

Enhancement of thermal conductivity in epoxy composites through the combined addition of expanded graphite and boron nitride fillers

Isaac Isarn,^a Leïla Bonnaud,^b Lluís Massagués,^c Àngels Serra,^d Francesc Ferrando^{a*}

a. *Department of Mechanical Engineering, Universitat Rovira i Virgili, C/Av. Països Catalans, 26, 43007 Tarragona, Spain. isaac.isarn@urv.cat, f.ferrando@urv.cat*

b. *Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), Materia Nova Research Center & University of Mons, 23 Place du Parc, B-7000, Mons, Belgium. leila.bonnaud@materianova.be*

c. *Department of Electronic, Electric and Automatic Engineering, Universitat Rovira i Virgili, C/Av. Països Catalans, 26, 43007 Tarragona, Spain. lluis.massagues@urv.cat*

d. *Department of Analytical and Organic Chemistry, Universitat Rovira i Virgili, C/Marcel·li Domingo s/n, 43007 Tarragona, Spain. angels.serra@urv.cat*

Abstract

Expanded graphite (EG) and boron nitride (BN) were used as fillers to impart thermal conductivity (K) while maintaining electrical insulation of a homopolymerized cycloaliphatic epoxy matrix. Even though EG leads to a higher increase of K than BN (550% of enhancement with only a 7.5 wt.% of EG), EG is also electroconductive and consequently its ratio within the epoxy system must be lower than the percolation threshold. Proportions between 2.5-7.5 wt.% of EG and a 40 wt.% of BN were polymerized in an oven and epoxy composites with 70 wt.% of BN and 2.5/5.0 wt.% of EG were also prepared under 74 MPa pressure. Over 2 W/m·K was achieved in the best composites (i.e. more than 1,500% of enhancement in reference to the neat epoxy). In the presence of BN, amounts of EG of 2.5 and 5 wt% were found to keep the insulation character. In addition, mechanical and thermal characteristics of the composites were also evaluated.

Keywords

Thermosetting resin, Layered structures, Polymer-matrix composites (PMCs), Thermal properties.

1. Introduction

Recently, the preparation and study of new nanocomposite materials has become a very important issue in different fields of science. Most of these composites are based on polymers.¹⁻⁴ Indeed, their low density makes these materials the most promising candidates to replace metals or ceramics when weight is a

restrictive parameter.⁵⁻⁷ Their good corrosion resistance, low production costs of industrial and easy processing, also make them more attractive than metals.^{1,6,8,9} In the sector of energy (production and storage systems such as solar cells, fuel cells, rechargeable batteries and supercapacitors), there is also a great interest in thermally conductive materials.¹⁰ Thermal conducting composites are used in electric and electronic industries as packaging and coating, heat dissipation structures of light emitting diodes and heat sinks.^{1,8,9} Unfortunately, most polymers exhibit insulating characteristics, both electrical and thermal. To tackle this lack of conductivity, usually thermally or electro conductive nanofillers are added to polymer matrices. While the electrical conductivity of polymer composites can drastically increase at a given electrical conductive particle concentration, in accordance with the percolation theory,^{9,11} the dependence of thermal conductivity and filler loading are in most cases practically linear and does not exhibit large changes until high filler loadings.¹²

Following the previous studies carried out by our group,¹³⁻¹⁶ the current work is focused on increasing the thermal conductivity of an epoxy resin while maintaining its electrical insulation. The prepared materials could be used as adhesives, coatings or packaging materials for electronic industry, usually called thermal interface materials (TIMs),¹⁷ thermally conductive adhesive (TCA),¹⁸ or electrical insulating layers of prepreg in a multilayer printed circuit boards (PCB). The selection of an epoxy resin as the matrix relies on the versatility of such a system in terms of curing agent and curing conditions and its good adhesion properties to a huge range of different surfaces, low shrinkage, good behaviour at elevated temperatures and high modulus and strength. All these characteristics make epoxy resins ideal matrices in composite material industries.¹⁹⁻²² However, it is well known that epoxy resins have low thermal conductivity and brittleness, which limit their use but the addition of inorganic particles can help to reduce both drawbacks.²¹ The introduction of particles in the epoxy matrix is still today the most economical and simplest method from the point of view of the application to increase thermal conductivity²³ than the costly alignment of polymer structures.²⁴

In the present study, a thermal latent epoxy system, which goes through a cationically initiated mechanism, was chosen to crosslink a cycloaliphatic epoxy resin (ECC). This system consists in a benzylanilinium salt, which is the cationic initiator and triethanolamine (TEA) as inhibitor of low temperature curing, which provides the latency. The system is distinguished for having a long pot life, fast curing once initiated and glass transition temperatures (T_g) of the cured material above 200 °C, which is considerable high in epoxy thermosets.^{14,16}

The main goal of this work is the preparation of new hybrid nanocomposites, by combination of a carbonaceous filler with an inorganic material, all of them dispersed in the epoxy matrix. By the application of pressure, a higher filler loading could be added to the composite. The mechanical properties and thermal conductivity of these materials have been evaluated together with the insulating electrical characteristics. Small proportions of carbon-based material (below the percolation threshold) were expected to improve some of these characteristics maintaining the electrical insulation. Considering different studies already reported in the scientific literature,^{9,25-27} we selected expanded graphite (EG) and boron nitride (BN) as the fillers, to determine potential synergic effects when added together to the formulation. EG is one of the most studied fillers in thermal energy storage systems.²⁸ Some authors^{25,28} state that this filler enhances the thermal conductivity much better than other carbon-based materials such as carbon nanotubes, carbon black or carbon fibres. Other fillers like graphene or graphene oxide result much more expensive, thus limiting their use in technological applications. Corcione and Maffezzoli²⁵ reported a good dispersion of the EG particles in the epoxy matrix and strong polar interactions of the filler with the matrix, attributable to the partially oxidized surfaces of the expanded graphite. The manufacturing process causes this partial oxidation since graphite, which is constituted by stacked layers of graphene, is converted in expanded graphite through chemical oxidation.^{8,25} When graphite is exposed to heat (thermal shock) it expands generating free space by evaporating the acid entrapped between the graphite layers.²² This space could be filled with the epoxy resin, which could homopolymerize, increasing in this way the filler-matrix interaction that is highly convenient to reach a good heat transfer. Among all the inorganic particles commonly used to increase thermal conductivity, hexagonal boron nitride (BN) provides the best combination of properties and therefore this material has been selected for the present study. BN platelets present a high thermal conductivity, low dielectric constant, high electrical resistivity, low coefficient of thermal expansion (CTE), low density, high mechanical strength and chemical and thermal stabilities.^{13,23}

2. Experimental

2.1. Materials

As the epoxy resin, 3,4-epoxy cyclohexylmethyl 3,4-epoxy cyclohexane carboxylate (EEW = 126.15 g/eq, from Sigma Aldrich, ECC) has been used. N-(4-methoxybenzyl)-N,N-dimethylanilinium hexafluoroantimonate, commercialized as CXC1612 from King Industries Inc., was mixed with 50 wt. % of propylene carbonate until dissolution. Propylene carbonate and triethanolamine (TEA) were provided

by Sigma-Aldrich and purified by distillation before use. Platelets of hexagonal BN of 180 μm of average, PCTP30D, were supplied by Saint Gobain Ceramic Materials. The particles were sifted with a sieve of 250 μm due to the high difference in particle size (manufacturer specifications state that product granulometry could include particle sizes of 1600 μm). Expanded graphite particles, BNB90, with an average of particle size of 85 μm and specific surface area (SSA) of 28.4 m^2/g were provided by Songhan Plastic Technology Co., Ltd.

2.2. Sample preparation

The epoxy neat formulation was prepared as described previously,^{14,16} by mixing 1 phr (parts of initiator per hundred parts of resin) of CXC1612 and 0.1 phr of TEA. Proportions of 2.5, 5.0 and 7.5 wt. % of expanded graphite were added to the epoxy system. Graphite particles were dispersed by sonication (NextGen Inside 500 from Sinaptec Ultrasonic Technology), using 35% of amplitude during 20 s, divided in batches of 5 s (leaving 10 s between each batch). After sonication, vacuum at room temperature were applied to the mixtures during 1 h to remove bubbles formed. The epoxy-graphite mixtures were used to prepare new formulations by mixing 60 wt. % of them and 40 wt. % of BN particles. In this case, manual stirring until homogeneity was performed, then the samples were cured in a ventilated oven. Other samples with a BN content of 70 wt % and 2.5 or 5 wt % of EG were also prepared and a pressure of about 74 MPa to compact and shape them was applied prior curing in the oven.

The curing of samples was carried out onto teflonated metallic moulds and following a multi-step temperature schedule at 100, 120, 150, 180 and 200 $^{\circ}\text{C}$, leaving them 1 h at each temperature.

2.3. Characterization techniques

A modulated differential scanning calorimeter 2920 (MDSC) from TA Instruments was used to analyse the epoxy reaction system. Samples of ca. 3-5 mg were tested in aluminium pans in a nitrogen atmosphere. The dynamic studies were performed in the range of 30-250 $^{\circ}\text{C}$ with a heating rate of 10 K/min . Enthalpy (Δh) of samples was calculated integrating the calorimetric signal (dh/dt) using a straight baseline, with the help of TA Universal Analysis software.

Rheologic experiments were carried out to the epoxy-EG blends in parallel aluminium plates of 25 mm diameter in oscillatory mode with an AR G2 rheometer from TA Instruments. The aim of the rheometric measurements were to determine the percolation threshold of the EG in the epoxy system. Linear viscoelastic range (LVR), a constant shear elastic modulus (G'), were determined at 1 Hz and 30 $^{\circ}\text{C}$,

varying strain applied. Viscoelastic properties, G' and shear viscous modulus (G''), were then determined in the LVR in frequency sweep experiments at 30 °C.

Dynamic mechanical thermal analyses (DMTA) were performed with a TA Instruments DMA Q800 analyzer. The prismatic rectangular samples (20 x 4.5 x 2.2 mm³) were analyzed by 3-point bending clamp at a heating rate of 3 K/min from 30 to 300 °C, using a frequency of 1 Hz and an oscillation of 0.1% of sample deformation. The Young modulus (E) was determined at 30 °C by means of a force ramp at a constant rate, 1 N/min, never exceeding 0.25 % of deformation to be sure that only elasticity was evaluated. E was calculated taken the slope between 0.1 and 0.2 % of deformation curve in accordance with the equation:

$$E = \frac{L^3 m}{4bt^3} \quad (1)$$

where E is the elastic modulus of composite sample (MPa), L is the support span (mm), b and t are the width and the thickness of test sample (mm) and m is the gradient of the slope (N/mm). A minimum of 4 experiments were made for each sample.

Thermomechanical analyses (TMA) were carried out on a Mettler TMA40 thermomechanical analyzer. Square cured samples (9 x 9 x 2.3 mm³) were supported by the clamp and a silica disc to distribute the force uniformly, and heated at 5 K/min from 35 to 100 °C. A minimum force of 0.01 N was applied to avoid results distortion. The coefficients of thermal expansion ($CTEs$) in the glassy state of the material were calculated as follows:

$$CTE = \frac{1}{L_0} \cdot \frac{dL}{dT} = \frac{1}{L_0} \cdot \frac{dL/dt}{dT/dt} \quad (2)$$

where L is the thickness of sample, L_0 the initial length, t the time, T the temperature and dT/dt the heating rate.

Thermal stability of the composites prepared were evaluated by a thermogravimetric analyser (TGA) Q50 from TA Instruments under N₂ atmosphere. Samples of ca. 6-9 mg were thermally decomposed on a platinum pan within the device. Global N₂ flow (100 mL/min) was divided between balance flow (40 mL/min) and sample flow (60 mL/min). A heating rate of 10 K/min was used between room temperature and 600 °C.

Surface hardness was evaluated through Knoop microindentation analysis being consistent with ASTM D1474-13. A minimum of 18 valid determinations were considered with a confidence level of 95% for each material. Knoop microindentation hardness (KHN) was calculated as follows:

$$KHN = \frac{L}{A_p} = \frac{L}{l^2 C_p} \quad (3)$$

where L is the load applied by the indenter (0.010 Kg), A_p is the area of indentation in mm^2 and C_p the indenter constant relating l^2 with A_p .

Measurements of X-ray diffraction (XRD) were performed with a Siemens D5000 diffractometer (Bragg-Brentano parafocusing geometry and vertical Θ - Θ goniometer) fitted with a curved graphite diffracted-beam monochromator, using incident and diffracted beam Soller slits, a 0.06° receiving slit and scintillation counter as detector. The angular 2Θ diffraction range was between 5 and 70° . The data were collected with an angular step of 0.05° at 3 seconds per step and sample rotation. $\text{Cu}_{k\alpha}$ radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA.

Environmental scanning electron microscopy (ESEM) was used to examine the fillers and breaking surfaces of the materials prepared. A Quanta 600 environmental scanning electron microscopy (FEI Company) allows collect micrographs at 10-20 kV and low vacuum mode without the necessary to coat the samples with poor electrical conductivity.

Electrical resistance of materials was tested using a multimeter 34410A 6½ Digit from Agilent Technologies at room temperature and based on ASTM D257-14. The samples with higher electrical resistance ($>10^8 \Omega \cdot \text{m}$) were evaluated with a Megohmmeter Resistomat 24508 at room temperature and the same standard. Samples of $9 \times 9 \times 2.3 \text{ mm}^3$ were tested between two stainless steel electrodes with a surface area of 19.635 mm^2 . A voltage of 500 V during 5 min was applied to thermoset composites.

Electrical resistivity (ρ) was determined as follows:

$$\rho = R \frac{A}{l} \quad (4)$$

where R is the electrical resistance measured by the device, A the electrode area and l the sample thickness.

Thermal conductivity was measured using the Transient Hot Bridge method by a THB 100 device from Linseis Messgeräte GmbH. A HTP G 9161 sensor was used with a $3 \times 3 \text{ mm}^2$ of area calibrated with

poly(methyl methacrylate) (PMMA), borosilicate crown glass, marble, Ti-Al alloy and titanium. Two equal polished rectangular samples (9 x 9 x 2.3 mm³) were placed in each one of the faces of the sensor. Due to the small size of sensor, side effects can be neglected. A measuring time of 100 s with a current of 10 mA was applied to each of the five measures done for the different formulations.

3. Results and discussion

3.1. Calorimetric analysis of the curing of the prepared formulations

In a previous study,¹⁴ the curing of the cycloaliphatic epoxy system (ECC) was performed. An optimal combination of 1 phr of benzylianium hexafluoroantimonate (CXC 1612) and 0.1 phr of triethanolamine (TEA) as initiating system ensured a complete epoxy group conversion with thermal latent characteristics. The benzylianium salt leads to a cationic homopolymerization of the epoxy monomers with high reactivity. In fact, the real catalytic groups, which initiate the attack to the oxiranic oxygen, are the benzyl cations released on heating the ammonium salt.²⁹⁻³¹ A high reactivity and an elevated degree of crosslinking were obtained because of the low nucleophilicity of the hexafluoroantimonate counter anion, which avoids the termination step in the epoxy homopolymerization. TEA was added as the thermal latent additive, since it converts the system in non-reactive until temperatures bordering 120 °C were achieved.³² The fact that the curing temperature is much higher than room temperature allows the reactive mixture to be stored for long periods, which is highly desirable for industrial applications.

Different proportions of EG were dispersed in the epoxy resin using a tip sonicator. Short sonication times were applied to the mixtures to avoid mechanical damage to the graphitic particles and to maintain the system unreacted, since the heat produced by the dispersion can lead to an undesired reaction if the temperature is highly increased. This technique results more efficient than the use of ultrasonic bath. To these mixtures a 40 wt % proportion of BN was added. Dynamic DSC scans of the different formulations are represented in **Figure 1**. If there is a great interaction between particles and matrix, some variations in the curing evolution must be expected. There are different facts that can affect this interaction: a) Both EG and BN have a similar crystalline structure, the surfaces are not reactive but the reactive groups at the particle edges could be bonded covalently with the resin and possibly participate in the curing process. b) The low viscosity and small size of the cycloaliphatic epoxy compound could allow its penetration into the EG interlayer spaces, which will lead to good interactions through partial oxidised surfaces. On the

other hand, the absence of aromatic moieties in the epoxy resin prevents in the present case π - π interactions between particles and matrix.

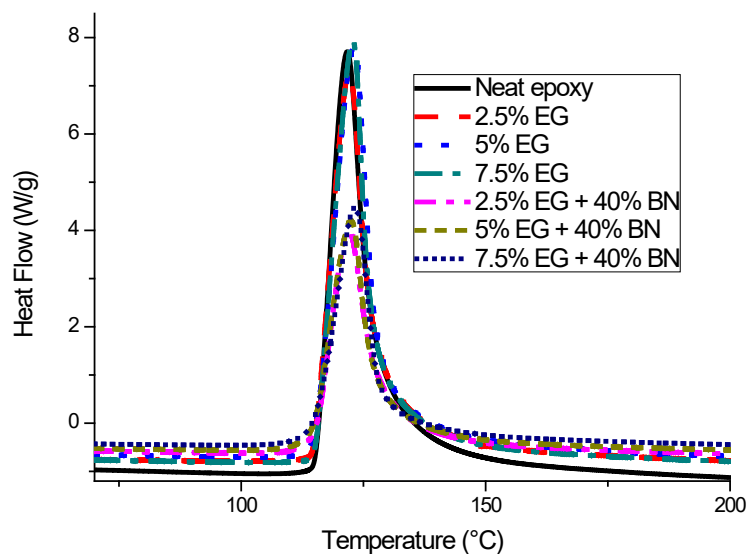


Figure 1. DSC analysis of the mixtures containing EG or EG and BN.

As it can be seen in the figure, neither the addition of EG nor the addition of BN affects the curing process, and the exotherm appears at the same temperature range, in contrast to what was observed in earlier studies with different fillers in ECC mixtures.^{14,16} **Table 1** collects the most important data extracted from the DSC experiments. It is clear that onset temperatures and the temperature of the maximum of the peak do not change. Enthalpy per epoxy equivalent evolved during the polymerization also remains similar, although the enthalpy released by gram is reduced on increasing the proportion of filler, as expected. These results also confirm that sonication does not produce any effect on the curing of the reactive mixture, confirming the stability of the formulation. The high crosslinking density of the network formed did not allow detecting, in a second dynamic DSC scan, the T_g of the final composites.

Table 1. Most important data extracted from DSC experiments.

Sample	Composition (ECC/EG/BN) wt %	T_{onset}^a (°C)	T_{peak}^a (°C)	Δh^b (J/g)	Δh^b (kJ/ee)
Neat epoxy	100/0/0	115	122	641	81
2.5% EG	97.5/2.5/0	115	122	615	80
5% EG	95/5/0	115	123	609	81
7.5% EG	92.5/7.5/0	115	122	600	82
2.5% EG + 40% BN	58.5/1.5/40	115	122	379	82
5% EG + 40% BN	57/3/40	115	122	370	82
7.5% EG + 40% BN	55.5/4.5/40	115	123	357	81

^a Onset and peak temperature of reaction determined by TA Universal Analysis software.

^b Enthalpy evolved by the reaction per gram of mixture or epoxy equivalent determined by the same software using a straight base line.

3.2. Rheological behaviour of epoxy-EG mixtures

The use of electrical semiconductors as carbon-based fillers leads to lose the electrical insulation character of the composites at a given filler loading. Moreover, to reach a high thermal conductivity, percolation of the particles should be reached. For this reason, it is of great importance to know at which proportion of filler the percolation occurs. Rheological percolation threshold is usually slightly lower than electrical conduction percolation,^{33,34} because conductive particles must be closer to each other. However, in some cases they could be similar or even identical.³⁵ In the present study, both EG and BN particles are added to the formulation but only EG particles can affect negatively electrical isolation. It should be noted that the 40% of the BN particles used in the present study have surely exceeded the percolation threshold, since the amount of BN particles to reach percolation, determined in a previous study with particles of average size of 6 μm , was determined to occur at 14.4% of BN's load.¹⁴ Because the addition of BN does not increase the electrical conductivity of the composite, we have selected a 40% of BN content that allows us to easily prepare by hand mixing the formulation and obtain homogeneous samples without the inclusion of bubbles. Therefore, only the rheological study of epoxy-EG mixtures was performed to determine the concentration needed to reach rheological percolation of EG particles in the formulation to know the maximum content of EG to keep electrical insulation.

To determine the viscoelastic properties of the formulation, the linear viscoelastic region (LVR) must be considered. This means to determine the deformation to be applied where the mixture present a Newtonian behaviour. One of the simplest method to determine this region is performing experiments keeping a constant frequency (1 Hz) varying the sample strain applied. **Figure 2** represents the elastic modulus (G') in front of strain, because of it is more sensitive than G'' . The less filled formulation exhibits a practically constant modulus in all the range of strain tested, typical of dilute solutions with Newtonian behaviour. When the concentration of EG is 5 wt %, its LVR shows a complex curve with a decrease of modulus, because the structure of the mixture breaks down. An increase of G' with a shoulder shape when the amplitude achieved certain value can also be observed. This behaviour can be explained as a particle structure reordering because of the deformation applied.³⁶ As expected for this type of mixtures, the LVR is shifted to lower strains when particle concentration increases, as it can be seen in the sample with a 7.5% of EG.

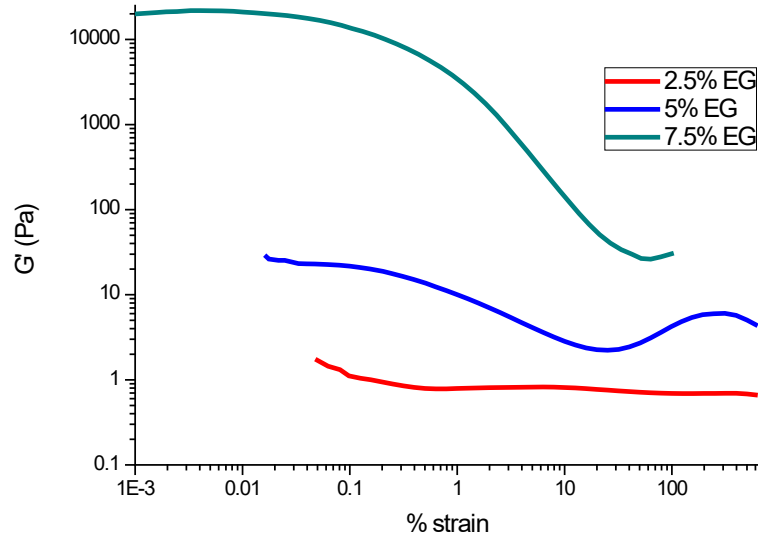


Figure 2. Elastic shear modulus (G') against deformation applied (%) from strain sweep experiments.

Once selected the appropriate amplitude for each mixture, frequency sweep experiments were carried out.

In **Figure 3** both elastic and viscous modulus are represented. Following the scientific literature, it is usually accepted that percolation threshold of a filled mixture is achieved when G' reached the same value as G'' at low frequencies.^{15,37} On increasing the filler proportion in a formulation it can be seen how the transition from liquid-like behaviour ($G'' > G'$) to solid-like ($G' > G''$) occurs. At low frequencies this transition occurs between the formulations of 2.5 and 5 wt % of EG, which means that the electrical percolation occurs at a filler loading of about 5% of EG.

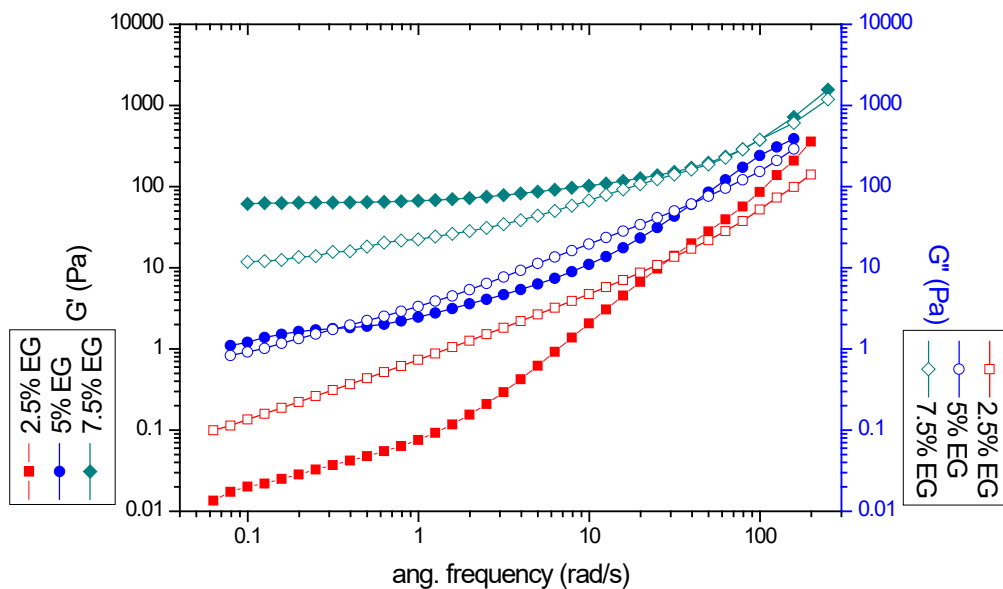


Figure 3. Elastic (G') and viscous (G'') modulus against frequency (ω) of epoxy-EG mixtures.

3.3. Thermal and mechanical behaviour

Once finished the study of the curing of the formulations, they were thermally cured in the oven in a multistep temperature program, selected according to the results obtained by DSC and improved testing the quality of the samples by DMA. The curing schedule that starts at 100 °C and ends at 200 °C has different steps with small temperature increases to avoid the generation of internal stresses within the materials. Although, because of the latency, the reaction is very fast, to reach the complete curing of the material requires temperatures about 200 °C to avoid vitrification. T_g s of the neat material and BN filled composites were determined in a previous study and resulted to be over 200 °C.¹⁴

Figure 4 presents the storage modulus (E'), related with the elastic response of materials (A), and the loss factor $\tan \delta$ (B), associated to the T_g , obtained by DMA and the main data are collected in **Table 2**.

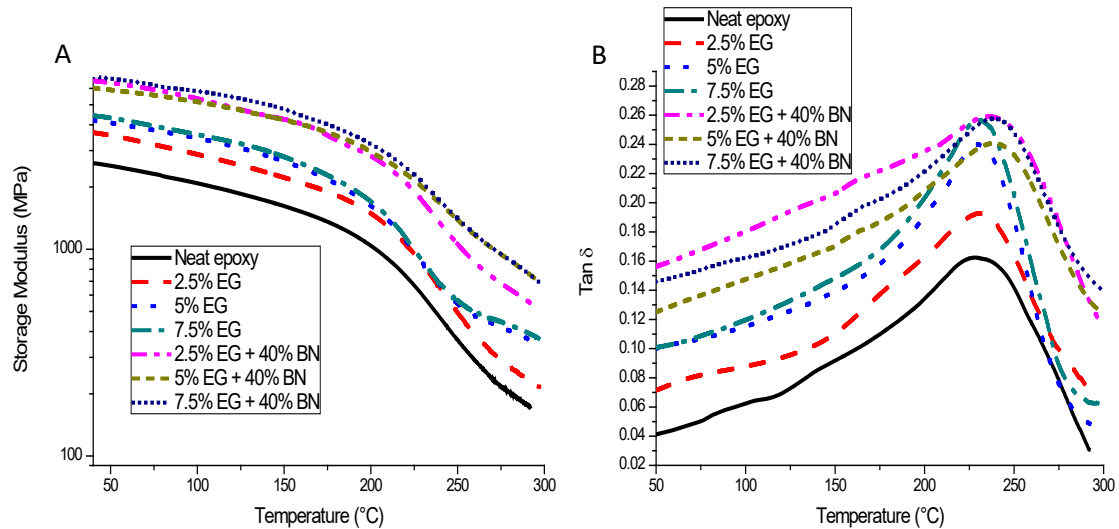


Figure 4. Storage modulus (E') (A) and $\tan \delta$ peak curves (B) against temperature.

Figure 4A shows the increase of the stiffness and the mechanical response of the composites when the proportion of filler increases. Once reached the mechanical percolation (at about 5% EG) the effect of increasing the proportion of EG on the storage modulus evolution is not noticeable. Similarly, when a 40% BN is in the formulation, the increase of EG content does not influence the mechanical performance. Moreover, the storage modulus is maintained up to 200 °C. These results demonstrated that the materials can be used in a long range of temperature without loss on their mechanical response. It should be noted the change in the slope of E' in composites with 5 and 7.5 wt% of EG at about 250 °C, which differs from the curve of the materials with lower EG content, in both series of materials with or without BN. This mechanical difference could be related to the percolation phenomenon, sensitive to the particle

interactions within the matrix. In Figure 4B the relaxation process of materials lengthens over a large temperature range, but the experiments, which were stopped at about 300 °C to avoid degradation, showed that the materials were not yet completely relaxed, accordingly to their high crosslinked character. The most important difference observed between these materials is the increase of $T_{\tan \delta}$ when BN particles are in the composite. However, the addition of EG does not lead to changes in the temperature of relaxation. As observed in previous studies^{14,16} the $\tan \delta$ peak is broad and low, indicating a slow relaxation process and low homogeneity of the polymer network, as a result of the homopolymerization by ring-opening mechanism in the curing process, which is inherently inhomogeneous.³⁸

By DMA, in static controlled force test at 30°C, the Young's moduli of the composites were determined. As can be seen from the values in the table, fillers play a reinforcing role into the matrix. There are clearly two sets of moduli, the first one in samples with only EG as filler, where about a 40% of enhancement is reached. In this case, once percolation is overpassed the EG particles seem not to increase rigidity. The second set is formed by the composites with both EG and BN. In these materials, rigidity more than doubles the value of pure material. (from 2.4 GPa till 5.1 GPa) and the addition of EG seems not to enhance much the Young modulus. The maximum value achieved is below the previously reported with the 40 wt % of BN (6.5 GPa).¹⁴ This lower value is due to the change of BN particles used, larger in the present study. As seen before, bigger filler particles worse the rigidity of the composites.¹⁵ Anyway, the rigidity is increased, and materials can be useful in some structural applications.

Table 2. Data obtained from DMA, TGA, TMA and microindentation tests.

Sample	$T_{\tan \delta}$ ^a (°C)	Young Modulus ^b (GPa)	$T_{5\%}$ ^c (°C)	Char yield ^c (%)	CTE_{glass} ^d ($10^{-6} \cdot \text{K}^{-1}$)	KHN ^e
Neat epoxy	229	2.4 ± 0.02	296	1.9	115	12.3 ± 0.67
2.5% EG	231	3.1 ± 0.02	306	4.9	110	17.6 ± 0.81
5% EG	230	3.4 ± 0.06	342	7.8	78	20.2 ± 1.12
7.5% EG	231	3.4 ± 0.09	339	11.0	77	20.2 ± 1.39
2.5% EG + 40% BN	240	4.7 ± 0.15	350	46.0	64	16.7 ± 0.78
5% EG + 40% BN	239	4.9 ± 0.23	356	46.5	64	16.5 ± 0.62
7.5% EG + 40% BN	239	5.1 ± 0.35	355	46.9	64	17.3 ± 0.75

^a Temperature of $\tan \delta$ peak determined at 1 Hz in an oscillatory experiment by DMA.

^b Rigidity of samples determined at 30 °C in DMA apparatus with a controlled force experiment.

^c Temperature of 5 wt % loss and final residue in TGA test at 10 °C/min in nitrogen atmosphere.

^d Coefficient of thermal expansion in the vitreous state determined by TMA, between 50 and 70 °C.

^e Microindentation Knoop hardness.

The thermal stability of the composites was analysed by TGA experiments under inert atmosphere.

Figure 5 shows the degradation curves and the main data extracted are collected in Table 2. The

degradation seems to occur in an only process, independently of the composition of the formulation and the main differences are observed in the char residue, due to the different proportion of filler added. There is a pronounced increase in the thermal stability of epoxy-EG when percolation threshold is surpassed of about 30°C, a sign of a good particle interaction. All the char residues correlate with the proportion of filler added except for the samples including 40 wt % of BN, where the residue is practically constant, because of the low relative variation of filler content among the samples. The increase of the initial temperature of decomposition is related with the decrease of the resin content that can be decomposed.

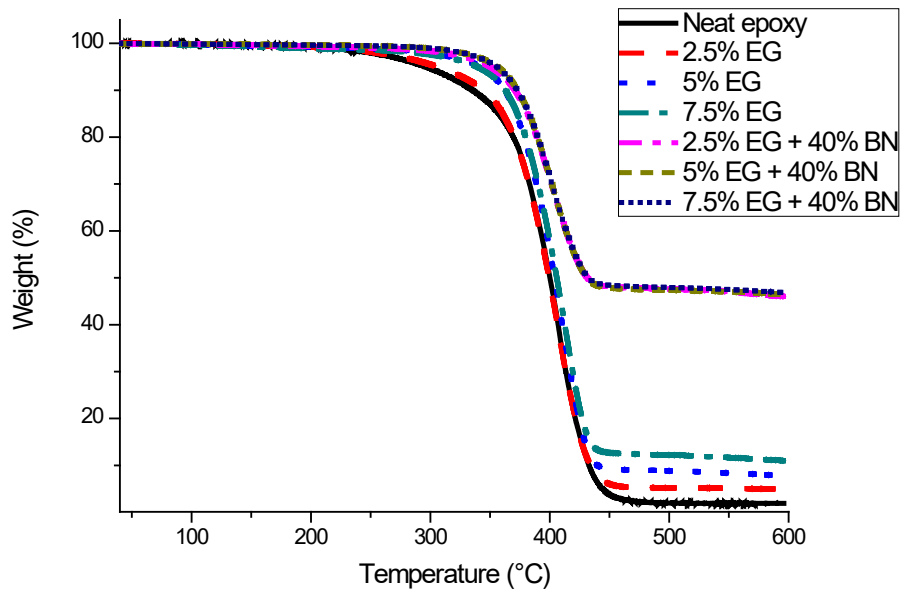


Figure 5. Decomposition curves performed by TGA experiments.

The dimensional stability of materials on changing the temperature is an important characteristic when they are used in devices where the temperature can change and are assembled with metals, such as occurs in electronic devices. To evaluate the effect of the incorporation of fillers to the matrix on the coefficient of thermal expansion (CTE), TMA analysis was performed. Generally, CTEs of polymers are larger than metals, and higher than ceramics. As it can be seen in Table 2, the inorganic fillers incorporated to the matrix, as expected, reduce the CTEs of composites approaching them to substrates they can coat. There is a sharp reduction of CTE on reaching EG percolation threshold, but a further addition of this filler does not produce any improvement. There is a reduction of CTEs in samples with 40% of BN, but the further addition of EG does not produce any change, since the percolation has been reached by the BN particles.

From the mechanical characteristics, the hardness of materials was evaluated since it is an important property for coatings, since it confers them durability. In addition, this property is used to correlate with ultimate tensile strength (or breaking strength). In Table 2 the Knoop values are collected. Also, in this

parameter, the addition of EG particles shows a high dependence on the filler loading until the percolation threshold is exceeded, and the addition of 7.5% of EG does not produce any improvement. The addition of BN particles led to a reduction of the surface hardness in comparison with materials filled with only EG. This result might be due to the decrease of cohesion of the material with such amount of filler, which is translated in an increase in the capacity to be deformed against penetration and a lower interaction epoxy-BN than epoxy-EG.

3.4. XRD characterization and microscopy inspection

X-Ray diffraction is a very powerful technique to characterize crystalline or semi-crystalline materials and to determine unit cell dimensions and sample purities. The fillers used in this work and two different composites were analysed by this technique and the registered diffractograms are represented in **Figure 7**. Figure 7A presents the diffractogram of the BN used with the characteristic peaks of hexagonal structure pattern of the BN in the ICDD database (card number 01-073-2095) in red colour. All the peaks fit well with the pattern as it was expected. However, it can also be observed small signals, the more visible ones in the range of 28-40° of 2 θ , related to the presence of calcium borate (Ca₂(B₂O₅)). The pattern of this impurity (card number 01-089-6630) fits well with these signals and a rough semiquantitative analysis (Reference Intensity Ratio method) determine a ~6% of concentration.

The X-Ray diffractogram of EG (figure 7B) is represented together with the graphite pattern (03-065-6212), in blue colour, because both have the same crystalline structure. Nevertheless, some differences are shown. Peaks at approximately 42° (crystallographic plane 100) and especially 44.5° (101) are broader than the others are. Such broadening could be related with the structure distortion due to the expanded graphite used. In addition, the peak at 54.6° (004) has a lower intensity than the one of the graphite pattern. No impurities were detected in this diffractogram.

Figures 7C and 7D correspond to the composites with 7.5% of EG and 7.5% + 40% of BN respectively. In both cases, they presented a broad peak at about 17°, representative of amorphous structure of the matrix. The peaks of the fillers are kept at the same diffraction angles, but partially covered by the epoxy resin, confirming that dispersion procedure did not affect filler crystal lattice. It should be noted, that the characteristic peaks of the two fillers appear at similar diffraction angles, since the two types of particles have the same crystalline structure, only differentiated by the cell size due to the different atoms in the structure. However, the peaks corresponding to expanded graphite have low intensity, because of its low proportion in the composites but BN peaks can be easily distinguished. The first and most intense peak at

about 26° , corresponding to the 002 plane of BN is partially overlapped by 002 plane of graphite. Despite this, in the figure 7E, it can be observed how the peak has a shoulder at low angles because the BN and graphite peaks do not have the same position because the obvious differences in cell sizes.

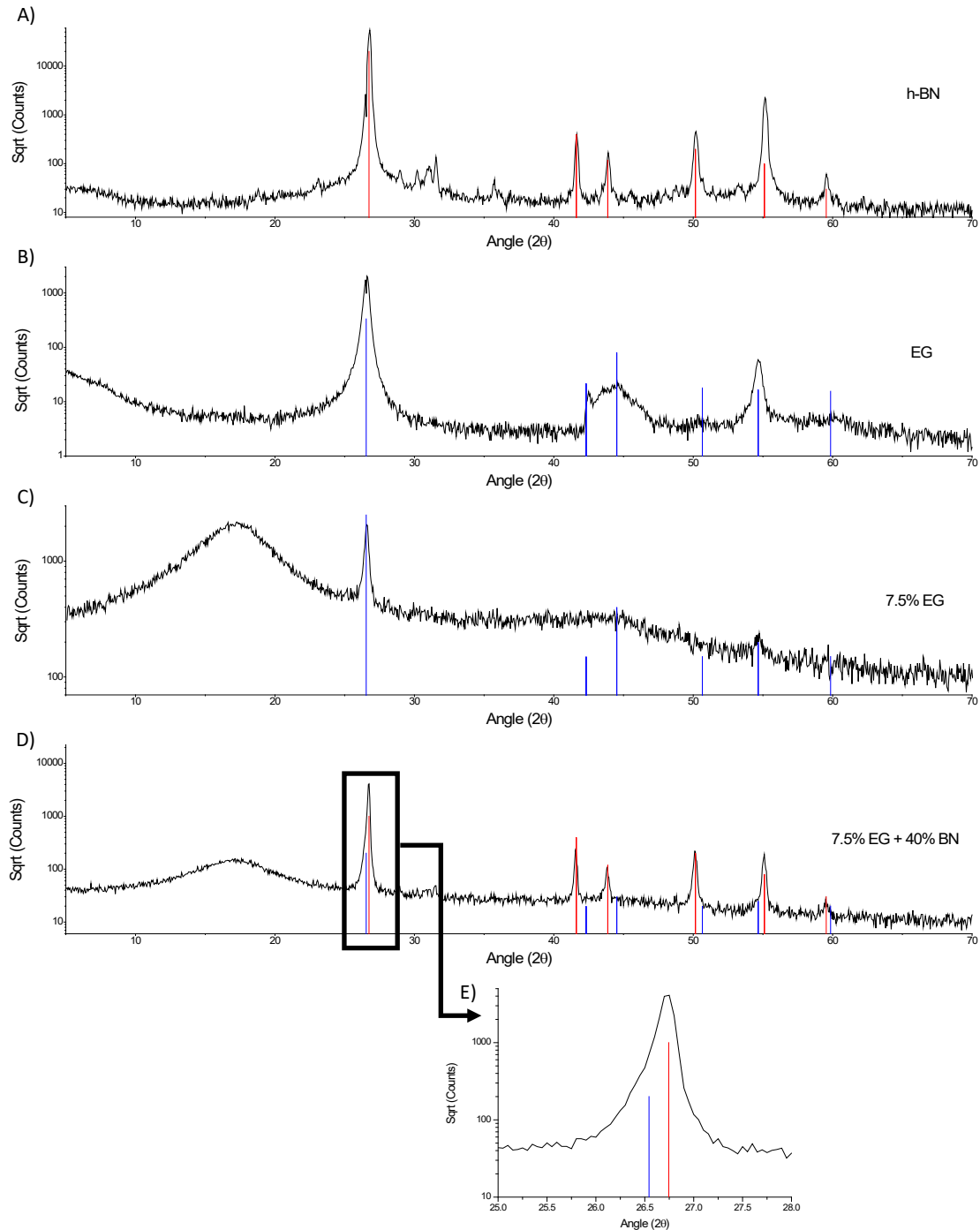


Figure 7. XRD diffractograms of the two fillers and two composite samples.

ESEM inspection can be used to determine the filler dispersion and the type of fracture by examining the surfaces of the fractured samples of the composites. We firstly examined the fillers used. **Figure 8**

presents a general view of the particles and a single particle (at higher magnifications) of BN and EG. BN particles exhibit a large dispersion of sizes, which might be appropriate to better fill the spaces within the matrix. In the micrograph of the single particles we can observe the laminar shape of BN. EG particles present an amorphous shape as consequence of the thermal shock after chemical oxidation.

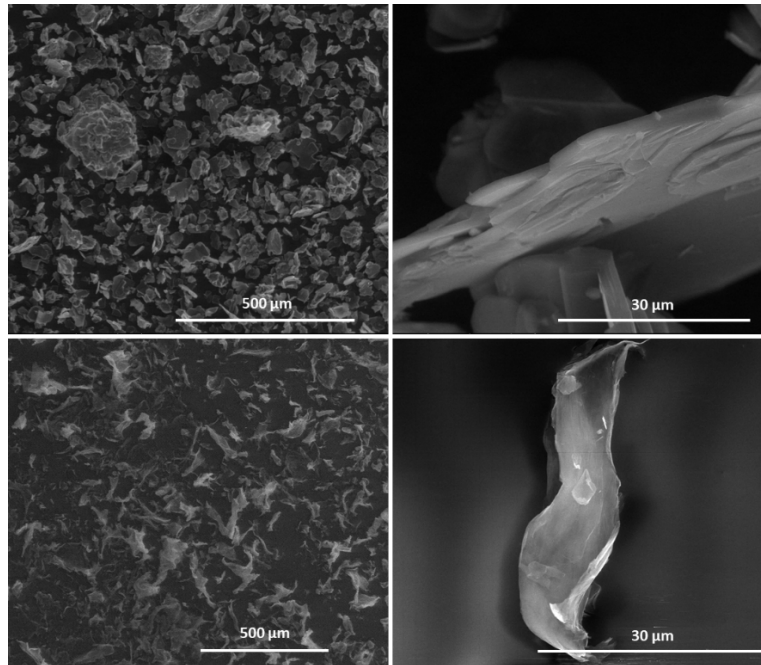


Figure 8. ESEM micrograph of fillers used in the study. BN in row above and EG in row below.

In **Figure 9** fracture surfaces of different composites are presented. The figures above correspond to the composites filled with EG at the three different proportions. In the first one (2.5 wt % of EG), it can be seen how most of the EG particles are isolated within the matrix whilst in the figure in the middle of the row (5 wt % of EG) the particles are closer to each other leading to the appearance of interconnected ways, which confirm that the percolation has been reached. A similar image is observed in the micrograph of the right, corresponding to the composite with the highest proportion of EG (7.5 wt %) that presents more interconnected EG particles and few parts of pure matrix. The particles in all the samples appear homogeneously distributed. From the left to the right it can be seen that the fracture roughness increases, indicating that the addition of EG enhances the toughness of the materials. In the line below, the first micrograph belongs to the neat epoxy breaking surface. It must be noted how cracks are straight meaning a fragile rupture typical of fragile thermosetting polymers. In the other samples containing BN+EG fillers, the fracture lines are more tortuous, changing their direction on finding a particle, which produces a great increase of the energy absorbed by the impact, increasing their toughness. The higher magnifications of the micrograph in the right below allow distinguishing some EG particles in the matrix.

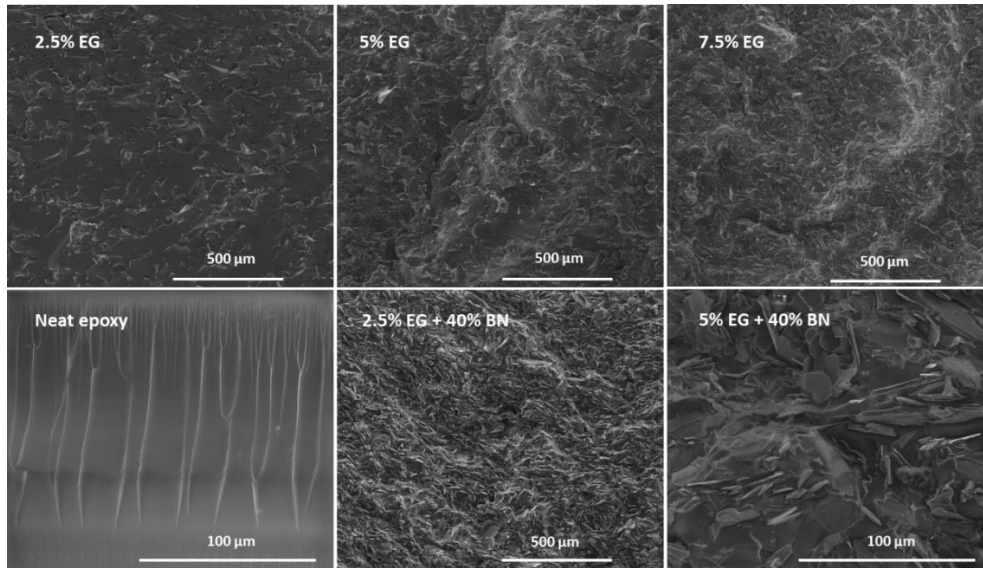


Figure 9. Fracture surfaces of the different composites at different magnifications (100 and 800).

3.5. Thermal conductivity and electrical resistivity

Since keeping electrical insulation of this type of composites is crucial for their use in electronic devices, we firstly determined the electrical resistivity of the composites to know the highest proportion of the semiconducting EG filler able to keep the insulating characteristics. It should be commented that although 40 wt % of BN is the proportion studied until now, samples with a proportion of 70% of BN have also been prepared, including proportions of 2.5 and 5 wt % of EG to maintain good electrical insulation character, in order to increase even further the thermal conductivity. When adding a 70 % of BN to the formulation the viscosity is highly increased and pressure molding is needed to prepare homogeneous samples without bubbles. These samples could not be characterized by rheometry or DSC, because of their low content in resin. As a comparison mode, a sample with 40 wt % of BN without EG was also prepared. Electrical resistivity and thermal conductivity are represented together in **Figure 10**.

Although by rheological measurements, the percolation threshold is found between the proportion of 2.5 and 5 wt % of EG, the measurement of electrical resistivity indicates a progressive reduction of this value on increasing the EG content till 7.5 wt %. However, the value of $4.5 \times 10^2 \Omega \cdot m$ for the composite with a 5 wt % of EG is too low to be considered as electrical insulator, which means that the electrical percolation has been overpassed.³⁹ The addition of a higher proportion of filler, up to 7.5 wt % lead to a further reduction in resistivity, with a value of $2.2 \times 10^1 \Omega \cdot m$. Thus, the proportion of EG in the epoxy matrix is limited to 2.5 wt% to keep electrical insulation. As in a previous study,¹⁴ the addition of BN particles to the epoxy formulation keep the electrical resistivity in the same value range of the neat epoxy ($7.9 \times 10^9 \Omega \cdot m$ for 40 wt.% of BN and $1.6 \times 10^{10} \Omega \cdot m$ for the neat material). When 40% of BN is added

to epoxy/EG samples, electrical resistivity increases in reference to the samples containing only EG as filler. Since BN particles are electrical insulators, they act as walls that hinder the EG particle to interact each other, avoiding tunnelling effect and increasing the distance between electrical conductive particles. In case of materials with both BN and EG, only the sample with a 7.5 wt % ($2.2 \times 10^1 \Omega \cdot m$) can be considered as conductive and therefore a 5 wt % of EG can be added without loss of insulating characteristics. On increasing the proportion of BN in the composite the resistivity is enhanced and the sample with a 70 wt % of BN and 5 wt% of EG has a resistivity of $2.4 \times 10^6 \Omega \cdot m$, which are typical values for insulating adhesives for electronic applications.

Thermal conductivities (TC) were determined at room temperature by the transient hot method. The results are also represented in Figure 10. It can be noticed the great impact on TC with the addition of low proportions of EG particles as reported by previous authors,^{1,25,28,40} with a much higher relative increase than in case of adding BN as the filler.¹⁴ The conductivity is almost tripled with the addition of 2.5% of EG (from 0.128 to 0.36 W/m·K) and almost doubled with the other two higher proportions (from 0.36 to 0.61 with a 5 wt % and 0.84 W/m·K with a 7.5 wt %). These values are higher than other reported using graphite nanoflakes¹⁹ (0.43 W/m·K at 8% of GN), probably due to aggregation phenomena of nanoparticles and the increased number of interfaces that results by the smaller size of the particles on comparison with ours.

The values of TC in BN filled formulations revealed that a higher proportion of filler is required to equal EG composites, since in a previous study¹⁴ a content of BN between 30 and 40 wt % was needed to reach conductivities comparable to composites with a 7.5 wt% of EG. In composites with a 40 wt % of BN, the increase of EG proportion lead to an increase in TC, although the enhancement in conductivity is less pronounced and no synergic effect can be observed. This is due to the fact that the particles of EG, with a higher conductivity, are isolated each other by the presence of BN platelets, less conductive, acting as walls, similarly to what happens in the electrical conductivity behaviour. The two samples with 70 wt % of BN, prepared under pressure, achieved TC over 2 W/m·K (2.08 with 2.5% of EG and 2.22 with 5% of EG). These good results, with enhancements over 1600 % in reference to the neat epoxy, seem to confirm that not only the amount of BN and EG but the pressure applied plays a main role on increasing the thermal conductivity, avoiding the appearance of bubbles inside the material.

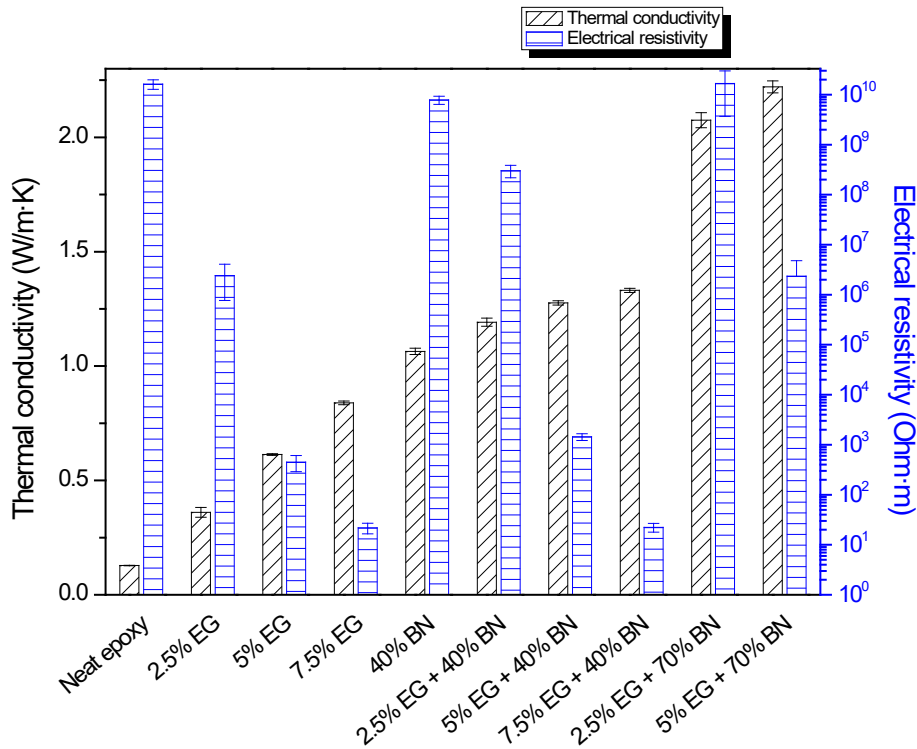


Figure 10. Thermal conductivities measured at room temperature by transient hot method and bulk electrical resistance (log scale) of samples prepared.

Taking into account electrical resistivity and thermal conductivity values we can state that the composite with a 70 % of BN and 2.5 % of EG is the best one to keep the electrical insulation of the neat epoxide with a high thermal conductivity. However, the material with 70 % of BN and 5% of EG, with an even higher TC, it still retains high insulating characteristics.

4. Conclusions

In the search for materials combining lightness, mechanical resistance, thermo-conductivity and electro-insulation for energy, electronic or aeronautic applications, epoxy resins modified with nanofillers appear as a promising approach. In this work, the potential of joint addition of BN and EG to impart thermal conductivity and maintain the electrical insulation of epoxy systems was studied.

It appears that the addition of BN and EG to the epoxy formulations does not affect the evolution of the curing progress. The thermomechanical performance of the prepared composites is well preserved up to temperatures as high as 200 °C, thanks to their high T_g s and the thermal stability of the network formed. Thermal expansion coefficients are highly reduced and the microindentation hardness enhanced on increasing the proportion of fillers. ESEM images of fractured samples confirmed the good dispersion of the particle fillers in the epoxy matrix and the enhancement in toughness. The addition of EG results

proportionally much more effective to enhance the thermal conductivity than the addition of BN. For large filler loadings, the use of pressure is highly recommended to further increase the thermal conductivity in composites.

In EG composites, the proportion of EG in the epoxy matrix is limited to 2.5 wt% to keep electrical insulation. However, when 40% of BN is added to epoxy/EG samples, electrical resistivity increases in reference to the samples containing only EG as filler and a 5 wt % of EG can be added without loss of electrical insulating characteristics.

The best compromise of properties was achieved for the composites containing 70 % of BN and 2.5 % of EG and 70 % of BN and 5 % of EG. More precisely, the composite obtained from the formulation with 70 % of BN and 2.5 % of EG shows the highest electrical resistivity, similar to the neat epoxy thermoset (about $10^{10} \Omega \cdot m$), with a high thermal conductivity (increase of 1500% in reference to the neat epoxy) whereas the material with 70 % of BN and 5% of EG, exhibits the highest thermal conductivity (1640 % keeping good insulating characteristics (about $10^6 \Omega \cdot m$).

Acknowledgments

The authors of URV would like to thank Ministerio de Economía y Competitividad and Fondo Europeo de Desarrollo Regional (MAT2017-82849-C2-1-R, MCIU/FEDER) and Generalitat de Catalunya (2017-SGR-77) for the financial support. The authors of Materia Nova wish to thank the “Région Wallonne” and the European Community for general support in the framework of the Interreg V program (“BIOCOMPAL” and “ATHENS” projects) and the FEDER 2014–2020 program (“HYBRITIMESURF” and “MACOBIO” projects).

References

- ¹ Chen X, Su Y, Reay D, Riffat S. Recent research developments in polymer heat exchangers - A review. *Renew Sust Energ Rev* 2016; 60: 1367-1386
- ² Huang X, Jiang P. A review of dielectric polymer composites with high thermal conductivity. *IEEE Electr Insul Mag* 2011; 27: 8–16.
- ³ *Epoxy Polymers: New Materials and Innovations*. Pascault JP, Williams RJJ, editors. Weinheim: Wiley-VCH, 2010.
- ⁴ Hong J, Park DW, Shim SE. A review on thermal conductivity of polymer composites using carbon-based fillers: carbon nanotubes and carbon fibers. *Carbon Lett*. 2010; 11: 347-356.

- ⁵ Cevallos JG, Bergles AE, Bar-Cohen A, Rodgers P, Gupta SK. Polymer heat exchangers - History, opportunities, and challenges. *Heat Transfer Eng.* 2012; 33: 1075-1093.
- ⁶ Viana ST, Scariot VK, Provensi A, Barra GMO, Barbosa Jr JR. Fabrication and thermal analysis of epoxy resin-carbon fiber fabric composite plate-coil heat exchangers. *Appl Therm Eng* 2017; 127: 1451-1460.
- ⁷ Im H, Kim J. Thermal conductivity of a graphene oxide-carbon nanotube hybrid/epoxy composite. *Carbon* 2012; 50: 5429-5440.
- ⁸ Li A, Zhang C, Zhang YF. Thermal conductivity of graphene-polymer composites: mechanisms, properties and applications. *Polymers* 2017; 9: 437-452.
- ⁹ Noh YJ, Kim HS, Ku B, Khil M, Kim SY. Thermal conductivity of polymer composites with geometric characteristics of carbon allotropes. *Adv Eng Mater* 2016; 18: 1127-1132.
- ¹⁰ Ahmed MMM and Imae T. Electrochemical properties of thermally expanded magnetic Graphene composite with conductive polymer. *Phys Chem Phys* 2016; 18: 10400-10410.
- ¹¹ Noh YJ, Pak SY, Hwang SH, Hwang JY, Kim SY, Youn JR. Enhanced dispersion for electrical percolation behavior of multi-walled carbon nanotubes in polymer nanocomposites using simple powder mixing and in situ polymerization with surface treatment of the fillers. *Compos Sci Technol* 2013; 89: 29-37.
- ¹² Chen H, Ginzburg VV, Yang J, Yang Y, Liu W, Huang Y, Du L, Chen B. Thermal conductivity of polymer-based composites: Fundamentals and applications. *Prog Polym Sci* 2016; 59: 41-85.
- ¹³ Isarn I, Massagués LI, Ramis X, Serra À, Ferrando F. New BN-epoxy composites obtained by thermal latent cationic curing with enhanced thermal conductivity. *Composites: Part A* 2017; 103: 35-47.
- ¹⁴ Isarn I, Gamardella F, Massagués LI, Fernández-Francos X, Serra À, Ferrando F. New epoxy composite thermosets with enhanced thermal conductivity and high T_g obtained by cationic homopolymerization. *Polym Comp* 2018; 39: 1760-1769.
- ¹⁵ Isarn I, Ramis X, Ferrando F, Serra À. Thermoconductive thermosetting composites based on boron nitride fillers and thiol-epoxy matrices. *Polymers* 2018; 10: 277-292.
- ¹⁶ Isarn I, Gamardella F, Fernández-Francos X, Serra À, Ferrando F. Enhancement of thermal conductivity by the addition of several conductive fillers to thermal cationic curing of cycloaliphatic epoxy resins. *Polymers* 2019; 11: 138-151.

- ¹⁷ Loeblein M, Tsang SH, Pawlik M, Phua EJR, Yong H, Zhang XW, Gan CL, Teo EHT. High-density 3D-boron nitride and 3D-graphene for high-performance nano-thermal interface material. *ACS Nano* 2017; 11: 2033-2044.
- ¹⁸ Singh AK, Panda BP, Mohanty S, Kumar S, Gupta NK, Gupta MK. Recent developments on epoxy based thermally conductive adhesives (TCA): a review. *Polym Plast Technol Eng* 2018; 57(9): 903-934.
- ¹⁹ Luo F, Wu K, Huang X, Hu X, Lu M. Encapsulation of graphite nanoflakes for improving thermal conductivity of mesogenic epoxy composites. *Ind Eng Chem Res* 2017; 56: 489-494.
- ²⁰ Asante J, Modiba F, Mwakikunga B. Thermal measurements on polymeric epoxy-expandable graphite material. *J Polym Sci A*, vol. 2016, Article ID 1792502, 12 pages.
- ²¹ Chatterjee S, Wang JW, Kuo WS, Tai NH, Salzmann C, Li WL, Hollertz R, Nüesch FA, Chu BTT. Mechanical reinforcement and thermal conductivity in expanded graphene nanoplatelets reinforced epoxy composites. *Chem Phys Lett* 2012; 531: 6-10.
- ²² Xie F, Qi SH, Wu D. Thermal conductive composites based on silver-plating graphite nanosheet and epoxy polymer. *Polym Composite* 2017; 38: 2822-2828.
- ²³ Rybak A, Gaska K. Functional composites with core-shell fillers: I. Particle synthesis and thermal conductivity measurements. *J Mat Sci* 2015; 50: 7779–7789.
- ²⁴ Chen H, Ginzburg VV, Yang J, Yang Y, Liu W, Huang Y, Du L, Chen B. Thermal conductivity of polymer-based composites: Fundamentals and applications. *Prog Polym Sci* 2016; 59: 41-85.
- ²⁵ Corcione CE, Maffezzoli A. Transport properties of graphite/epoxy composites: Thermal, permeability and dielectric characterization. *Polym Test* 2013; 32: 880-888.
- ²⁶ Kim HS, Kim JH, Kim WY, Lee HS, Kim SY, Khil M-S. Volume control of expanded graphite based on inductively coupled plasma and enhanced thermal conductivity of epoxy composite by formation of the filler network. *Carbon* 2017; 119: 40-46.
- ²⁷ Wang Z, Qi R, Wang J, Qi S. Thermal conductivity improvement of epoxy composite filled with expanded graphite. *Ceram Int* 2015; 41: 13541-13546.
- ²⁸ Badenhorst H. A review of the application of carbon materials in solar thermal energy storage. *Sol Energy*. In press. <https://doi.org/10.1016/j.solener.2018.01.062>
- ²⁹ Nakano S, Endo T. Cationic polymerization of glycidyl phenyl ether by benzylammonium salts. *J Polym Sci: Part A Polym Chem* 1995; 33: 505-512.

- ³⁰ Nakano S, Endo T. Thermal cationic curing by benzylpyridinium salts. *Prog Org Coat* 1994; 23: 379-385.
- ³¹ Nakano S, Endo T. Thermal cationic curing with benzylammonium salts. *Prog Org Coat* 1993; 22: 287-300.
- ³² Tejkl M, Valis J, Kaplanová M, Jasúrek B, Syrový T. Inhibition of premature polymerization of cationically polymerizable low viscosity systems. *Prog Org Coat* 2012; 74: 215-220.
- ³³ McClory C, Chin SJ, McNally T. Polymer/Carbon nanotube composites. *Aust J Chem* 2009; 62: 762-785.
- ³⁴ McCrossan K, McClory C, Mayoral B, Thompson D, McConnell D, McNally T, Murphy M, Nicholson T, Martin D, Halley P. Composites of poly(ethylene terephthalate) and multi-walled carbon nanotubes. Book: *Polymer-carbon nanotube composites: Preparation, properties and applications*. Editors: Tony McNally and Petra Pötschke. Oxford: Woodhead Publishing Limited, 2011, p. 545-586.
- ³⁵ McNally T, Pötschke P, Halley P, Murphy M, Martin D, Bell SEJ, Brennan GP, Bien D, Lemoine P, Quinn JP. Polyethylene multiwalled carbon nanotube composites. *Polymer* 2005; 46(19): 8222-8232.
- ³⁶ Laun H.M. Rheological properties of aqueous polymer dispersion. *Angew Makromol Chem* 1984; 123/124: 335-359.
- ³⁷ Jouault N, Vallat P, Dalmas F, Said S, Jestin J, Boué F. Well-dispersed fractal aggregates as filler in polymer-silica nanocomposites: Long-range effects in rheology. *Macromolecules* 2009; 42: 2031-2040.
- ³⁸ *Thermosetting Polymers*. Pascault JP, Sautereau H, Verdu J, Williams RJJ. New York: Marcel Dekker AG, 2002.
- ³⁹ Sancaktar E, Bai L. Electrically Conductive Epoxy Adhesives. *Polymers* 2011; 3: 427-466.
- ⁴⁰ Ramakrishnan S, Wang X, Sanjayan J, Wilson J. Heat transfer performance enhancement of paraffin/expanded perlite phase change composites with graphene nano-platelets. *Energy Procedia* 2017; 105: 4866-4871.