10. If this sample is heated to above its T_g, and then cooled again to room temperature, it will arrive at state B. This has been demonstrated in our published paper [Paper III] by DSC. The same effect can be seen in the thermal conductivity. The same densified sample used for DSC, which had a thermal conductivity of 6.86 $Wm^{-1}K^{-1}$, was reheated to above its $T_{g\infty}$ and then cooled again to room temperature, and the thermal conductivity was again measured. The obtained value was 5.44 $Wm^{-1}K^{-1}$, which is much lower than that of the densified sample. This value is still larger than the sample (undensified) cured at ambient pressure which was 3.44 $Wm^{-1}K^{-1}$. This difference between two undensified samples refers to the effect of curing under pressure, which results in a more compact epoxy matrix and hence a better interface of matrix-particle, while the other part of the enhancement would be achieved using “permanent” densification which was obtained by cooling to room temperature while maintaining pressure. Thus this former increase from 5.44 $Wm^{-1}K^{-1}$ to

6.86 $Wm^{-1}K^{-1}$ refers to the “permanent” densification. The densification is permanent until the sample is heated up to above $T_{g\infty}$.

If the undensified sample (the sample cured at ambient pressure) is heated above $T_{g\infty}$ while the pressure (2 MPa) is applied, it will reach a state between A and D in Figure 3.10; due to lack of the effect of curing under pressure, it will not reach state D because there will be no effect of curing under pressure. Following cooling to room temperature under pressure will result in a state between G and E in Figure 3.10, and releasing the pressure will lead to a final state between B and G in Figure 3.10, for which the anticipated thermal conductivity would be between that of the sample cured at ambient pressure and that cured under pressure.

With a similar idea, a measurement was performed for the same undensified sample which had previously been densified (6.86 $Wm^{-1}K^{-1}$) and then for which the densification had been removed by heating above the glass transition region (5.44 $Wm^{-1}K^{-1}$). This sample was again heated up to its above $T_{g\infty}$ under 2MPa pressure and then cooled to room temperature while maintaining pressure. After releasing the pressure, a value of 6.76 $Wm^{-1}K^{-1}$ was obtained [Paper III] from the thermal conductivity measurement. This experiment confirms that the densification is reversible.

4. Future Work

1. This thesis concentrates on BN; other fillers are possible, such as AlN, SiC…
2. The importance of matrix-filler interface has been demonstrated; so surface treatments and coupling agents would be interesting to study in detail.
3. The use of hybrids has been shown to be advantageous, principally by allowing higher filler contents to be achieved. This avenue remains to be explored: hybrids of different sizes, different shapes, different types (BN, AlN, SiC, . . .).
4. Use of dual cure technique for the epoxy-BN composites in order to apply the orientation effect in order to reach a higher thermal conductivity. The dual cure method can be performed by means of a curing agent in an amount less than the stoichiometric proportion with respect to the epoxy. Leaving such a sample in the oven for an appropriate time at a temperature less than $T_{g\infty}$ (in order to prevent the formation of the fully cured sample), provides a partially cured sample with formability. Applying pressure using hot-pressing or rolling [mills] methods to this sample to reach the desirable orientation (only in the case of BN platelets), followed by a fully cured stage by heating up to above $T_{g\infty}$ for a sufficient time

leads to an oriented composite which would have a much higher thermal conductivity compared with the composites with random direction.

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[Paper I] S. Moradi, Y. Calventus, F. Román, J. M. Hutchinson, "Achieving high thermal conductivity in epoxy composites: effect of boron nitride particle size and matrix-filler interface", *Polymers*, vol. 11, issue. 7, no. 1156, 2019, doi: http://dx.doi.org/10.3390/polym11071156.

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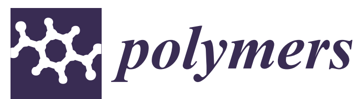
Paper I

Achieving high thermal conductivity in epoxy composites: effect of boron nitride particle size and matrix-filler interface



Article

Achieving High Thermal Conductivity in Epoxy Composites: Effect of Boron Nitride Particle Size and Matrix-Filler Interface

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Abstract: For the thermal management of high watt density circuit layers, it is common to use a filled epoxy system to provide an electrically insulating but thermally conducting bond to a metal substrate. An epoxy-thiol system filled with boron nitride (BN), in the form of 2, 30 and 180 µm platelets, has been investigated with a view to achieving enhanced thermal conductivity. The effect of BN content on the cure reaction kinetics has been studied by differential scanning calorimetry and the thermal conductivity of the cured samples has been measured by the Transient Hot Bridge method. The heat of reaction and the glass transition temperature of the fully cured samples are both independent of the BN content, but the cure reaction kinetics is systematically affected by both BN content and particle size. These results can be correlated with the thermal conductivity of the cured systems, which is found to increase with both BN content and particle size. For a given BN content, the thermal conductivity found here is significantly higher than most others reported in the literature; this effect is attributed to a Lewis acid-base interaction between filler and matrix.

Keywords: epoxy; thiol; boron nitride; thermal conductivity; differential scanning calorimetry (DSC)

1. Introduction

Composite systems consisting of epoxy resin filled with boron nitride (BN), or other suitable fillers such as aluminium nitride or silicon carbide, are widely used for the thermal management of electronic devices on account of their high thermal conductivity and electrical insulating properties, combined with ease of manufacture. There are several commercial systems available with thermal conductivities of approximately 3.0 W/mK, for example VT-4B3 from Ventec [1] and Cool-CladTM from AI Technology [2], while even higher values can be found, though these often require some special preparation procedures. However, given the very high thermal conductivity of the boron nitride, up to 600 W/mK parallel to the basal plane and 30 W/mK perpendicular to the basal plane for hexagonal BN [3,4], one might expect that values considerably higher than 3.0 W/mK could be achieved with relatively simple preparation procedures. Such an outcome, though, is generally not observed, and there have been numerous studies aimed at understanding how the thermal conductivity depends on the epoxy-BN composite fabrication process, and what are the important parameters involved; these aspects are discussed in some recent reviews of thermal conductivity in polymer-based composites [5,6].

The BN content in the epoxy matrix composite is clearly of prime importance, and a systematic increase of thermal conductivity as the BN content increases is almost universally observed, the rate of increase accelerating for higher BN contents [7,8]. However, there is a practical limit to the BN content, as the viscosity of the simple epoxy-BN mixture increases rapidly and the mixture becomes essentially

intractable for contents greater than 40 to 50 vol %; to achieve higher vol % contents requires the use of solvents or other procedures.

Besides this basic parameter of BN content, though, there are other parameters which play an important role in determining the thermal conductivity of the composite. These other parameters include the use or otherwise of surface treatments of the particles or of coupling agents and, in particular in the present context, the size and shape of the BN particles. As regards these last parameters, there is no universal consensus about the effect of particle size on the thermal conductivity, although the large majority of workers find that the thermal conductivity increases with BN particle size e.g., [9–14]. This correlation is somewhat confounded, however, by the fact that the BN particle shape is not always the same in these studies. For example, Huang et al. [12] compare the performance of small spherical BN particles, 0.2 to 0.4 μm in size, to larger "flakes", or platelets, with sizes in the range 3 to 6 μm, while Gaska et al. [13] compare 13 μm platelets with 25 μm agglomerates. In both cases the larger particles give higher thermal conductivities, but the question remains of whether this is a consequence of the particle size or of the particle shape.

On the other hand, some authors report higher thermal conductivities for composites filled with smaller BN particles [15,16], while Wattanakul et al. [17] report that higher mixing speeds and sonication, which both have the effect of reducing the original agglomerate size of 300 μm, give composites with higher thermal conductivity. Indeed, these authors state that "small particles generally give higher thermal conductivity than large particles due to the formation of greater number of conductive pathways", citing Zhou et al. [18] with reference to silicone rubber filled with BN particles. To complete the picture, Permal et al. [19] report that, for epoxy composites filled with either 1 or 5 μm BN particles, there is no significant effect of particle size, though their values of thermal conductivity are very low for the rather high content (40 vol %) of BN used.

All of the above discussion is further complicated by the possible effects of coupling agents or of surface treatments of the BN particles, which were used in all except three [12,13,17] of the references cited in the above paragraphs. In summary, therefore, there is no clear conclusion that can be drawn about the effect of BN particle size on the thermal conductivity of epoxy-BN composites. The purpose of the present work is to clarify this situation by fabricating epoxy-BN composites filled with BN particles in the form of platelets covering a wide range of sizes, and without the use of any coupling agents or surface treatments. The thermal conductivity of the cured composites is measured, and in parallel we study the cure kinetics by differential scanning calorimetry (DSC), which has been shown earlier [7,8] to mirror, in a consistent and systematic way, the dependence of the thermal conductivity on BN content.

2. Materials and Methods

2.1. Materials

The epoxy resin was a commercial diglycidyl ether of bisphenol-A, DGEBA (Araldite GY240, Huntsman Advanced Materials, Salt Lake City, UT, USA), with a nominal molecular weight per epoxy equivalent (eq) of 182 g/eq and a density of 1.17 g/cm^3. The cross-linking agent was a thiol, pentaerythritol tetrakis (3-mercaptopropionate) (Sigma-Aldrich, Saint Louis, MO, USA), with a molecular weight of 488.66 g/mol and a density of 1.28 g/cm^3. The thiol reacts with the epoxy in a "click" mechanism, with the formation of hydroxyl and thioether groups in a single step [20,21]. The curing reaction was initiated using a latent initiator, encapsulated imidazole LC-80 (Technicure, A&C Catalysts, Linden, NJ, USA), in the form of a powder, which was added in the proportion of 2 parts per hundred resin (phr).

The boron nitride (BN) particles were obtained commercially (Saint-Gobain Boron Nitride, Amherst, NY, USA), and were of different sizes within the same product category of CarboTherm platelets. The average platelet size, maximum particle size, tap density and specific surface area,

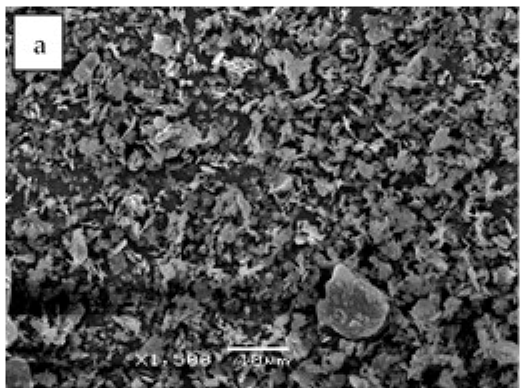
as given in the manufacturer's literature [22] for the three types of BN particles used here, were as follows:

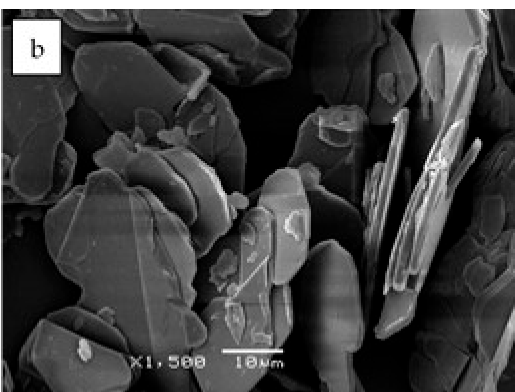
PCTP2: 2 μm, 10 μm, 0.2 g/cm^3, 10 m^2/g

PCTP30: 30 μm, 100 μm, 0.6 g/cm^3, 1 m^2/g

PCTP30D: 180 μm, 1600 μm, 0.6 g/cm^3, 1 m^2/g

Figure 1 shows the BN platelets of three different sizes in the as-received condition. Figure 1a,b, at the same magnification of 1500×, clearly show both the individual platelet characteristic of the 2 and 30 μm particles, respectively, and the significant difference in average size. There is inevitably a distribution of particle sizes, and according to the manufacturer's information [22] the maximum particle sizes are 10 μm for PCTP2 and 100 μm for PCTP30. For example, in Figure 1a, a particle of 10 μm can be seen, and likewise, for PCTP30, particles as large as 100 μm have been observed.





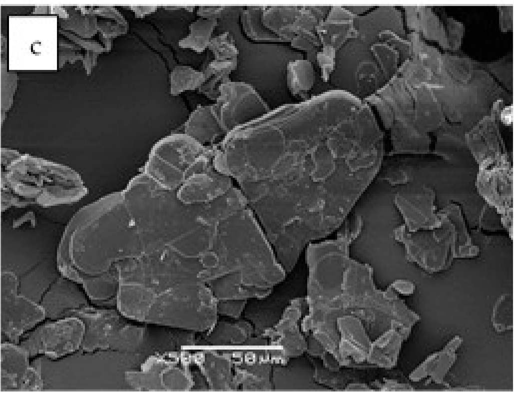


Figure 1. Scanning Electron Microscopy (SEM) images of the as-received BN platelet particles: (**a**) PCTP2, 2 μm, magnification 1500×, scale bar 10 μm; (**b**) PCTP30, 30 μm, magnification 1500×, scale bar 10 μm; (**c**) PCTP30D, 180 μm, magnification 500×, scale bar 50 μm.

The PCTP30D particles have been engineered for high shear mixing processes, for example for their incorporation into thermoplastics and, while being classified as platelets [22], they are slightly different from the other two platelets used here. These particles are stated by the manufacturer to be a "loosely agglomerated powder", and there is a much wider distribution of particle sizes, with a maximum of 1600 μm. At the center of the image in Figure 1c, for example, there is a large (broken) particle, about 180 μm in the largest dimension, surrounded by much smaller particles.

2.2. Methods

2.2.1. Sample Preparation

The epoxy and thiol were mixed by hand in a stoichiometric ratio, approximately 60:40 by weight, the latent initiator LC-80 previously having been added in the proportion of 2 phr. The BN particles

were then added in the proportion required, to give contents of 10%, 30%, 50%, 60% and 70% with respect to the combined weight of epoxy and BN, and again were mixed by hand for approximately 10 min until a homogeneous mixture was obtained. This final mixture was then degassed in a vacuum chamber at room temperature and less than 26 hPa pressure for approximately 15 min. The sample denominations and proportions of all the components in each sample are given in Table 1.

Table 1. Composition by weight of epoxy-thiol samples filled with BN particles with size x = 2, 30, 180 μm.

Sample	Epoxy	BN	Thiol	LC-80
ETL	100	0	67	2.0
ETLBNx-10	90	10	60.3	1.8
ETLBNx-30	70	30	47	1.4
ETLBNx-50	50	50	33.5	1.0
ETLBNx-60	40	60	27	0.8
ETLBNx-70	30	70	20	0.6

The viscosity of the epoxy-thiol-BN mixture increases strongly with increasing BN content, and the mixture becomes a very stiff paste at the highest BN content. This is particularly so for the smallest BN particles (2 μm), for which the 70% BN content could not be achieved, because for the same BN content, the surface area to volume ratio increases as the particle size decreases. In fact, the specific surface area quoted by the manufacturer is ten times larger for PCTP2 than it is for the other two particle types. Furthermore, it is not possible to degas the samples with such high BN contents, and as a consequence it is likely that some air bubbles remain, which would tend to reduce the thermal conductivity. The preparation of these composites by this simple mixing technique therefore implies a limit to the BN content, which for the 70% samples represents a volume percentage of just less than 45%. To achieve higher vol % loadings of BN, as have been reported in the literature e.g., [10,14,23,24], involves more elaborate preparation procedures, such as the use of solvents, allowing filler contents as large as 80 vol % to be attained [10,14]. Even then, though, it is not uncommon to find that the thermal conductivity decreases beyond 50 or 60 vol %, probably because of the existence of voids.

2.2.2. Differential Scanning Calorimetry (DSC)

DSC in both isothermal and non-isothermal (constant heating rate) modes was used to characterize the cure kinetics of these composite systems. The DSC instrument (Mettler-Toledo DCS821e, Greifensee, Switzerland) equipped with a robot sample handler and intracooler (Haake EK90/MT, Vreden, Germany), was calibrated for both heat flow and temperature using indium, and a flow of dry nitrogen at 50 mL/min was used throughout. The data analysis was made using the STARe software of the instrument.

For the isothermal cure experiments, the composite samples of about 10 mg, enclosed in an aluminium pan crimped with a lid, were weighed on an analytical balance and then immediately introduced into the DSC furnace, previously heated to the required isothermal cure temperature. The heat flow was measured as a function of time until the cure reaction was complete, the cure time depending on the cure temperature; cure temperatures of 60, 70 and 80 °C were used, all of which are sufficiently high temperatures such that no vitrification will occur during cure. The cure kinetics is characterized by the time, t_p, at which the exothermic heat flow is a maximum, and by the exothermic heat of reaction, determined from the area under the cure curve. Subsequently, a second (non-isothermal) scan was made at 10 K/min to determine the glass transition temperature of the fully cured sample, $T_{g\infty}$, and to check that there was no residual heat of reaction. This second scan is made immediately after cooling at 20 K/min, and hence the glass transition temperature can be determined in the standard way as the mid-point of the transition in the specific heat capacity on heating from the glassy to the rubbery state.

For the non-isothermal cure experiments, the weighed samples were introduced into the DSC at 25 °C, cooled at 20 K/min to −65 °C, and then scanned at the required rate (2, 5 and 10 K/min) to 200 °C. The cure kinetics is characterized by the temperature, T_p, at which the exothermic heat flow is a maximum, and by the exothermic heat of reaction, determined from the area under the cure curve. Subsequently, a second (non-isothermal) scan was made at 10 K/min to determine the glass transition temperature of the fully cured sample, $T_{g\infty}$.

2.2.3. Thermogravimetric Analysis (TGA)

The TGA experiments were performed in a combined TGA/DSC (Mettler-Toledo TGA/DSC1, Greifensee, Switzerland), equipped with a robot sample handler and a cryostat (Huber ministat 125, Offenburg, Germany). The equipment was calibrated using indium with a dry air flow of 200 mL/min. For the TGA experiments, samples of 5 to 10 mg were heated at rates of 2 and 10 K/min from 40 to 600 °C with a dry nitrogen flow of 200 mL/min.

2.2.4. Thermal Conductivity

The thermal conductivity was measured using the Transient Hot Bridge method (Linseis GmbH, THB-100, Selb, Germany), in which a heat pulse is applied to a sensor placed between two surfaces of the sample material and the resulting heat dissipation, quantified by the temperature change, ΔT, is used to determine the thermal conductivity directly [25]. The Kapton Hot Point sensor was calibrated with five standards, covering a range of thermal conductivities from 0.2 to 10 W/mK: polymethyl methacrylate, borosilicate crown glass, marble, a Ti-Al alloy, and titanium. The epoxy-BN composite samples were prepared by casting the uncured mixture into a silicone mold, 10 mm × 40 mm × 4 mm, degassing under vacuum at room temperature, and curing isothermally at 70 °C for 1 h. The surfaces of the cured samples were carefully polished by hand, using emery paper (120, 400 and 600 grit size sequentially), to give smooth and flat surfaces for contact with the Hot Point sensor. For the measurement, the sensor was clamped between these two smooth and flat surfaces, in a manual screw-actuated press, and a series of four repeated measurements were made, each with a heating power of 50 mW and a duration of 100 s, and allowing sufficient time between each measurement for the sample to return to the same initial state. The linear range of a plot of ΔT as a function of the inverse square root of the measurement time is extrapolated to zero on the abscissa (infinite time), and the thermal conductivity is then inversely proportional to ΔT (∞).

2.2.5. Density

The density of the cured samples, ρ_s, was determined by Archimedes principle, the samples being the same as those used for the thermal conductivity measurements. The weight of the sample in air, m_{air}, and the weight of the same sample suspended by a fine wire in ethanol, m_{eth}, for which the density, ρ_{eth}, is tabulated as a function of temperature, were determined using an analytical balance. The sample density is calculated as:

$$\rho_s = m_{air} / (m_{air} - m_{eth}) \times \rho_{eth} \quad (1)$$

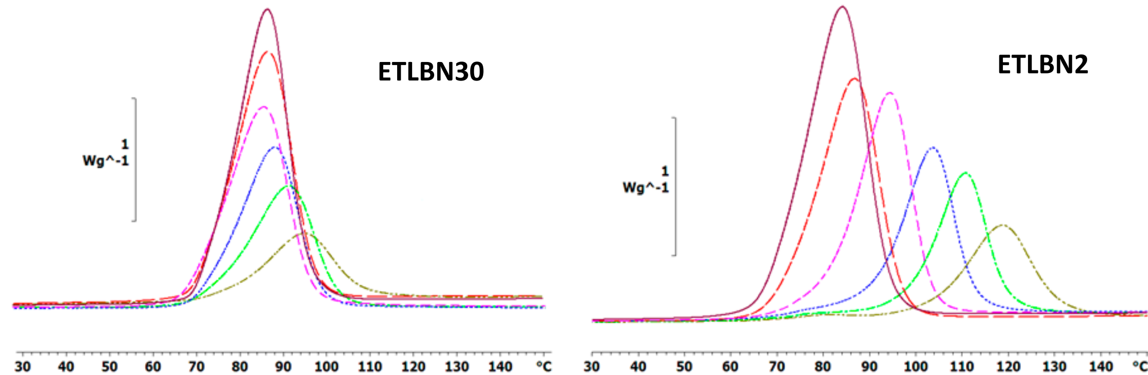
2.2.6. Scanning Electron Microscopy (SEM)

Fully cured samples, similar to those used for the thermal conductivity measurements and prepared using the same isothermal curing procedure, were fractured and then the fracture surface was sputter-coated with gold (Baltec SC-005, Leica Biosystems, Wetzlar, Germany) and examined in a Scanning Electron Microscope (JEOL JSM-5610, Tokyo, Japan). Typically, an accelerating voltage of 10 kV was used to give magnifications of 100× to 5000×.

3. Results and Discussion

3.1. Differential Scanning Calorimetry (DSC)

The non-isothermal DSC curves at a heating rate of 5 K/min for the epoxy-thiol system without any filler (ETL) and for the epoxy-thiol-BN composite systems filled with 2, 30 and 180 µm BN platelets are shown in Figure 2, while similar results were obtained for heating rates of 2 and 10 K/min. These DSC scans were made from −60 °C, but only the temperature region in which the exothermic cure reaction occurs is shown here. At lower temperatures, however, the glass transition temperatures of the uncured mixtures, T_{g0}, with 2, 30 and 180 µm BN platelets are observed at the average temperatures (±1 standard deviation) of −38.6 ± 0.5, −38.0 ± 0.7 and −37.5 ± 0.7 °C, respectively, compared with −38.4 ± 0.5 °C for the unfilled ETL system. The glass transition temperature of the uncured mixture is therefore essentially independent of the heating rate and of the BN content; the small increase in T_{g0} with increasing BN particle size may be a result of an increased restriction to the molecular mobility of the epoxy-thiol mixture with the larger particles, and is of no further consequence here.



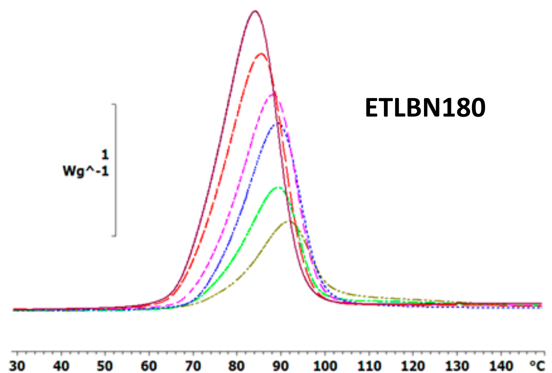


Figure 2. Non-isothermal DSC scans at 5 K/min for ETLBN2-*y*, ETLBN30-*y* and ETLBN180-*y*, in which *y* refers to the different BN contents given in Table 1: purple, full line, *y* = 0; long dash, red, *y* = 10; short dash, pink, *y* = 30; dash-dot, blue, *y* = 50; dotted, light green, *y* = 60; dash-double dot, dark green, *y* = 70.

In a second scan after the non-isothermal cure shown in Figure 2, the glass transition temperature of the fully cured system, $T_{g\infty}$, is determined, and is found to be approximately independent of BN particle size and content, with values of 54.0 ± 0.4, 53.7 ± 1.2 and 52.7 ± 1.3 °C for the 2, 30 and 180 µm BN platelets, respectively. Likewise, the heat of reaction, ΔH, is also found to be essentially independent of BN particle size and content, as well as of the heating rate, with an average value of 127.2 ± 8.3 kJ/ee. The constancy of both $T_{g\infty}$ and ΔH implies that the network structure of the cured epoxy composites is not influenced by the presence of the BN filler.

On the other hand, the kinetics of the cure reaction clearly is influenced by the BN filler, as can be seen from two particular aspects of the cure curves in Figure 2. The first aspect is the displacement of the curves as a function of BN content. The addition of BN particles results in a shift of the curves to higher temperatures. This is consistently observed for all BN platelet sizes, but is most dramatic for the smallest particle size of 2 μm, for which the exothermic peak is shifted by as much as 30 °C. The explanation for this observation probably lies in the relationship between surface area and volume of the BN platelets. If, as we argue here, there is an interaction between the epoxy-thiol matrix and the BN filler, which is a surface effect, then the surface area to volume ratio will have an important influence. In fact, it is probably only the edge surfaces of the platelets which are involved in this interaction, for which the area to volume ratio is inversely proportional to the particle size. Furthermore, the 180 μm platelets have a much wider distribution of particle sizes than do the other platelet sizes (see Figure 1), and there is also a tendency for the larger platelet sizes to break during fabrication, evidenced by the fracture surfaces of the cured composites (to be discussed below). Consequently, the area-to-volume ratio for the 30 and 180 μm platelets is rather similar, whereas that for the 2 μm platelets is an order of magnitude larger.

The second aspect is that the cure curves become increasingly asymmetric as the BN content increases, this being particularly noticeable in Figure 2 for the composites filled with 30 and 180 μm platelets. For the composites filled with the 2 μm platelets, on the other hand, this asymmetry takes the appearance of a shoulder at low temperatures, which becomes more prominent as the BN content increases, eventually even being manifest as a small peak for the highest BN content. The explanation for this behavior probably lies in the action of the LC-80 initiator, which is an encapsulated imidazole. This encapsulation means that, in principle, the initiation of the epoxy-thiol reaction by the LC-80 occurs when the temperature of 70 to 80 °C is attained during non-isothermal cure. In addition, though, the reaction kinetics is influenced also by the presence of the BN platelets, and in a different way depending on the platelet size, as discussed immediately above. The consequence of this combination of effects is the different asymmetry observed in Figure 2 for the 2 μm platelets in comparison with that observed for the 30 and 180 μm platelets.

The shift of the peaks to higher temperatures with increasing BN content can be seen more readily in Figure 3, where the peak exothermic temperature, T_p, relative to that for the unfilled system, T_{p0}, is plotted as a function of the vol % of BN for each particle size and for each heating rate. The temperature shift is clearly greatest for the 2 μm platelets, and then reduces in turn for the 30 and 180 μm particles.

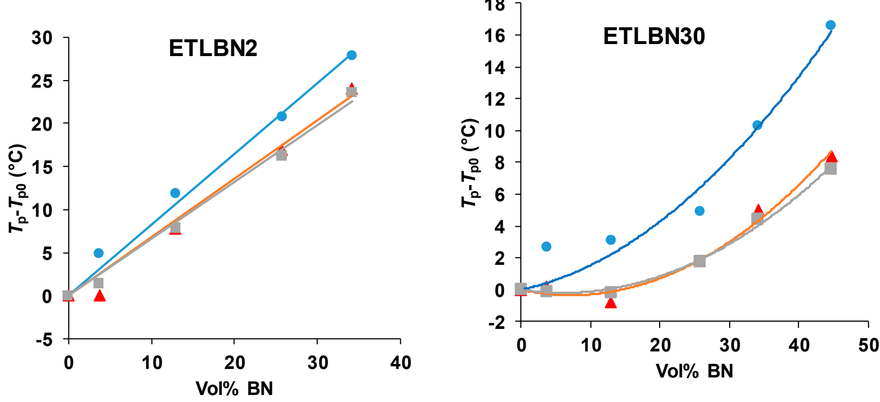


Figure 3. *Cont.*

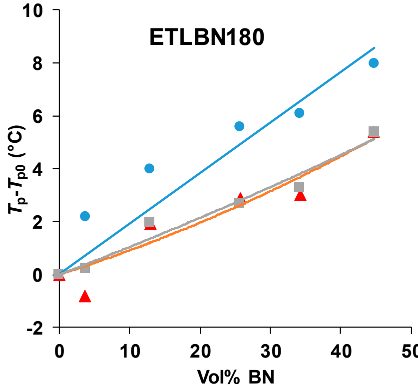


Figure 3. Peak temperature during non-isothermal cure relative to that for the unfilled system, $T_p - T_{p0}$, as a function of BN content for different platelet sizes, as indicated, and for different heating rates: 10 K/min, blue circles; 5 K/min, red triangles; 2 K/min, grey squares.

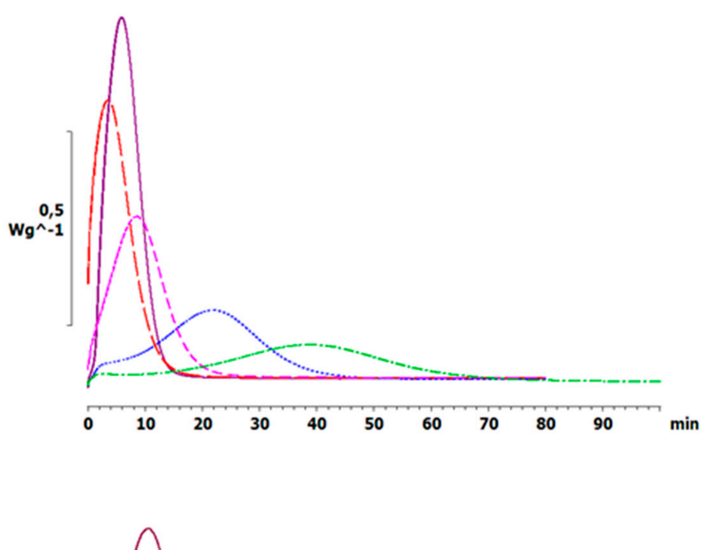
For all particle sizes, it is interesting to observe that there is no significant difference between the shifts for the two lower heating rates of 2 and 5 K/min. At first sight, this may appear strange, but it must be remembered that it is the *difference* between the peak temperatures of the filled and unfilled systems that is plotted in Figure 3; in all cases, the peak temperature itself always increases with increasing heating rate, as would be expected. What the results for the heating rates of 2 and 5 K/min probably indicate is that the cure reaction is not simple, as has already been commented in respect of the results presented in Figure 2, and that there may be competing effects of the BN filler particles. In particular, there appears to be a tendency, especially for the 30 μm composites, for the reaction first to be accelerated on the addition of BN particles, before being slowed.

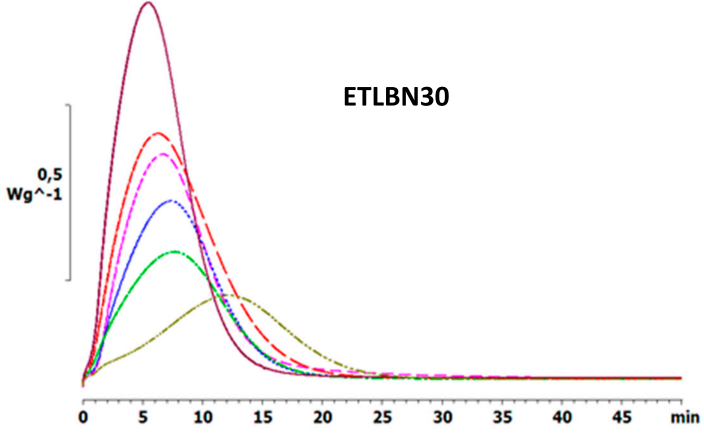
Similar effects are observed also for the isothermal cure. Figure 4 shows the isothermal cure at 70 °C of samples with different contents of the three BN particle sizes: ETLBN2, ETLBN30 and ETLBN180. For each cure condition, the heat of reaction (122.8 ± 9.6 kJ/ee) and the glass transition temperature of the fully cured sample (52.7 ± 0.8 for ETLBN2, 53.0 ± 0.9 for ETLBN30, 51.8 ± 1.3 °C for ETLBN180), obtained from a second scan, are essentially independent of the filler content and of the isothermal cure temperature. On the other hand, the cure kinetics is significantly influenced by the BN content. In general, with increasing amount of filler, whatever the size of the platelets, the exothermic peak is displaced to longer times, similar to the displacement to higher peak temperatures in the non-isothermal cure curves in Figure 2. However, for the smallest BN content (y=10), the cure is actually accelerated for the 2 and 180 μm platelets, an effect that can be observed also in some of the non-isothermal results, for example for the 30 μm platelets, shown in Figure 3. Similar results were found for the other isothermal cure temperatures of 60 and 80 °C.

The variation of the peak exotherm time, t_p, with the BN content is shown in Figure 5 for the three BN platelet sizes and for the three isothermal cure temperatures. Here can be seen the tendency for the reaction first to accelerate, with a reduction in t_p, and then to be slowed as the BN content increases. There is a systematic variation with the BN platelet size, whereby the peak time t_p, for a given cure temperature and BN content, decreases as the BN platelet size increases, and dramatically so on going from 2 μm to 30 μm; this behavior mirrors that shown in Figure 3 for the non-isothermal cure.

In order to understand the role of the thiol cross-linking agent in the kinetics of the cure reaction, it is of interest to compare these results for the cure of these epoxy-BN composites with a thiol with those for the same epoxy-BN system cured with a diamine, Jeffamine D-420. This comparison has been made for just one of the BN platelet sizes (30 μm). The corresponding results for the non-isothermal cure of the EJBN30-y samples at 2 and at 5 K/min are shown together with the results for the ETLBN30-y samples at the same heating rates in Figure 6. It is evident that the peak temperature for the epoxy-diamine system is essentially independent of the BN filler content, in clear contrast to the behavior for the

epoxy-thiol system. This was also reported earlier in the comparison of epoxy-thiol and epoxy-diamine systems filled with aluminium nitride, AlN [7].





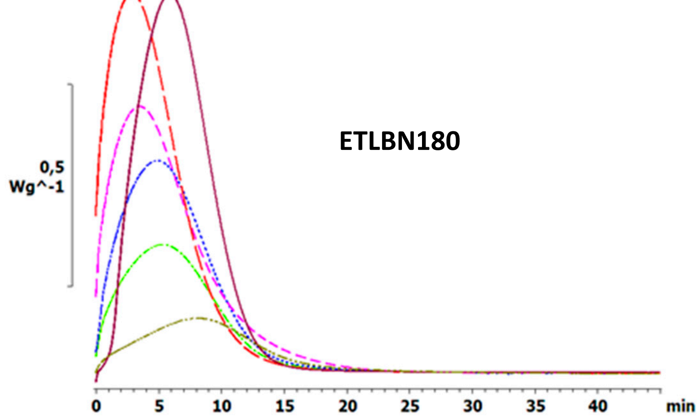


Figure 4. Isothermal DSC scans at 70 °C for ETLBN2-y, ETLBN30-y and ETLBN180-y, in which y refers to the different BN contents given in Table 1: purple, full line, y = 0; long dash, red, y = 10; short dash, pink, y = 30; dash-dot, blue, y = 50; dotted, light green, y = 60; dash-double dot, dark green, y = 70.

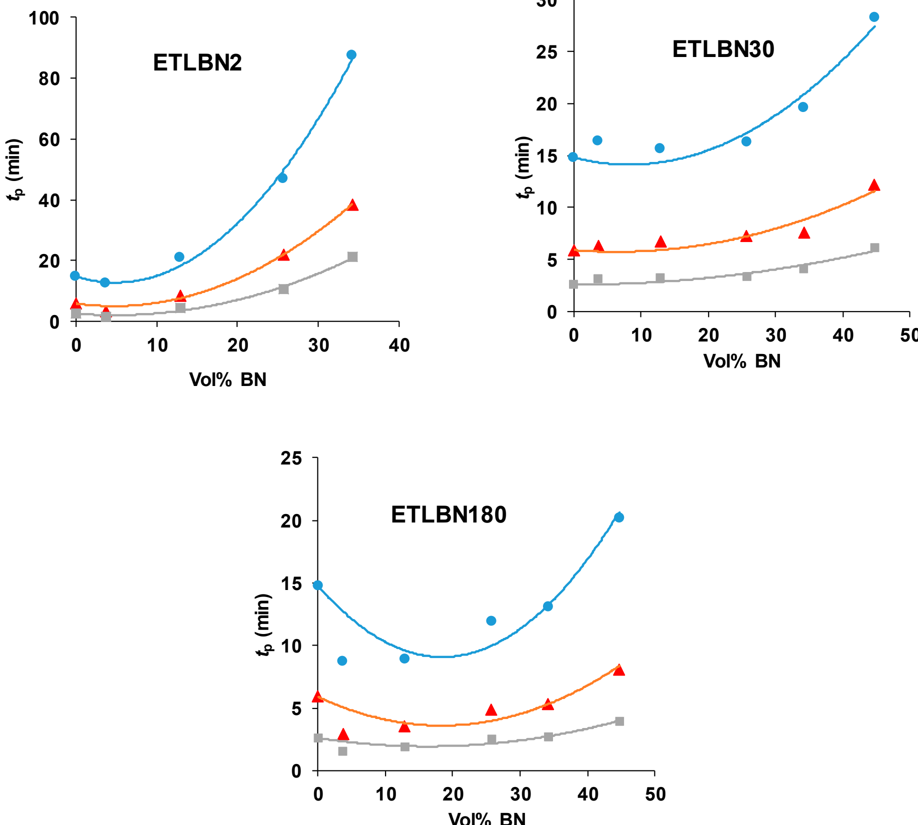


Figure 5. Time of exothermic peak during isothermal cure, t_p, as a function of BN content for different platelet sizes, as indicated, and for different isothermal cure temperatures: 60 °C, blue circles; 70 °C, red triangles; 80 °C, grey squares.

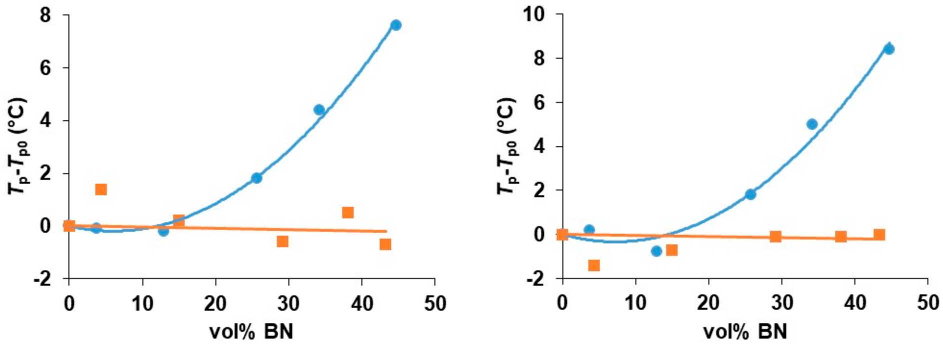


Figure 6. Peak temperature during non-isothermal cure relative to that for the unfilled system, $T_p - T_{p0}$, as a function of BN 30 µm content for the heating rates of 2 K/min (**left**) and 5 K/min (**right**). Epoxy-thiol system, blue circles; epoxy-diamine system, red squares.

There is clearly an influence of the BN filler on the cure kinetics of the epoxy-thiol system, though the fully cured epoxy network structure is unaffected, and this effect is related to the presence of the thiol as it is not observed for the epoxy-diamine system. In this context, the effect of the BN particle size is important. Figure 7 shows how the peak exotherm temperature in non-isothermal cure at 5 K/min depends on the platelet size. It can be seen that the greatest effect of retarding the reaction occurs for the smallest platelets, while there is very little difference between the effects of the 30 and 180 µm platelets. This behavior occurs also for the heating rates of 2 and 10 K/min, and the systematic effect of the particle size and of the filler content has been noted in earlier work [7,8].

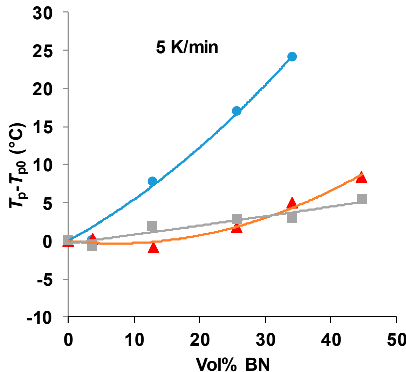


Figure 7. Peak temperature during non-isothermal cure of the epoxy-thiol system relative to that for the unfilled system, $T_p - T_{p0}$, as a function of BN content for the heating rate of 5 K/min. Effect of platelet size: 2 µm, blue circles; 30 µm, red triangles; 180 µm, grey squares.

Since this interaction between the epoxy matrix and the BN filler is fundamental in respect of the heat transfer by phonon transport in the composite material, this systematic behavior should be compared with the thermal conductivities of these epoxy-thiol composites filled with BN platelets of different sizes. First, however, it is of interest to consider the composition of the cured composites by means of thermogravimetric and density measurements.

3.2. Thermogravimetric Analysis (TGA)

The thermal degradation of the cured systems has been determined by TGA under an inert atmosphere of dry nitrogen, and the weight loss at 10 K/min for the composites with the 30 µm BN platelets is shown in Figure 8; similar results were obtained for the composite samples with 2 and with 180 µm platelets, and for the heating rate of 2 K/min. In addition, the degradation behavior of the epoxy-thiol system without any filler (ETL) was also determined, and that of the BN particles alone were also studied by TGA, though these results are not shown in Figure 8. The degradation behavior is very similar for the composites fabricated with BN platelets of different sizes, as would be expected from our earlier observation that the epoxy network structure is independent of the BN platelet size and content. For each platelet size, the important difference between the various curves is the residual mass at 600 °C, which increases as the BN content increases.

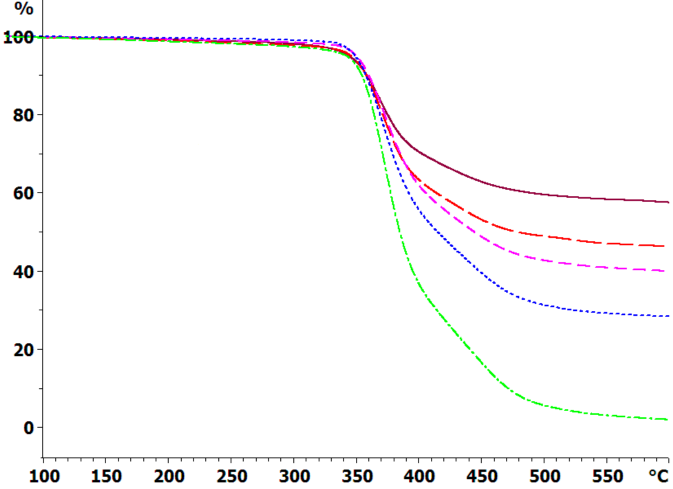


Figure 8. TGA curves of sample mass versus temperature for the fully cured ETLBN30-*y* system at 10 K/min in an inert atmosphere: dash-dotted, green, *y* = 0; dotted, blue, *y* = 30; short dash, pink, *y* = 50; long dash, red, *y* = 60; full line, purple, *y* = 70.

The cured epoxy-thiol without any filler, ETL, leaves a residue of 4.5 ± 2.5%, while the BN particles alone leave a residue of 97 ± 2%. Taking a 60:40 mass ratio for the stoichiometric epoxy:thiol ratio, with 2 wt % LC-80 initiator, then the anticipated residues for the different BN contents can be calculated as: 10.2 ± 2.5% for ETLBN*x*-10; 23.2 ± 2.4% for ETLBN*x*-30; 38.9 ± 2.3% for ETLBN*x*-50; 48.0 ± 2.2% for ETLBN*x*-60; 58.2 ± 2.2% for ETLBN*x*-70, independently of the size, *x*, of the platelets. The average values obtained by TGA for the two different heating rates of 2 and 10 K/min are plotted as a function of these theoretical values in Figure 9. It can be seen that the correlation is very good, confirming thus the BN contents of the different composite samples as well as supporting the conclusion that the epoxy network structure is independent of the filler size and content.

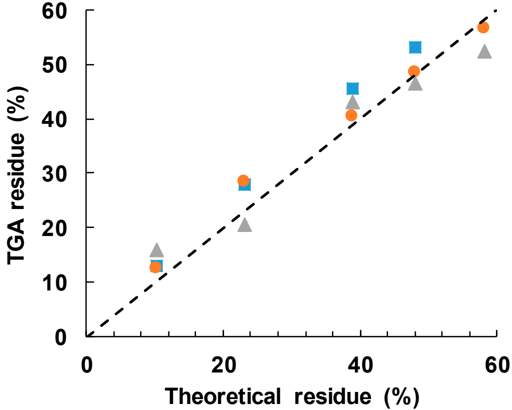


Figure 9. Measured TGA residue after degradation to 600 °C as a function of the theoretical value: 2 μm, blue squares; 30 μm, orange circles; 180 μm, grey triangles. The dashed line has a slope of unity.

3.3. *Density Measurements*

In order to achieve a high thermal conductivity in these samples, it is important that they be free from voids. A good way to check for the absence of voids in the cured samples is by means of density measurements, and the results are shown in Figure 10 as a function of BN vol %. If it is assumed that the volumes of the components that make up the epoxy-thiol-BN composite are additive, then, using the densities of the various components (epoxy 1.17; thiol 1.28, BN 2.1 g/mL), an approximate calculation of the anticipated density of any of the compositions listed in Table 1 can be made. The dependence of this calculated density on the BN content is indicated in Figure 10 by the full yellow line, where it can be seen that, apart from the results for the highest BN content of 44.7 vol %, the measured densities are all higher than the predicted values. The reason for this is that, during the epoxy-thiol reaction, the volumes are not in fact additive, but there is typically a 4% volume shrinkage on cure. When this shrinkage is taken into account, the predicted densities follow the dashed blue trend-line shown in Figure 10, in good agreement with the measured values except for those at 44.7 vol %. There is probably a significant void content in this composite with the highest BN content; the uncured mixture was a very stiff paste, and the degassing procedure would not eliminate any air bubbles introduced during the mixing process. This is likely to have an impact on the thermal conductivity, discussed shortly.

3.4. *Thermal Conductivity*

The dependence of thermal conductivity on BN content is shown in Figure 11. As expected, and as has been observed in the large majority of studies of such systems [reference 8 gives a compilation], the thermal conductivity increases with BN content, and more so the greater is the BN content, giving an upward curvature to the dependence. The highest vol % of 44.7% represents the approximate limit that can be achieved with the simple mixing procedures adopted here, as the mixture becomes a very stiff paste at these BN contents, and is intractable for higher concentrations. Indeed, the vol % of 44.7% cannot be achieved for the samples with 2 μm platelets, as explained in an earlier section.

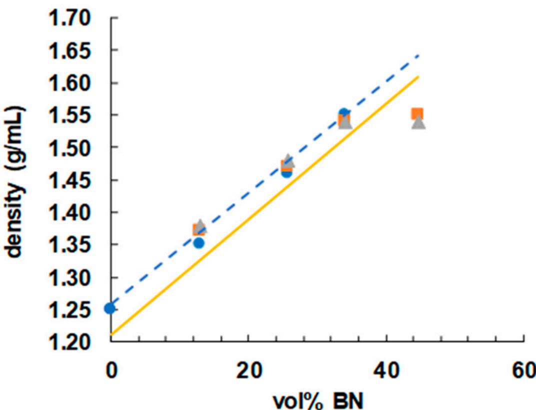


Figure 10. Density as a function of vol % BN for epoxy-thiol samples with different BN platelet sizes: 2 µm, blue circles; 30 µm, orange squares; 180 µm, grey triangles.

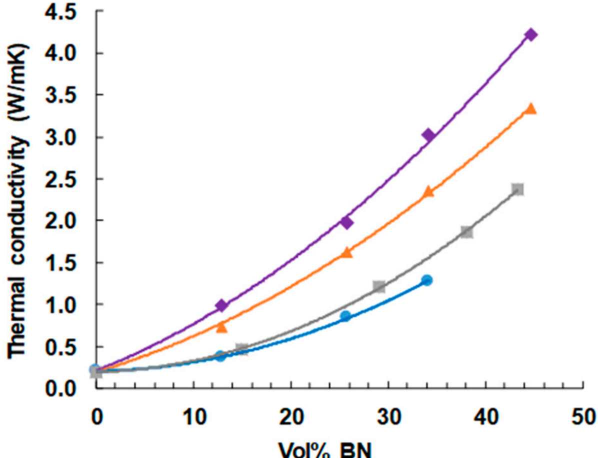


Figure 11. Thermal conductivity of ETLBN and EJBN samples as a function of the BN content: ETLBN2, blue circles; EJBN30, grey squares; ETLBN30, orange triangles; ETLBN180, purple diamonds.

It can also be seen very clearly that the thermal conductivity increases systematically with increasing BN platelet size. In this study, we have not made use of any surface treatment of the BN particles or of any coupling agent to improve the contact between particles and matrix. Furthermore, the BN particles all have the same shape (platelets), as well as all being from the same supplier (Saint Gobain). There can therefore be no doubt that increasing BN particle size results in an increase in the thermal conductivity when composites with the same filler content are compared. This confirms what the majority of studies have suggested, but which until now has been unclear as a consequence of the possible influence of the other parameters, which have been eliminated in the present study.

The increase of thermal conductivity with BN particle size can be understood from a consideration of the interface between particles and matrix, and of the geometry of the particles. In view of the very high value of thermal conductivity of hexagonal BN (600 W/mK parallel to the basal plane; 30 W/mK perpendicular to the basal plane), the fact that more limited values are obtained for epoxy-BN composites in general is evidently in part a consequence of the interface between particles and matrix, which presents a resistance to heat flow. Indeed, this is the reason why coupling agents and surface treatments are often introduced into the composite preparation procedure, though not always with a significant improvement in the thermal conductivity. For a given BN content, the larger is the particle size, the smaller is the interfacial area, and hence increased particle size is clearly beneficial. However, if the platelets are considered to be hexagonal with edge size d/2 and thickness t, then the ratio of area:volume is $A/V = 2/t + 8/d\sqrt{3}$. With $t = 0.2$ µm this gives values of A/V of 12.3, 10.2 and 10.0 μm^{-1} for the 2, 30 and 180 µm platelets, respectively; with $t = 1.0$ µm the corresponding values of A/V are

4.3, 2.2 and 2.0. The increase of 20 to 30% in the thermal conductivity between the samples with 30 and 180 µm platelets is difficult to reconcile with the much smaller increase in the corresponding area:volume ratio.

It is in this respect that the geometry of the particles is believed to play an important part, and in particular the anisotropy of the thermal conductivity. The larger platelets provide significantly more continuity in the parallel direction, with a thermal conductivity of 600 W/mK, than do the smaller platelets, and this additional factor results in the highest thermal conductivities of the 180 µm composites.

In fact, these composites with BN platelets of 180 µm, and also those with 30 µm platelets to a certain extent attain values that are significantly larger than most published values for the same BN content [8]. We believe that the reason for this is associated with the improved interface between matrix and particles as a consequence of the use of thiol as the cross-linking agent. This improvement results from the Lewis acid-base interaction between the sulphur of the thiol and the boron of the particles. In order to investigate this interpretation, epoxy-BN composite samples with the 30 µm platelets (EJBN30-*y*) were prepared in which the cross-linking agent was a diamine rather than the thiol. The resulting thermal conductivities as a function of the BN content are included in Figure 11, where it can be seen that they fall significantly below the corresponding values for the epoxy-BN composites cross-linked with thiol. The explanation for this is the matrix-filler interface is enhanced when the sulphur-containing thiol is used.

This distinction between the behaviors of the epoxy-BN composite system filled with 30 µm BN platelets and cured with thiol on the one hand and with diamine on the other was seen earlier in the cure kinetics monitored by DSC, shown in Figure 6. For the composites cured with thiol there is a strong and systematic dependence of the peak temperature on BN content, whereas for the diamine the peak temperature is essentially independent of the filler content. This confirms that there is an interaction between the epoxy-thiol matrix and the BN particles which influences both the cure kinetics and the matrix-filler interface, this latter leading to an increased thermal conductivity, whereas there is no such interaction when epoxy-diamine is used for the matrix. None of the results published by other authors and discussed here made use of thiol as a cross-linking agent, and we attribute the higher thermal conductivity values reported here to the advantageous interactions between the thiol and the filler particles.

3.5. Scanning Electron Microscopy

The nature of the interface between BN particles and epoxy matrix has been investigated by examining the fracture surfaces of the cured samples by Scanning Electron Microscopy (SEM). The fracture surfaces of composite samples with different BN platelet sizes x, where x is 2, 30 and 180 µm, and different contents (ETLBN*x*-30, 12.9; ETLBN*x*-50, 25.7; ETLBN*x*-60, 34.2 vol %) are shown in Figure 12.

It can be seen, particularly for the larger platelet sizes, that there are many BN particles with no epoxy matrix adhering to the flat and smooth surfaces. This is an indication that the interface between the surfaces of the BN particles and the epoxy-thiol matrix is relatively poor, since the fracture has simply separated the matrix and filler along this interface. Nevertheless, this interface is better for the epoxy-thiol composites in comparison with the epoxy-amine composites, as can be seen by a comparison with the fracture surface of a corresponding epoxy-amine composite with a similar vol % of BN, shown in Figure 13. In this Figure, it can be seen that there are distinct resin-rich regions, indicative of a less homogeneous mixture, there is significant porosity, and the separation between the platelets and their surrounding epoxy matrix appears larger for the epoxy-amine composites in comparison with the epoxy-thiol composites. This is consistent with our hypothesis that the epoxy-thiol system gives an improved interaction between matrix and filler.

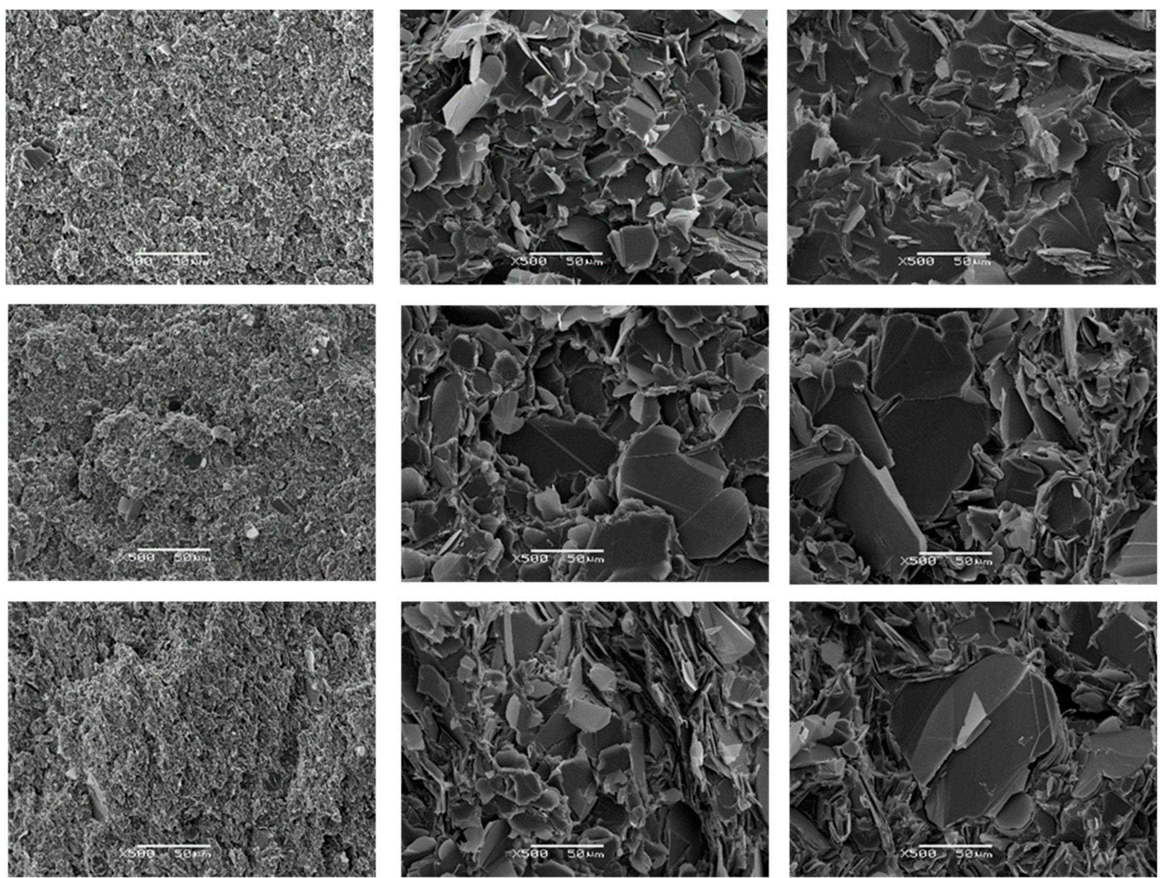


Figure 12. SEM micrographs of epoxy-thiol composites. Left hand column, top to bottom: ETLBN2 -30, -50, -60; middle column, top to bottom: ETLBN30 -30, -50, -60; right hand column, top to bottom: ETLBN180 -30, -50, -60. Magnification 500×, scale bar 50 µm.

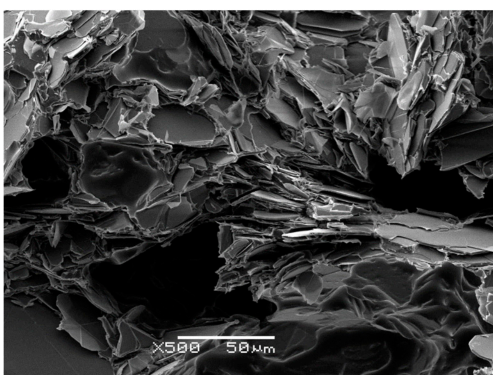


Figure 13. SEM micrograph of an epoxy-composite, EJBN30-60. Magnification 500×, scale bar 50 µm.

In spite of the significant increase in thermal conductivity achieved here by the addition of BN particles, this relatively poor interface, which represents a barrier to phonon transport, is one of the main reasons why the thermal conductivity of these composites does not achieve higher values. Many attempts have been made to improve this interface, for example by surface treatment of the BN particles or the use of coupling agents, with mixed success, as has been discussed briefly above. Likewise, the use of high pressure during the fabrication of these composites, which might be expected to improve the interface, has also been reported [10,14,15,17,26–28], though no direct comparison to observe the effect of pressure has been shown; this is currently under investigation in our laboratory, and will be reported in due course.

4. Conclusions

The thermal conductivity of epoxy-thiol composites filled with boron nitride, BN, particles in the form of platelets has been shown to increase with BN content in the usual way. However, for the same vol% of BN, the thermal conductivity increases with increasing BN particle size; this result clearly demonstrates the effect of the size of the particles, independent of other factors such as particle shape and surface treatment. The thermal conductivities of these epoxy-thiol-BN composites are higher than many reported in the literature, and this is attributed to an improved matrix-particle interface as a consequence of the Lewis acid-base interaction between the thiol and the BN particles. This interpretation is supported by similar experiments with an epoxy-diamine system, for which the thermal conductivity for the same BN content and the same BN platelet size is significantly lower. The cure kinetics likewise shows a difference between the epoxy-thiol and epoxy-diamine composites. For the former, there is a systematic dependence of the cure kinetics on the BN content, which mirrors the thermal conductivity results, whereas for the latter the cure kinetics is essentially independent of the BN content. This result again supports the conclusion that the use of thiol as a cross-linking agent enhances the matrix-filler interface, and hence increases the thermal conductivity.

Author Contributions: The project was conceived by J.H. and the experimental work was undertaken by S.M. as part of his doctoral studies, under the supervision of Y.C., F.R. and J.H. All authors contributed to the analysis of the experimental data, the discussion of the results, and the drafting of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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Paper II

Epoxy composites filled with boron nitride: cure kinetics and the effect of particle shape on the thermal conductivity

ATTENTION¡¡
Pages 90 to 100 of the thesis, containing the article mentioned above are available at the editor's web
https://link.springer.com/article/10.1007/s10973-020-09743-3

Paper III

Densification: a route towards enhanced thermal conductivity of epoxy composites

Article

Densification: A Route towards Enhanced Thermal Conductivity of Epoxy Composites

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Abstract: When an amorphous polymer is cooled under pressure from above its glass transition temperature to room temperature, and then the pressure is released, this results in a densified state of the glass. This procedure applied to an epoxy composite system filled with boron nitride (BN) particles has been shown to increase the density of the composite, reduce its enthalpy, and, most importantly, significantly enhance its thermal conductivity. An epoxy-BN composite with 58 wt% BN platelets of average size 30 µm has been densified by curing under pressures of up to 2.0 MPa and then cooling the cured sample to room temperature before releasing the pressure. It is found that the thermal conductivity is increased from approximately 3 W/mK for a sample cured at ambient pressure to approximately 7 W/mK; in parallel, the density increases from 1.55 to 1.72 ± 0.01 g/cm^3. This densification process is much more effective in enhancing the thermal conductivity than is either simply applying pressure to consolidate the epoxy composite mixture before curing or applying pressure during cure but then removing the pressure before cooling to room temperature; this last procedure results in a thermal conductivity of approximately 5 W/mK. Furthermore, it has been shown that the densification and corresponding effect on the thermal conductivity is reversible; it can be removed by heating above the glass transition temperature and then cooling without pressure and can be reinstated by again heating above the glass transition temperature and then cooling under pressure. This implies that a densified state and an enhanced thermal conductivity can be induced even in a composite prepared without the use of pressure.

Keywords: thermal conductivity; epoxy composites; boron nitride; densification; glass transition; differential scanning calorimetry (DSC)

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1. Introduction

The enhancement of the thermal conductivity of electrically insulating materials used for heat management in many modern electrical and electronic devices has been the objective of a large research effort in recent years. The use of higher frequencies and more compact structures leads to ever increasing service temperatures in such devices, and in order to maintain a satisfactory performance, including a high degree of stability and an acceptable lifetime of operation, it is essential to remove and dissipate the heat generated, usually by conduction through the dielectric layer to a metallic substrate. The dielectric layer must satisfy a number of practical requirements, including good adhesion, ease of processing and low cost, in addition to the physical attributes of electrical insulation and high thermal conductivity. The importance of achieving these objectives can be gauged from the large number of publications devoted to this topic, which have conveniently been collected in several recent comprehensive reviews [1–8].

The requirement for good adhesion leads to epoxy resins being adopted widely as the matrix material, and the present paper is restricted to epoxy composites filled with a suitable inorganic filler. It is well known that the thermal conductivity increases with

filler content, but there are numerous other parameters which can influence the thermal conductivity: filler size, shape and type, and surface functionalization to improve the matrix-filler interface are some of the most widely studied aspects, while three-dimensional structuring and other orientation techniques give significant increases in thermal conductivity in preferred directions, though usually at the expense of fabrication complexity. On the other hand, one approach that has not received much attention to date is the application of pressure during cure of the epoxy matrix. In fact, the rather few studies which make use of pressure for the purpose of enhancing the thermal conductivity appear somewhat unsystematic, so that it is difficult to identify what the advantages are of the use of pressure. For example, some workers simply apply pressure to the uncured mixture to improve its compactness before curing at ambient pressure [9–11], others only partially cure the sample under pressure followed by a post-cure at higher temperature and only at ambient pressure [12,13], while there are several reports of composites cured under pressure but without the magnitude of the pressure being specified [14–18].

In addition, while there are several reports of samples being fully cured under pressure [19–29], no direct comparison is made with a sample prepared without pressure, and in some cases the preparation method is designed specifically to introduce orientation of the filler particles [25,28,29]. More importantly in the present context, though, these studies do not indicate whether or not the samples were cooled from the cure temperature whilst maintaining the applied pressure. This aspect is important because it determines whether or not the final composite is in a densified state. The purpose of the present paper is to demonstrate the efficacy of densification, and for this it is appropriate to explain the process by which a densified state is achieved.

When a glassy polymer such as an epoxy, or indeed any glass-forming system, is cooled at ambient pressure from above to below its glass transition temperature, the resulting glassy state is one of non-equilibrium. This is illustrated schematically in the volume-temperature (*V*-*T*) or enthalpy-temperature (*H*-*T*) diagram in Figure 1: the initial state is equilibrium at A, the final state is the glassy state B at a temperature which is taken here to be room temperature (*RT*), and the transition at C from the equilibrium liquid-like region (AC) to the glassy region (CB) defines the glass transition temperature, T_g, for the cooling rate used. If the sample is allowed to remain at *RT*, it will display physical aging [30], whereby both the volume and the enthalpy decrease and approach the equilibrium state at that temperature, indicated in Figure 1 by the dashed line extrapolation of the equilibrium liquid-like region. As is well known, this physical aging resulting from the structural (volume, enthalpy) changes in the glass is manifest as a change in many mechanical and physical properties of the material.

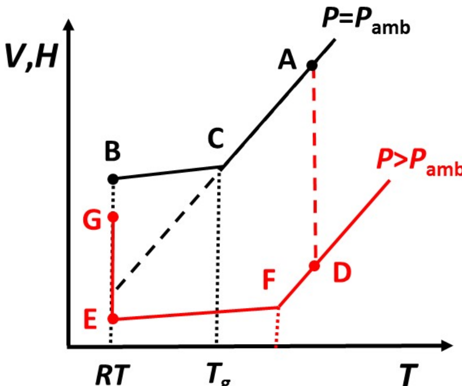


Figure 1. Schematic illustration of the glass transition region and the effect of pressure.

If an epoxy composite system is cured at ambient pressure and at a temperature corresponding to point A in Figure 1, which is above the glass transition temperature of the fully cured system, $T_{g\infty}$, then on cooling to *RT* it will transform to a glass and reach

state B. If, on the other hand, the epoxy composite system is cured under pressure and at the same temperature as before, its initial state after cure will be at D in Figure 1, which we assume here to be above $T_{g\infty}$ for the cured system under pressure, state F in Figure 1; note that the increase in T_g with pressure is much less than 1 °C per MPa [31], and often almost an order of magnitude smaller, which means that the difference between the glass transition temperatures represented by C and F in Figure 1 will be very small under most circumstances.

Once the epoxy composite system has been fully cured under pressure, if it is cooled while maintaining the pressure then it will transform into a glass at point F in Figure 1 and reach state E at *RT*. If the pressure is now released, the sample will recover to state G, the important aspect being that this state is at a volume (and enthalpy) lower than that at state B for the same epoxy system cooled from above T_g at ambient pressure. In other words, the sample is "densified", and this has important consequences for many properties, and in particular for the thermal conductivity, as will be demonstrated in this paper.

Several years ago, Senapati et al. [32] investigated the effect of pressure on one such property, the fast ionic conductivity of some silver iodomolybdate glasses, and reported that the ionic conductivity increased with the application of pressure. The application of pressure during use of these glasses in order to profit from the enhanced ionic conductivity would not be feasible in practice, but densification would offer a practical alternative: the densified glasses would retain the enhanced ionic conductivity induced by the high pressure even after the removal of this pressure. Unfortunately, it was later demonstrated [33] that densifying the silver iodomolybdate glasses in fact resulted in lower ionic conductivities, as a consequence of the ionic conductivity actually decreasing on the application of pressure. In fact, this seems more reasonable; the effect of pressure would be to inhibit the pathways for ion transport.

Nevertheless, the procedure of densification remains valid; indeed, one might anticipate the opposite effect to that observed for ionic conductivity when thermal conductivity is considered. In the epoxy composites considered here, the heat transfer occurs preferentially between the highly conducting filler particles, and the effect of pressure might be envisaged as two-fold: both the reduction of the inter-particle distance and the improvement of the particle-matrix interface. The present work investigates just this effect of densification and demonstrates that it presents a highly effective means of enhancing the thermal conductivity of epoxy composites.

2. Materials and Methods

2.1. Materials

The epoxy resin was a commercial diglycidyl ether of bisphenol-A, DGEBA (Araldite GY240, Huntsman Advanced Materials, Salt Lake City, UT, USA), with a nominal molecular weight per epoxy equivalent (eq) of 182 g/eq, a viscosity of 7000 to 9000 mPa.s at 25 °C, and a density of 1.17 g/cm^3. A thiol, pentaerythritol tetrakis (3-mercaptopropionate) (Sigma-Aldrich, Saint Louis, MO, USA), with a molecular weight of 488.66 g/mol, a viscosity of 500 mPa.s at 23 °C, and a density of 1.28 g/cm^3, was used as the cross-linking agent. The cross-linking reaction of the epoxy with the thiol was initiated by a latent initiator, encapsulated imidazole (LC-80, Technicure, A&C Catalysts, Linden, NJ, USA), in the form of powder.

The filler was boron nitride in the form of platelet particles (Saint-Gobain Boron Nitride, Amherst, NY, USA), with a mean size of 30 μm (code PCTP30). According to the manufacturer's literature [34], these particles have a maximum size of 100 μm, a tap density of 0.6 g/cm^3, and a specific surface area of 1 m^2/g. The filler particles were used as received, without any surface treatment.

2.2. Methods

2.2.1. Sample Preparation

The epoxy and thiol were mixed by hand in a stoichiometric proportion (approximately 60:40 by weight), and the latent initiator was added in the proportion of 2 parts per hundred resin. While a wide range of filler contents has been used in earlier work on these epoxy composite systems [35,36], for the investigation of the effect of densification in this work only a single filler content was used, namely 70% by weight of boron nitride (BN) with respect to the combined weight of epoxy and BN. The weight percentages of each component in the mixture for this sample, denoted ETLBN30-70, are: epoxy, 24.9%; thiol, 16.6%; BN, 58.0%; LC-80, 0.5%. Making an approximate calculation based on the densities of the constituent components, this corresponds to 44.7 volume% of BN.

In order to obtain compressed samples, the required amount of epoxy-thiol-BN mixture was introduced into a Teflon cylinder of internal diameter 15 mm, outside diameter 60 mm, and height 52 mm. A spring, with a constant of 5.95 kN/m acting on a piston, was used to compress the sample by a measured distance and then locked in place, thus maintaining a constant force. The force on the piston was calibrated by measuring the distance by which the spring was compressed; the maximum pressure that could be achieved in this way was 3.0 MPa. The whole assembly was placed in an air-circulating oven at 70 °C for 3 h to effect the cure under the applied pressure. After cure, the pressure was maintained during cooling, and the cured sample was removed at *RT*. The cured samples, in the form of solid cylinders 15 mm diameter and between 25 and 35 mm in length, were cut in half using a diamond wafering saw to give two smooth and flat surfaces for the measurement of the thermal conductivity.

2.2.2. Thermal Conductivity

The thermal conductivity was measured using the Transient Hot Bridge method (Linseis THB-100, Selb, Germany). A heat pulse is applied to a sensor placed between two surfaces of the sample material, and the thermal conductivity is determined from the temperature change ΔT as a function of time [37]. The instrument was calibrated with 5 different standards covering the range from 0.2 to 10 W/mK.

2.2.3. Differential Scanning Calorimetry (DSC)

The DSC instrument (Mettler-Toledo DCS821e, Greifensee, Switzerland) was equipped with a robot sample handler and intracooler (Haake EK90/MT, Vreden, Germany), and was calibrated for both heat flow and temperature using indium. For all experiments, a flow of dry nitrogen at 50 mL/min was used, and the data analysis was made using the STARe software of the instrument.

Powder samples were obtained from the cured composite cylinders by chipping a small amount from the centre of the faces opposite to those used for the measurement of thermal conductivity. Heating scans were made by inserting the encapsulated and weighed samples into the DSC at *RT*, cooling at −20 K/min to 0 °C and then scanning at 10 K/min to 100 °C, well above the T_g of these composites, which is around 52 °C. A second scan, also at 10 K/min, was performed immediately after cooling to 0 °C at −20 K/min when the first scan had been completed.

2.2.4. Density Measurement

The density of the cured samples was measured by Archimedes method. The samples were first weighed in air at room temperature, and then when immersed fully in ethanol, suspended by a fine thread.

3. Results and Discussion

3.1. Effect of Pressure on Thermal Conductivity

The thermal conductivities of samples of composition ETLBN30-70 cured under pressures of 1.4 and 2.0 MPa, and then cooled to *RT* whilst maintaining the pressure, are

given in Table 1, and the effect of pressure on the thermal conductivity is shown in Figure 2. Two samples were prepared at the pressure of 2.0 MPa to check the reproducibility of the results. In addition, data for samples cured at ambient pressure and at 175 kPa, taken from work published elsewhere [38], are also included for comparison. For the pressure of 175 kPa, the pressure was obtained simply by placing a weight on the piston rather than using the compression spring.

Table 1. Thermal conductivity and density of ETLBN30-70 samples.

Sample	Pressure (MPa)	Thermal Conductivity (W/mK)	Density (g/cm^3)
S1	ambient	3.34	1.55
S2	0.175	4.77	1.56
S3	1.4	6.47	1.63
S4	2.0	7.67	1.71
S5	2.0	6.86	1.73

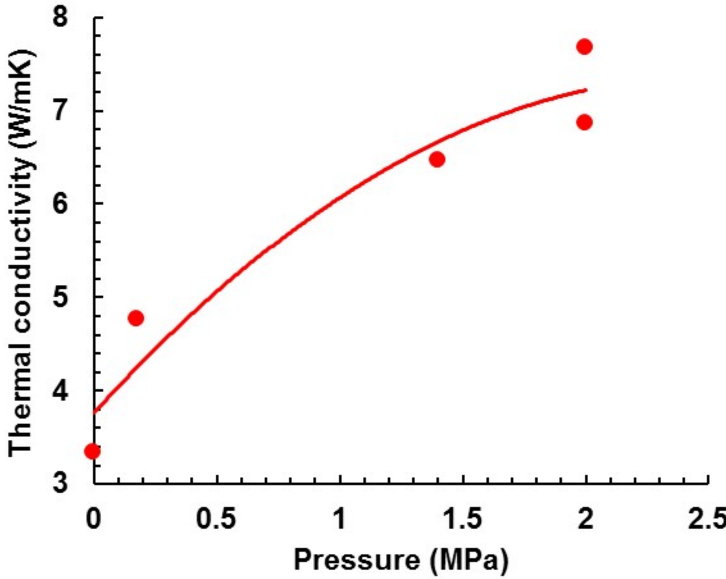
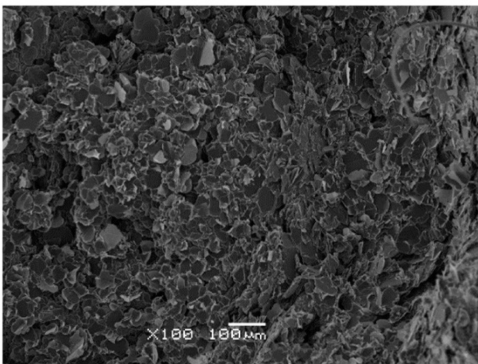


Figure 2. Dependence of thermal conductivity on pressure.

It is evident that the thermal conductivity increases with pressure applied during cure. In fact, the increase in thermal conductivity for the sample cured at 2.0 MPa is remarkable. This increase in thermal conductivity is accompanied by an increase in the density, as can be seen from the values listed in Table 1. With reference to Figure 1, the final states at *RT* of all the samples (S3, S4, S5) cured under high pressure, state G, are confirmed to have higher densities than that of sample S1 cured at ambient pressure, state B. We should point out, however, that although there is some correlation between density and thermal conductivity [38], the latter cannot simply be related directly to the former.

It is interesting to speculate about the mechanism for the enhancement of the thermal conductivity by densification. Figure 3 shows Scanning Electron Microscopy micrographs of the fracture surfaces of two samples: sample S1 cured at ambient pressure, and sample S4 which was densified at a pressure of 2.0 MPa. There can be seen to be a certain amount of consolidation of the composite in the densified state, with a closer connection between matrix and filler particles, implying an improved interface. The closer approach of the individual platelets in the densified sample will also contribute to the enhanced thermal conductivity.



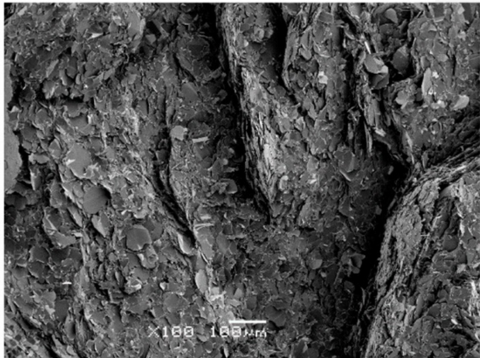


Figure 3. Scanning Electron Microscopy micrographs of two samples of composition ETLBN30-70: left-hand photo for sample cured at ambient pressure, right-hand photo for sample densified at 2.0 MPa. Magnification ×100, scale bar 100 μm.

3.2. Effect of Densification on Enthalpy

In a similar way, a sample in state G would be expected to have a lower enthalpy, which should be manifest in a DSC scan. The DSC scan for sample S5, cured under 2.0 MPa pressure, is shown in Figure 4 together with the second scan. It can be seen that there is indeed an enthalpy difference between the two scans; the greater area under the first scan, by 0.50 J/g with respect to the second scan, represents the enthalpy difference between states B and G in Figure 1, the lower enthalpy of state G being recovered on heating to above the glass transition region.

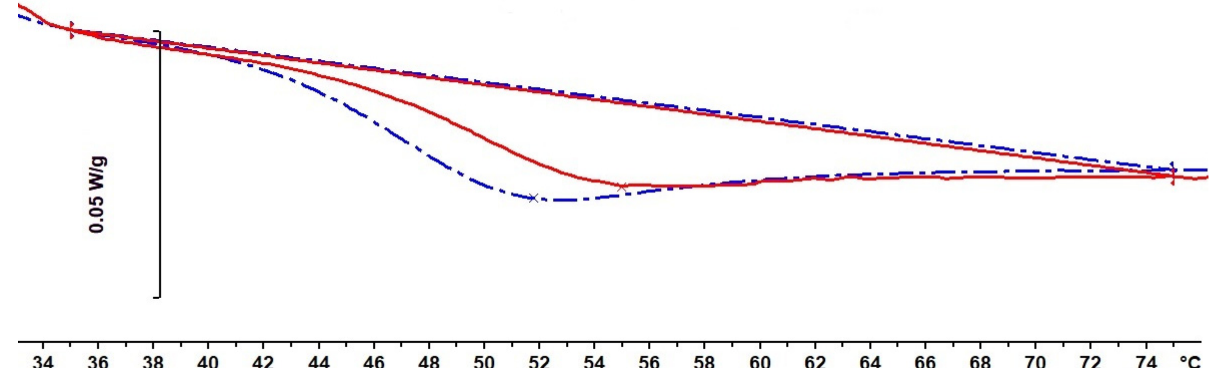


Figure 4. Differential Scanning Calorimetry (DSC) scan at 10 K/min of sample S5 (dash-dotted blue curve), densified at 2.0 MPa, followed by second scan (full red curve). Baselines for the determination of the areas are constructed from 35 °C to 75 °C. Endothermic direction is downwards.

A further demonstration of the effect of densification can be seen in the aging behavior of the densified sample S4. This sample, after curing and then cooling to *RT* under the pressure of 2.0 MPa, and then releasing the pressure, was left for two weeks at *RT* before scanning in the DSC. This meant that the densified sample had aged for two weeks at a temperature about 25 °C below its T_g, and the effect of this aging will be manifest as an enthalpy recovery peak in a DSC scan. Such a scan, together with a second scan immediately afterwards, is shown in Figure 5, where it can be seen that there is an area difference between these two scans, the magnitude being 1.23 J/g, with the endothermic peak of the first scan occurring at 52.5 °C. This area difference corresponds to the enthalpy recovered on heating as a consequence of the combined effects of both densification and aging. The same sample S4, after the recovery of both the densification and aging effects, was again subjected to an aging period of two weeks at *RT*, in order to compare the effects of aging of the densified and "undensified" samples. The DSC scan for this aged

"undensified" sample is also shown in Figure 5, together with another second scan, which superposes almost exactly on the earlier second scan.

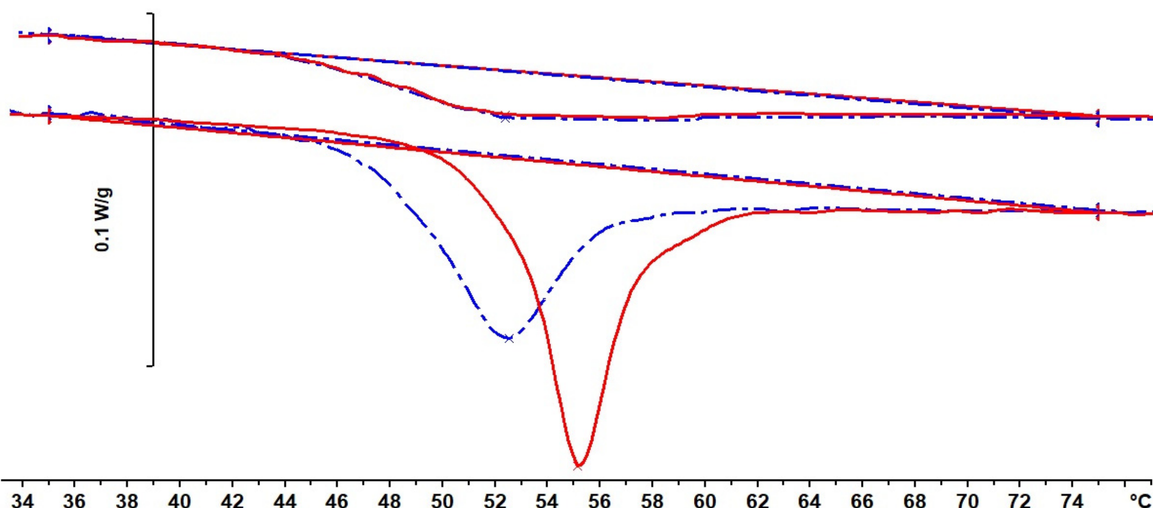


Figure 5. Comparison of DSC scans after aging for two weeks at *RT* for densified (dash-dotted blue curve) and "undensified" (continuous red curve) samples, together with their respective second scans. Baselines for the determination of the areas are constructed from 35 to 75 °C, and the second scans have been displaced vertically for clarity. Endothermic direction is downwards.

It can be seen that the enthalpy recovery of the aged densified and "undensified" samples is quite different: the latter exhibits a much sharper peak, with a maximum at 55.1 °C, significantly higher than that of the densified sample, and the area difference between first and second scans for the "undensified" sample represents an enthalpy recovery of 1.19 J/g. Given that a part of the enthalpy recovered in the densified and aged sample is that corresponding to the densification, which is 0.50 J/g according to the result for sample S5, the effect of aging in the densified sample is evidently much less than that in the "undensified" sample. The reason for this can be understood by reference to Figure 1. The densified sample, immediately after cure and release of the pressure at *RT*, is in state G, at a lower enthalpy than that of the "undensified" sample in state B. Since state G is closer to equilibrium at *RT*, indicated by the dashed line in Figure 1, the rate of aging of the densified sample will be slower than that of the "undensified" sample.

3.3. Reversibility of Densification

An important aspect of the densification is that it is reversible. Consider the densified sample in state G (Figure 1). If it is heated to above its glass transition temperature, and then cooled again to *RT*, it will arrive at state B. This has been demonstrated above by DSC, whereby the second scans are the same, indicating that they always begin from the same state B. The same effect can be seen in the thermal conductivity. The densified sample S5, which had a thermal conductivity of 6.86 W/mK, was reheated to above its glass transition temperature and then cooled again to *RT*, and the thermal conductivity was again measured. It was found now to be 5.44 W/mK, much lower than that of the densified sample, though still larger than that of the "undensified" sample, S1, which was 3.44 W/mK. This implies that the effect of curing under pressure, which results in a more compact epoxy matrix and hence a better matrix-particle interface, but much of which would be recovered on removal of the pressure at the cure temperature, is just one part of the enhancement; the other part results from the "permanent" densification resulting from cooling to *RT* while maintaining the applied pressure. In the present case, for example, the increase in thermal conductivity from 3.44 to 5.44 W/mK would be attributed to the effect

of curing under pressure, while the further increase from 5.44 to 6.86 W/mK would be a consequence of the “permanent” densification.

The term “permanent” is written in this way, in inverted commas, because the densification is only “permanent” until the sample is heated above its glass transition temperature, whereupon the densification effect is removed, while the effect on the thermal conductivity of curing under pressure still remains. Likewise, a densified state can be induced in a sample already cured without the application of pressure. With reference to Figure 1, a sample cured without pressure would be in state B when at *RT*. If pressure is applied and the sample is heated above T_g, it will reach a state between A and D; it will not reach state D because there will be no effect of curing under pressure. Subsequent cooling to *RT* under pressure will lead to a state between G and E, and releasing the pressure will result in a final state between B and G, for which one would anticipate a thermal conductivity between that of the sample cured at ambient pressure and that cured under pressure.

This can be illustrated by the results obtained for sample S5, which had previously been densified (6.86 W/mK) and then for which the densification had been removed by heating above the glass transition region (5.44 W/mK). This sample was then returned to the compression cell, a pressure of 2.0 MPa was applied, and the sample was heated above the glass transition region, allowed to equilibrate for several minutes, and then cooled back to *RT* while maintaining the pressure. After releasing the pressure, the thermal conductivity was then measured and found to be 6.76 W/mK. This demonstrates that the densification is reversible and, importantly, that an enhancement of the thermal conductivity can be achieved, retroactively, in a sample already cured without pressure.

3.4. Comparison with Literature Values

In Figure 2, the effect of pressure and densification on the thermal conductivity of epoxy-BN composites was demonstrated for a single composition, denoted as ETLBN30-70. The effect of pressure on the thermal conductivity of various epoxy-BN composites has been reported on a number of occasions, but the concept of densification has never been considered in this respect. Furthermore, the use of pressure can be made in many different ways, and in many cases it is not possible to identify clearly the experimental procedure. In order to compare our results presented here, for a single composite composition, with other literature values for a wide range of composite compositions, it is necessary to consider also the effect of BN content on the thermal conductivity. A convenient way in which to do this is to make use of the trend curves in a plot of thermal conductivity as a function of BN content, taken from reference 6 and included in Figure 6.

In the compilation of this figure, the values of the maximum thermal conductivity, together with the corresponding BN content, were taken from more than one hundred references for epoxy-BN composites [6]. In order to simplify and display the overall tendency for the dependence of thermal conductivity on BN content, three trend curves were drawn: an upper trend curve, below which more than 95% of the values fell, including values for both isotropic and anisotropic samples; an intermediate trend curve, which represented an approximation to the upper limit of the isotropic thermal conductivities, thus excluding all those samples for which orientation had been deliberately introduced; and a lower trend curve, below which fewer than 5% of all the values of thermal conductivity fell. These trend curves permit the comparison of our present results with the majority of results reported in the literature.

In the simplest case, pressure can be applied to the uncured mixture at RT simply to consolidate it, to remove voids, or to induce some orientation of the BN particles, the pressure being removed before heating the sample in order to cure it [9–11]. On the other hand, there are several reports of samples prepared by curing under controlled pressure-temperature schedules [13,19–29], though some authors do not specify the magnitude of the pressure applied [14–18]. Unfortunately, in no case is there any specific indication of whether or not the cured samples were then cooled under pressure, and hence whether or not they are densified. In contrast, in some cases it is possible to infer that

there is no densification, because the samples are post-cured without the application of pressure [12–14,16,25]. The maximum values of thermal conductivity taken from these references are plotted as a function of the wt% BN in Figure 6, where they are compared with the upper, intermediate, and lower trend curves discussed above.

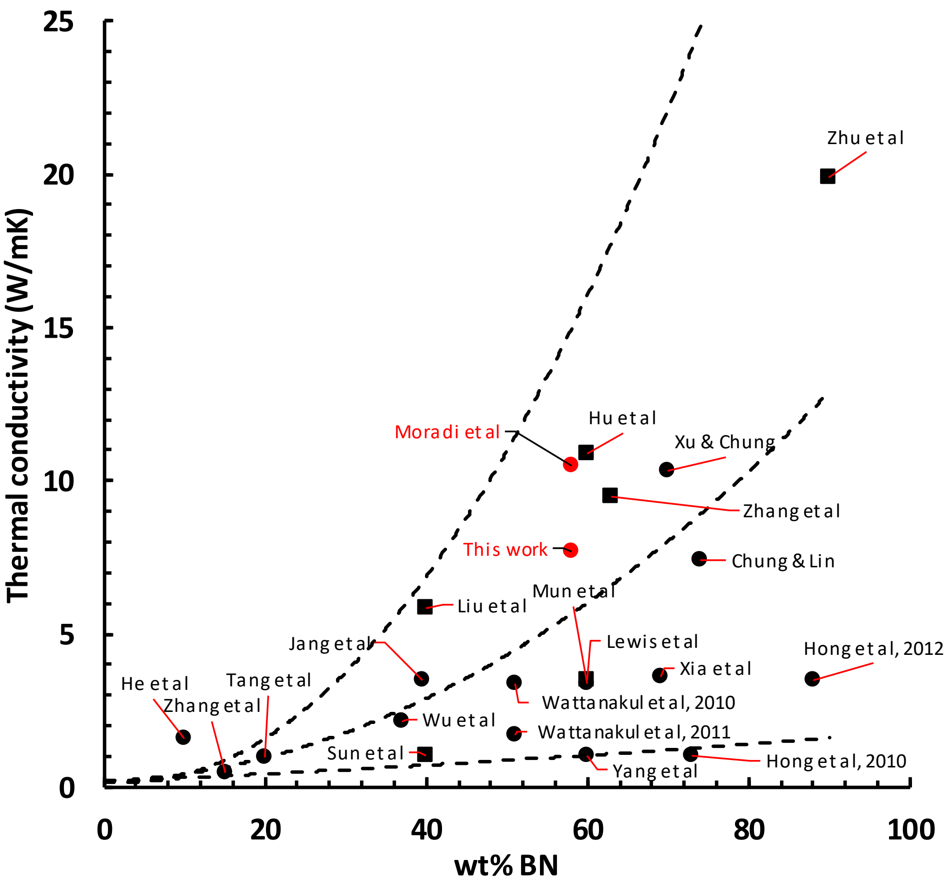


Figure 6. Thermal conductivity as a function of boron nitride (BN) content (wt%) for epoxy-BN samples prepared under pressure. Dashed lines represent upper, intermediate, and lower trend curves [6]. Squares represent oriented samples.

There are several results that are worthy of some comment. First, there is only one value, that of He et al. [14], which falls above the upper trend curve. With only 10 wt% of functionalized BN nanoparticles, these authors achieve a thermal conductivity of 1.6 W/mK, in comparison with a value of only 0.5 W/mK when the BN particles are not surface treated. This result is particularly remarkable as pressure (though an unspecified value) is applied during cure at 100 °C, and then the sample is post-cured without pressure at 150 °C, implying that the final composite is not densified.

Second, many of the values which fall in the region between the intermediate and upper trend curves are a consequence of orientation, the values included in Figure 6 being those in the preferentially oriented direction [9,13,25,28]. Of the remaining values lying in this same region, the results of Jang et al. [15], the present work, and Xu and Chung [19] all follow approximately the same dependence of thermal conductivity on BN content. In the work of Jang et al. [15] and Xu and Chung [19], the BN particles were surface treated, which often leads to improved thermal conductivity, whereas in the present work, the particles were untreated. It is possible, therefore, that the disadvantage of using untreated particles in the present work is compensated by the effects of densification.

The data presented in Figure 6 are for epoxy-BN composites, but for comparison we have also included the data of Tang et al. [27] and Zhang et al. [29], for both of which the composite was a hybrid in which the epoxy matrix was filled with both glass fibres (or

cloth) and BN particles. The thermal conductivity enhancement of the epoxy matrix is therefore due to both the glass and the BN, while the manufacturing procedure introduced significant orientation. Tang et al. [27] report that the addition of 20 wt% BN increases the thermal conductivity of the epoxy/glass/BN hybrid by factors of 5.4 and 3.0 in the in-plane and through-plane directions, respectively. To compare this result with our own values, we have applied an average factor of 4.2 to the unfilled epoxy (0.23 W/mK) to obtain the value of 0.97 W/mK plotted in Figure 6, which falls just on the intermediate trend curve. Likewise, Zhang et al. [29] report an increase in the thermal conductivity by a factor of 2.5, in both the in-plane and through-plane directions, for epoxy/glass/BN hybrids filled with 15 wt% BN. Applying the same factor to the unfilled epoxy (0.2 W/mK) gives a value of 0.50 W/mK for the thermal conductivity of an epoxy/BN composite for comparison with our own results. This is plotted in Figure 6, where it can be seen to fall close to the intermediate trend curve. The application of pressure during cure, 5 MPa in both these cases [27,29], appears therefore to raise the thermal conductivity to the level of the intermediate trend curve, but these values still fall below that which can be obtained by densification.

Finally, the very high value of 10.5 W/mK at 58 wt% BN reported by Moradi et al. [38] corresponds to BN in the form of agglomerates, densified at 2.0 MPa pressure. The effect of pressure on agglomerates has been suggested to be different from that on platelets; whereas pressure brings the matrix and platelets closer and hence improves the interface, the agglomerates are deformed by the pressure such that the surface area of contact between matrix and filler, and between one filler particle and another, is considerably increased, with a resulting dramatic increase in the thermal conductivity [38].

4. Conclusions

It has been demonstrated that the application of pressure during the cure of composites of epoxy and boron nitride has two separate effects: curing under pressure results in a more compact matrix and a better matrix-filler interface, whereas subsequently cooling from the cure temperature to room temperature while maintaining the pressure results in densification. Both effects contribute to an enhancement of the thermal conductivity of the composite. The densification is reversible: heating the densified sample, at ambient pressure, to above its glass transition temperature removes the densification, and the thermal conductivity is consequently reduced. Likewise, though, the densified state can be reintroduced by heating the sample again to above its glass transition temperature, applying pressure, and then cooling to room temperature before releasing the pressure, whereupon the thermal conductivity returns to its original densified value. Comparison is made between these results and others reported in the literature for samples prepared under pressure.

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Paper IV

Thermal conductivity and cure kinetics of epoxy-boron nitride composites—a review

Review

Thermal Conductivity and Cure Kinetics of Epoxy-Boron Nitride Composites—A Review

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Abstract: Epoxy resin composites filled with thermally conductive but electrically insulating particles play an important role in the thermal management of modern electronic devices. Although many types of particles are used for this purpose, including oxides, carbides and nitrides, one of the most widely used fillers is boron nitride (BN). In this review we concentrate specifically on epoxy-BN composites for high thermal conductivity applications. First, the cure kinetics of epoxy composites in general, and of epoxy-BN composites in particular, are discussed separately in terms of the effects of the filler particles on cure parameters and the cured composite. Then, several fundamental aspects of epoxy-BN composites are discussed in terms of their effect on thermal conductivity. These aspects include the following: the filler content; the type of epoxy system used for the matrix; the morphology of the filler particles (platelets, agglomerates) and their size and concentration; the use of surface treatments of the filler particles or of coupling agents; and the composite preparation procedures, for example whether or not solvents are used for dispersion of the filler in the matrix. The dependence of thermal conductivity on filler content, obtained from over one hundred reports in the literature, is examined in detail, and an attempt is made to categorise the effects of the variables and to compare the results obtained by different procedures.

Keywords: epoxy; boron nitride; thermal conductivity; cure kinetics

1. Introduction

Power electronics devices and other applications, such as solid-state relays and light emitting diodes (LED) in which high power density occurs, require an efficient means for the removal of the heat generated during operation. This has become increasingly important because the frequency of operation and power levels have risen in recent years. A good example of this is a consequence of the advances made in respect of LEDs, where technological developments have already brought three watt and five watt LEDs to the market-place, with even higher wattages predicted within the next few years [1]. Examples of applications involving ever increasing power levels include illuminated signs and displays; LED headlights and power steering in the automotive industry; and switches, relays, inverters and power supplies in the power electronics industry. The heat generated by these high power densities results in an increase in the temperature of the devices, which can have a detrimental effect on performance and significantly reduce the lifetime of operation. There are various rules of thumb to estimate the effect of such an increase in operating temperature, for example that the failure rate of an electronic device doubles with every 10 °C increase [2], or that every increase in operating temperature of 10% reduces the service life by 50% [3]. It is crucially important to be able to remove the heat from such devices, and considerable effort has been devoted to this end in recent years. In practice, this is commonly achieved by the use of insulated metal substrates (IMS), in which the copper conductor is bonded to a metal substrate by a dielectric layer, as shown schematically in Figure 1.

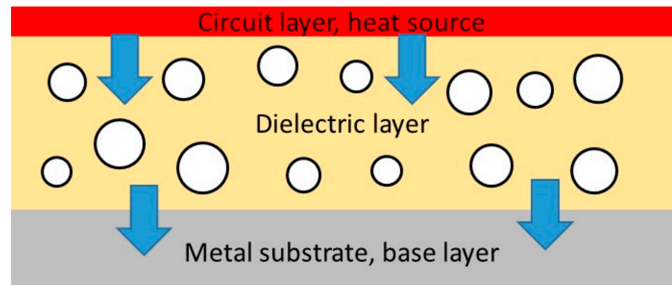

Figure 1. Schematic illustration of an insulated metal substrate (IMS).

There are many commercial IMS systems available, from companies such as Bergquist [1], AI Technology [2], Technoboards Kronach [4] and Ventec International Group [5]. At the heart of all these systems is the dielectric layer, which must offer a variety of properties, including electrical insulation, thermal conductivity, ease of processing and adhesive strength. There are some additional requirements of this dielectric layer, for example the need for the thermal expansion coefficient to be matched to that of the other components, as well as limitations on its thickness, which is usually in the range from 50 to 150 μm. However, the most important aspect from the perspective of this review is thermal conductivity, while bearing in mind the need to accommodate the other requirements. Adhesion is generally achieved by using an epoxy resin as the matrix material, which satisfies the requirement of electrical insulation but has a very low thermal conductivity, typically around 0.2 W/mK [6]. In order to increase the thermal conductivity, a filler is commonly added. This filler must be thermally conductive but electrically insulating, and examples of suitable materials include oxides, such as Al_2O_3, SiO_2 and ZnO [7–10]; carbides, such as silicon carbide (SiC) [11,12]; and nitrides, such as AlN, BN and Si_3N_4 [13,14]. In this way, commercial IMS products are available that offer thermal conductivities typically in the range from 0.8 to 4.2 W/mK [1–5], though values as high as 7.0 [5] and 7.5 W/mK can be found [1]. This represents a significant improvement in the range of from 0.2 to 0.4 W/mK for the traditional FR-4 printed circuit board technology.

There is clearly a wide variety of candidate materials for the dielectric layer, but in this review we consider only boron nitride (BN), on account of its wide application and that it has one of the highest values of thermal conductivity for electrically insulating materials. Hexagonal boron nitride is a white solid material, often referred to as "white graphite" because it has the same plate-like hexagonal structure as graphite and has lubricating properties but, in contrast to graphite, BN is a good electrical insulator and is therefore suitable for IMS application. The thermal conductivity of hexagonal BN is reported to be up to 30 W/mK in the direction perpendicular to the hexagonal planes, and up to 600 W/mK parallel to these planes [15,16]. BN is usually available in the form of powder, the powder particles being either in the form of platelets or agglomerates, and with a range of possible sizes. An example of the grades on offer can be seen in the product list provided by Saint-Gobain [17], which includes platelets with average particles sizes from 2 to 180 μm, and agglomerates, both low density and high density as well as spherical powders, with average sizes from 80 to 300 μm. Figure 2 shows scanning electron microscopy (SEM) micrographs of some of these grades of BN particles.

The fabrication procedure for epoxy-BN composites involves mixing the epoxy resin, curing agent and BN particles, as well as some other components such as the catalyst or accelerator in some cases, and then effecting the cure, usually isothermally or in a series of isothermal stages. Although the thermal conductivity of the final cured product is essentially determined by the BN particles, it might be expected that the curing process could affect the interaction between the epoxy matrix and the BN filler particles. In particular, the matrix-filler interface plays a crucial role in the development of the thermal conductivity in the composite, and any interaction between the matrix and filler would be evident in the curing reaction. Thus, we begin with a review of the cure kinetics of epoxy composites in general, and then of epoxy-BN composites in particular. We then examine in more detail how

the thermal conductivity of the cured composites depends on the numerous parameters involved in their fabrication.

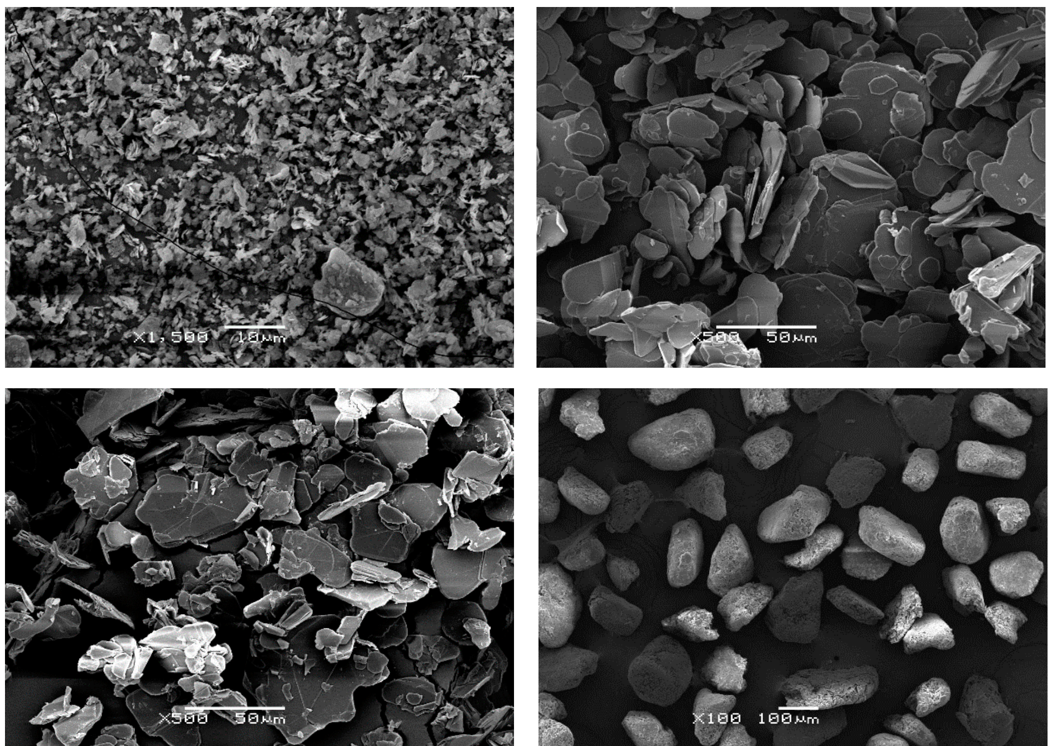

Figure 2. SEM micrographs of boron nitride (BN) particles from Saint-Gobain [17]: top left, 2 µm platelets, PCTP2; top right, 30 µm platelets, PCTP30; bottom left, 180 µm platelets, PCTP30D; bottom right, 120 µm low density agglomerates, PCTL7MHF.

2. Cure Kinetics

2.1. General Aspects

The fabrication of epoxy-BN composites requires the curing of the epoxy matrix. In practice, this will usually be an isothermal cure, either in a single stage or in two stages, with an initial partial cure at a temperature less than the glass transition temperature of the fully cured system, $T_{g\infty}$, followed by a post-cure at a temperature higher than $T_{g\infty}$. It might be expected that the details of the cure procedure, for example the isothermal cure temperature, could have an influence on the properties of the cured composite, such as the mechanical and thermal properties, and including the thermal conductivity. For this reason, it is interesting to investigate the cure kinetics, the analysis of which usually involves not only isothermal but also non-isothermal cure.

The experimental study of cure kinetics is typically made by differential scanning calorimetry (DSC), and the analysis is based on one of a number of relatively simple kinetic equations. All of these equations describe the time (t) dependence of the degree of cure (α), the latter being determined experimentally as the ratio of the heat of reaction at time t, $\Delta H(t)$, to the total heat of reaction, ΔH_∞, for a fully cured sample:

$$\alpha = \frac{\Delta H(t)}{\Delta H_\infty} \tag{1}$$

The heat of reaction at time t is obtained from the area under the DSC curve of heat flow up to this time, while the total heat of reaction requires the area under the complete cure curve, and both are usually expressed per unit of mass of sample, in J/g. If no vitrification occurs during the curing

process, then the cure can be described by a chemical rate equation in which the rate of cure is both temperature (T) dependent and a function of the degree of cure:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{2}$$

In this equation, $k(T)$ is the rate constant and depends on temperature according to an Arrhenius equation:

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \tag{3}$$

where A is the pre-exponential factor or frequency factor, R is the universal gas constant and E is the activation energy.

The function $f(\alpha)$ depends on the kinetic model considered most appropriate for the given circumstances. For epoxy cure, the autocatalytic model is one of the most widely used, and the function can be expressed by the Sestak–Berggren equation:

$$f(\alpha) = \alpha^m(1-\alpha)^n \tag{4}$$

where the kinetic exponents m and n often sum to approximately two. One problem with this equation is that, without an initial non-zero value for the degree of cure, α, the reaction will never start. Furthermore, the equation requires that the initial reaction rate be zero, whereas this is not necessarily the case. An alternative equation for the chemical reaction rate, which overcomes these problems, is the Kamal equation:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \tag{5}$$

where both rate constants k_1 and k_2 have Arrhenius temperature dependences, with different activation energies and pre-exponential factors. The initial reaction rate in the Kamal equation is given by k_1.

The above equations have been rather widely used for the analysis of the cure kinetics of unfilled epoxy systems, with a variety of different resins, curing agents and initiators or accelerators. This approach has been adopted by many authors (e.g., [18–24]) to interpret aspects of the reaction and of the cured system in terms of the parameters of the model (A, E, m and n).

2.2. Epoxy Composites

In epoxy composite systems, on the other hand, there is the additional effect of the filler to be considered, and here two different aspects can be identified: the effect of the filler on the cure kinetics and the effect on the properties of the cured composite. Considering the latter aspect, the purpose of the filler is clearly to modify the properties of the composite. For example, glass, carbon or aramid fibres are incorporated into an epoxy matrix in order to improve the mechanical properties, and many fillers are added to reduce the thermal expansion coefficient or even simply to reduce the cost of the material. In this context, the boron nitride filler is added in order to enhance the thermal conductivity of the composite. Besides these changes deliberately induced in the properties of the overall composite material, there is the question of the effect of the filler on the epoxy matrix, and here the situation is not well understood. For example, it is commonly believed that increasing the filler content will lead to an increase in the glass transition temperature, T_g, of the cured composite because the filler particles will provide a restriction of the molecular mobility of the epoxy matrix. However, a literature search using the key words or phrases "effect of fillers", "glass transition temperature" and "epoxy" gives nearly 400 results in the Web of Science database, many of which conclude that there is no significant effect of filler on T_g, though there are reports of both an increase and a decrease in T_g on the addition of a filler, as the following examples illustrate.

Many years ago, Filyanov [25] alluded to the generally held view that fillers restrict molecular mobility when he wrote "in contradistinction to the majority of cases where the glass transition

temperature of an epoxy resin rises during filling", referring to his own results for an epoxy resin filled with glass microspheres, which instead featured a marked reduction in T_g. This effect was attributed to an "adsorptive-adhesional interaction between resin components and the filler surface". The dominant role of the matrix-filler interface, and in particular "enhanced polymer dynamics", was also cited by Sun et al. [26] to explain why they observed a decrease in T_g for epoxy-silica nanocomposites in comparison with the corresponding composites with micron-sized fillers. However, it is not clear why these very general interface attributes should apply in these situations and not in others. Indeed, Stevens and Richardson [27] investigated a silica-filled epoxy-anhydride system, for which silanol groups at the silica surfaces were potential hydrogen-bonding sites for hydroxyl and epoxide groups, and therefore with much greater potential for filler-matrix interaction, but they concluded that there was no significant filler effect on T_g in the fully cured composites. That the situation is complicated by other interfacial aspects was highlighted more recently in a review [28] of the effect of carbon nanotubes on the T_g of epoxy nanocomposites; the bundling tendency of single-wall nanotubes can lead to a reduction in T_g, whereas T_g increases or remains constant for multi-wall nanotubes.

On the other hand, the following examples are representative of many (probably the majority of) reports which suggest that T_g is essentially independent of the filler content in epoxy composites. Linec and Music [29] investigated the effects of the addition of silica of different shape, specific surface area and chemical structure, including crystalline and fused silica, in epoxy moulding compounds and found that T_g remained almost constant. Dorigato and Pegoretti [30] introduced both carbon black (CB) and carbon nanofibers (NF) into an epoxy matrix with in situ generated silver nanoparticles and concluded that T_g was "slightly reduced"; for example, for 4 wt.% nanofiller the reduction was about 5.5 °C for the CB nanofiller, but only about 2.6 °C for NF. In particular, these authors could not detect any clear trend of T_g with the relative proportions of the two carbonaceous nanofillers, in agreement with their earlier observations with various other nanofilled thermosets. They attributed this result to two competing effects of the nanofillers: an increase in T_g due to "chain blocking mechanisms", and a reduction in T_g due to a reduction in the degree of cross-linking as a consequence of matrix-filler interactions and increased viscosity.

The complexity of the situation is illustrated by another result. In ternary epoxy nanocomposites filled with 5 wt.% titanium dioxide nanoparticles and halloysite nanotubes (HNT), Vijayan et al. [31] found a small decrease (about 3 °C) in T_g for epoxy-TiO_2 composites, a significant increase (>10 °C) for epoxy-HNT composites, but essentially no change for the ternary composites. While the authors asserted that HNT can restrict the segmental motion of cross-links near the matrix-HNT interface, thus giving rise to the observed increase in T_g, they did not explain why T_g remained essentially constant for the ternary composites. More generally, Kang et al. [32] concluded that composites with a weak filler-matrix interface show essentially no change in T_g, whereas a strong interface promotes an increase in T_g.

In the above discussion of the properties of the epoxy matrix in cured composites, the glass transition is associated with the network structure of the cured epoxy, which is developed during the course of the previous curing schedule. Consequently, we turn now to the second aspect mentioned above, namely the effect of the filler type and content on the cure kinetics in epoxy composites. First, we will consider the situation in general, before reviewing the curing process of epoxy-BN composites in particular.

Although many of the fillers used for epoxy composites are essentially inert with respect to epoxy, and hence might not be expected to have any effect on the cure reaction, in practice there are several chemical species which can occur at the surface of filler particles that can influence the reaction. Consequently, it is common to see reports on the effect of fillers in an epoxy composite cure, and the most obvious effect is whether the reaction is accelerated or retarded by the presence of the filler. This can be assessed simply by examining whether there is a reduction or increase, respectively, in the peak temperature, T_p, during a non-isothermal cure or in the time to the peak exotherm, t_p, in an isothermal cure. Alternatively, the kinetic Equations (1)–(5) can be used to fit the cure curves and

obtain the values of the parameters, in particular the activation energy, E, and the pre-exponential factor, A. In this respect it should be pointed out that it is sometimes assumed that a reduction in E implies an acceleration of the reaction, but this is incorrect: the reaction rate is described by the rate constant k, which is a function of both E and A. Thus, it is possible for there to be a reduction in E and yet a slowing down of the reaction as a consequence of a concurrent reduction in A. Comment on this will be made when discussing some of the examples considered below.

The most common observation is that the cure reaction of epoxy composites is accelerated by the addition of fillers (e.g., [33–43]), most of these systems being based on DGEBA epoxy resin, and cured with methylene dianiline [33,34], anhydride [36,42], or amines [35,39,43]. A wide variety of fillers is included here: zeolite [33,34,36], zirconium tungstate [37], alumina [39,42], barium ferrite/aniline [41], carbon black and carbon fibres [35], aluminium nitride [40], silica [38] and mallow fibres [43]. The advance of the curing process is typically identified by a reduction in the peak exotherm temperature in a non-isothermal cure or by a decrease in the time to the peak exotherm in an isothermal cure. However, while a systematic effect of filler content might be expected, in some cases [37,40,42] the effect reported is an initial acceleration, apparently simply as a consequence of the addition of the filler, but with no further significant or systematic change as the filler content is further increased.

Nevertheless, the acceleration effect of adding fillers is not always clearly evident. For example, Olivier et al. [44] monitored the cure kinetics of a polyepoxy cured with polyamineaniline and filled with either polyamide-12 or a ceramic. During non-isothermal cure, the peak temperature clearly decreased as the content of either filler increased, indicating an acceleration effect. However, when these authors analysed the isothermal cure, they found that, for a given cure time, the degree of cure was lower for the filled samples than for the pure epoxy, and hence concluded that the fillers slow down the reaction. However, there is some inconsistency, in that the heat of reaction, apparently per unit mass of epoxy, decreased as the filler content increased, which could affect the isothermal cure analysis. Likewise, Sanctuary et al. [45] reported different effects in non-isothermal and isothermal cures for a DGEBA epoxy resin filled with alumina nanoparticles and cured with a triamine. Since the isothermal cure was carried out at 25 °C, which is less than $T_{g\infty}$, it involves vitrification, which is detected by temperature-modulated DSC. With increasing filler content in the isothermal cure, the magnitude of the heat flow increased and the vitrification time was reduced, indicating an acceleration of the reaction by the filler. On the other hand, these authors obtained the surprising result that the non-isothermal cure kinetics is essentially unaffected by filler content and discuss this in terms of an interphase region between the nanoparticles and the epoxy matrix, in which there is reduced molecular mobility.

Differences between the effects of fillers in non-isothermal and isothermal cure can also be inferred from the early results of Dutta and Ryan [46]. The isothermal cure of a DGEBA epoxy resin cured with a diamine and filled with carbon black or silica at 6 wt.% content was advanced relative to the unfilled system, and more so for the former filler. However, in the non-isothermal cure, while for the same 6 wt.% content the peak exotherm temperature was reduced for both fillers compared to the unfilled system, and more so for the carbon black, there was no systematic effect of other filler contents. For carbon black the cure was apparently retarded for 1 wt.% and 4 wt.% but was slightly advanced for 2 wt.%, while for silica it was also retarded for 4 wt.% content. In the non-isothermal cure of a DGEBA epoxy filled with quartz flour, de Miranda et al. [47] also reported that the effect of the filler on cure kinetics depends on the range of the filler content. For up to 10 wt.% filler, the rate constants for the filled and unfilled systems are the same for any given degree of cure, whereas at 20 wt.% and 30 wt.% content, the rate constants are approximately equal but lower than that for the unfilled system. This suggests that a filler content greater than 10 wt.% will slow down the reaction, in contrast to the generally observed effect. However, the reported peak exotherm temperatures at 10 °C/min for the filled systems, from 2 to 30 wt.%, did not vary systematically, and their variation is much smaller than the difference between their average value and that of the unfilled resin. Accordingly, it is difficult to draw any firm conclusions from these results.

There are a few other reports of a decrease in the cure rate as a consequence of the presence of fillers. Omrani et al. [48] studied a DGEBA epoxy filled with barium carbonate at up to 15 parts per hundred resin (phr) and found that the peak exotherm temperature increased by 10 °C for the highest filler content, indicating a slowing down of the reaction rate. However, a large variability in the heat of reaction between repeated experiments suggested a heterogeneous filler dispersion, which could have influenced the cure kinetics and may also have been responsible for an anomalous variation of the glass transition temperature. Zabihi et al. [49] investigated a DGEBA epoxy, anhydride cured and filled with polythiophene nanoparticles, and found that in non-isothermal cure the peak exotherm temperature increased by between 10 and 15 °C with an addition of only 1% nanoparticles. Just as for Omrani et al. [48], however, they also reported a large variation in the heat of reaction for filler loadings greater than 1%, again attributed to an inhomogeneous distribution and agglomeration of the nanoparticles. Similar results were presented by Karasinski et al. [50], who studied the cure kinetics of a DGEBA epoxy cured with *o*-tolyl biguanidine and filled with nanoparticles of either γ-alumina or zinc oxide at a loading of 3 phr, corresponding to volume percentages of 1.2 and 0.6, respectively. These authors also reported a slight tendency of the nanoparticles to cluster, with the more homogeneous distribution being found for zinc oxide. For these epoxy composites, the peak exotherm temperature increases markedly, for example by more than 10 °C for the alumina composites and by more than 30 °C for the zinc oxide composites, at the heating rate of 10 K/min. However, this is accompanied by a significant increase in the heat of reaction for the nanocomposites, which is attributed to a higher cross-linking density. This is consistent with an increase in $T_{g\infty}$ for the nanocomposites with respect to the unfilled system, but probably indicates that the presence of benzoin as a degassing agent and of poly(*n*-butylacrylate) as a plasticizer have modified the cure reaction, thus making it difficult to distinguish the effect of the filler nanoparticles on the cure kinetics.

In summary, it is probably true to say that it is not possible to draw any firm conclusions from the reports in the literature where the cure of epoxy composites is apparently retarded by the addition of the filler particles: the heat of reaction is often not constant, there are different effects in isothermal and non-isothermal cure, there are unsystematic variations with the filler content, and sometimes inhomogeneous dispersion or agglomeration of filler particles occurs.

There are also reports of the fillers having no effect on the cure kinetics of epoxy composites. Tarrío-Saavedra et al. [51] show DSC non-isothermal curves for an amine-cured epoxy filled with up to 50 wt.% fumed silica, where the peak exotherm temperature is unaffected by the filler content. As the title of their paper suggests, however, there are some unusual observations, which throw some doubt on the interpretation of the effect of the filler on the cure kinetics. For example, the heat of reaction varies in a non-systematic way with filler content, which the authors themselves interpret as agglomeration of the nanoparticles and a possible loss of stoichiometry in the reaction. On the other hand, Ghaffari et al. [52] investigated the cure kinetics of a DGEBA epoxy cured with polyaminoamide, but with only a single and very small (1 wt.%) content of either micro- or nano-sized zinc oxide particles. Furthermore, they used only isothermal cure, for which there is very little difference between the iso-conversional cure times as a function of the inverse temperature for the different composite systems. These plots, as well as a model-fitting procedure, allowed the evaluation of the activation energy, E, which decreased for the micro-composite and, to an even greater extent, for the nano-composite. This reduction in E should not, however, be associated with an advance of the reaction for the filled systems, as it was accompanied by a significant reduction in the pre-exponential factor, A, and again to a greater extent for the nano-filler compared with the micro-filler.

Finally, another effect, namely that of the surface treatment of the filler particles, was investigated by Harsch et al. [53], who analysed the cure kinetics of a cycloaliphatic epoxy cured with anhydride and filled with a variety of fillers, including silica, both with and without a surface treatment. These authors found that the addition of the surface-treated filler reduced the activation energy, E, and the pre-exponential factor, A, while they remained unaffected by the untreated filler, and they

concluded that the surface-treated filler accelerates the reaction. These authors did not, however, offer any explanation for this observation.

A compilation of all the results for non-isothermal cure is given in Figures 3 and 4. The filled symbols correspond to the data obtained for epoxy composites with fillers other than BN, while the open symbols correspond to epoxy-BN composites. In Figure 3, data are included for the heating rate of 10 K/min only, whereas in Figure 4 all heating rates are included. The correspondence between the symbols used in Figures 3 and 4 and the references from which the data were obtained is given in the legends, but can be seen more clearly by accessing Supplementary Material 1. For filler particles other than BN, the filled symbols in Figures 3 and 4 demonstrate the tendency for the peak temperature T_p to decrease with the addition of filler particles in the epoxy composites, particularly at higher filler contents.

In the light of the compilation and discussion above, where it might be concluded that the cure reaction of epoxy composites is usually accelerated by the addition of fillers, it is interesting to consider the explanations that are given for why this acceleration might occur. In nearly all cases in which acceleration of the reaction occurs, this is attributed to the catalytic effect of hydroxyl groups present on the surface of the various filler particles, be they zeolite [33,34,36], zirconium tungstate [37], nano-SiO_2 [38], nano-alumina [39], or nano-AlN particles [40]. It should be noted that there is no need for the surface of the filler particles to be modified for there to be a catalytic effect; for example, for the epoxy-zeolite composites [33,34,36], the filler was natural zeolite without any surface treatment. Likewise, Sanctuary et al. [45] attributed the acceleration of the isothermal cure of epoxy/nano-alumina composites to the surface catalytic action of –OH groups and argued that the lack of any acceleration effect in non-isothermal cure was a consequence of the reduction of the molecular mobility by the "interphases". More generally, Dutta and Ryan [46] considered that the acceleration of epoxy cure when filled with carbon black was due to the presence of numerous constituents found on the surface of the carbon black, principally phenolics, carboxylics, quinones, hydroquinones and lactones. In contrast, they attributed the lack of any catalytic effect when the epoxy is filled with silica to either the lower specific surface area (SSA) or the relatively complex-free surface of the silica.

In some cases, the catalytic effect is reported to be modified by surface treatment of the filler particles, though there is no consensus on the effect. Haman et al. [37] consider that silane functionalisation of zirconium tungstate particles retards the cure as a consequence of the shielding of –OH groups by silane, while Yu et al. [40] consider that the catalytic effect of their silane treated nano-AlN particles results from both –OH and –NH_2 groups on the surface. The catalytic effect of the amino group was also proposed by Bi et al. [42] for the cure of their epoxy composites filled with amino-functionalised alumina particles. Similarly, Harsch et al. [53], as noted above, only found an acceleration of the cure rate when the filler particles are surface treated.

Some other explanations have been given for the acceleration of the cure for some particular circumstances. Wu et al. [35] observed that the incorporation of activated carbon fibres into their composites accelerated the reaction, and that the activation of the carbon fibres simultaneously increased their SSA significantly. On the other hand, when the carbon fibres were ozone treated, there was neither an acceleration of the cure nor any significant change in the SSA of the fibres. Accordingly, these authors associated the acceleration of the reaction with an increase in the SSA, an observation that accords with that of Dutta and Ryan [46]. In another particular situation, for epoxy/barium ferrite/polyaniline composites, Saad et al. [41] considered that the protonated amine-imine groups of polyaniline act as epoxy-opening initiators to accelerate the cure reaction. Finally, in a quite different epoxy composite system, in which mallow fibres give rise to a very slight acceleration of the cure, Nascimento et al. [43] concluded that mallow fibres act as "nucleation sites".

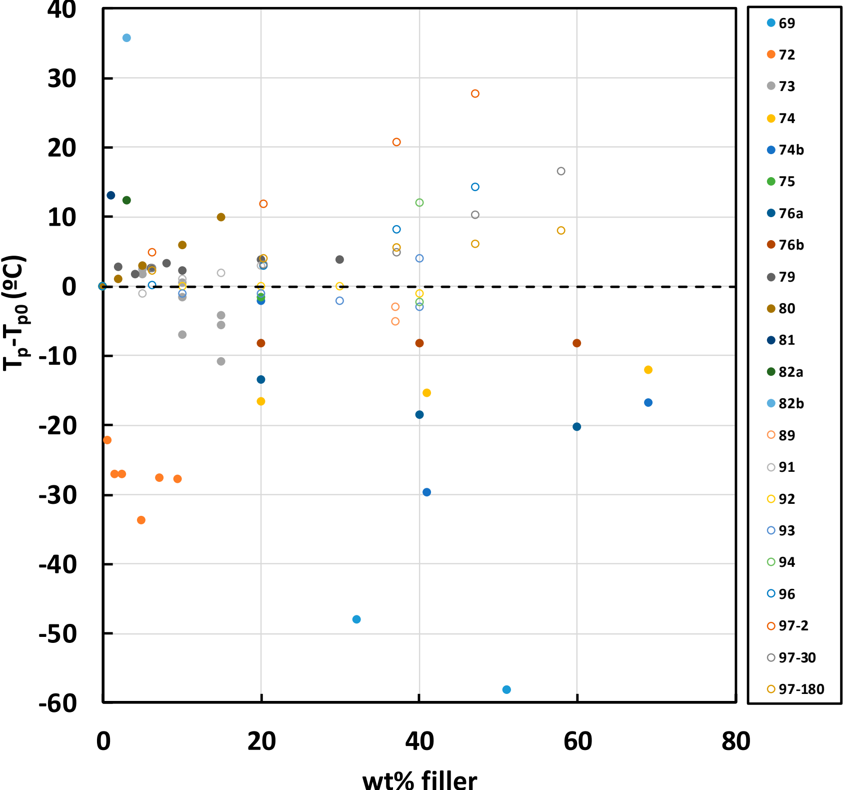

Figure 3. Effect of filler content in epoxy composites on the peak temperature, in non-isothermal cure at 10 K/min, relative to that of the unfilled system. Heating rate 10 K/min. Open symbols: boron nitride filler; filled symbols: other fillers.

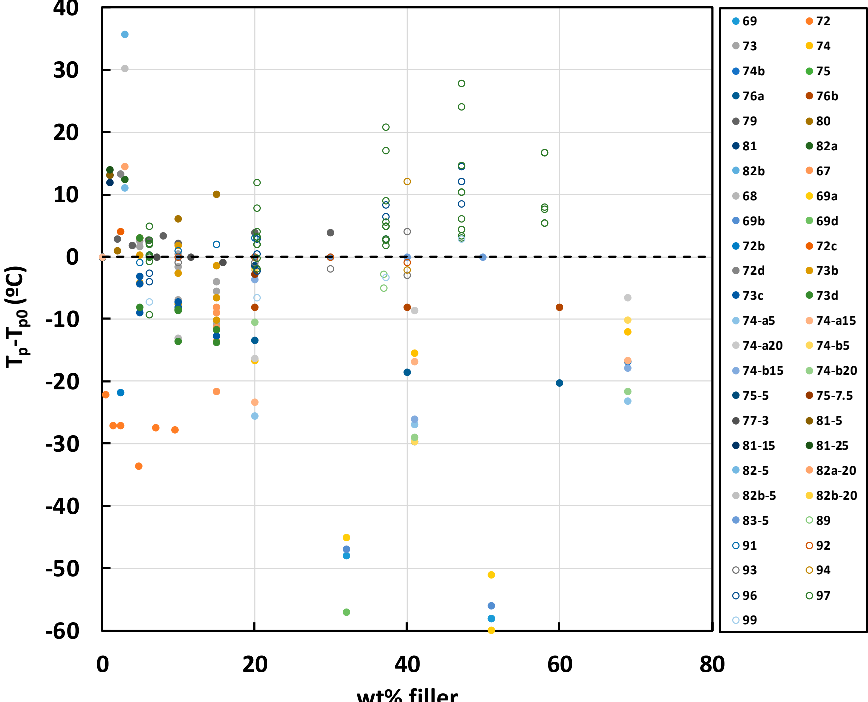

Figure 4. Effect of filler content in epoxy composites on the peak temperature in non-isothermal cure, relative to that of the unfilled system. No distinction is made here between results obtained at different heating rates. Open symbols: boron nitride filler; filled symbols: other fillers.

2.3. Epoxy-BN Composites

The general aspects of the cure kinetics of epoxy composites discussed above can now be compared with the particular behaviour of epoxy-BN composites. However, apart from the contributions of two particular research groups—Isarn et al. and Hutchinson and co-workers—considered in more detail below, there is rather little work reported on the cure kinetics of epoxy-BN composites, despite the fact that such composites are very widely studied in respect of their thermal conductivity. Furthermore, in some instances [54–56], unfortunately, the calorimetric cure data are either poorly presented or confusing, to the extent that no reliable conclusions can be drawn about the influence of the filler on the cure kinetics. The results of Teng et al. [57] are more interesting. These authors used a DGEBA epoxy matrix cured with diamino diphenyl sulphone and filled with combinations of BN, both unmodified and modified with a zirconate coupling agent, and both functionalised and non-functionalised multiwall carbon nanotubes (MWCNT). The peak temperature in non-isothermal cure at 5 °C/min decreased slightly, by about 3 °C and 5 °C for the modified and unmodified BN, respectively, for a loading of 25 vol% BN, which is consistent with the usually observed acceleration of the cure reaction with added filler, as discussed above. However, at the same time there was a large difference between the heats of reaction for the composites with unmodified fillers and those with the modified and functionalised fillers, the heat of reaction for the latter being about twice that of the former. These authors allude to the steric hindrance of the filler particles as an explanation for these observations, although this might be expected to slow down rather than accelerate the reaction, and also conclude that the reactive sites of the functionalised hybrid filler react with the epoxy resin, which does not occur for the pristine hybrid filler. This additional reaction is believed to reduce the free volume and hence improve the matrix-filler interface, which was correlated with an increase in thermal conductivity. This interpretation is interesting and is a good illustration of how calorimetric cure data can be related to the thermal conductivity of the cured composite; further examples of such a relationship will be presented below. Nevertheless, the thermal conductivities achieved by these authors remain rather low for the BN filler loadings used, as will be seen in Section 3.1 of this review. Another report, by Wu et al. [58] on bisphenol-A epoxy composites filled with nano-BN particles, is ambiguous and inconsistent in reporting the dependence of the peak exotherm temperature in non-isothermal cure on BN content, so no conclusions can be drawn from this work.

For various reasons, it is not possible to draw any reliable conclusions from the references discussed above [54–58] about the effect of the addition of BN particles on the cure kinetics of epoxy-BN composites, for comparison with the generally observed acceleration. It is, therefore, interesting to note that Isarn et al. [59–62] and Hutchinson and co-workers [63–67] present many results which show the opposite effect, namely a retardation of the cure upon addition of BN, and accordingly these are examined now in some detail. There are some differences in the matrix materials and fillers used by the two groups. The former group used two types of epoxy: DGEBA and a cycloaliphatic resin, 3,4-epoxy cyclohexylmethyl 3,4-epoxycyclohexane carboxylate (ECC), and effect the cure reaction in two separate ways. In most of their work, these authors induced epoxy homopolymerisation by cationic initiation, but in one of their studies they used a thiol, pentaerythritol tetrakis (3-mercaptopropionate) (PETMP), as a cross-linking agent, with 4-(N,N-dimethylamino)pyridine (DMAP) as the initiator. The filler is principally BN, but carbon nanotubes (CNT) were added occasionally.

For composites with a DGEBA epoxy matrix, for which only an antimonate cationic initiator was used, BN particles of around 6 μm size in non-isothermal cure gave rise to a very slight increase in the peak exotherm temperature, T_p, from 120 °C to 123 °C, when increasing the BN content up to 20 wt.%; this was attributed to “the hindrance produced by the BN particles” or “the increased viscosity of the formulation” [59]. For a higher BN content of 40 wt.%, with the same epoxy/initiator system, a much greater increase in T_p, from 121 °C to 133 °C, was reported, essentially independent of whether or not 1 wt.% of CNT was also included in the composite [62]. This retardation of the cure upon addition of BN particles was attributed to “the dilution effect of the high quantity of filler”. Isoconversional analysis shows that the cure curves all follow a second order kinetic model, the retardation on the addition

of BN particles being demonstrated by a reduction in the rate constant, k. Furthermore, the heat of reaction, measured in kJ/ee, and the glass transition temperature of the fully cured composite, $T_{g\infty}$, were both essentially independent of the filler content, indicating that the network structure was not influenced by the presence of the filler.

For the other epoxy matrix material, ECC, the peak exotherm temperature remains very much independent of the BN content. When the cure is cationically initiated [60,62], T_p either remains constant [60] or at most decreases by only 2 °C [62] for the non-isothermal cure of composites with 40 wt.% BN, though for the hybrid with 1 wt.% CNT a slightly greater decrease of 3 °C was observed. This was interpreted as indicating a cooperative effect between the two different fillers; possibly the protons formed during the oxidation of the CNT help to catalyse the ring-opening polymerisation. Likewise, when the ECC epoxy was cured with a thiol, PETMP, and initiated with DMAP, there was only a small change in T_p on addition of 40 wt.% BN, though the direction of the change depended on the BN particle size: for 6 μm particles there was a 3 °C decrease, whereas for 80 μm particles there was a 4 °C increase [61]. The authors concluded that DGEBA resin systems are likely to interact better with BN than ECC resin systems.

The dependence of the peak exotherm temperatures in non-isothermal cure for epoxy-BN composites is plotted together with the data for the other fillers in Figures 3 and 4 as the open symbols. Here, it can be seen that the tendency is quite the opposite of that for the other fillers, though the reason for this is not clear.

In nearly all cases, Isarn et al. found that the heat of reaction per epoxy equivalent in the non-isothermal cure and the glass transition temperature of the fully cured systems, when it could be measured, were essentially independent of the filler content. They concluded that BN has an inert character with respect to the final network structure for both cationic epoxy homopolymerisation and when cured with a thiol. A slight decrease, from 120 kJ/ee for the unfilled epoxy to 114 kJ/ee for 40 wt.% of the 6 μm BN filler, and to 116 kJ/ee for the 80 μm BN filler in the ECC/PETMP system, was attributed to topological restrictions. The same explanation was given for the rather stranger decrease for cationic homopolymerisation, from 88 kJ/ee for the unfilled system to, initially, 69 kJ/ee for low BN content, but it then remained constant as the BN content increased.

The conclusion that BN is an inert filler in epoxy composites was also reached by Hutchinson and co-workers in all their work on DGEBA epoxy composites cured with thiol (PETMP), where the heat of reaction and $T_{g\infty}$ were consistently independent of the BN content [63–67]. However, these authors also consistently observed an underlying retardation of the epoxy-thiol cure kinetics with the addition of BN particles, and they carried out a systematic study of the effects of various parameters in addition to the fundamental one of filler content, namely particle size [64,65], particle shape (i.e., platelets or agglomerates) [67], and surface modification [66]. Furthermore, they investigated the effect of using a diamine rather than thiol as the curing agent [63–65]. An illustration of some of these effects, and a comparison with the results of Isarn et al. [62] is shown in Figure 5.

The interesting aspects of this dependence of the cure kinetics on BN content are as follows. First, the DGEBA epoxy composite system cured either with thiol or cationically shows a similar retardation with the addition of 30 μm BN platelets. In contrast, the composite system based upon ECC epoxy resin does not display this retardation. Second, the DGEBA epoxy composite cured with diamine did not display any retardation of the cure with the addition of filler. This difference between the epoxy-thiol and epoxy-diamine composites was attributed to a Lewis acid-base interaction between the BN particles and thiol in the former, which does not exist in the latter [63–65]. The authors suggest that this could have a positive impact on the thermal conductivity of these composites as a consequence of the enhanced filler-matrix interaction. Third, there was a significant increase in the retardation effect when 2 μm BN platelets were used as the filler. Kinetic analysis of the cure curves for these 2 μm composites shows that the activation energy E decreased, which would be inconsistent with the observed retardation unless the pre-exponential factor A also decreased, and markedly so. Hutchinson and co-workers propose that the Lewis acid-base interaction between filler and matrix, coupled with

the very large surface area of these much smaller particles, results in a large proportion of the epoxy matrix being immobilised at the particle surface [67].

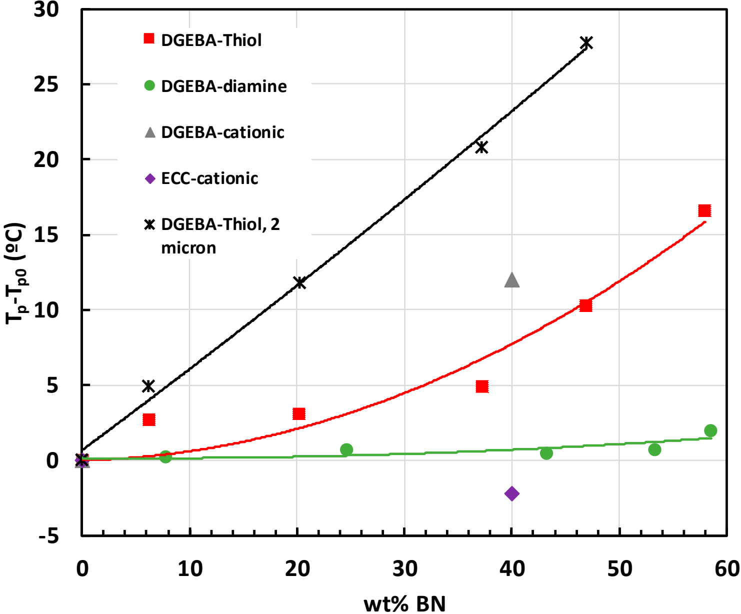

Figure 5. Dependence of peak temperature, T_p, on filler content relative to unfilled epoxy, T_{p0}, for epoxy-BN composites in non-isothermal cure at 10 K/min. 30 µm platelets: red squares, DGEBA-thiol [65]; grey triangle, DGEBA-cationic [62]; purple diamond, ECC-cationic [62]; green circles, DGEBA-diamine [65]. 2 µm platelets: black asterisks, DGEBA-thiol [65].

Besides this overall tendency for the cure reaction to be retarded by the BN filler reported by Hutchinson and co-workers, they also point out that, with a low BN content, there can be an acceleration effect. This is illustrated in Figure 6 for an epoxy-thiol system filled with 2 µm platelets and cured isothermally at three different temperatures [65], and is even more apparent in some other epoxy-BN systems [63,64,67]. In fact, this effect can also be seen in the cationic cure of DGEBA epoxy at the lowest BN concentration in the work of Isarn et al. [59]. It is argued that this could be a consequence of the improved heat transfer of the sample, hence representing a physical rather than a chemical effect.

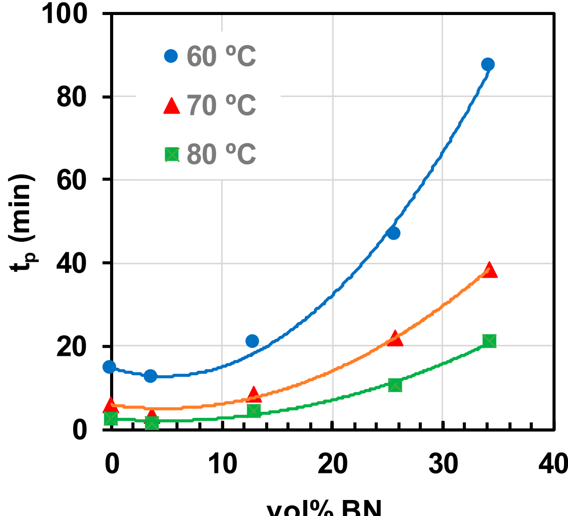

Figure 6. Dependence of time to peak exotherm, t_p, on content of 2 µm BN platelets for epoxy-BN composites in isothermal cure at 60 °C (blue circles), 70 °C (red triangles) and 80 °C (green squares).

3. Thermal Conductivity

3.1. *Effect of BN Content*

In the foregoing Sections 2.2 and 2.3, the effect of fillers in general, and of BN in particular, on the cure kinetics of epoxy composites was considered. Although no unequivocal conclusions can be drawn from the results presented in the literature, there is one notable aspect, namely that there is nearly always *some* effect: in the majority of cases, the filler causes an acceleration of the cure, but sometimes there is a retardation. This implies that there is a certain interaction between the filler and the matrix, which might be expected to have some consequences for the properties of the cured composite, and in particular for the thermal conductivity. However, the primary relationship to consider is the effect of BN content on thermal conductivity. It is generally observed not only that the thermal conductivity of epoxy-BN composites increases with BN content, but also that this increase becomes more rapid as the BN content increases, giving rise to an upward curvature in a plot of thermal conductivity as a function of BN content. This upward curvature is usually attributed to increased connectivity between the BN particles beyond the percolation threshold. A compilation of data obtained from the literature is plotted in this way in Figure 7. The relationship between the symbols and the references from which the data were obtained is given in the legend, but can be seen more clearly in Supplementary Material 2.

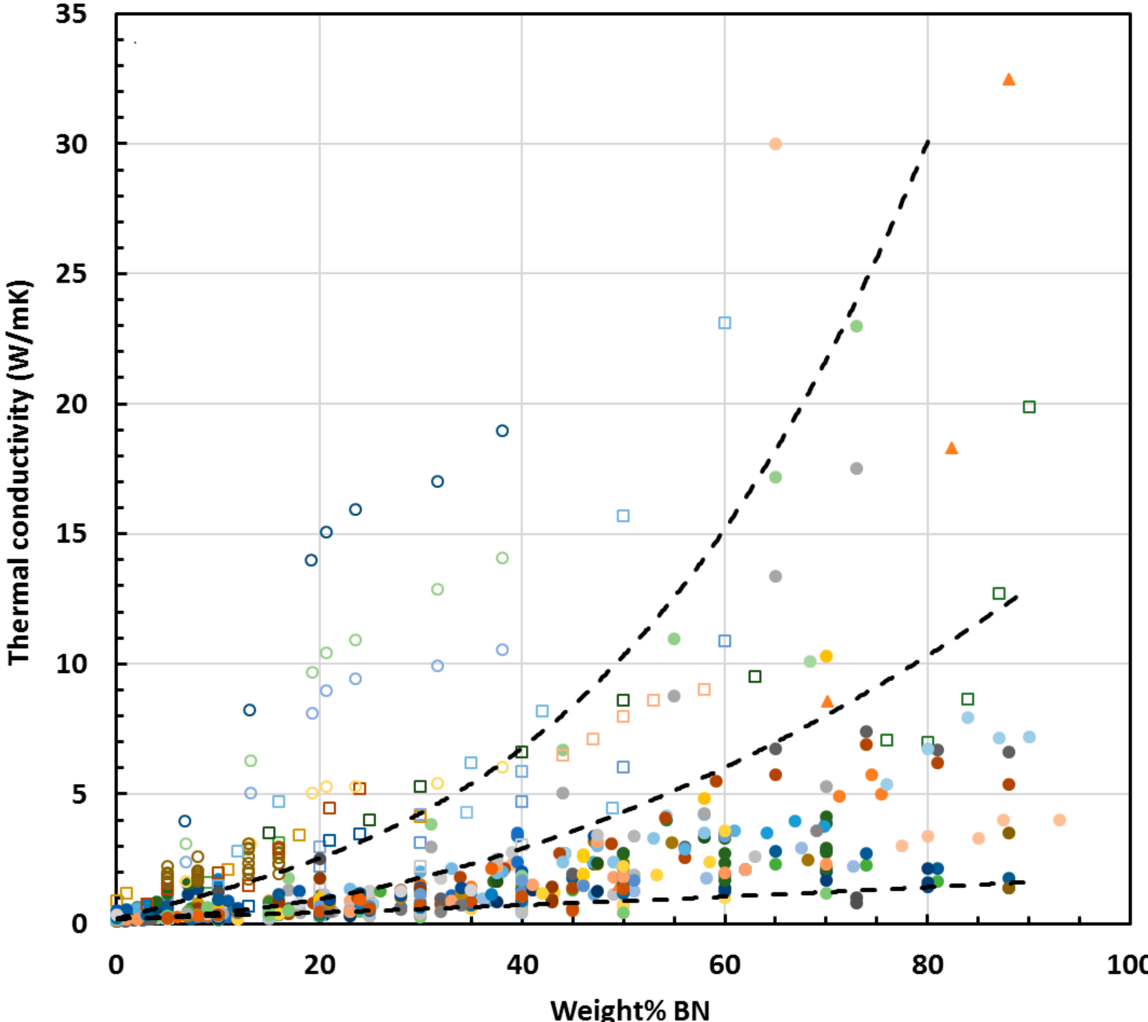

Figure 7. *Cont.*

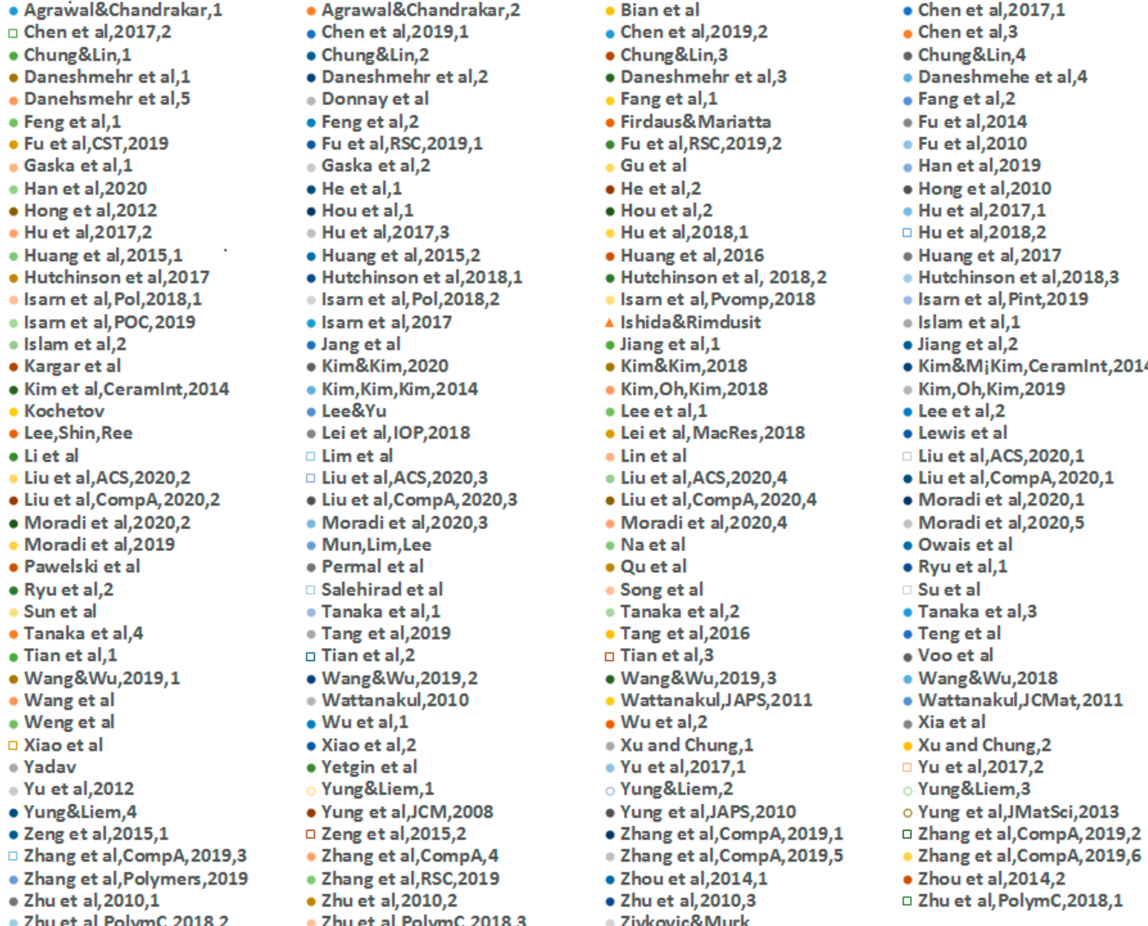

Figure 7. Thermal conductivity of epoxy-BN composites as a function of the BN content by weight. Data taken from references [54,57,59–159]. Open circles refer to data from references [54,151], open squares refer to data from references [89,90,114,116,125,127,132,143,147,153,158]. The dashed trend lines indicate the overall tendency for the dependence of thermal conductivity on BN content (excluding the data represented by the open circles): an upper trend line, below which more than 95% of the values fall; and a lower trend line, below which fewer than 5% of the values fall. The intermediate trend line is an approximation to the upper limit for isotropic samples.

Included in this compilation are the results obtained for any epoxy composite material containing BN. In particular, many of these references are to hybrids in which BN is incorporated with one or more other type of particle for the enhancement of thermal conductivity. For such hybrid materials, the data plotted in Figure 7 refer only to the limiting situation in which only BN is present. There is a total of approximately 900 data points included in Figure 7, but two series of data are worthy of special mention—the results of Yung and Liem [54] and Yung et al. [151], which are presented as open circles, and which show significantly higher thermal conductivities than any others for the same BN content.

In reference [54], the authors use a bisphenol-A type brominated epoxy resin, which has application in flame-retardant printed circuit boards. The epoxy is cured with a dicyandiamide and filled with silane-treated BN particles of different sizes: hexagonal (h-BN), with sizes from about 0.2 μm to 0.6 μm, or cubic (c-BN), with a size of 1.0 μm. In reference [151], the authors use an anhydride-cured bisphenol-A phenolic resin, filled with BN particles of sizes 1.5, 5, 10 and 15 μm, and treated with a silane coupling agent. There is no obvious explanation for why the thermal conductivities are so high. Nevertheless, two aspects are worthy of mention. First, the usually observed upward curvature in the dependence of the thermal conductivity on BN content is not displayed by the results of Yung and Liem [54], which are shown separately in Figure 8; instead, there appears to be a tendency to

reach a limiting value as the BN content increases. Second, the results of Yung et al. [151] show a trend of increasing thermal conductivity as the BN particle size decreases, which contrasts with the usual observed effect of particle size [64,65]. This is also illustrated in Figure 8, for the case of the BN particles not treated with silane; the same trend was reported for the silane-treated particles, for which higher thermal conductivities were observed, but for clarity these are not included in Figure 8.

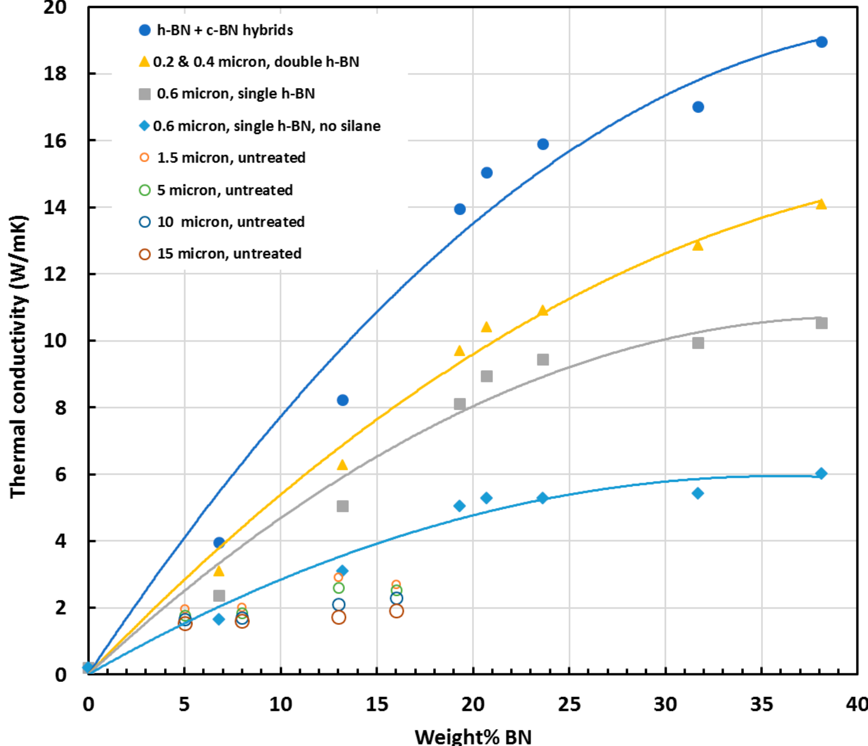

Figure 8. Dependence of thermal conductivity on BN content for epoxy-BN composite systems; data replotted from Yung et al. [54,151]. Filled symbols for silane-treated particles unless otherwise stated [54]: light blue diamonds, 0.6 µm single h-BN, without silane; grey squares, 0.6 µm single h-BN; yellow triangles, 0.2 µm and 0.4 µm double h-BN; dark blue circles, hBN+cBN hybrids. Open symbols [151]: 1.5 µm, 5 µm, 10 µm and 15 µm BN, untreated, symbol size increasing with BN particle size.

Even setting aside the results of Yung et al. [54,151], there is still evidently a very wide dispersion of the data. In an attempt to clarify the situation, we have included in Figure 7 some trend lines to indicate the overall tendency for the dependence of thermal conductivity on BN content: an upper trend line, below which more than 95% of the values fall (excluding the data of Yung et al. [54,151]); and a lower trend line, below which fewer than 5% of the values fall.

To simplify the picture further, some particular results can be singled out. These are the data which correspond to samples in which orientation of the BN particles has deliberately been introduced. The orientation can be induced by various means: gravity alignment and subsequent resin infiltration [147]; the application of high pressure to partially cured samples before the final cure [90,153,158]; spin-coating of films and hot pressing after pre-cure [116]; magnetic alignment of Fe_3O_4-decorated BN particles [114,125,127]; or by resin infiltration of hierarchically ordered 3-dimensional templates [89,132,143]. The orientation induced usually results in a highly anisotropic thermal conductivity. In Figure 7, the results corresponding to the thermal conductivity measured in the orientation direction are shown as open squares, where it can be seen that they almost all lie well above the data for the thermal conductivity of isotropic samples, indicated as the filled data points. Accordingly, we have included a further, intermediate trend line which represents an approximation

to the upper limit of these isotropic thermal conductivities. It can be seen that the vast majority of data fall between the lower and intermediate trend lines. The remaining scatter in these data points is a consequence of the many differences in the epoxy-BN composites, which arise from the different parameters involved: the matrix epoxy resin and curing agent; the BN particle size and shape, and the use of hybrids; the use or otherwise of surface treatment of the particles or of coupling agents; and the cure schedule and fabrication procedure. Many of these aspects will be considered below.

Before looking at these aspects, though, there still remain some data points in Figure 7 which have thermal conductivities significantly higher than those indicated by the intermediate trend line, and are worthy of special mention. Ishida and Rimdusit [94] reported, some twenty years ago, "extraordinarily high" thermal conductivities for large BN contents, indicated by the filled triangles in Figure 7, giving the highest value of 32.5 W/mK for 88 wt.% BN. In fact, these authors used a benzoxazine resin and so these results should not strictly be compared with those for epoxy-BN composites, but the very high values for thermal conductivity suggest that there may be some important aspects to consider. There are several points of particular interest. The benzoxazine monomer is solid at room temperature and was first ground to a powder, mixed with the BN particles and heated to about 80 °C, when it took the form of a paste, which was then compression moulded before finally curing under 0.1 MPa pressure at 200 °C. The compression moulding may have introduced an orientation of the BN particles, which would have an important effect on the thermal conductivity. The BN particles were large, with an average size of about 225 μm and a bimodal size distribution; according to the authors, this bimodal distribution facilitated the very high filler contents achieved. Finally, under the composite preparation conditions used, the benzoxazine matrix had a very low viscosity, around 1000 cP, in comparison with that of a typical bisphenol-A epoxy, which is around 12,000 cP; this may have contributed to the ability to obtain very high filler contents. The authors measured the density of the composites and noted that the measured density was slightly higher than that calculated using the densities of the components, which might be expected as a consequence of shrinkage on cure, and they concluded from this that there were no voids in the samples, which is essential for the achievement of high thermal conductivity. Indeed, attempting to add more BN beyond 88 wt.% resulted in a significant decrease in density, which they attributed to void formation. All of these observations are interesting, but do not really explain such high values of thermal conductivity. In fact, the increase in thermal conductivity is dramatic only beyond about 70 wt.%, where the value coincides approximately with the intermediate trend line in Figure 7; for a lower filler content, for example at 50 wt.% BN, the value was unremarkable, and close to the lower trend line. If the dramatic increase is due to the establishment of connectivity between the filler particles, then it suggests that the percolation threshold is much higher than that proposed by the authors, around 20 vol% or 33 wt.%. Nevertheless, the value of 32.5 W/mK for the thermal conductivity remains remarkable, and in 2013 it was stated that it "remains the highest reported thermal conductivity value in the literature" [160].

A value "higher than 30 W/mK" was reported by Song et al. [126] for an epoxy-BN composite with 50 vol% filler, the highest filler content used by these authors and which we estimate to be approximately 65 wt.%. It is important to note here, though, that this value was measured in a thin film, and in the in-plane direction; consequently, there is a strong likelihood that there are significant orientation effects here. It seems reasonable, then, that this value appears to extend, to a slightly higher filler content, the tendency corresponding to the values of the samples in which orientation has been deliberately introduced, discussed above and indicated in Figure 7 by the open squares.

The results discussed immediately above may be considered as special cases, for the reasons presented. There are still two sets of data in particular which stand out from the rest in Figure 7, and which fall between the upper and intermediate trend lines. Both sets of data, indicated by grey-blue and green filled circles, are from Islam et al. [95], and correspond to composites in which the matrix was a liquid crystalline epoxy resin. These results will be discussed in more detail below. The values of thermal conductivity of close to 10 W/mK reported by Tanaka et al. [129] and Xu and Chung [144], indicated in Figure 7 by green and orange circles, respectively, are also worthy of special

mention; both use about 70 wt.% BN and the data lie significantly above the intermediate trend line. Nevertheless, the vast majority of the remaining results included in Figure 7 fall between the lower and intermediate trend lines. This still leaves a significant amount of scatter, and the following sections consider the possible reasons for this, and how they might influence the thermal conductivity.

3.2. Effect of Surface Treatments and Coupling Agents

It is well known that the interface between the epoxy matrix and the filler particles is a major source of thermal resistance, and for this reason considerable attention has been paid to finding ways in which the quality of this interface can be improved. One problem is that the flat surfaces of the hexagonal BN platelets, which correspond to the hexagonal planes of the BN crystal structure, are molecularly smooth, and present little opportunity for chemical bonding with the matrix or for other interactions. However, there are some functional groups, such as hydroxyls and amino groups, which are present on the narrow edge planes of these platelets, and these edges do offer the possibility of bonding in order to improve the matrix-particle contact. It is, therefore, quite common to aminate [71] or hydroxylate these edges, for example by sol-gel treatment with a strong alkali. These functionalised BN particles may be used directly in the epoxy-BN composite [69,71,85,124], or may additionally be treated with a coupling agent to further enhance the matrix-filler interface. Teng et al. [57] used a zirconate coupling agent, but by far the most common are the silanes, of which numerous variants have been used, including (3-mercaptopropyl) trimethoxysilane, [97], (3-aminopropyl) triethoxysilane, APTES [88,109,138,155], epoxy-terminated dimethyl siloxane, ETDMS [101], and (3-glycidyloxypropyl) trimethoxysilane, GPTMS [66,138]. Jang et al. [96] found that increasing the carbon chain length of the silane, from propyl trimethoxysilane to hexadecyl trimethoxysilane, improved the affinity of BN with epoxy and led to an increase in thermal conductivity. A similar observation was made by Wattanakul et al. [137], who found that increasing the chain length of four cationic surfactants, from dodecyl-, tetradecyl-, hexadecyl- to octadecyl trimethyl ammonium bromide, adsorbed onto the surface of BN particles was increasingly effective for enhancing the thermal conductivity, as a consequence of better wetting of the epoxy resin. In many cases the coupling agent, N-(β-aminoethyl)-γ-aminopropyl trimethoxysilane [54], APTES [68,74,82,131,138,148], or GPTMS [72,73,138,144,156], is added directly in the preparation of the epoxy-BN composite, usually with the help of a solvent such as acetone or ethyl alcohol, and without any prior functionalisation of the BN particles.

Other approaches to the functionalisation of the BN particles involve the use of dopamine [69], 1-pyrenebutyric acid, which reportedly avoids structural defects induced in BN particles by covalently-bonded functional groups [85], ionic liquid flame-retardant functionalisation [113], and aniline trimer, which is considered to provide π-π interactions with the BN particles [124]. Wattanakul et al. [138] also investigated the effect of admicellar polymerisation of polystyrene and polymethylmethacrylate onto the BN surfaces to improve the interfacial adhesion, and found a significant enhancement of the thermal conductivity.

Attention was drawn in the previous section to the high value of thermal conductivity—just over 10 W/mK at about 70 wt.% BN—reported by Xu and Chung [144]. It is interesting to note that these authors compared a variety of different surface treatments in the fabrication of epoxy composites, with BN contents of 44 vol% and 57 vol%, which is approximately 58 and 70 wt.%, respectively. In all cases, the thermal conductivity increased with BN content, so we consider here only those with 70 wt.%. The composites with untreated BN particles, equiaxial and from 5 to 11 μm in size, have a thermal conductivity of 5.27 W/mK, which increases sequentially for acetone, nitric acid and sulphuric acid treatments. For the silane treatment, the thermal conductivity increases with increasing proportion of silane, from 0.7% to 2.4%, and at the highest proportion is the most effective treatment, giving a thermal conductivity of 10.31 W/mK. This increase in thermal conductivity of 96% as a consequence of the surface treatment of the BN particles is remarkable, and represents the most dramatic effect of all the surface treatments considered here. This is illustrated in Figure 9, which presents the data of Figure 7 in a slightly different way. First, only the maximum value from each of the references

is plotted, rather than showing the data for all BN contents from a given reference source. Second, the scales are limited to 11 W/mK and 90 wt.% BN; in this way, it is possible to show more clearly the region in which most of the experimental data lie and to identify the effects of the parameters, namely the surface treatment and the particle size.

The data of Xu and Chung [144] can be seen at 70 wt.% BN in Figure 9, indicated by filled and open orange circles. A similar increase in thermal conductivity, of almost 75%, when the BN particles were surface treated can be seen in the data of Yung and Liem [54] at 38 wt.% BN, indicated by light blue circles, though the unusual nature of these results was pointed out above. Similarly, a significant increase in thermal conductivity was found by Kim et al. [102] for an epoxy-terminated dimethyl siloxane matrix filled with BN particles which had been treated with either GPTMS or 3-chloropropyl trimethoxysilane (CPTMS). These authors found, for BN contents from 50 to 70 wt.% (indicated in Figure 9 by open and filled brown circles for 70 wt.%), that GPTMS was more effective than CPTMS, although both increased the thermal conductivity when compared with composites fabricated without any coupling agent. In fact, an increase in thermal conductivity as a consequence of surface functionalisation and/or of using a coupling agent is nearly always observed, though the effects are often much smaller than those reported by Xu and Chung and by Yung and Liem. However, there is one report in which the thermal conductivity decreases in nearly all cases after surface treatment [66], and it is argued that for the surface treatment to be effective, the BN particles must be platelets rather than agglomerates, since the latter have fewer edges available for modification. In this respect, it would appear strange that the dramatic increase observed by Xu and Chung [144] should be for what these authors call "equiaxial" particles.

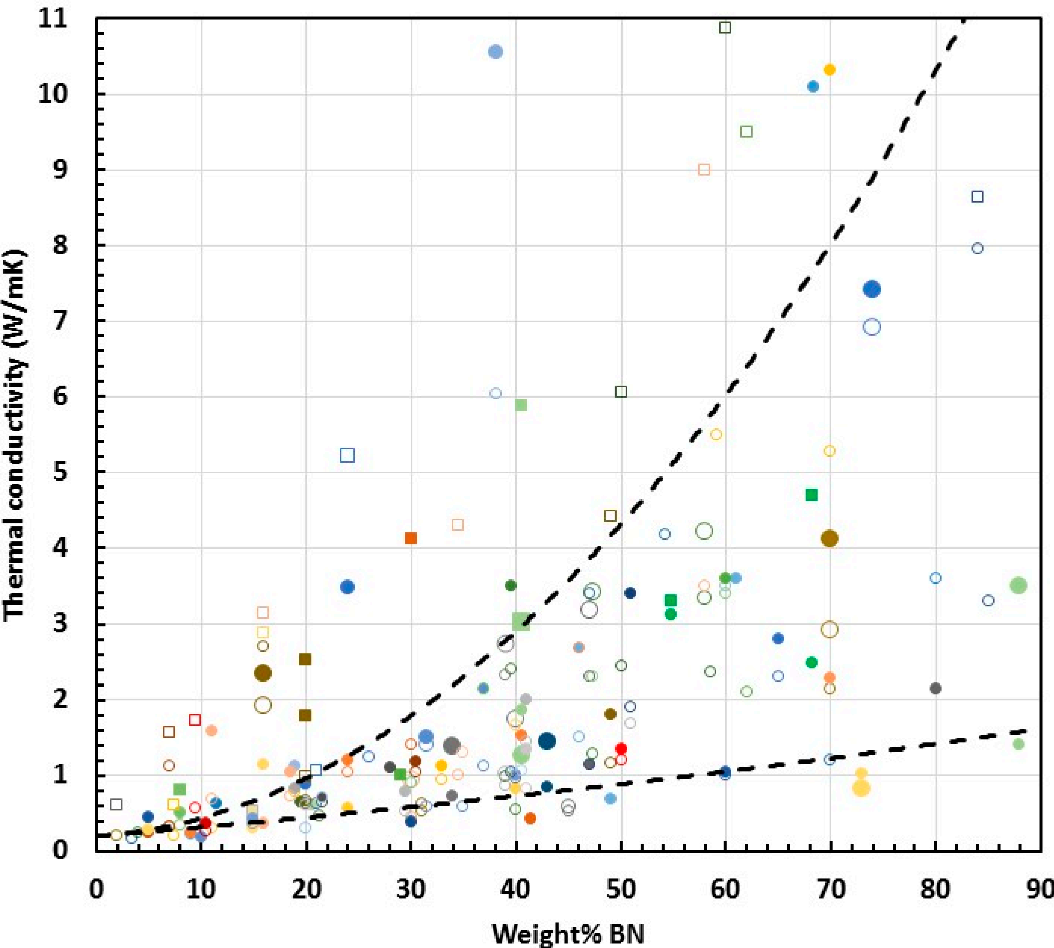

Figure 9. *Cont.*

Figure 9. Maximum values of thermal conductivity as a function of BN content for data taken from references [54,57,59–159]. Colour coding for references is given in the legend but can be seen more clearly in Supplementary Material 3. Open circles: untreated particles; filled circles: treated particles. Squares correspond to data from oriented samples. Increasing size of particles within any set of data is represented by increasing size of symbol. Dashed lines are the intermediate and lower trend lines, and are drawn to guide the eye. Some of the data at 20, 30 and 40 wt.% BN have been shifted slightly to lower or higher BN contents to avoid overlapping, for clarity.

In some instances, the effect of surface treatment is so small as to be virtually negligible [71,74,82,123,131,148,155]. On the other hand, when the thermal conductivity is low (close to the lower trend line in Figure 9), a small absolute increase can translate into a significant percentage increase. This effect can be seen in the results of Lee et al. [109], where for 10 wt.% BN the conductivity increases from 0.27 to 0.36 W/mK after sulphuric acid treatment and silanisation, and in the results of Zhang et al. [155], where it increases from 0.37 to 0.43 W/mK at 15 wt.% BN after oxidisation in air and the addition of APTES. In contrast, again at a low BN content of only 10 wt.%, the non-covalent functionalisation with pyrenebutyric acid by He et al. [85] results in a remarkable increase in thermal conductivity from 0.68 to 1.58 W/mK, well above the intermediate trend line.

There are some other results which should be commented on. Chung and Lin [72] achieved high BN content, but found that the thermal conductivity passes through a maximum at 50 to 60 vol% for two different BN particle sizes, 3.6 and 10.6 µm, the latter exhibiting higher thermal conductivity. When the GPTMS coupling agent was used without prior functionalisation of the BN particles, the maximum thermal conductivity increased by about 0.5 W/mK for each size of particle, leading to a value of 7.42 W/mK for the larger particle, which is approaching the intermediate trend line in Figure 9. Jang et al. [96] observed an increase from 2.4 to nearly 3.5 W/mK for a BN content of close to 40 wt.%, which represents a move from below to well above the intermediate trend line; this was for BN which had been surface modified by a sol-gel reaction with NH_4OH and a silane coupling agent with a C16 carbon main chain. Similarly, Wattanakul et al. [137,138] investigated various strategies, including the use of admicellar polymerisation modification of the BN surfaces and the use of cationic surfactants of different chain length. These treatments resulted in significant increases in thermal conductivity, with maximum values of 3.4 W/mK at 51 wt.% BN and 2.69 W/mK at 46 wt.% BN, both of which are close to the intermediate trend line.

Other results for which thermal conductivity values fall close to the intermediate trend line should also be mentioned. Jiang et al. [97] used a strong alkali to attach –OH groups to the BN particles and then grafted the mercaptopropyltrimethoxysilane coupling agent. The increase in thermal conductivity as a consequence of the surface treatment resulted in a maximum value of 1.2 W/mK, which is relatively high for a BN content of only 24 wt.%. Likewise, Li et al. [113] achieved a relatively high value of 1.04 W/mK for only 20 wt.% BN in a flame-retardant epoxy-BN nanocomposite. At slightly higher BN contents, Tang et al. [131] achieved a value of 1.51 W/mK at 30 wt.% BN with APTES as the coupling agent.

It is evident that in virtually all cases the surface treatment of the BN particles and/or the use of coupling agents, in all their varieties, result in an enhancement of thermal conductivity. However, this comes at a certain cost in many instances. One of the important parameters with respect to the use of these epoxy-BN composites in insulated metal substrates is the simplicity of the fabrication process, as mentioned in the Introduction, but many of the results discussed above make use of a solvent in the dispersion of the functionalised BN particles in the epoxy resin system, which is generally an undesired industrial practice. The solvents most widely used are acetone [57,74,85,113,131,141,148] and ethanol [68,82,97,155], but others include methyl ethyl ketone and dimethyl formamide [96], and tetrahydrofuran [71]. On the other hand, "dry" or "direct" mixing, which obviates the use of any solvents in this composite fabrication step, was adopted by many researchers [54,88,109,113,123,137,138,144,149,156]. Chung and Lin [72] used dry mixing for BN contents ≤40 vol% but required acetone as a solvent for dispersion in order to achieve higher filler loadings.

While there seem to be clear advantages in the use of surface treatment to enhance thermal conductivity, it should be pointed out that there are several researchers who did not make use of such treatments yet achieved notable values of thermal conductivity. These results, represented by open circles in Figure 9 and which lie close to the intermediate trend line, are worthy of some comment. Gaska et al. [81] used a DGEBA epoxy cured with anhydride, and reported thermal conductivity values of 2.32 W/mK and 2.75 W/mK at a filler loading of 25 vol% (approximately 39 wt.% BN), for untreated

BN particles with average sizes of 13 μm and 25 μm, respectively. The effect of particle size will be considered later, but it is remarkable that such values of thermal conductivity are achieved with simple mixing with untreated BN particles. Approximately the same value of thermal conductivity as that for the smaller particles above was reported by Jang et al. [96], namely 2.40 W/mK at approximately 39 wt.% BN, for untreated platelets with sizes in the range of from 5 to 10 μm; the unspecified epoxy resin was cured with dicyandiamide, but the composite preparation required the use of methyl ethyl ketone and dimethylformamide.

At slightly higher BN contents, Hutchinson et al. [64–66] reported values from 3.2 to 3.4 W/mK at about 47 wt.% BN for particles of various sizes and types, and values of approximately 4.2 W/mK at 54 wt.% and 58 wt.% BN. These values, higher than the majority of other values reported in the literature, both with and without surface treatment, were all obtained with untreated BN particles, and with a DGEBA epoxy resin matrix cured with a thiol, PETMP. These authors suggested that the Lewis acid-base interaction between the sulphur in the thiol and the boron in the filler leads to an improved matrix-filler interface, which was the reason for the enhanced thermal conductivity. In support of this hypothesis, they reported that the same epoxy-BN system cured with a diamine does not give such high thermal conductivities, for example only 1.7 W/mK at 53 wt.% BN [65]. They also noted that the cure kinetics of the epoxy-thiol system and the epoxy-diamine system are quite different in their dependence on the BN content, as discussed in Section 2, and consider this to be further evidence of the favourable matrix-filler interaction in the epoxy-thiol-BN composite system.

The result obtained by Kargar et al. [98] is also noteworthy. These researchers used an unspecified epoxy and curing agent and obtained high volume fractions of untreated BN platelets, with sizes in the range from 3 to 8 μm, without the use of solvents. The reported thermal conductivity of 5.5 W/mK at a filler loading of 59 wt.% (open yellow circle) is very close to the intermediate trend line in Figure 9.

3.3. *Effect of BN Particle Size and Shape*

Another parameter that is of prime importance in respect of the thermal conductivity of epoxy-BN composites is the size and shape of the particles used as the filler. The interface between filler particles and matrix is important because it represents a thermal barrier in the pathway for phonon transport between the highly conducting BN particles. There will inevitably be some heat conduction through the epoxy resin between the filler particles, and it is for this reason that much effort has been expended in attempting to minimise the thermal barrier of the interface by surface treatments of the BN particles and by the use of coupling agents, as discussed in the previous section. For a given filler loading, however, the amount of interfacial region depends on the size of the filler particles, which decreases as the particle size increases. Consequently, one might expect that the thermal conductivity of an epoxy-BN composite with a given weight fraction of filler would be greater the larger the filler particles are. We examine this idea by referring to the data collected in the literature.

In Figure 9, the results obtained for a given system in which BN particles of different sizes are used are presented such that the size of the data point increases with increasing particle size. In nearly all cases, thermal conductivity increases as the particle size increases, as expected. For Chung and Lin [72], who also investigated the effects of using a coupling agent, this increase was quite dramatic, going from about 2.3 to 7.0 W/mK with no coupling agent, and from about 2.8 to 7.5 W/mK with a coupling agent, when the average particle size increased from 3.6 to 10.6 μm (dark blue circles, open and filled, at 65 and 74 wt.%). Hong et al. [87] investigated the effect of a bimodal distribution of polygonal aluminium nitride particles and platelet-shaped BN particles, with a view to increasing the packing efficiency and maximum filler content, but also reported the thermal conductivity of highly filled composites containing only BN particles, with average sizes of 6 μm and 18 μm. For a very high content of 70 vol%, which approximates to 88 wt.% BN, and with APTES as the coupling agent, the thermal conductivity increased from 1.4 to 3.5 W/mK with increasing particle size. Although these values of thermal conductivity are low for such a high filler content, as is evident from Figure 9 (filled light green circles), they display the usual dependence on particle size. The slight decrease

in thermal conductivity at 73 wt.% BN with increasing particle size, for values taken from earlier work by the same group [86] (filled yellow circles), is misleading. In this earlier work, the authors were studying the effect of different quantities of the APTES coupling agent; the maximum thermal conductivity occurred for different silane contents for the two particle sizes (1 and 5 µm) and the variation in thermal conductivity was small, so this result is not likely to be significant.

Kim et al. [102], who investigated the effect of different coupling agents, as discussed in the previous section, also studied the effect of different sizes of BN particles, namely 1, 8 and 12 µm, and observed a systematic increase in the thermal conductivity with increasing particle size for each of their filler contents of 50, 60 and 70 wt.%. The result for 70 wt.% BN is included in Figure 9 (open brown circles), where it can be seen that the thermal conductivity was rather low for such a high filler content, though the use of the coupling agent improved it (filled brown circle).

There are several results where the thermal conductivity for composites with a given filler content lies close to the lower trend line in Figure 9, but with an increase in the particle size the thermal conductivity increases, sometimes even approaching the intermediate trend line. Isarn et al. [61], in their studies of composites with a cycloaliphatic epoxy cured with a thiol, obtained a value close to 1.0 W/mK for 40 wt.% of 6 µm particles, which increased significantly to 1.7 W/mK for the same loading of 80 µm particles, a value mid-way between the lower and intermediate trend lines. In another example, Tang et al. [131] obtained a thermal conductivity of 0.6 W/mK at a filler loading of 18 vol% (approximately 30 wt.%) for 1.5 µm particles, which lies on the lower trend line. This value increased to 1.4 W/mK for 30 µm particles (open blue circles, displaced to 31 wt.% for clarity), a value close to the intermediate trend line. Furthermore, this value increased slightly when a coupling agent was used (filled blue circle). Similar results were reported by Yung et al. [149] with a particle size increase from 53 nm to 4 µm for 43 wt.% BN, and by Zhu et al. [157] with a particle size increase from 70 nm to 7 µm for 34 wt.% BN. The same effect of increasing thermal conductivity with increasing particle size is therefore also seen in the size range from nanometre to micrometre.

While the majority of researchers have found that thermal conductivity increases with BN particle size, there are some, though rather few, reports of almost no effect, or even a decrease. Pawelski et al. [121] used a Novolac epoxy matrix cured with diethylmethyl benzenediamine and filled with 45 wt.% BN particles 2, 12 and 45 µm in size, all in the form of platelets. The thermal conductivities measured were 0.53, 0.59 and 0.66 W/mK, respectively, thus increasing systematically with particle size, but very little when viewed in the context of other values reported in the literature. This is seen clearly in Figure 9, where these values are all clustered just below the lower trend line (open purple circles). Likewise, Permal et al. [122] observed no effect of particle size, for BN platelets with average sizes of 1 and 5 µm, in their composites with 30 wt.% filler. They used an epoxy matrix that was a mixture of DGEBA, Novolac and cycloaliphatic epoxy, cured with anhydride. Similar to the study by Pawelski et al., the value of the thermal conductivity was very low for the filler content used, and lies just below the lower trend line in Figure 9 (dark blue filled circle).

The notable report of a decrease in thermal conductivity as BN particles size increases can be found in the work of Yung et al. [151]. These authors investigated epoxy-BN composites with a bisphenol-A phenolic matrix cured with an anhydride and filled with platelets with sizes ranging from 1.5 to 15 µm, both with and without a silane coupling agent. The use of the silane coupling agent resulted in an increase of thermal conductivity, but there was a decrease in thermal conductivity for increasing particle size, typically by between 20% and 30%, whether or not the coupling agent was used, and for all the filler contents used, from 3 to 10 vol%, equating to about 5 to 16 wt.%. These data can be seen to fall well above the intermediate trend line in Figure 9 at 16 wt.% BN (open and filled brown circles), and even above the upper trend line in Figure 7. The fact that these authors found trends of thermal conductivity as a function of BN content and particle size that are opposite to nearly all other reports in the literature suggests that there may be some other factors at play here, such as orientation or sedimentation of the particles during the fabrication of the composites.

Finally, it is important to point out that it is not always straightforward to deduce the effect of particle size from results presented in the literature, as there is a simultaneous effect of particle shape which can complicate the situation. For example, Gaska et al. [81], in a study of epoxy composites filled with hybrids of aluminium nitride, boron nitride and silica, compared the thermal conductivity of two epoxy-BN composites, one filled with platelet-shaped particles with an average size of 13 μm and the other filled with agglomerates with an average size of 25 μm. The thermal conductivity of composites filled with 25 vol% (approximately 39 wt.%) of the larger agglomerate particles was 2.75 W/mK, falling on the intermediate trend line in Figure 9, in comparison with only 2.32 W/mK for the same content of the smaller platelet particles (open light brown circles). This seems to accord with the usually observed increase in thermal conductivity with increasing particle size, but this conclusion does not take into consideration the effect of the shape of the particles.

Likewise, Huang et al. [91] used BN fillers in different forms, namely spherical particles with a narrow size distribution from 200 to 400 nm, and "flakes" with a diameter from 3 to 6 μm and a thickness from 100 to 300 nm. These authors found that, for filler loadings up to 30 wt.%, the thermal conductivity was 0.95 W/mK for the composites fabricated with flakes compared with 0.45 W/mK for the composites fabricated with the smaller spherical particles. Both of these values are rather low for the filler content used, the latter falling on the lower trend line. Again, though, the particles with the larger diameter give a higher thermal conductivity, but in this case, in contrast to the findings of Gaska et al., it is the platelet-shaped particles which had the higher conductivity.

Similar to Gaska et al., Sun et al. [128] compared composites fabricated with up to 40 wt.% of larger (30 μm) spherical particles with those fabricated with smaller (18 μm) platelets and found that the thermal conductivity was higher for the larger spherical particles. For example, at 40 wt.% the thermal conductivity was 1.03 W/mK for the spherical particles in comparison with 0.86 W/mK for the platelets. These values fall well below those found by Gaska et al. for particles of similar sizes, and in fact are only slightly above the lower trend line in Figure 9, but nevertheless show this same trend of increasing thermal conductivity with particle size. In fact, the preparation procedure for these composites involves a hot pressing stage; this induces a certain amount of in-plane orientation for the platelets, which does not occur for the equiaxial spherical particles. The values quoted above correspond to the through-plane direction, and hence disadvantage the platelets, for which the through-plane thermal conductivity of the platelets themselves (2 W/mK according to Sun et al.) is much smaller than the in-plane value (185 to 300 W/mK according to Sun et al.). This effect of orientation will be considered later, but is clearly a further complication in the analysis of the effect of particle size.

The findings of Gaska et al. [81], Huang et al. [91] and Sun et al. [128] demonstrate an increase of thermal conductivity with increasing particle size, but it is not possible to draw any unequivocal conclusions from them about the effect of particle size, as there are other intervening factors. On the other hand, Hutchinson and co-workers [63–67] conducted a systematic study of the effects of both BN particle size and shape. Moradi et al. [65] fabricated epoxy-thiol composites filled with BN particles of different average sizes, namely 2, 30 and 180 μm, all in the form of platelets, and found an increase of thermal conductivity with increasing particle size for a given filler content. For example, for 47 wt.% BN the thermal conductivity increased from 1.28 W/mK for the 2 μm particles to 2.36 W/mK for the 30 μm particles and reached 3.02 W/mK for the 180 μm particles. In Figure 9, this can be seen to represent an increase from just above the lower trend line for the smallest particles to slightly below the intermediate trend line for the largest particles (open dark green circles). This filler content of 47 wt.% was the limiting amount for the 2 μm platelets, but higher contents were achieved for the larger particles, with the thermal conductivity reaching a value of 4.22 W/mK at 58 wt.% filler content; this value can also be seen in Figure 9 to be approaching the intermediate trend line. The same effect of particle size was reported also by this group for agglomerates: for example, at 47 wt.% filler content, the thermal conductivity for composites made with lightly agglomerated 6 μm particles was 2.31 W/mK [63], whereas a significantly higher value of 3.40 W/mK was measured when 80 μm agglomerates were used [64]. It is interesting to note that with the use of hybrids, in which BN particles

of different sizes are incorporated simultaneously, in particular 80/6 μm and 80/2 μm [64], the thermal conductivity did not increase for a given filler content, but decreased. This result is consistent with larger particles giving higher thermal conductivity. What the hybrids do permit, on the other hand, is a higher packing density, and hence higher thermal conductivities were achieved as a consequence of higher filler contents [64]. This same group also compared the effects of particles of different shapes, namely platelets and agglomerates [67], and found that agglomerates are more effective in enhancing the thermal conductivity. For example, for all the filler contents investigated, 120 μm agglomerates gave a higher thermal conductivity than the larger 180 μm platelets.

The reason why larger particles should result in higher thermal conductivities for a given filler content is probably related to the effect of the matrix-particle interface, which represents a certain barrier to heat transfer. It is for this reason that much attention has been paid to improving this interface, as discussed in Section 3.2. For a given filler content, this interfacial area is smaller for larger filler particles, and hence one would expect the effect of particle size that is generally observed. However, increasing particle size has its limitations as a strategy for increasing the thermal conductivity of insulated metal substrates; in practice, the dielectric layer is usually between 50 and 150 μm in thickness, and filler sizes of less than about 30 μm are preferred.

4. Special Procedures

4.1. Orientation

The quest for higher values of thermal conductivity of epoxy-BN composites has encouraged a large number of researchers to investigate novel fabrication procedures in recent years. In many cases these procedures involve orientation of the BN platelets in some way or another in order to benefit from the much higher in-plane thermal conductivity of the BN platelets themselves in comparison with the through-plane direction. In general, these specialised fabrication procedures create a structured assembly for which there is a highly anisotropic thermal conductivity and often a significant enhancement of thermal conductivity. This can be seen clearly in Figure 7, where the open squares represent data obtained from composites fabricated by such procedures. Many of these data points fall close to the upper trend line. Here, we review some of these special procedures.

Orientation of the filler particles can be achieved in a number of ways, possibly even simply by sedimentation of the particles in a low viscosity mixture. Kim and Kim [100] fabricated composites with an epoxy-terminated dimethyl siloxane matrix cured with diaminodiphenylmethane, in which the BN particles, either as 12 μm h-BN platelets or exfoliated BN nanosheets (BNNS), were incorporated in solution in ethanol. During solvent removal by filtration, the larger h-BN particles were preferentially oriented to a greater extent than the BNNS, which resulted in an anisotropic thermal conductivity, with higher values and a greater degree of anisotropy for the former. For a composite with 68 wt.% h-BN, the thermal conductivity increased from 2.5 W/mK in the through-plane direction to 4.7 W/mK in the in-plane direction, as can be seen in Figure 9 (filled dark green symbols). In a slightly different procedure, orientation was also induced by gravity alignment of 10 to 30 μm size h-BN platelets by Yu et al. [147] during vacuum filtration from an ethanol solution to form a h-BN "cake", in the form of a cylinder of diameter 4 cm and thickness 3 cm, in which the BN platelets were oriented parallel to the base of the cylinder. This cake was then sliced thinly, with the BN platelets perpendicular to the plane of the slices, infiltrated with an acetone solution of DGEBA epoxy resin, hexahydro-4-methylphthalic anhydride curing agent and dimethylaminomethylphenol accelerator, degassed under vacuum, and cured at 100 °C for 2 h. For 44 vol% BN content, this significant amount of orientation gave a thermal conductivity in the through-plane direction of 9.0 W/mK in comparison with 3.5 W/mK for a simple random dispersion of the same BN content in the epoxy system. These results are included in Figure 9 at an estimated 58 wt.% BN (open dark pink symbols), where it can be seen that the orientation increases the thermal conductivity from approximately mid-way between the lower and intermediate

trend lines to well above the intermediate trend line; nevertheless, Figure 7 shows that the oriented sample still lies significantly below the upper trend line.

Filtration through a die was also the technique adopted by Xiao et al. [143] to induce orientation of BNNS in composites. They used a more elaborate fabrication procedure, in which the BNNS were first exfoliated from 12 µm BN platelets by sonication in isopropyl alcohol and were then both functionalised with GPTMS and decorated with SiC nanowires (SiC_w, 0.1 to 0.6 µm in diameter and 50 to 100 µm long) in an ethanol solution before being vacuum filtrated through a die. They achieved a vertically-oriented SiC_w/BNNS framework which was vacuum-assisted infiltrated with epoxy resin and anhydride curing agent, and finally cured. Samples were prepared with different proportions of SiC_w and BNNS, and while the thermal conductivity increased with BNNS content as usual, for a given filler content the thermal conductivity increased with increasing proportion of BNNS, leading us to question why the SiC_w was incorporated. The highest thermal conductivity obtained was 4.22 W/mK in the direction of orientation for a sample containing 21.9 vol% filler (approximately 30 wt.%) with a 1:9 mass ratio of SiC_w and BNNS. The corresponding value in the orthogonal direction was 1.43 W/mK, and these values can be compared with 1.6 W/mK for a randomly distributed epoxy/BNNS composite. The thermal conductivity of the oriented sample lies on the upper trend line in Figure 7 and well above the intermediate trend line in Figure 9 (filled maroon square), and hence represents a significant result. In fact, this result is quite similar to those obtained by Yu et al. [147], Hu et al. [90], Liu et al. [116], and Lim et al. [114]. All these values of thermal conductivity, at different filler contents for each of these groups, increased as a consequence of the various methods of orientation, from a value approximately mid-way between the lower and intermediate trend lines to a value well above the intermediate trend line.

Similarly, Lee et al. [108] observed a significant increase, from 0.6 W/mK in the through-plane direction to 1.7 W/mK in the in-plane direction, for composites with only 10 wt.% BN. This is again clearly seen in Figure 9 (open red symbols). The fabrication procedure involved the use of a solvent, acetone, to incorporate the 1.5 to 2.0 µm BN particles into the epoxy-diamine mixture, and the low viscosity and low filler loading probably resulted in sedimentation, though this is not specifically stated by the authors.

Perhaps a more direct way in which to induce orientation, and one which has been used by a number of researchers, is by hot-pressing. This is well illustrated by the results of Hu et al. [90] on composites with an anhydride-cured epoxy matrix and 18 µm BN particles. In the first stage of the fabrication procedure, illustrated in Figure 10, the composite was mixed and partially cured for 15 min at 120 °C to provide sufficient viscosity for the subsequent stage, in which a pressure of 10 MPa at 150 °C was applied to the composite sample between copper foils. The hot-pressed composite was then moulded into a disc shape with diameter 25.4 mm and thickness 200 µm, and finally cured at temperatures from 120 °C to 200 °C for programmed times. The particle orientation induced by the hot-pressing was detected by X-ray diffraction (XRD), and the degree of orientation was found to increase as the filler loading increased from 40 to 60 wt.%. The anisotropy induced at 50 wt.% was notable: 6.09 W/mK for the oriented sample in comparison with 2.44 W/mK for a sample with random orientation of the BN particles. In Figure 9, this orientation effect can be seen to increase the thermal conductivity from well below the intermediate trend line to well above it (open black symbols). A more dramatic increase, to 10.87 W/mK, was found for the higher filler loading of 60 wt.%, as can be seen in Figure 9, but the increased viscosity of this mixture required the use of acetone as a solvent. In fact, these authors carried out a systematic study including different temperatures (130, 150 and 170 °C) and pressures (7, 10, 13 MPa) for the pre-curing stage, as well as different particle sizes of 5, 18 and 25 µm. In this respect, it is interesting to note that increasing pressure results in higher thermal conductivity, as does increasing the size of the BN particles.

Similar results were reported by Liu et al. [116] for a low viscosity epoxy-amine filled system using isopropanol as a solvent, with either 1 to 2 µm h-BN platelets or exfoliated BNNS of about 300 nm lateral dimension. The fabrication procedure of composite films involved spin-coating followed by

evaporation of the solvent, and then pre-curing for 5 h at room temperature to provide the necessary viscosity of the mixture. This mixture was then cured under pressure at 5 MPa and 80 °C for 30 min before completing the cure over 5 h at 60 °C. The 40 wt.% BN composites showed considerable anisotropy, more so for the BNNS than for the h-BN. For example, in the through-plane direction the thermal conductivity was 1.9 W/mK for the BNNS composite and 1.3 W/mK for the h-BN composite, which increased to 6.0 W/mK and 3.0 W/mK in the in-plane direction, respectively; in Figure 9, these in-plane values lie well above and just on the intermediate trend line, respectively (filled sage green squares). The greater thermal conductivity for the BNNS filler was attributed to a reduction, by an order of magnitude, in the interfacial thermal resistance between filler and matrix in comparison with the h-BN filler, as a consequence of the use of a surface coupling agent (APTES).

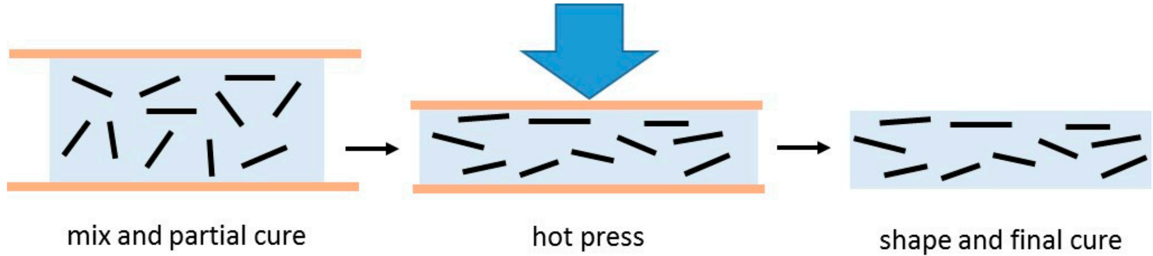

Figure 10. Schematic illustration of the hot-pressing procedure used to introduce orientation into epoxy-BN composites.

An even more dramatic enhancement of thermal conductivity by orientation was reported by Zhang et al. [153]. These authors investigated an anhydride-cured bisphenol-A epoxy system in which the 18 μm BN platelets were decorated with Ag nanoparticles, an approach that will be further discussed in Section 4.3. The fabrication procedure included the use of hot-pressing, and the effect of this can be considered separately from that of the Ag nanoparticles as the authors used a control sample with undecorated particles, prepared following the same procedure of hot-pressing ("Hot-pressed BN/epoxy"), as well as a sample prepared without hot-pressing ("Random BN/epoxy"). The hot-pressing was made under a relatively low pressure of 30 psi (≈200 kPa) at 100 °C for 10 min, followed by a final cure schedule at temperatures up to 200 °C for programmed times. For a filler content of 62 wt.%, the random BN/epoxy sample had the same thermal conductivity of 2.1 W/mK in both the in-plane and through-plane directions, as would be expected, while the hot-pressed BN/epoxy sample had a thermal conductivity of 9.5 W/mK in the in-plane direction compared with 2.6 W/mK in the through-plane direction. This orientation can be seen in Figure 9 (open dark green symbols) to increase the thermal conductivity from somewhat above the lower trend line to well above the intermediate trend line, even at this relatively low pressure.

Much higher pressures and filler contents were used by Zhu et al. [158], but there seems to be very little effect of the magnitude of the pressure on thermal conductivity. In some way this is consistent with the observation by Zhang et al. [153] that a low pressure can induce significant orientation and hence dramatically enhance thermal conductivity. Zhu et al. fabricated their composites by incorporating their BN platelets into an amine-cured epoxy using tetrahydrofuran as solvent, and compressed their samples at pressures of 43, 108 and 215 MPa for 5 min in a 24 mm diameter mould before curing them in an oven at 80 °C for 30 min and then at 120 °C for 60 min. It should be noted that this procedure is significantly different from the hot-pressing used by Hu et al. [90], Liu et al. [116] and Zhang et al. [153], in which the pre-cure took place under pressure. From SEM images of fracture surfaces of the cured composites, Zhu et al. concluded that there is a certain orientation of the BN platelets as a consequence of the compression process, but that this orientation is not significantly affected by the magnitude of the pressure applied. In contrast, for samples prepared without the application of pressure there was no observable orientation. This lack of dependence of orientation on the magnitude of the pressure is reflected in the thermal conductivity; although there is a fair amount of scatter in the data, there does

not appear to be any systematic or significant dependence on pressure, but the thermal conductivity is significantly higher than that for samples prepared without pressure. For example, at 84 wt.% BN and 215 MPa pressure, the through-plane and in-plane thermal conductivities were 7.95 W/mK and 8.63 W/mK, respectively, in comparison with only 3.3 W/mK for the sample prepared without compression. This effect of pressure can be seen very clearly in Figure 9 (open navy blue symbols). The rather small difference between the through-plane and in-plane thermal conductivities for a filler content of 84 wt.% is perhaps surprising, but it becomes much more marked for higher filler contents, and a thermal conductivity of over 20 W/mK was achieved in the in-plane direction at filler contents of about 90 wt.%.

An alternative way in which orientation can be introduced into epoxy-BN composite systems is by magnetic alignment, an approach that has been used by several researchers, most notably Lim et al. [114] and Kim and Kim [99], both groups following similar procedures for decorating the BN platelets with Fe_3O_4 nanoparticles. In order to obtain the desired orientation, the uncured epoxy-BN-Fe_3O_4 mixtures were placed in a magnetic field before curing. Lim et al. [114] cast 1 mm thick films with 20 vol% (≈34 wt.%) of 8 μm BN platelets from an epoxy solution in methylethylketone to obtain a vertical orientation of the platelets with respect to the plane of the film. Without magnetic orientation, the thermal conductivity was less than 1.0 W/mK, whereas for the oriented film it was 4.3 ± 0.5 W/mK in the vertical direction, thus increasing from just above the lower trend line in Figure 9 to close to the upper trend line in Figure 7. More recently, Kim and Kim [99] used Fe_3O_4-decorated BN nanoplatelets, which had previously been liquid phase exfoliated by ultrasonication from 12 μm h-BN particles in dimethylformamide. These decorated particles were then dispersed in proportions up to 20 wt.% in a DGEBA epoxy/acetone solution, before removal of the acetone and addition of the diaminodiphenylmethane curing agent. The doping of the surface of the BN nanoplatelets with Fe_3O_4 was confirmed by XRD and X-ray photoelectron spectroscopy (XPS), while the orientation of the nanoplatelets was also confirmed by XRD. Compared with composites fabricated with the raw h-BN particles, for which the thermal conductivity at 20 wt.% was 0.62 W/mK, the same content of the Fe_3O_4-doped nanoplatelets gave a slightly lower value of 0.48 W/mK without alignment, but a higher value of 1.07 W/mK with magnetic alignment. This last value falls just on the intermediate trend line and so is somewhat disappointing, while the lower value for the unaligned composite was attributed to the effect of additional Kapitza resistance introduced by the Fe_3O_4 nanoparticles.

In terms of enhancing thermal conductivity by the magnetic orientation procedure, the recent results reported by Kim and Kim [99] do not compare very favourably with the earlier work of Lim et al. [114]. Some other relatively recent results were also less successful. Salehirad et al. [125] adopted the same magnetic alignment principle but used a slightly modified procedure in which 70 nm h-BN nanoparticles were first exfoliated into nanosheets by sonication, polyacrylamide was then grafted and the nanosheets were finally modified with Fe_3O_4 nanoparticles. Epoxy composites with filler loadings up to 20 wt.% were cast in a mould located between two magnets, but the results were not definitive. Indeed, at the filler content of 20 wt.%, the highest thermal conductivity was found for the polyacrylamide-grafted BN nanosheets without Fe_3O_4 modification, while there was no systematic difference in thermal conductivity between the two orthogonal directions after orientation. The lower values found for the Fe_3O_4-modified nanosheets are possibly again due to increased Kapitza resistance, while the highest thermal conductivity of only about 0.4 W/mK at 20 wt.% is very close to the lower trend line in Figure 9. Similarly, the results of Su et al. [127] for flexible cycloaliphatic epoxy-BN composites are rather disappointing. Again, there is essentially no significant difference between in-plane and through-plane thermal conductivity after magnetic alignment, and the maximum value of thermal conductivity of about 1.0 W/mK at 30 wt.% filler content lies only mid-way between the lower and intermediate trend lines in Figure 9.

4.2. Three-Dimensional Structures

The basic objective of inducing orientation in composites by means of hot-pressing or magnetic alignment is to create preferential pathways for heat transport. In recent years, the same objective of creating pathways for phonon transport has been met in a number of ingenious ways, which rely essentially on the construction of a three-dimensional framework into which the BN particles can be introduced in an ordered way. In most cases, a further aim is to obtain high thermal conductivity at low filler loadings, for reasons of processability, and consequently many of the examples presented here use relatively low filler contents.

One quite common procedure is to create an aerogel-type structure with a vertically aligned anisotropic 3-dimensional BNNS network into which the epoxy resin system is infiltrated, as illustrated schematically in Figure 11. The aerogel fabrication often [70,89,134,152], but not always [79], makes use of the ice-templated assembly method, and the skeleton support can be constructed with materials other than BNNS such as cellulose [70] or polyamide 6,6 [79]. In these aerogel-type epoxy-BN nanocomposites, the thermal conductivity is nearly always measured only in the alignment direction, but Zeng et al. [152] compared the parallel and perpendicular directions. They found that the parallel direction gave significantly higher values of thermal conductivity at very low loadings, from 2 to 4 vol%, but that at higher loadings of around 10 vol% there was rather little difference, which they attributed to a microstructural change from a well-ordered wall-like to a honeycomb-like morphology. At 9.29 vol% BNNS, for example, the thermal conductivities in the parallel and perpendicular directions were 2.85 W/mK and 2.40 W/mK, respectively, compared with 1.13 W/mK for a composite with randomly distributed BNNS and with 0.16 W/mK for the epoxy alone. For a similar BNNS content of 9.6 vol%, Chen et al. [70] reported a thermal conductivity of 3.13 W/mK. The BNNS, with a lateral size of around 1.3 μm and thickness of about 2.5 nm, and previously exfoliated from h-BN particles, were incorporated into a cellulose supporting structure, which was infiltrated with a cycloaliphatic epoxy resin with methyl-hexahydrophthalic anhydride as a curing agent and neodymium acetylacetonate trihydrate as a latent catalyst. These values of thermal conductivity obtained by Zeng et al. [152] and Chen et al. [70] are remarkable for such a low filler content. If the 9 vol% content is approximated as 15 wt.% based on the densities of BN and epoxy, it can be seen from Figure 7 that they fall well above the upper trend line.

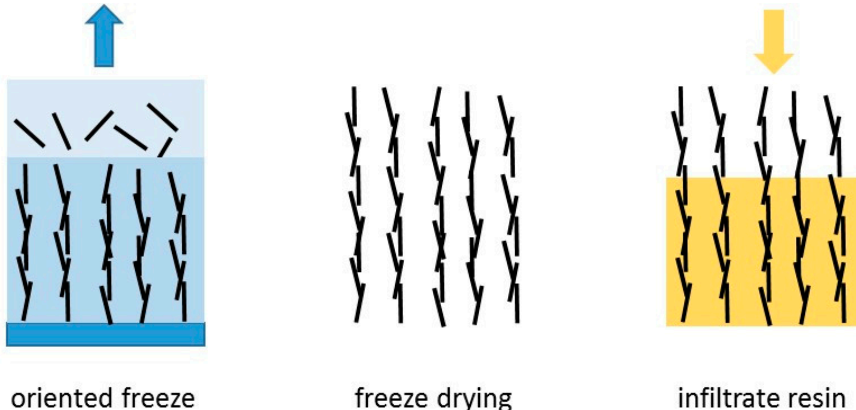

Figure 11. Schematic illustration of aerogel procedure for fabricating 3-dimensional oriented epoxy-BN nanosheets (BNNS) composites.

At even lower filler contents, this aerogel procedure also produces some impressive thermal conductivity results. Wang and Wu [134] infiltrated bisphenol-F epoxy and *o*-dichloroaniline methane as curing agent under vacuum into the vertically aligned 3-dimensional BNNS network and measured a value of 1.56 W/mK in the cured composite with only 4.4 vol% filler. This was significantly higher than the value of 0.32 W/mK for the same content of randomly dispersed BNNS. If the filler content is approximated as 8 wt.%, this result can be seen to lie well above the intermediate trend line in Figure 9

(open maroon symbols), and just above the upper trend line in Figure 7. On the other hand, the results reported by Fu et al. [79] for a filler content of 4 vol% are not quite so impressive. These workers prepared a polyamide 6,6 aerogel structure, to which the BN platelets, with sizes between 3 and 5 μm, adhered and formed a continuous thermal conduction network. After infusion of the epoxy resin and diaminodiphenyl methane curing agent, and subsequent curing of the composite, they measured a value of 0.6 W/mK. Although this is three times higher than the thermal conductivity of a composite with the same content of a random dispersion of the same BN platelets, it lies only just above the intermediate trend line in Figure 9 (open yellow square).

In contrast to the low filler contents used in the works described above, Hu et al. [89] introduced large quantities of filler into their three-dimensionally structured composites. Their aerogel was prepared by ice-templating and then freeze-drying an aqueous slurry of 10 μm h-BN platelets with sodium carboxymethyl cellulose, which acts as both a dispersion agent and organic binder. The epoxy resin, anhydride curing agent and imidazole catalyst were mixed and infused into the aerogel, and the composite was finally cured at 120 °C for 1 h and then at 160 °C for 2 h. The thermal conductivity increased with BN content in the usual way, and at the highest filler content of 34.2 vol% (approximately 49 wt.%) a value of 4.42 W/mK was measured, compared with a value of only 1.16 W/mK for a randomly dispersed sample. This represents an increase from somewhat above the lower trend line in Figure 9 for the random sample to just above the intermediate trend line for the 3-dimensionally structured sample (open dark brown square). In comparison with the values of thermal conductivity obtained for other epoxy-BN composites prepared by the aerogel procedure and discussed above, this result is not so noteworthy for such a high filler content. It is also worth remarking that, although the cure schedule only reached 160 °C as a maximum, these authors reported glass transition temperatures for the composite of up to 240 °C and decreasing markedly as the BN content increased; it is difficult to reconcile these observations.

The above procedures usually introduce some anisotropy of thermal conductivity in the cured epoxy-BN composite. Tian et al. [132] argue that such anisotropy is not always desirable and describe an alternative way in which BN can be incorporated into a 3-dimensional structure, but with an isotropic thermal conductivity. These authors added BN particles to an aqueous solution of sodium dodecyl sulphate, which acts as both a foaming agent and surfactant, and gelatine, which provides the structural integrity of the BN foam. Foaming was induced by rapid stirring, and the slurry was then poured into a mould and stored at low temperature to solidify. After further drying at 70 °C, the previously mixed epoxy, anhydride curing agent and imidazole catalyst were poured into the porous BN foam, degassed, and then cured at 120 °C for 1 h and 160 °C for 3 h to obtain the epoxy-BN composite. The procedure is schematically illustrated in Figure 12. X-ray tomography shows that the BN filler formed a continuous 3-dimensional structure and that the epoxy filled the pores.

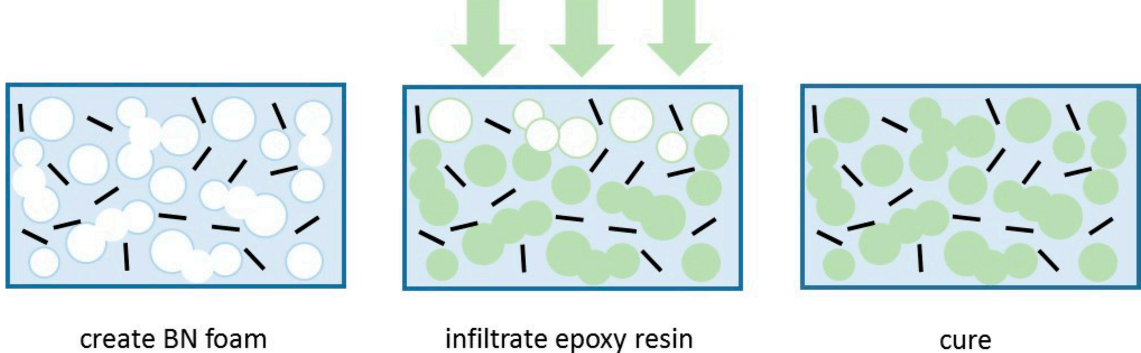

Figure 12. Schematic illustration of the fabrication of porous BN foam and epoxy-BN composite.

This procedure resulted in some remarkable thermal conductivity values. For composites fabricated with 24.4 wt.% of 8.7 μm BN platelets, the thermal conductivity in the in-plane direction was

5.19 W/mK and in the through-plane direction was 3.48 W/mK. In principle, this fabrication procedure should not give rise to anisotropic thermal conductivity; while not exactly isotropic, both of these values represent high thermal conductivities for the given filler content, as can be seen in Figure 9 (dark blue symbols), the former even lying well above the upper trend line in Figure 7, while the latter falls almost on it. Considerably lower values of thermal conductivity were found for composites fabricated in the same way but using smaller BN particles of sub-micron size (0.7 µm); at 25.1 wt.% filler content, these composites had a thermal conductivity of only 1.27 W/mK, just on the intermediate trend line in Figure 9 (open dark blue circle). The authors attributed the difference between the results for the micron-sized and sub-micron-sized BN particles to an alignment of the larger particles within the pore walls in the foam structure, in comparison with a random distribution for the sub-micron particles. It should be noted that these filler contents represent approximately limiting values for this procedure; according to the authors, any further increase of loading results in serious aggregation of the BN particles and poor structural uniformity of the composite. This can be noted from their graph of thermal conductivity as a function of BN content, for which there is a noticeable downward curvature at the highest contents.

A similar approach was adopted by Wang and Wu [135]. Melamine foam with an average pore size of ≈100 µm was repeatedly immersed in an aqueous solution of polyethyleneimine and then in a dispersion of exfoliated BNNS in isopropanol. In this way, they achieved a layer-by-layer deposition of BNNS on the melamine foam structure by virtue of the electrostatic attraction between the positively charged polyethyleneimine and the negatively charged BNNS, with up to 30 deposition cycles. Scanning electron microscopy and element mapping show that the BNNS coat the surfaces of the melamine foam cells rather homogeneously. The epoxy resin and curing agent, *o*-dichloroaniline methane, were then infiltrated into the foam under vacuum, followed by degassing and finally curing at 150 °C for 2 h and 180 °C for 2.5 h. It was found that the thermal conductivity increased with the number of deposition cycles, reaching a value of 0.53 W/mK after 20 cycles. Increasing the number of deposition cycles to 30 further increased the thermal conductivity to 0.6 W/mK, but the relative increase was markedly reduced, similar to the downward curvature in the results of Tian et al. [132]. Nevertheless, this value remains remarkable. The authors estimated the filler content to be about 1.1 vol%, approximately 2 wt.% calculated on the basis of the densities, and it can be seen that this value at a very low filler content lies well above the intermediate trend line in Figure 9 (open purple square). Indeed, the authors point out that to achieve this thermal conductivity with a random dispersion of BNNS in epoxy would require a filler loading of almost 20 vol%, which would correspond closely with the lower trend line in Figure 9.

4.3. Surface Decoration

There are a number of recent reports in which the surfaces of BN particles have been decorated with a variety of different nanoparticles or nanostructures, and following a variety of different procedures, some much more elaborate than others, with a view to achieving increased thermal conductivity. This has met with mixed success. Furthermore, since many of these decorating particles are themselves thermally conducting, such as graphene, silver and gold, the corresponding composites are no longer strictly epoxy-BN composites, but hybrids, and direct comparison with epoxy-BN composites fabricated in different ways is no longer valid. Nevertheless, some of these reports are considered here for the sake of interest.

Some of the simpler procedures were used by Han et al. [84] and Zhang et al. [155]. In the former case, hetero-structured SiC-BNNS fillers, fabricated by sol-gel and in situ growth methods, were mechanically mixed with the epoxy resin and curing agent and cured at 120 °C for 5 h. SEM images showed SiC nanoparticles on the surface of the BNNS, and that the number of SiC nanoparticles increased with the amount of Si powder used in the fabrication process. The mass proportions of SiC:BNNS used were 2:1, 1:1 and 1:2. The thermal conductivity of the epoxy alone was 0.22 W/mK, and those of the epoxy-SiC and epoxy-BNNS composites with 20 wt.% filler were 0.43 W/mK and

0.61 W/mK, respectively; this simply reflects the higher thermal conductivity of BN in comparison with SiC. There was a synergistic effect with the SiC-BNNS fillers, the thermal conductivity being higher than that of the composites with each filler separately. The optimum proportion was 1:1, at which a thermal conductivity of 0.89 W/mK was achieved at 20 wt.% filler content, but this value only just reaches the intermediate trend line in Figure 9.

Zhang et al. [155] used hybrids of small h-BN particles and larger cubic BN (c-BN) spherical agglomerates with a diameter of 59 μm. The procedure used was to modify the particles with a silane coupling agent, APTES, and then add them to an Au salt preloaded micellar solution to give Au-decorated BN. These particles were added in various proportions to the epoxy and curing agent in an ethanol solution, mixed thoroughly, degassed under vacuum, and then cured, first at room temperature for 3 h and then at 80 °C for a further 4 h. Similar to the findings of Han et al. [84], a synergistic effect was again observed: the thermal conductivity enhancement for 6 vol% was 50% for c-BN and 80% for h-BN, but a significantly higher enhancement of 120% was found for a hybrid with 4 vol% h-BN and 2 vol% c-BN. Despite this, the values of thermal conductivity reported are disappointing: 0.512 W/mK for a composite with 10.5 vol% (approximately 17 wt.%) filler without Au-decoration, increasing to 0.656 W/mK with Au-decoration, only just reaching the intermediate trend line.

Feng et al. [75] used a more elaborate fabrication procedure, devised to enhance both thermal conductivity and flame retardancy. By means of a simple hydrothermal process, they produced $Ni(OH)_2$ nanoribbons that were 15 to 20 nm wide and 1 to 2 μm long, the purpose of which was to provide flame retardancy by endothermic decomposition. These nanoribbons were coated onto reduced graphene oxide (RGO) sheets by electrostatic self-assembly to give what the authors denoted as RGO@$Ni(OH)_2$. An ethanol solution of RGO@$Ni(OH)_2$ was mixed with an acetone solution of the diglycidyl ether of bisphenol-F epoxy and imidazole curing agent, the solvents were evaporated and then the 5 to 10 μm h-BN platelets were dispersed in the mixture and the composite was cured following a schedule of 2 h at 60 °C, 2 h at 100 °C, and 5 h at 150 °C. Composites were fabricated with up to 40 wt.% h-BN. Compared with composites of epoxy and h-BN platelets alone, for which a thermal conductivity of 1.44 W/mK was obtained for 40 wt.% filler content, composites with the same content of h-BN and only 2 wt.% RGO@$Ni(OH)_2$ had a thermal conductivity of 2.00 W/mK, an increase of nearly 40%. In fact, a significant increase upon addition of 2 wt.% RGO@$Ni(OH)_2$ occurred only with h-BN contents greater than 20 wt.%. The authors explained this on the basis of the dispersion of the h-BN platelets being too "dilute" at low filler contents, whereas at higher filler contents the RGO@$Ni(OH)_2$ forms bridges between the h-BN platelets, creating thermal conduction pathways. Nevertheless, with respect to the thermal conductivity, even though this value is almost an order of magnitude greater than that of the epoxy alone (0.21 W/mK), at a filler content of 40 wt.% it still falls only about mid-way between the lower and intermediate trend lines.

Significantly more enhancement of thermal conductivity was achieved by Fu et al. [78], though at a much lower filler content of 4.7 vol%, through a combination of orientation and decoration procedures. BNNS were decorated with 10–20 nm Ag nanoparticles, denoted Ag-BNNS, and mixed with Ag nanowires (AgNW), previously synthesised by a modified polyol procedure, to give Ag-BNNS/AgNW. This mixture was ice-templated by freezing and freeze-drying to give a 3-dimensional network, which was then infiltrated by epoxy resin and the anhydride curing agent and cured for 2 h at 160 °C. The BNNS content was 4.7 vol%, which corresponds to approximately 8 wt.%. The thermal conductivity in the out-of-plane direction, which is the orientation direction of the BNNS, increased with AgNW content, which rose to 40 wt.% with respect to the BNNS content. The thermal conductivity at approximately 8 wt.% filler content was 0.34 W/mK for the epoxy-BNNS composite with untreated BNNS particles, 0.50 W/mK for epoxy/Ag-BNNS, and 0.80 W/mK for epoxy/Ag-BNNS/AgNW with the highest nanowire content. Although the thermal conductivity was low, as a consequence of the filler content being very low, these represent significant enhancements, the value of 0.80 W/mK falling well above the intermediate trend line, as can be seen in Figure 9 (filled green square). The authors attributed

the enhancement to AgNW improving heat transfer between BNNS, termed a "physical connection", and the Ag-decoration improving the interface between the BNNS and the AgNW, termed a "welding connection". It should be borne in mind that these composites, even without the AgNW, are hybrids with the Ag nanoparticles decorating the surface of the BNNS, and direct comparison of their thermal conductivity with the other epoxy-BN composites discussed here should be made with caution.

The combination of surface decoration and a "densely-assembled and oriented" structure was introduced in an innovative way by Liu et al. [117], making use of 3-D printing technology, in order to optimise the thermal pathways and promote efficient heat transfer within the epoxy-BN composite. The 15 μm h-BN platelets were first exfoliated by sonication in dimethylformamide, and then aqueous $AgNO_3$ was gradually added and stirred for 1 h at 150 °C to reduce the Ag^+ to Ag nanoparticles (AGNPs) decorating the BN surfaces; this filler is denoted BN-Ag. The printing inks were prepared by mixing the DGEBA epoxy and amine curing agent with silica, as a thixotropic agent, to give a modified epoxy (MEP), and then adding the BN or BN-Ag particles to give loadings of 5, 10 and 20 wt.% in the final composites. The 3-D printing was carried out using single-material and multi-material printing. For single-material printing (S-BN/MEP and S-BN-Ag/MEP for undecorated and decorated BN platelets, respectively), the sample was printed by repeated passes of the MEP ink with the above filler loadings. For the multi-material printing (M-BN-Ag/MEP), the passes were made successively of MEP ink loaded with 40 wt.% BN-Ag filler and 1, 3 or 7 passes of MEP ink alone. This procedure gave the same 5, 10 and 20 wt.% filler loadings in the final composite, but with the conducting pathways "densely-assembled and oriented". High resolution SEM and XRD show that the BN particles were oriented along the printing direction by shear alignment. The printed samples were cured for 3 h at 40 °C and 6 h at 80 °C. The thermal conductivity was measured in two orthogonal directions—the printing direction (PD) and the transverse direction (TD)—and in all cases was found to increase with BN content. In the TD, all the samples had approximately the same thermal conductivity, reaching 0.6 to 0.7 W/mK at a filler loading of 20 wt.% in comparison with 0.23 W/mK for the MEP alone. In the PD, on the other hand, there was a much more dramatic increase in the thermal conductivity with filler loading, increasing in the order S-BN/MEP (0.98 W/mK) → S-BN-Ag/MEP (1.77 W/mK) → M-BN-Ag/MEP (2.52 W/mK). The increase from S-BN/MEP to S-BN-Ag/MEP can be attributed to the presence of silver nanoparticles distributed on the surface of BN-Ag platelets, which reduce the contact thermal resistance, while the increase from S-BN-Ag/MEP to M-BN-Ag/MEP results from the dense filler loading of 40 wt.% in the heat-conducting phase, such that there is always contact between BN platelets. Once again, it should be borne in mind that these composites with BN-Ag are hybrids, with the Ag nanoparticles providing thermal pathways in addition to the BN. It is at least partly for this reason that the value of 2.52 W/mK for M-BN-Ag/MEP falls on the upper trend line in Figure 7, and the value of 1.77 for S-BN-Ag/MEP falls well above the intermediate trend line in Figure 9 (filled sage green symbols). On the other hand, without the Ag decoration on the BN platelets, the value of 0.98 W/mK for S-BN/MEP falls just on the intermediate trend line in Figure 9.

5. Concluding Remarks

This review has examined the cure kinetics and thermal conductivity of a large number of epoxy-BN composites reported in the literature. As regards the cure kinetics, the effect of fillers in general is most commonly to accelerate the cure reaction, usually attributed to the catalytic effect of, for example, hydroxyl groups present on the surfaces of the filler particles. For epoxy-BN composites in particular, there are rather limited studies of the cure kinetics, but it is interesting to note that for these epoxy-BN systems the reaction is more often retarded than accelerated by the filler particles. Since many of these cure kinetics studies of epoxy-BN systems involve thiol as a curing agent, it is surmised that this might be a consequence of a Lewis acid-base interaction between matrix and filler, and that this interaction might have some corresponding influence on the thermal conductivity of the cured composites. It transpires that such composites do indeed have a thermal conductivity which is higher than that of many other systems with the same filler content.

The discussion of the thermal conductivity considers composites which have been fabricated using a wide variety of methods, from simple mixing to much more elaborate procedures involving such aspects as orientation and other means of creating improved pathways for heat conduction. The composite systems include diverse epoxy resins and curing agents, and incorporate BN particles of different sizes and shapes, both with and without surface treatment and/or coupling agents. The dependence of the thermal conductivity on BN content in almost all cases follows the same tendency, namely to increase with increasing filler content and displaying an upward curvature. Within this broad tendency, however, there is great variation, and we attempt to analyse the reasons for this variation by defining three trend lines in the graph of thermal conductivity as a function of wt.% BN. The lower trend line indicates the approximate limit below which very few results lie; the vast majority of values of thermal conductivity reported for composites prepared without "special procedures" or orientation of the BN platelets lie between the lower and intermediate trend lines; and the upper trend line represents the approximate limit below which 95% of the reported values lie.

By locating reported values of thermal conductivity with respect to these trend lines it is possible to discuss the effects of the many variables involved. For example, the use of surface treatments and/or coupling agents nearly always increases the thermal conductivity. Thermal conductivity generally increases with BN particle size, and agglomerates are often better than platelets for any given filler content. To obtain thermal conductivities above the intermediate trend line usually requires some special preparation procedures, or the introduction of orientation of the BN platelets, though there are a few notable exceptions in which very high thermal conductivities were obtained without such procedures. Furthermore, in a majority of cases these special procedures apply to rather low filler contents, for example less than 20 wt.%, for which even a very significant increase in thermal conductivity relative to a simple mixing procedure results in a thermal conductivity which is still less than about 3 W/mK.

In general, if the use of these epoxy-BN composites is considered for application in IMS devices, there are some fundamental requirements that must be met, including high thermal conductivity and ease of processing. Many of the notable reports of enhancement of thermal conductivity discussed here, and principally those involving special procedures, do not meet either of these requirements, while many other procedures involve the use of solvents in the preparation of the composites, a practice which is not desirable for industrial applications. Likewise, from a consideration of the intermediate trend line, it is evident that to obtain a thermal conductivity greater than, for example, 5 W/mK using "simple" preparation techniques would require a filler content greater than about 50 wt.%, which also introduces practical difficulties as a consequence of the reduced manageability of such stiff pastes.

For IMS devices, therefore, there may be several procedures that could offer some practical advantages in attempting to achieve higher thermal conductivity. One is the use of pressure, which can be applied in practice quite easily, for example in an autoclave, and which allows the consolidation of relatively stiff resin-filler mixtures and elimination of voids. Another is to induce orientation in a type of pre-preg, which could then be laid up in a manner similar to that used in the fabrication of fibre-reinforced composites, to obtain the orientation in the required direction of heat transfer. Finally, the use of hybrids, for which several examples discussed exhibited synergistic behaviour, could provide a relatively simple means of enhancing the thermal conductivity, with combinations of different particle sizes and shapes. To date, it does not appear that these approaches have been exhausted.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1944/13/16/3634/s1, Supplementary Material 1: Excel spreadsheets giving correspondence between symbols and references in Figures 3 and 4. Supplementary Material 2: Excel spreadsheets giving correspondence between symbols and references in Figure 7. Supplementary Material 3: Excel spreadsheets giving correspondence between symbols and references in Figure 9.

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Paper V

Remarkable thermal conductivity of epoxy composites filled with boron nitride and cured under pressure

Article

Remarkable Thermal Conductivity of Epoxy Composites Filled with Boron Nitride and Cured under Pressure

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Abstract: This work demonstrates that the application of even moderate pressures during cure can result in a remarkable enhancement of the thermal conductivity of composites of epoxy and boron nitride (BN). Two systems have been used: epoxy-thiol and epoxy–diamine composites, filled with BN particles of different sizes and types: 2, 30 and 180 μm platelets and 120 μm agglomerates. Using measurements of density and thermal conductivity, samples cured under pressures of 175 kPa and 2 MPa are compared with the same compositions cured at ambient pressure. The thermal conductivity increases for all samples cured under pressure, but the mechanism responsible depends on the composite system: For epoxy–diamine composites, the increase results principally from a reduction in the void content; for the epoxy–thiol system with BN platelets, the increase results from an improved matrix-particle interface; for the epoxy–thiol system with BN agglomerates, which has a thermal conductivity greater than 10 W/mK at 44.7 vol.% filler content, the agglomerates are deformed to give a significantly increased area of contact. These results indicate that curing under pressure is an effective means of achieving high conductivity in epoxy-BN composites.

Keywords: Thermal conductivity; epoxy composites; boron nitride; density; pressure; differential scanning calorimetry (DSC)

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1. Introduction

Epoxy composites filled with boron nitride (BN) are widely used for heat management in Insulated Metal Substrates (IMS). Such materials must satisfy a number of requirements, including adhesion, processability, electrical insulation, and high thermal conductivity. The last of these has attracted considerable attention, and the state of the art in polymer-based composites in general [1,2], and in epoxy-BN composites in particular [3], has been reviewed recently. There are numerous parameters which play a role in determining the thermal conductivity, perhaps the most important being the filler content, size and type (shape) of filler particles, and the surface treatment or the use of coupling agents.

It is widely recognized that the thermal conductivity of epoxy-BN systems increases with increasing BN content [3,4], at least up to about 50 vol.% BN. However, higher BN contents present difficulties for processing on account of their being very stiff pastes, and the thermal conductivity often decreases as a consequence of the presence of voids which are difficult to remove. The effects of BN filler size and type have been investigated previously [5,6], and it has been shown that, for a given filler content, the thermal conductivity generally increases with particle size; the usual interpretation is that larger particles have a smaller interfacial contact area with the matrix, this interface presenting a barrier to phonon transport. As regards filler type, it was found [6] that agglomerates result in a higher thermal conductivity than do platelets.

The effect of BN filler size highlights the importance of the matrix–particle interface, and attempts have been made to improve this interface by the surface treatment of the particles or with the use of coupling agents. The results, however, are not entirely conclusive. While many authors report significant increases in the thermal conductivity [7–14] there are also reports that these treatments have much less effect [15–17].

The drive towards increasing the thermal conductivity of epoxy composites for IMS applications, occasioned by the demand for the use of electronic devices at ever higher frequencies and power densities, should take into consideration all of the above aspects, but must also be governed by some more practical motives. For example, the electrical insulation properties can be affected by the migration of copper ions in the formation of conductive anodic filaments in humid conditions [18,19], which can mitigate against the use of amines as a cross-linking agent. Similarly, the requirement for good adhesion of the dielectric layer to the metallic substrate of the IMS would imply a preference for filler particles such as Al_2O_3 rather than BN, despite the intrinsically lower thermal conductivity of the former. Processability is also a factor that must be borne in mind; although significantly higher thermal conductivities have been achieved in epoxy composites by the alignment of the filler particles by various means (e.g., [20]), these procedures are usually rather elaborate, and hence the composites are not easily fabricated.

In the light of the above discussion, it would be interesting to find a more generic way in which the thermal conductivity of epoxy composites might be increased. There is, indeed, just such a possibility, though it has received little attention to date; this is the effect of the application of pressure during cure. In the first place, it might intuitively be expected that applying pressure would consolidate the material, improving the matrix–filler interface, and hence enhancing the thermal conductivity. Additionally, though, there is also the possibility of densifying the material, by cooling the epoxy matrix through its glass transition region under pressure [21,22]. In view of the occasionally noted correlation between density and thermal conductivity [22,23], this would imply a further possible route towards increasing the thermal conductivity. Accordingly, it would be appropriate to summarize here the state of the art as regards the use of pressure during the cure of epoxy-BN composites for high thermal conductivity applications.

Several authors have reported the use of pressure during fabrication of their epoxy-BN composites, but there are very few systematic studies of this effect on the thermal conductivity. Furthermore, there are several different ways in which the pressure can be applied. Some workers apply pressure to the composite mixture before curing at ambient pressure [23–25]. The principal objective is presumably to consolidate the sample, though a wide range of pressures is used, and other objectives are noted: Lewis et al [25] use approximately 1.6 MPa to "break … agglomerations and flatten the material"; Isarn et al [24] use approximately 74 MPa to "compact and shape" cylindrical samples before cure, while Zhu et al [23] compression mold samples, at pressures in the range from 43 to 215 MPa, in such a way as to introduce significant orientation, as evidenced by a marked difference between the thermal conductivities measured in the in-plane and through-plane directions.

On the other hand, several workers simply use pressure, without specifying the magnitude, in a process often referred to as "hot pressing", as part of the fabrication procedure of their epoxy composites [13,26–29]. The primary objectives of each of these studies are manifold, and do not necessarily include the investigation of the effect of pressure. For example, Jang et al [13] and He et al [26] study the effect of coupling agents and functionalization of the BN particles on the thermal conductivity of their hot-pressed composites, while Mun et al [28] and Wu et al [29] report the thermal conductivity of hybrid epoxy-BN composites with expanded graphite and silver nanoparticles, respectively, in both cases after compression molding at an unspecified pressure. In contrast, Sun et al [27] use the hot pressing process to deliberately introduce orientation into their cured composites fabricated with BN platelets, in comparison with composites fabricated with BN microspheres, which are essentially isotropic. Thus, although these composites are all cured

under pressure, the effect of pressure *per se* on the thermal conductivity cannot be identified.

In the majority of studies, though, the composite is either first partially cured under pressure [8,12,30–33] and subsequently post-cured without pressure, or is directly fully cured [7,34–36], in all cases under specified conditions of pressure, temperature and cure time. Distinction should be made here between two different modes in which the pressure is applied: (i) the pressure is applied uniaxially (hot-pressing) [31–33], which deliberately introduces orientation and yields composites with significant differences between the in-plane and out-of-plane thermal conductivities; and (ii) the sample is compressed in a mold [8,12,30,34–36], thus implying effectively hydrostatic pressure and no orientation of the BN filler particles. A variety of pressures is employed in the fabrication of the composites, but for the hot-pressing technique [31–33] the pressures tend to be lower, in the range from 200 kPa (30 psi) to 13 MPa, in comparison with pressures of 5 MPa [12], 10.5 MPa [7], 13.2 MPa [36], 20.6 MPa (3000 psi) [8,30], and 42 MPa [34,35] for samples cured in a mold.

In the latter category, the large number of additional factors which play a role in determining the thermal conductivity of these composites (e.g., BN particle size and shape, filler content, surface treatments and coupling agents [3]) make it impossible to identify the effect of pressure. For example, the increasing pressures listed immediately above give rise to the following maximum thermal conductivities: 2.7 W/mK and 10.6 W/mK for 60 vol.% of surface treated 3.6 μm and 10.6 μm platelets, respectively, cured at 5 MPa [12]; 10.31 W/mK for 57 vol.% of 5-11 μm silane treated agglomerates, cured at 10.5 MPa [7]; 3.6 W/mK for 69 vol.% of untreated BN particles, cured at 13.2 MPa [36]; 1.5 W/mK and 3.5 W/mK for 80 vol.% of surface treated 6 μm and 18 μm particles, respectively, cured at 20.6 MPa [30]; 3.4 W/mK for 37 vol.% of surface treated BN platelets, cured at 42 MPa [34].

In order to identify the effect of pressure on the thermal conductivity of these epoxy-BN composites, it would clearly be necessary to make a systematic study. However, of all the studies discussed above, only Zhu et al [23] and Hu et al [33] include such an investigation. Zhu et al [23], as noted earlier, used pressures between 43 and 215 MPa to introduce significant orientation to the uncured epoxy-BN mixture at room temperature before curing without pressure at higher temperature. For example, these authors reported a large increase in the thermal conductivity, reaching ~20 W/mK for 90 wt.% BN in the in-plane (oriented) direction in comparison with about 10 W/mK in the through-plane direction and with only about 4 W/mK for samples with the same filler content prepared without pressure. There was no significant effect on the thermal conductivity of the magnitude of the pressure applied, which suggests that 43 MPa pressure is sufficient to introduce significant orientation, which is not further improved by higher pressures. In contrast, Hu et al [33] used lower pressures and a much more elaborate fabrication procedure. Samples were prepared by first pre-curing the epoxy-BN mixture to increase its viscosity, then hot-pressing at different pressures (7, 10, 13 MPa) and temperatures (130, 150, 170 °C) before shaping the samples in a cylindrical mold and finally curing them without pressure at 120 °C for 1 h, 160 °C for 2 h, and 200 °C for 2 h. These authors found that the thermal conductivity increased with pressure, for example from 8.3 W/mK to 10.9 W/mK and then to 11.9 W/mK for 60 wt.% of 18 μm BN particles at 7, 10, and 13 MPa. Thus, at these pressures, significantly lower than those used by Zhu et al [23], the degree of orientation *is* a function of the pressure applied.

From the foregoing discussion, it is evident that it is not possible to obtain any clear idea about the effect of pressure during cure on the thermal conductivity of epoxy-BN composites from the results presented in the literature. Consequently, in the present work we make a systematic investigation of the effect of pressure during cure on the thermal conductivity of a number of different epoxy-BN composite systems, and show that significant increases can be achieved. The mechanisms by which these increases are obtained depend on the composite system, and demonstrate that enhancement of the thermal conductivity can occur in ways other than by orientation.

2. Materials and Methods

2.1. Materials

The epoxy resin used was diglycidyl ether of bisphenol-A, DGEBA (Araldite GY240, Huntsman Advanced Materials, Salt Lake City, UT, USA), with a nominal molecular weight per epoxy equivalent (eq) of 182 g/eq, density of 1.17 g/cm^3 and viscosity of 7000 to 9000 mPa.s at 25 °C. The principal cross-linking agent used was a thiol, pentaerythritol tetrakis (3-mercaptopropionate) (Sigma-Aldrich, Saint Louis, MO, USA), with a molecular weight of 488.66 g/mol, density of 1.28 g/cm^3, and viscosity of 500 mPa.s at 23 °C. In order to initiate the cross-linking reaction of the epoxy with the thiol, a latent initiator, encapsulated imidazole (LC-80, Technicure, A&C Catalysts, Linden, NJ, USA) in the form of powder, was used. In addition, a polyoxypropylene diamine, Jeffamine D-230 (molecular weight 230 g/mol, density 0.948 g/cm^3, viscosity 9000 mPa.s at 25 °C), and a dicyandiamide, N,N-dimethyl-N-phenyl urea (PDU-250M, Technicure, A&C Catalysts, Linden, NJ, USA), were also used as alternative cross-linking agent and initiator, respectively, for comparative purposes.

Different grades of hexagonal BN filler (Saint Gobain Ceramic Materials, Amherst, NY, USA) were used, shown in Figure 1, with average and maximum particle size, tap density and specific surface area, respectively, as given in the manufacturer's literature [37], as follows:

- PCTP2: 2 μm, 10 μm, 0.2 g/cm^3, 10 m^2/g;
- PCTP30: 30 μm, 100 μm, 0.6 g/cm^3, 1 m^2/g;
- PCTP30D: 180 μm, 1600 μm, 0.6 g/cm^3, 1 m^2/g;
- CTS7M: 120 μm, 180 μm, 0.5 g/cm^3, 3.5 m^2/g.

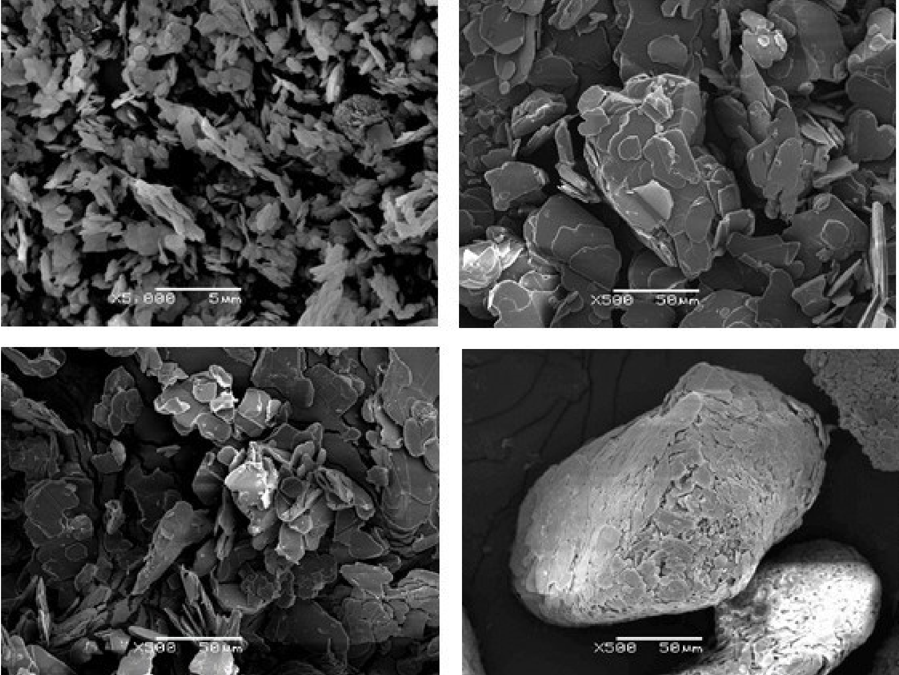


Figure 1. Scanning Electron Microscopy (SEM) images of the as-received BN particles: (top left) PCTP2, 2 μm, magnification 5000×, scale bar 5 μm; (top right) PCTP30, 30 μm, magnification 500×, scale bar 50 μm; (bottom left) PCTP30D, 180 μm, magnification 500×, scale bar 50 μm; (bottom right) CTS7M, 120 μm, magnification 500×, scale bar 50 μm.

Various important aspects of these filler particles can be appreciated from this Figure. The 2 μm and 30 μm particles are both in the form of platelets, but the specific surface area is 10 times higher for the smaller particles; this has the effect that it is difficult to fabricate composites with a large content of the 2 μm particles. The 180 μm particles are

also in the form of platelets, but there is a very wide distribution of particle sizes; according to the manufacturer, these particles are engineered for high shear mixing processes. On the other hand, the 120 μm particles are in the form of agglomerates, denoted as spherical powder by the manufacturer. The filler particles were used as received, without any surface treatment.

2.2 Methods

2.2.1. Sample Preparation

The epoxy-BN composites were fabricated in the proportions given in Table 1, where the sample nomenclature is also given. In all cases, a stoichiometric ratio of epoxy to curing agent was used, and for the epoxy–thiol composites the initiator was added in a proportion of 2 parts per hundred resin. For each epoxy system cured under pressure (except for the 2 μm composites, for which only the lower filler content was used, for the reasons given above), two BN filler loadings were used, specified with respect to the combined weight of epoxy and BN: For epoxy–thiol, 60% and 70%; for epoxy–diamine, 60% and 65%. The reason why a lower maximum filler content was used for the epoxy–diamine composites lies in the significantly higher viscosity of the diamine (9000 mPa.s) in comparison with the thiol (500 mPa.s); epoxy–diamine composites with a filler content higher than 65% by weight of BN with respect to the combined weight of BN and epoxy resulted in a paste that was so stiff that it was unworkable in practice. Likewise, no 70% epoxy–thiol samples could be prepared at ambient pressure with the 120 μm agglomerates, though this was possible when pressure was applied during cure. This ability to obtain epoxy-BN composite samples with higher filler contents by the application of pressure was earlier noted by Hu et al [33]. Table 1 also includes data for the 30% and 50% epoxy–thiol systems, which were prepared at ambient pressure.

Table 1. Compositions by weight of epoxy–thiol samples, ETLBN, with BN particles (particle size, x = 2, 30, 120s, 180 μm) and epoxy–diamine samples, EJBN, with BN particles (x = 30). Note that ETLBN2-70 samples could not be prepared. The weight per cent of BN particles is converted into volume per cent in the final column.

Sample	Epoxy	BN	Thiol	LC-80	Diamine	BN vol.%
ETL	100	0	66.7	2.0	-	0
ETLBNx-30	70	30	46.7	1.4	-	12.9
ETLBNx-50	50	50	33.4	1.0	-	25.7
ETLBNx-60	40	60	26.7	0.8	-	34.2
ETLBNx-70	30	70	20.0	0.6	-	44.7
EJ	100	0	-	-	33.3	0
EJBNx-60	40	60	-	-	13.3	38.1
EJBNx-65	35	65	-	-	11.7	43.3

All the components were mixed by hand for 15 minutes to ensure homogeneity and were then degassed under vacuum (< 26 hPa) at room temperature for about 10 minutes. The quality of the dispersion can be evidenced by examination by Scanning Electron Microscopy (SEM) of the fracture surfaces of cured composite samples. An illustration of one such SEM micrograph is shown in Figure 2, for the sample ETLBN2-60, with 60% of 2 μm platelets. In comparison with composites fabricated with the other BN particles, these 2 μm particles present the greatest difficulty for dispersion in view of their high specific surface area. Nevertheless, it can be seen from Figure 2 that the dispersion is excellent; the particles appear to be uniformly distributed across the fracture surface, and there are no agglomerations of particles or regions rich in epoxy matrix. Similar SEM micrographs for

other samples shown later demonstrate that this quality of dispersion is maintained for other compositions.

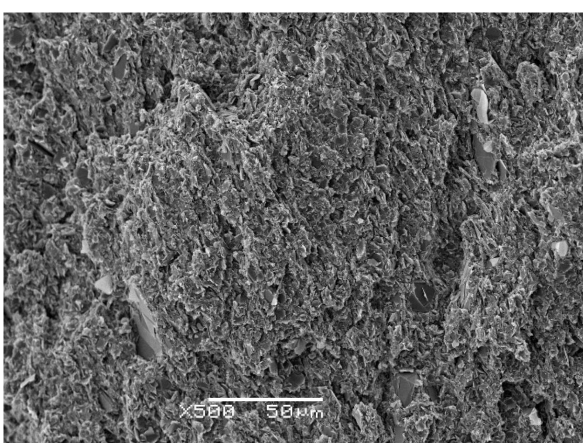


Figure 2. Scanning electron microscopy (SEM) image of the fracture surface of sample ETLBN2-60, magnification 500×, scale bar 50 µm.

2.2.2. Thermal Conductivity

The thermal conductivity was measured using the Transient Hot Bridge method (Linseis THB-100, Selb, Germany), in which a heat pulse is applied to a sensor placed between two surfaces of the sample material and the instrument measures the temperature change ΔT as a function of time, t, following the heat pulse input. The thermal conductivity, λ, was obtained [38] from an extrapolation of the linear part of a plot of ΔT as a function of the inverse square root of time, $1/\sqrt{t}$. The instrument was calibrated with five different standards covering the range from 0.2 to 10 W/mK. The samples prepared at ambient pressure were cast in silicone molds 10 mm × 40 mm × 4 mm, and cured isothermally in an air-circulating oven at 70 °C for 3 h. Four measurements were made of the thermal conductivity of each of the samples, and the average value was taken. Typically, the standard deviation of these four measurements was ± 0.1 W/mK.

2.2.3. Compressed Samples

In order to obtain compressed samples, the device illustrated in Figure 3 was used. The required amount of epoxy–thiol or epoxy–diamine mixture was introduced into the Teflon cylinder of internal diameter 15 mm, outside diameter 60 mm and height 52 mm, and the spring (with spring constant 5.95 kN/m) was compressed by a measured distance and then locked in place. The force on the piston could be calibrated to give pressures up to 3 MPa, though results are presented here only for a maximum pressure of 2 MPa. The whole assembly was placed in an air-circulating oven such that the temperature of the sample remained at 70 °C for 3 h in order to effect the cure under the applied pressure. After cure, the pressure was maintained during cooling, and the cured sample was removed at room temperature. The cured samples, in the form of solid cylinders 15 mm diameter and between 25 and 35 mm in length, were cut in half using a diamond wafering saw to give two smooth and flat surfaces for the measurement of thermal conductivity. In an earlier arrangement, a weight was used in place of the spring, giving rise to a much smaller pressure of 175 kPa; results obtained with this much lower pressure are also included in the present work.

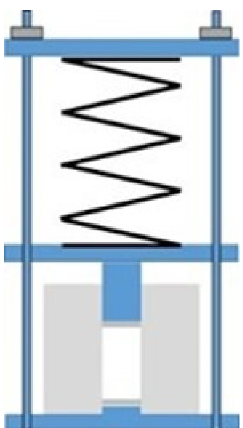


Figure 3. Schematic illustration of the compression device.

2.2.4. Density

The density of the cured samples was measured by Archimedes method. The samples were first weighed in air at room temperature, and then when immersed fully in ethanol, suspended by a fine thread. From repeated measurements on the same sample, the uncertainty in the density is estimated as ± 0.02 g/cm^3.

2.2.5. Scanning Electron Microscopy (SEM)

Fully cured samples, similar to those used for the thermal conductivity measurements and prepared using the same isothermal curing procedure, were fractured and then the fracture surface was examined in a Scanning Electron Microscope (JEOL JSM-5610, Tokyo, Japan). An accelerating voltage of 10 kV was used to give magnifications from 100× to 5000×.

3. Results and Discussion

3.1. Density Measurements

The density of epoxy–thiol-BN platelet composites, samples ETLBN*x*-30, -50, -60, and -70, with x = 2, 30, and 180, cured in open molds without the application of pressure, was measured experimentally in earlier work [5], and is shown as a function of the vol.% of BN by the open symbols in Figure 4.

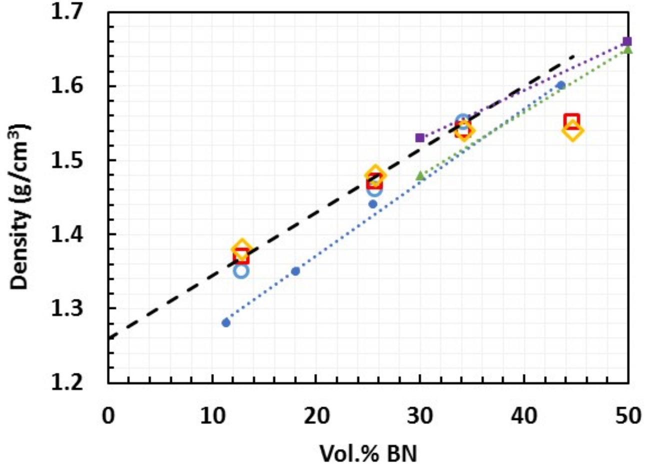


Figure 4. Density as a function of BN content for epoxy–thiol composites prepared at ambient pressure with different BN platelet sizes: 2 µm, open blue circles; 30 µm, open red squares; 180 µm, open yellow diamonds [5]. Filled symbols for data taken from the literature: blue circles,

Lewis et al [25]; green triangles, Chung and Lin, 3.6 μm [12]; purple squares, Chung and Lin, 10.6 μm [12].

Here it can be seen that, for BN contents less than 40 vol.%, the density of the composites is independent of the BN particle size, and increases linearly with increasing filler content from a value of 1.25 g/cm^3 for the epoxy–thiol system without any filler. In fact, the composite density calculated from the densities and weight fractions of the three components (epoxy, thiol, BN) and allowing for a 4% shrinkage on cure gives the dashed line, which agrees very closely with the experimental values, implying that there is an insignificant void content for filler volume fractions less than 34%. For the highest filler content of almost 45 vol.%, however, there is a significant deviation from this linear relationship, which is attributed to the presence of voids in the sample; at such high filler contents the composite is a very stiff paste, and the mixing procedure introduces air bubbles which cannot be removed by degassing.

Comparison can be made with literature values for other epoxy-BN composites, though this is not straightforward: the density depends on the nature of the epoxy and hardener system as well as on the BN content, and there are also rather few studies in which density measurements are reported. For epoxy-BN composites prepared by curing at ambient pressure, data are available from two references in addition to Zhu et al [23]. Lewis et al [25] use a DGEBA epoxy (1.17 g/cm^3) cured with triethylenetetramine (0.982 g/cm^3) and filled with 3-8 μm BN platelets (2.29 g/cm^3), which gives a calculated density of the composite (without any allowance for shrinkage on cure) which falls on the same dashed line as given in Figure 4. The data of Lewis et al are included in Figure 4 as the filled blue circles, and fall below the calculated line, as well as below our experimental values except for the highest BN content for which we noted above the presence of voids. The deviation of the data of Lewis et al from the calculated line may be a result of their rather high value for the density of the BN particles, taken from the manufacturer's literature [39]. If the value of 2.1 g/cm^3 used in our calculations is applied instead, together with a 4% volume shrinkage on cure, the calculated density corresponds very closely with the data of Lewis et al, suggesting that their composites are essentially void-free, as are ours for volume fractions up to 34%. This is consistent with their thermal conductivity results, which compare well with ours and with others in the literature [3].

The second reference for comparison of the density values is Chung and Lin [12], who use two different sizes of BN platelets, 3.6 μm and 10.6 μm, in a matrix of cresol novolac epoxy cured with a phenol novolac hardener and 1-benzyl-2-methylimidazole catalyst. These data are included in Figure 4 as filled green triangles and purple squares, respectively, where it can be seen that they fall close to the calculated dashed line, thus following approximately the trend displayed by our own results.

It should be noted that both Lewis et al [25] and Chung and Lin [12] compact their epoxy-BN mixtures before curing, using pressures of 1.6 MPa and 5.0 MPa, respectively. Zhu et al [23] investigate the use of much higher consolidation pressures in a DGEBA epoxy system cured with phenolic aldehyde amine (1.01-1.10 g/cm^3), and with very high BN contents, well beyond those used here. The reported densities, for BN contents between 74 wt.% and 95 wt.% do not appear to show any systematic variation with either BN content or consolidation pressure, and fall well below the "theoretical" density, which increases from about 1.8 g/cm^3 to about 2.2 g/cm^3 over this filler range. Indeed, the reported density of approximately 1.0 g/cm^3 for composite samples fabricated without consolidation before cure is apparently less than that of the unfilled epoxy system (1.14 g/cm^3). This would appear to be consistent with the reported values of thermal conductivity for these composites cured without prior consolidation, and hence without significant orientation, which, at less than 4.0 W/mK, are very low for such highly filled systems [3], implying significant void content.

The effect on the density of curing the samples under a pressure of 175 kPa is illustrated in Figure 5 for epoxy–thiol and epoxy–diamine composites filled with 30 μm

BN platelets. For both composite systems the filler loadings used were the two highest weight proportions. For the epoxy–thiol system, the compressed samples, denoted ETLBN30-60C and ETLBN30-70C, had filler contents of approximately 34 and 45 vol.%. For the epoxy–diamine system, the compressed samples, denoted EJBN30-60C and EJBN30-65C, had filler contents of approximately 38 and 43 vol.%.

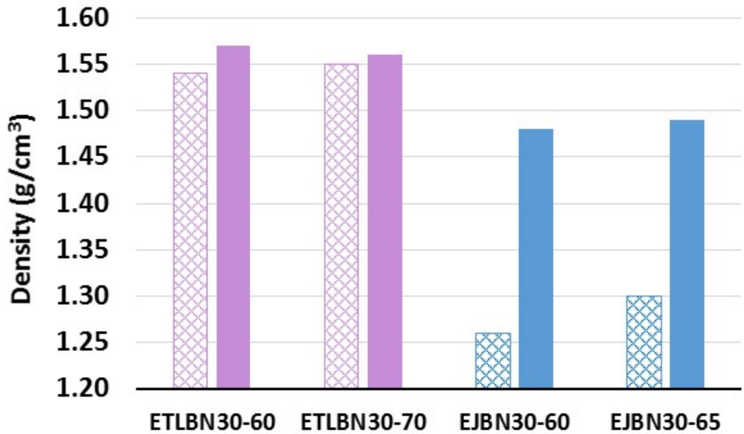


Figure 5. Effect of compression during cure on the density of epoxy–thiol and epoxy–diamine composites with 30 μm BN platelets, as indicated; cross-hatched = ambient pressure, filled = compressed at 175 kPa.

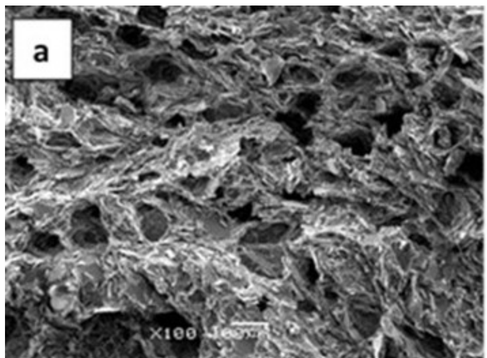
The difference between the effects of curing under pressure for the two composite systems is remarkable. For the epoxy–thiol composites, the increase in density resulting from curing under this rather low pressure of 175 kPa is small, as can be seen in Figure 5, but can be considered significant when the results for all the composites systems, collected in Table 2, are examined. The values listed in Table 2 show that the density increases systematically, albeit in a modest way, for the epoxy–thiol composite samples with both 60% and 70% of the 30 μm and 180 μm platelets when they are cured under a pressure of 175 kPa.

Table 2. Densities and thermal conductivities (TC) of composites, ETLBN*x*-*y* and EJBN*x*-*y*, cured at ambient pressure, P_{amb}, and those cured with 175 kPa and 2 MPa pressure, where *x* refers to the particle size and *y* refers to the filler content. Samples cured under 175 kPa pressure are labelled ETLBN*x*-*y*C and those cured under 2 MPa pressure are labelled ETLBN*x*-*y*C2.

Sample	Density (g/cm³)			TC (W/mK)		
	P_{amb}	175 kPa	2 MPa	P_{amb}	175 kPa	2 MPa
ETLBN2-60	1.55	1.52	-	1.28	1.49	-
ETLBN30-60	1.54	1.57	-	2.36	4.44	-
ETLBN30-70	1.55	1.56	1.70	3.34	4.77	7.67
ETLBN180-60	1.54	1.54	-	3.02	3.80	-
ETLBN180-70	1.54	1.61	1.69	4.22	5.38	8.52
ETLBN120s-60	1.42	1.43	-	3.42	5.34	-
ETLBN120s-70	-	1.42	1.43	-	5.55	10.49
EJBN30-60	1.26	1.48	-	1.87	4.19	-
EJBN30-65	1.30	1.49	-	2.37	4.32	-

Strangely, however, the density appears to decrease for the samples filled with 2 μm platelets, though the difference is small and close to experimental uncertainty. This is probably related to the much higher specific surface area, 10 m^2/g, for these platelets in comparison with that for the larger platelets, 1 m^2/g, which made it very difficult to fabricate composites with a high filler content of 2 μm platelets. It can be seen, for example, that no data are included in Figure 4 for the 70% content of 2 μm platelets; the texture of the uncured mixture was quite different from that for the other platelet sizes, being somewhat powdery and unable to be compacted.

In comparison with the very limited effect of the pressure of 175 kPa on the density of the epoxy–thiol composites illustrated in Figure 5, even this rather low pressure is sufficient to cause a dramatic increase in density for the epoxy–diamine composites. This can be understood from the SEM micrographs of the fracture surfaces, shown in Figure 6, where the voids in the sample prepared at atmospheric pressure (Figure 6a) have largely been eliminated by curing under 175 kPa pressure (Figure 6b). The reason why the problem of voids is not apparent in the epoxy–thiol samples is explained by the much lower viscosity of the epoxy–thiol mixtures.



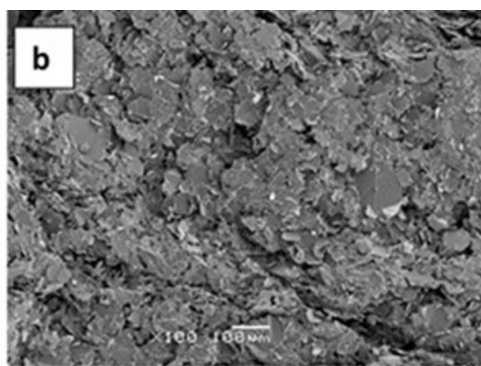


Figure 6. SEM micrographs of epoxy–diamine samples: (**a**) EJBN30-60 and (**b**) EJBN30-60C. Magnification 100×, scale bar 100 μm.

It is remarkable that the large density changes observed in the epoxy–diamine composites shown in Figure 5 should occur at the pressure of only 175 kPa, which is very low in comparison with many of the pressures used by other workers, as summarised in the Introduction. However, there are other examples of similarly low pressures having a significant effect on the properties of epoxy composites. Zhang et al [31] hot press their epoxy-BN composites at just 207 kPa (30 psi) and obtain a significant orientation of the BN platelets, with a corresponding enhancement of the thermal conductivity in the in-plane direction. In the present case of the epoxy–diamine composites, we attribute the increase in density to the elimination of voids, which is an important consideration for fibre-reinforced epoxy composite systems. For example, Thomason [40] and Gu et al [41] show that large reductions in the void content can be achieved using pressures well below 1 MPa; in fact, increasing the pressure from 90 to 270 kPa can reduce the void content by more than a factor of 2 [41].

At the higher pressure of 2 MPa, it can be seen from the results included in Table 2 that there is a significantly greater increase in density for the epoxy–thiol composites fabricated with both 30 μm and 180 μm platelets. In fact, it appears that the densities of these samples, 1.70 g/cm^3 and 1.69 g/cm^3, respectively, are greater than the calculated density for 70% epoxy–thiol-BN composites, 1.64 g/cm^3 (see Figure 4); this value is calculated assuming simple additivity of stoichiometric amounts of epoxy and thiol, with densities of 1.17 g/cm^3 and 1.28 g/cm^3, respectively, and the appropriate proportion of BN platelets with a density of 2.1 g/cm^3, and allowing for a 4% shrinkage on cure. These results for the densities of the epoxy–thiol-BN composites cured at 2 MPa pressure therefore require some comment.

One possibility is related to the effect of pressure on the cure process, and in particular on the density of the cured epoxy. Although there is one report that the density is independent of the cure pressure, in the range up to 1000 MPa [42], the majority of studies suggest that increasing the cure pressure results in a higher density of the cured epoxy [43–46]. Beloshenko and co-workers [43,44] investigated various epoxy resins and found that increasing pressure during cure results in a higher density of the cured epoxy, attributing this effect to the inhibition of voids and a reduction of the free volume. This latter aspect is equivalent to the effects of densification, discussed elsewhere [22], which requires not only that the cure be made under pressure but also that the pressure be maintained while the sample is cooled from the curing temperature. Hwang and Chang [45] used a plunger-type dilatometer to measure the volume shrinkage during cure of an epoxy molding compound (EMC), and observed an increase in the volume shrinkage with increasing pressure in the range from 2 to 10 MPa. Hopmann et al [46] used a specially constructed dilatometer to measure the cure shrinkage and found that, for a low viscosity epoxy resin cured with an amine, the shrinkage increased from about 4% to about 7% when the pressure was increased to 2.5 MPa. Accordingly, it is possible that, for our epoxy–thiol system, the combined effects of the increased shrinkage due to curing under pressure and the densification as a consequence of maintaining the pressure during cooling could have increased the density of the cured epoxy-BN composite beyond the anticipated value.

In clear contrast to the increase in the density observed for the epoxy–thiol composite systems with BN particles in the form of platelets discussed above and illustrated in Table 2, there is no significant increase in density for composites fabricated with the 120 µm spherical agglomerates; the reason for this is considered below.

3.2. Thermal Conductivity

The effect of curing under pressure on the thermal conductivities of the epoxy–thiol and epoxy–diamine composites with 30 µm BN platelets is shown in Figure 7, the complete set of data being given in Table 2. For comparison, additional results for epoxy–thiol samples cured at ambient pressure and covering a wider range of BN contents (filled symbols) are taken from earlier work [3–6], and show how the thermal conductivity increases non-linearly with increasing BN content. To achieve higher thermal conductivities than about 3 W/mK in composites prepared at ambient pressure (filled symbols) would require an increased BN content, but the problem is that the uncured mixture becomes such a stiff paste at BN contents greater than about 45 vol.% that it is essentially unworkable. On the other hand, the application of pressure during cure, a feasible fabrication procedure using, for example, an autoclave, results in a large increase in the thermal conductivity for the two BN contents used here, as can be seen in Figure 7. For both the epoxy–thiol-BN and epoxy–diamine-BN composite systems, the use of even the rather low pressure of 175 kPa results in an increase in thermal conductivity by as much as a factor of 2, as indicated by the arrows. For the epoxy–thiol system and a cure pressure of 2 MPa, the increase in thermal conductivity is even more dramatic.

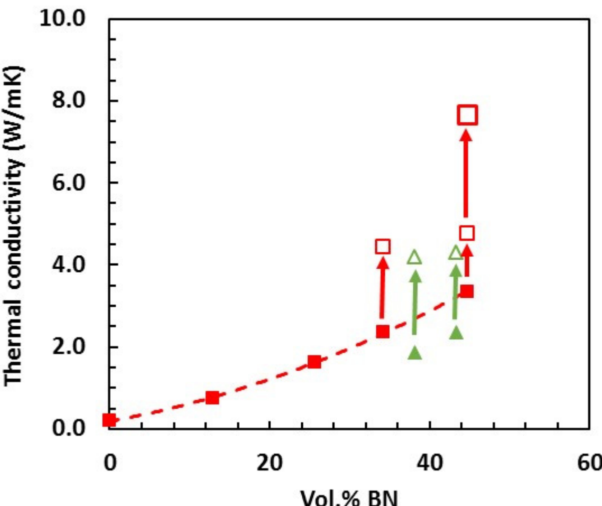


Figure 7. Thermal conductivity as a function of BN content for ETLBN30 samples (red squares) and EJBN30 samples (green triangles): filled symbols, samples cured at ambient pressure [3–6]; small open symbols, samples cured under 175 kPa pressure; large open symbol, sample cured under 2 MPa pressure.

The preceding observations, which show that both the density and the thermal conductivity increase when the samples are cured under pressure, and more so the higher is the pressure, raise the question of whether or not these two properties are inter-related in respect of the effect of pressure. In Figure 8, the thermal conductivity is plotted as a function of the density for all the epoxy-BN composites studied. Included here also are earlier results for the epoxy–thiol system cured at ambient pressure using either PDU (shaded symbols) or LC-80 (full symbols) as the initiator [3–6].

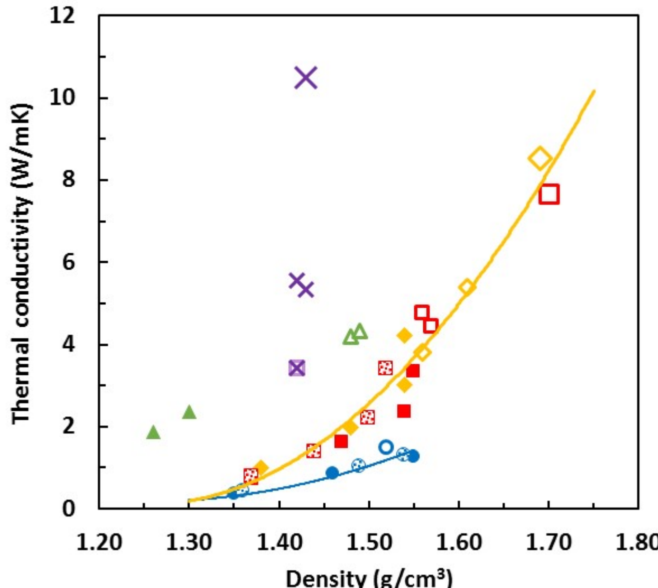


Figure 8. Thermal conductivity as a function of the density for the epoxy-BN composites. Full symbols, ambient pressure cure with LC-80 [3–6]; shaded symbols, ambient pressure cure with PDU [3–6]; small open symbols, cured under 175 kPa pressure; large open symbols, cured under 2 MPa pressure. ETLBN2, blue circles; ETLBN30, red squares; ETLBN180, yellow diamonds; EJBN30, green triangles; ETLBN120s (agglomerates), purple crosses.

There appears to be quite a strong correlation between the thermal conductivity and the density, within certain groups of BN filler types. For the 30 μm and 180 μm platelets, for both of which the specific surface area is 1.0 m^2/g, an increase in the density as a consequence of applying pressure during cure results in an increase in the thermal conductivity which follows the trend of the increase resulting from higher BN contents, indicated by the full yellow curve. This may be explained on the basis of the thermal conductivity depending on the pathways for heat conduction between the BN particles.

A similar correspondence between thermal conductivity and density was noted by Zhu et al [23], though the pressure was applied in quite different circumstances, specifically for consolidating and orienting the BN platelets within the samples before curing at ambient pressure. Nevertheless, the thermal conductivity in the in-plane direction increases in an apparently non-linear manner, similar to our results in Figure 8, and reaches a maximum value just greater than 21 W/mK, even though this was not for the highest pressure applied. No report is made for the equivalent relationship for the thermal conductivity in the through-plane direction, which reaches a value of approximately 12 W/mK at the highest BN content, between 90 and 95 wt.%.

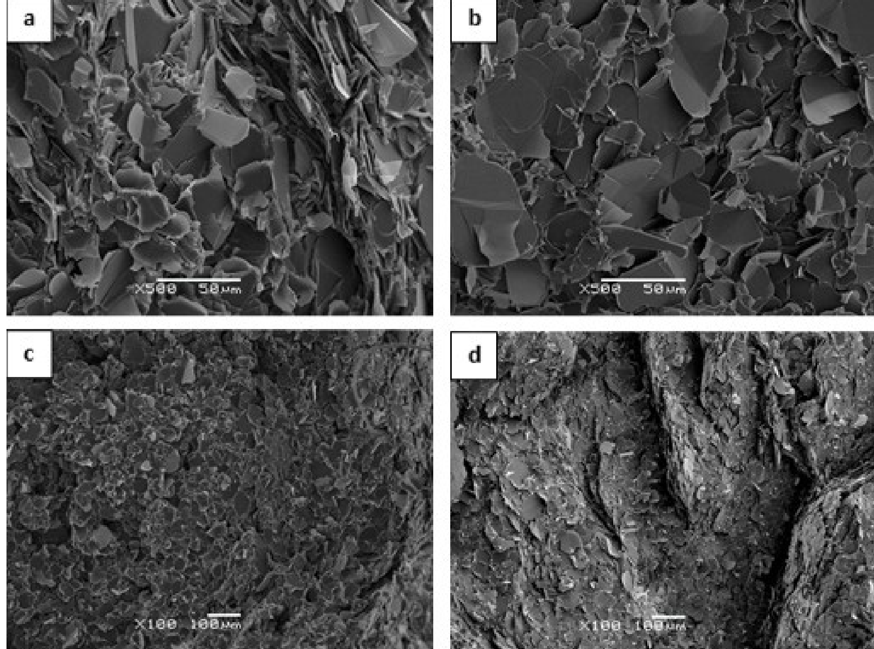
These very high values of thermal conductivity obtained by Zhu et al [23] are a consequence of two particular aspects: the BN platelets are oriented by the application of pressure, and the filler contet is very high. To compare our present results for thermal conductivity with others in the literature, we set aside those, such as Zhu et al, in which significant orientation is introduced by the composite preparation process, and we make use of the compilation of data presented in an earlier review [3]. It is remarkable that our values for samples with 58.0 wt.% BN and prepared under 2 MPa pressure, namely 7.67 W/mK and 8.52 W/mK for composites with 30 μm and 180 μm platelets, respectively, and 10.49 W/mK for composites with 120 μm agglomerates (see Table 2), are higher than any others reported, with one exception. The one exception is Islam et al [47], who make use of a liquid crystalline epoxy resin cross-linked either with an amine or a cationic initiator. This unfilled resin has an intrinsically higher thermal conductivity than DGEBA, 0.34 ± 0.02 W/mK for amine cure and 0.45 ± 0.03 W/mK for cationic cure, and when filled with 55 wt.% (the closest to the content of our ETLBN*x*-70 samples, 58.0 wt.%) of 30 μm BN platelets gives values of 8.77 W/mK and 10.96 W/mK for amine and cationic cure, respectively. These composite samples are prepared by hot-pressing at 20 MPa, but the authors verify that there is no orientation induced by this procedure. Our values for the epoxy–thiol system at 2 MPa are therefore only slightly less than those of Islam et al at 20 MPa, which represent the highest values reported for isotropic epoxy-BN composites. It is possible that the epoxy–thiol values could be increased further by pressures higher than 2 MPa.

For comparison, we note the following studies in which thermal conductivities are reported with values which most closely approach our own. Xu and Chung [7] report a thermal conductivity of 10.31 W/mK for samples with 57 vol.% (~70 wt.%) of silane treated BN particles, 5-11 μm in size, prepared at 10.5 MPa pressure, but at 44 vol.% (~58 wt.%) the corresponding values is only 4.84 W/mK. Chung and Lin [12] prepared composites with 10.6 μm silane treated BN platelets, cured in a vacuum oven after pressing a mold at 5 MPa, and found a strong dependence of thermal conductivity on BN content, which passed through a maximum between 50 and 60 vol.%. Their values of 6.75 W/mK at 50 vol.% (~65 wt.%) and 7.42 W/mK at 60 vol.% (~74 wt.%) are less than our values at a lower filler content of 58 wt.%. Lastly, Kargar et al [48] reported a value of 5.50 W/mK for their highest content of 45 vol.% (~59 wt.%) of 3-8 μm BN platelets, which, though higher than many other values reported in the literature [3], is still significantly less than our values at a similar filler content.

The apparent correlation between thermal conductivity and density demonstrated by Figure 8 can be explained as follows. Both increased BN content and the application of pressure during cure increase the thermal conductivity and improve the heat transfer. In

the former case, increasing the BN content increases the number of heat conduction pathways and simultaneously increases the density, as a consequence of the higher density of the BN particles in comparison with the epoxy matrix. In the latter case, the application of pressure during cure improves the matrix–filler interface as a consequence of the increased density. A similar trend is seen for the 2 µm platelets, indicated by the blue curve, though it is displaced to much lower thermal conductivities. This results from the much higher specific surface area, 10 m²/g, for these BN particles, which creates a much larger interfacial area between matrix and filler.

The effect of applying pressure during cure on the pathways for heat conduction is illustrated in Figure 9 by the SEM micrographs of the epoxy–thiol composites fabricated with 30 µm platelets. Samples ETLBN30-60, cured at ambient pressure, and ETLBN30-60C, cured at 175 kPa pressure, are shown in Figures 9a and 9b; samples ETLBN30-70, cured at ambient pressure, and ETLBN30-70C2, cured at 2 MPa pressure, are shown in Figures 9c to 9h at different magnifications.



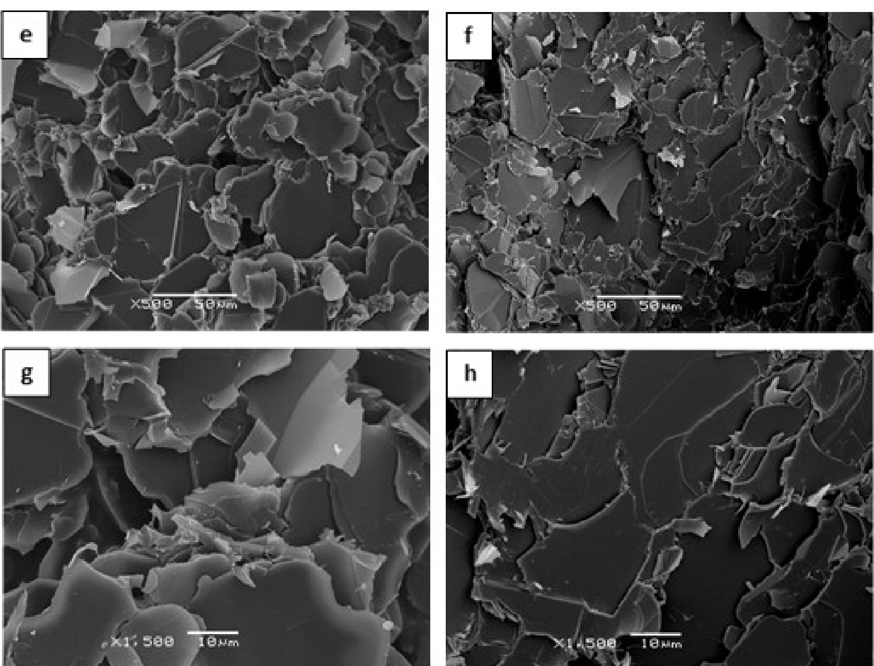


Figure 9. SEM micrographs of fracture surfaces of epoxy–thiol composites filled with BN platelets: (**a**) ETLBN30-60 and (**b**) ETLBN30-60C, with magnification 500×; (**c**), (**e**), (**g**) ETLBN30-70 and (**d**), (**f**), (**h**) ETLBN30-70C2 with magnifications 100×, 500×, 1500×, respectively. Scale bars are indicated on each micrograph.

In comparison with the fracture surfaces of the epoxy–diamine composites, shown above in Figure 6 and which demonstrate that for the epoxy–diamine system the increase in thermal conductivity results principally from a reduction in the void content on the application of pressure during cure, the SEM micrographs for the epoxy–thiol system in Figure 9 show that the void content is not an issue here: there are no voids visible in these micrographs, neither in the samples cured at ambient pressure nor in those cured at 2 MPa. Here the comparison is made between the 60% composites fabricated without and with 175 kPa pressure, Figures 9a and 9b, respectively, and between the 70% composites fabricated without and with 2 MPa pressure, Figures 9c, 9e, and 9g on the one hand and 9d, 9f, and 9h on the other.

It can be seen that for the samples cured under pressure there is much better contact between the BN particles and an improved matrix–filler interface. The improvement noted between Figures 9(c), 9(e), and 9(g) on the one hand and Figures 9(d), 9(f), and 9(h) on the other, as a consequence of curing at 2 MPa, is significantly better than the improvement between Figures 9(a) and 9(b), for cure at 175 kPa. Similar observations were made for the ETLBN180 composites. This supports our view that the effect of pressure in the epoxy–thiol system filled with BN platelets is to bring the BN particles into closer and better contact, and hence increase the thermal conductivity.

On the other hand, the epoxy–thiol composites with 120 µm agglomerates display a quite different relationship between thermal conductivity and density, in which the thermal conductivity increases dramatically without a significant increase in the density. This is very clearly seen in Figure 8 where the data for the composites fabricated with agglomerates are shown as the open purple crosses. The value of over 10 W/mK for the composite filled with approximately 45 vol.% of 120 µm spherical agglomerates (about 58 wt.%) is higher than any other value reported in the literature for the same filler content [3], except for those for which elaborate fabrication techniques are required, which are not usually practical. This suggests that the increased thermal conductivity for these composites with BN agglomerates occurs for reasons other than simply having an improved matrix–filler

interface, and this can indeed be shown by reference to the fracture surfaces observed by SEM.

The SEM micrographs for the epoxy–thiol composites filled with BN agglomerates are shown in Figure 10, both for the ETLBN120s-60 composites prepared at ambient pressure (Figure 10a) and with 175 kPa pressure (Figure 10b), and for the ETLBN120s-70 composites prepared at ambient pressure (Figure 10c) and at 2 MPa pressure (Figure 10d).

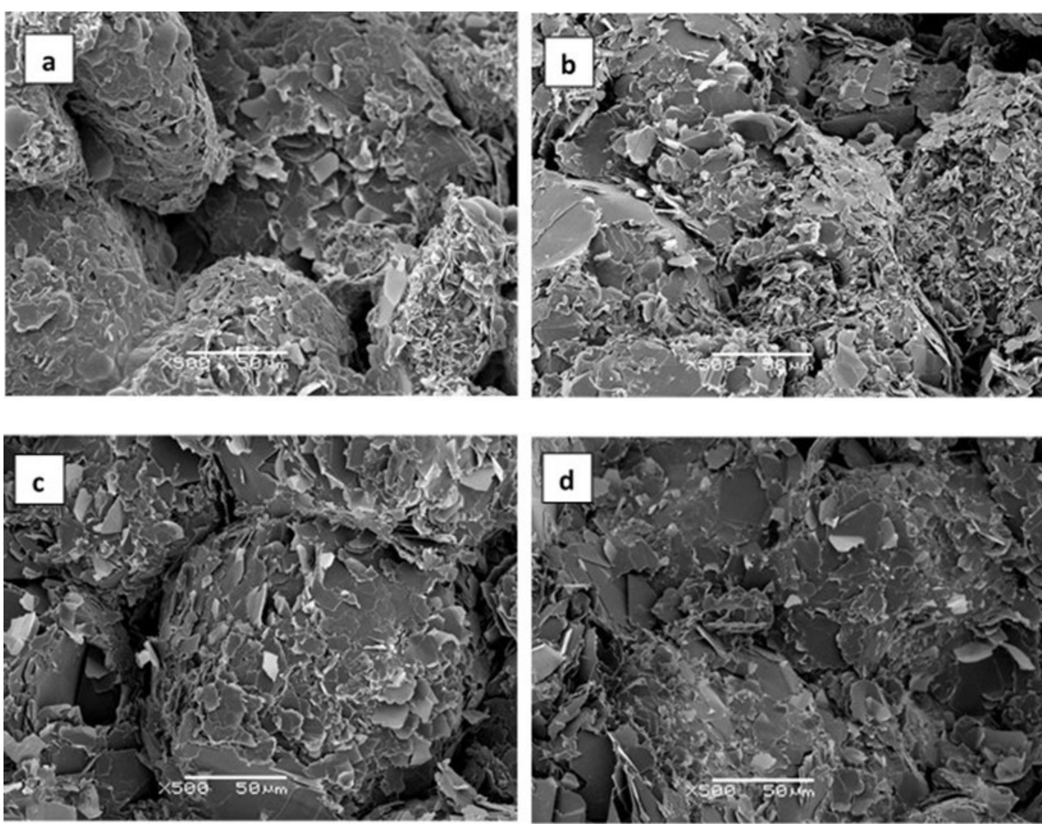


Figure 10. SEM micrographs of fracture surfaces of epoxy–thiol composites filled with BN agglomerates: (**a**) ETLBN120s-60, (**b**) ETLBN120s-60C, (**c**) ETLBN120s-70, and (**d**) ETLBN120s-70C2. Magnification 500×, scale bar 50 μm.

In Figure 10a the individual agglomerates can clearly be seen, essentially with their original approximately spherical form as shown in Figure 1, and with a certain, but limited, area of contact with their neighbouring particles. In Figure 10b, though, these agglomerates can be seen to have been deformed by the pressure, such that the area of contact between neighbouring particles is now considerably greater. The same observations can be made for the ETLBN120s-70 composites in Figure 10c and 10d for the samples formed without pressure and with 2 MPa pressure, respectively. It is this deformation of the agglomerates and the consequent increase in thermal contact between the particles which leads to the dramatically increased thermal conductivity seen in Figure 8. Since particles in the form of agglomerates are the most efficient for increasing the thermal conductivity of epoxy-BN composites with a given filler content [3–5], the application of pressure would therefore appear to be an excellent way in which to enhance the thermal conductivity.

4. Conclusions

The application of pressure during the cure of several different epoxy-BN composite systems has been shown to increase both the density and the thermal conductivity of these composite materials. In most cases there is a correlation between the density and the thermal conductivity, but the mechanisms for enhancing the thermal conductivity depend on

the particular epoxy-BN system. For the epoxy–diamine system, the principal effect of applying pressure is to reduce the void content, which leads to a large increase in the thermal conductivity. On the other hand, for the epoxy–thiol system in which the BN filler particles are in the form of platelets, the enhancement in thermal conductivity results from an improvement in the matrix–filler interface, and the closer proximity of the particles. In contrast, for the epoxy–thiol system filled with BN particles in the form of agglomerates, the effect of pressure is to deform the agglomerates, leading to a greatly increased area of contact between the particles and a correspondingly dramatic increase in the thermal conductivity. The use of pressure during cure, particularly for epoxy-BN composites filled with particles in the form of agglomerates, is therefore considered to be an excellent procedure for achieving high thermal conductivities in these systems.

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