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NOVEL BN-EPOXY/ANHYDRIDE COMPOSITES WITH ENHANCED THERMAL CONDUCTIVITY

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Abstract

Boron nitride (BN) composites formed by an epoxy-anhydride matrix and different BN contents, between 30 and 80% w/w of agglomerates of 120 μ m BN, were prepared and characterized by several thermal techniques.

The curing process evolution of the epoxy system was studied by calorimetric measurements to see if there was an influence of the filler particle on the curing rate. Rheological measurements were performed to obtain the percolation threshold.

The addition of high ratio of BN (> 60% w/w) to the epoxy matrix required the use of pressure to eliminate voids and to improve the compactness of the material.

BN filler has no pernicious effect on the thermomechanical properties of the materials and allowed to enhance the thermal conductivity from $0.17 \text{ W/m} \cdot \text{K}$, in the case of the neat epoxy, to 3.06 W/m·K, when 80 wt. % of BN agglomerates were added, which represents an improvement of 1700%.

Keywords: Composites, thermal properties, mechanical properties

1. Introduction

The expansion of technology in all aspects of our lives requires adequate thermal management of integrated electronic components to achieve greater performance and efficiency. This is the reason why the next generation of packaging materials must possess superior thermal dissipation characteristics, since it is known, that the reliability of an electronic equipment is exponentially correlated to the operating temperature.

In most cases the thermal conductivity (TC) of thermosets is within the span of 0.1-0.5 W/m·K, insufficient for heat conduction applications [1]. This is since the dominant thermal conduction mechanism is performed through lattice waves (phonons), instead of electrons, as in

most of non-metallic materials [2]. The absence of free electrons able to transfer the heat, and the lack of an ordered structure in polymeric chains are two of the most important reasons why polymers present this low conductivity. Thus, in amorphous polymers, phonons are the responsible of heat transmission and their scattering needs to be reduced as much as possible to get high TC.

The addition of thermally conductive fillers to thermosetting matrices is still today the easiest way to increase the thermal conductivity [3], but for several electronic and electrical applications, the fillers must be electrically insulating. In polymer composite materials, the thermal conductivity relies on many factors, which the most important ones are the nature of the matter, crystallinity of the filler, the presence of defects or grain boundaries, their size and shape, among others [4]. Thus, the selection of the filler and its proportion takes an essential role in the TC of composites. The formation of a conductive network usually occurs at elevated filler ratio and it is connected to the percolation threshold that can be worked out by rheology experimental results. However, it has been reported that a good compatibility between filler and matrix, especially if there is covalent bonding, leads to a notable increase of thermal conductivity. At the filler-matrix interfaces phonon scattering may occur extensively, reducing the heat transmission. Therefore, BN particles adequately functionalized can provide an effective route with interconnected conductive networks and may finally solve the heat dissipation problem. According to that, several articles reported the chemical modification of conductive particles to enhance the adhesion filler-matrix and subsequently the thermal conductivity [5, 6, 7, 8]. However, the high chemical inalterability of BN makes extremely difficult its modification.

The modification of BN particles is not an easy task, and from the point of view of commercial applicability it would be a better strategy to improve the matrix-filler interaction by the proper selection of a matrix that can interact with the BN surface or with the reactive groups present in the edges of the BN sheets. For example, high conductivities (4.17 W/mK) were reported in thiol-epoxy BN thermosets with a ~ 40% vol/vol of BN, probably due to the interaction of sulfur with the BN structure [9].

The hexagonal form of BN has emerged as one of the best prospect for high thermal conductivity composites and electrical insulating applications. This synthetic material combines a set of properties optimum for these purposes [10,11]. Optimizations of h-BN production processes are continuously reducing cost and increasing purity and, as a consequence, enhancing their thermal conductivity [12]. However, platelets of BN possess remarkable anisotropic properties depending on the direction measured. For this reason, we have selected agglomerates to obtain an isotropic TC in all the directions of the material. In addition, the use of agglomerates has two good responses. By increasing the filler size, the number of interfaces where the phonons can be scattered is reduced [13], and if there was also phonon scattering within each agglomerate,

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it is reduced by being interfaces of the same material, and then acoustic phonons can better transmit the heat energy. The use of pressure replies the demand to avoid voids in high viscous mixtures, which can be the principal defects at which phonons can be scattered. Also, reduce the interfacial resistance play an important role. Most of the studies using pressure to BN platelets are conducted to obtain the maximum value of TC in only one direction [14,15,16].

Yu *et al.* [16] used a compression molding before curing with three different pressures, at 43, 108 and 215 MPa, held during 5 min and the in plane conductivity resulted more than double than in through-plane, with a marked anisotropy. Xu *et al.* [15] used a high temperature vacuum laminating machine under different temperatures and pressures (7, 10 and 13 MPa). In the same way, the TC achieved in the aligned filler composites was more than the double than in the random filler distribution. However, this method is only applicable to produce thin films. Hill *et al.* [17] applied pressure (28 MPa) to different ceramic fillers: Al₂O₃, BN, TiB₂ and SiC. They found that the hexagonal form of BN is more compactable and deformed than the other fillers. They demonstrate that on increasing the density of the powders goes in benefit of the TC. Then, the mixture of epoxy and fillers was also compressed applying a force of 22.2 kN in a 25.4 mm die. They conclude that at high filler loadings, soft fillers as BN, can improve the connectivity of particles and thus, enhance the TC. The group of Peng-Gang [18] got better results in TC with compression at room temperature than at 190°C.

This work delves on the addition of agglomerates of hexagonal platelets of boron nitride (BN) in an epoxy-anhydride matrix and the use of pressure to compact the mixtures when the filler proportion is elevated (>50 wt. %). We expect that the high reactivity of anhydrides would help to increase the interaction between filler and matrix, establishing covalent bonds with the functional groups of BN in the edges. Although the most studied matrix in epoxy-BN composites is formed by using amines as the curing agent, there are several authors that reported the use of anhydrides [19,20]. The research includes the study of the curing process, the determination of the percolation threshold and the thermal and mechanical characterization of the composites prepared.

2. Experimental

2.1 Materials

DGEBA (EPIKOTE Resin 828; EEW=187 g/epoxy equivalent) was supplied by Hexion Specialty Chemicals (Stuttgart, Germany). Hexahydro-4-methylphtalic anhydride (HH4MA; 168.19 g/mol), and N,N-dimethylbenzylamine (BDMA) were purchased from Sigma-Aldrich Inc. (Darmstadt, Germany). BN agglomerates (PCTL7MHF) of 120 µm were used as received from Saint-Gobain (Valley Forge, PA, USA).

2.2. Sample preparation

Stoichiometric mixtures of DGEBA and HH4MA were stirred until homogeneity. Then, 1 phr (parts of initiator per hundred parts of resin) of BDMA was added to the mixtures and stirred and degassed under vacuum for 10 mins. To the desired amount of agglomerates of BN, from 30 to 80 wt. %, were added the proportion required of epoxy system prepared and stirred till homogeneity. Mixtures were kept to -10 °C before their use to prevent polymerization. Samples were cured in molds at 150 °C for 4h and post-cured for 2h at 200 °C. In the case of mixtures with 60 wt. % or higher of BN, a pressure of approximately of 75 MPa was applied during 1 min in a cylindrical mold of 13 mm of diameter to compress and shape the sample before curing.

2.3 Characterization techniques

A differential scanning calorimeter (DSC-3+, Mettler Toledo, Columbus, OH, USA) was used to analyze the epoxy curing progress. Dynamic tests between 30 and 250 °C were performed with a heating rate of 10 K/min. Heat evolved during the experiment (Δh) was work out by integrating the calorimetric signal (dh/dt) using a straight baseline in the spectrum of the exotherm. Data were analyzed by STARe software. The glass transition temperature (T_g) of cured samples in the oven was determined in a same dynamic scan taking the temperature of the halfway point of the jump in the heat capacity when the material experiments the transition from glassy to rubbery state, under 50 mL/min of N₂ atmosphere.

Rheological test were conducted for non-filled mixture and mixtures between 30 and 50 wt. % of BN using parallel aluminum plates (20 mm in diameter) in oscillatory manner with an AR G2 rheometer equipped with a Peltier temperature controller accessory from TA Instruments (New Castle, DE, USA). The linear viscoelastic range (LVR) was determined at 1 Hz and 30 °C varying the % of strain used. Viscoelastic properties, shear elastic modulus (G') and viscous modulus (G') were determined in the LVR using frequency sweep experiments at 30 °C.

Dynamic mechanical thermal analyses (DMTA) were carried out with a TA Instruments DMA Q800 analyzer. The prismatic rectangular samples ($20 \times 4.5 \times 2.5 \text{ mm}^3$) were examined by 3-point bending clamp at a heating rate of 3 K/min from 30 to 210 °C, using a frequency of 1 Hz and an oscillation of 0.1% of sample deformation. The Young's modulus (*E*) was determined at 30 °C by means of a force ramp at constant rate, 1 N/min, until reaching a deformation that never exceeds 0.25% of overall strain, to guarantee that only the elastic part of the material is evaluated. *E* was calculated taken the slope between 0.1 and 0.2 % of the deformation curve in accordance with the equation:

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

where *E* is the elastic modulus of epoxy sample (MPa), *L* is the support span (mm), *b* and *t* are the width and the thickness of test sample (mm) respectively, and *m* is the gradient of the slope (N/mm).

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Thermal stability of cured samples was analyzed in a Mettler TGA2 thermo-balance. All the experiments were performed under N_2 atmosphere (50 mL/min). Portions of polymerized samples of 3-6 mg were heated between 30 and 600 °C at a heating rate of 10 °C/min.

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

Thermal conductivity was measured using the Transient Hot Bridge method by a THB 100 device from Linseis Messgeräte GmbH (Selb, Germany). A HTP G 9161 sensor was used with a 3 x 3 mm² of area calibrated with polymethylmethacrylate (PMMA), borosilicate crown glass, marble, Ti-Al alloy and titanium. Two equal polished circular samples (10 mm² in diameter and 2.3 mm of thickness) were placed in each face of the sensor. Due to the small size of sensor, side effect can be neglected. A measuring time of 100 s with a current of 10 mA was applied to the five measures done for each different formulations.

3. Results and Discussion

3.1 Calorimetric analysis

As it is known, ring opening polymerization of epoxy resins produces the evolve of heat, by releasing the stress of epoxide group and forming new bonds. Moreover, Hutchinson *et al.* [9] reported variations in the temperature of the calorimetric signal depending on the amount of filler added, and this was correlated with an increment in TC of the composites. In addition, DSC analysis is of crucial importance to evaluate the curing process. For this reason, the study of the calorimetric changes with the addition of fillers becomes important.

We started the DSC study, by testing the compositions with \leq 50 wt. % of BN, since higher filler loadings led to small and broad exotherms, difficult to be accurately evaluated. In any case, the samples tested were adequate to observe the calorimetric behavior. **Figure 1** shows the curves of the dynamic DSC analysis. Apart of the difference in the height of the signal, due to the decrease in the resin/filler ratio, the curves are similar, showing no effect on the addition of fillers and proving that BN particles did not have any kinetic influence in the reactive process, in contrast to the behaviour previously mentioned [9].

From the DSC exotherms some important values could be extracted, and they are reported in **Table 1**. As told before, the temperature of the peak of the exotherm scarcely vary with the addition of BN agglomerates. Despite the high reactivity of anhydrides, the inert character of BN seems to avoid any chemical reaction, which could improve the filler-resin interaction. The heat evolved from the samples is reduced in agreement with the amount of filler added and it can be seen that the enthalpy liberated per epoxy equivalent is maintained in similar values, in the range of 111 and 117 kJ/ee, without any trend related to the amount of filler. To define the glass transition temperature (T_g) of the materials, isothermally cured samples in the oven were analyzed as well by DSC. T_g 's of composites were practically constant around 112 °C and again, showing no effect with the addition of filler.

3.2 Rheological study

 An important property that makes epoxies widely used, especially as coatings and in microelectronics, is their ability to strongly adhere to many different substrates during the curing process [21] together with the low viscosity of the mixture. This leads to the possibility to prepare a huge number of thermosetting coatings, filled with fibers or fillers, with improved properties. At a given concentration of fillers, certain properties can experiment an abrupt change in their values. This point is known as percolation threshold and it is the concentration that allow the formation of an interconnected network constituted by the filler particles. By rheology experiments it is possible to determine this point. As developed in previous studies [22, 23], this phenomenon is observed when the unreacted formulations, change their behavior from liquid like to solid like, or what is the same, when the signal of G' (elastic shear modulus) appears over G'' (viscous shear modulus) at a given concentration of filler, in an oscillatory frequency sweep experiment.

As in the calorimetric studies, by rheology only the pre-cured mixtures with \leq 50 wt. % of BN were tested. To determine the viscoelastic properties (*G*', *G*''), the linear viscoelastic range (LVR) must be first determined for each different mixture. This means that it is necessary to know at what deformation, with a constant frequency (1 Hz), the mixtures behave like a Newtonian fluid. Then, maintaining that determined deformation, different for each mixture, we proceed to perform the frequency sweep experiments.

The results obtained are depicted in **Figure 2**. It can be seen a sharp increase in the viscoelastic property values between the formulations of 30 and 40 wt. %. Also, the transformation from liquid like (G' < G'') to solid like (G' > G'') behavior is observed between these samples. Overpass the threshold percolation is accompanied by a kind of plateau of G', observed as well before. As calculated in previous studies of our research group it is also possible to determine the percolation threshold more precisely using the following expression [22, 24]:

$$G' \propto (m - m_c)^{\beta}$$
 Eq. (2)

where G' is the storage modulus, m is the mass fraction of BN, m_c is the mass fraction at the rheological percolation and β is the critical exponent. Taking the results at 1 rad/s the rheological percolation was calculated to be 38.01 wt. % and the critical exponent 2.00. The concentration calculated is the lowest that allows the BN particles to interact among them and therefore, the minimum required to enhance notably, the TC of the composites.

3.3. Thermal and thermomechanical analysis

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 Once cured, samples prepared were examined by thermogravimetry (TGA) and thermomechanical analysis (DMA) to study the thermal behavior of the composites. The most important data extracted from these tests are collected in **Table 2**.

From TGA curves (**Figure 3**) it can be observed the thermal degradation of the materials. All the plots are comparable with a single degradation step, showing a degradation pattern similar to that of the neat epoxy matrix. This indicates that the addition of BN agglomerates does not influence the degradation mechanism. It is observed that the initial temperature of degradation, evaluated as $T_{5\%}$ (Table 2) is highly increased with the increase in the proportion of filler, however this behavior is explained by the reduction of the ratio of epoxy matrix that can be degraded. The char residue is related to the inorganic filler content, although it is slightly higher, because of the residue produced by the degradation of the matrix present in each composite. The carbonaceous residue formed by the polymeric matrix is due to the presence of aromatic molecules in the DGEBA moieties.

The thermomechanical effect of the presence of BN agglomerates were analyzed by DMTA tests. Due to the shape of compressed samples, they could not be analyzed by this technique. At 30 °C the rigidity of the samples was tested. In Table 2 it can be seen that the addition of 30 wt. % of agglomerates causes an improvement of the Young's modulus higher than a 60%, from 2.7 to 4.3 GPa. Nevertheless, higher proportions of fillers reduce this improvement which can be explained by two reasons. The first one is related with the filler size. As observed previously [22, 25], the tinier the filler, the better rigidity (in micro-size scale). Moreover, the shape of the filler is also important: the regular shape of the agglomerates, with a low aspect ratio, is not the best shape to increase the rigidity. The second reason is associated with the loss of cohesion in the sample due to the amount of filler. For this reason, higher proportions of filler were compressed under pressure to ensure a solid compaction. The T_g of the materials, related with the tan δ peak in a DMTA experiment (Table 2), is steadily increased few degrees with the increase in the quantity (%) of filler added. It must be mentioned the difference of more than 50 °C found comparing the T_g determined by DSC and the one by DMTA. The first one is defined as the change in the heat capacity of the material. In the other, the mechanical response of the filler that acts as reinforcement comes into play. Whereas the T_g determined by DSC is practically independent of the amount of filler, the tan δ temperature increases steadily few degrees with the amount of filler, because of the reinforcing effect of the BN agglomerates.

3.4. Microscopic examination of composites

Neat and composite samples were cooled down to produce a brittle fracture. Then, fracture surfaces were examined by ESEM microscopy and the most illustrative micrographs are shown in **Figure 4**.

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It can be observed in the micrograph of the neat epoxy, the typical lines of breakage of a brittle thermoset. They are straight lines of rupture due to the fragile behavior of epoxies with a slight resilience capacity. The second micrograph shows the rupture surface of the composite with 30 wt. % of BN, where resin enclaves can be seen. This shows that the percolation threshold has not yet been reached, in concordance with that observed by rheology results. Single BN platelets can also be seen within the matrix, probably they detached from the agglomerates during the manufacturing process. On the other hand, on the sample with 50 wt. % BN, no isolated pure resin is observed, which means that the percolation has been exceeded. The low resin content is shown in the inadequate cohesion aspect that presents, with the agglomerate particles with hardly any matrix coating to bind them. This may be the reason for the decrease in the stiffness of the material, determined by DMTA, with the additional proportion of particles. Finally, the last sample, with a 70 wt. % of BN content manufactured under pressure, shows a well differentiated appearance. From the immaculate aspect of the agglomerates of the previous sample, it is possible to see how the action of pressure has deformed the particles. This benefits the cohesion of the material. Although not determined, the rigidity of the material is presumed to be superior to samples not made with compression, avoiding any void. From the inspection of the SEM micrographs and the fracture lines which appears, it is clear that the addition of BN specks favors the toughness characteristics, making a more tortuous crack propagation pathway.

3.5. Thermal conductivity

The principal intention of this study was to enhance the TC of epoxy composites by adding a high ratio of BN with the help of pressure to shape the samples before curing. In **Figure 5** the values obtained by THB method are represented and the numerical data and confidence level are collected in Table 2.

The TC is enhanced from 0.17 W/m·K for the neat epoxy to 3.06 W/m·K, the highest value obtained, with the incorporation of 80 wt. % of BN agglomerates. This represents an improvement of 1700%. However, the enhancement of conductivity is not linear with respect to the amount of filler added. Two kind of jumps can be seen in the middle of different wt. % of filler. The first one is observed between 30 and 40 wt. % and can be related to exceeding the percolation threshold determined by rheology. The improvement between 50 and 60 wt. %, with a little jump, is attributed to the use of pressure. The other jump can be noticed with the increase in the ratio of BN from 60 to 70 wt. %. To explain this behavior, some parameters must be taken into account. The proportion to overpass the percolation threshold can depend on the property measured [26] and this sudden increment ($2.03 \rightarrow 2.83$ W/m·K) is more pronounced than the first one ($0.89 \rightarrow 1.41$ W/m·K) at same filler proportion increment. Some authors state that this would be the percolation threshold of the thermal conductivity [3], usually at very high filler loadings.

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An important response observed is the excellent enhancement in TC of composites when pressure has been applied to mold the samples. The use of pressure produces two opposite effects. The first one, enhances the TC avoiding any gap within the sample, as it has been put in evidence by the micrographs in Figure 4. The second effect can be detrimental, since the pressure can deform the particles causing defects, forming points at which phonons can be scattered. Seeing the results, the first effect seems to be much more important than the other, in accordance with Hill *et al.*[17]. They conclude that the deformable fillers, as h-BN, produces higher enhancements in composites than other not deformable ceramic particles. Similar conclusions were obtained by the French National Centre for Scientific Research with the use of compressed expanded graphite (with analog chemical structure as h-BN), which its conductivity was function of its density, depending on the pressure applied [27].

Comparing these results with previous studies of our group, it can be seen the difference among the type of filler used at the same loading (40 wt. %), without forgetting the class of matrix. In a homopolymerized cycloaliphatic epoxy matrix, a 40 wt. % of 6 μ m h-BN platelets the conductivity measured was 1.03 W/m·K [23]. The same type of filler in an epoxy-thiol matrix obtained 0.97 W/m·K [22]. However, when agglomerates of 80 μ m are used in the thiol-epoxy matrix, the conductivity grow up till 1.75 W/m·K [22]. The previous cycloaliphatic epoxy matrix with BN platelets of 180 μ m achieved a value of 1.06 W/m·K [25] and 0.99 W/m·K when the platelets used sizes 30 μ m of average [26]. In this work, the addition of 40 wt. % of agglomerates of 120 μ m reports 1.41 W/m·K. Thus, we can state that the filler shape possesses more importance than the filler size in the microscale. All the platelets types reach values of about 1 W/m·K while agglomerates increase the conductivity between 1.43-1.75 W/m·K.

4. Conclusions

Boron nitride (BN) composites from epoxy-anhydride matrix and BN agglomerates were prepared. The addition of 30-50 % w/w of the filler did not affect the curing evolution. The rheological percolation was worked out to be 38.01 wt. % of BN and the critical exponent 2.00 at 1 rad/s.

Glass transition temperatures, determined by DSC, were practically unaffected on increasing the BN ratio in the material, but slightly enhanced the *tan* δ temperature, because of the mechanical effect of the particles on relaxation phenomena. Young modulus growth with the addition of a 30 wt. % of BN, but further addition did not lead to a steadily increase of this property, which can be associated with the loss of cohesion in the sample.

Thermal conductivity enhancements of 1700% in reference to the neat epoxy were reached. Whereas the neat epoxy thermoset had a TC value of 0.17 W/m·K, a TC of 3.06 W/m·K was obtained when 80 wt. % of BN agglomerates were added. However, with proportions higher than

50 wt. % of BN, the use of pressure was necessary to get compact samples. The shape of the BN particles, which were agglomerates and their sizes, $120 \mu m$, also favours reaching these high thermal conductivity values.

Taking into account the current results and those obtained in previous studies, we can conclude that agglomerates, due to their size and shape, work better to increase thermal conductivity than platelets. Furthermore, it has been determined that the application of pressure has more benefits than detriments to increase this property.

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Table 1. Calorimetric data extracted from DSC experiments

Sample	T_{peak}^{a} (°C)	$\Delta h^{\rm b}$ (J/g)	$\Delta h^{\rm c}$ (kJ/ee)	$T_g^{\rm d}(^{\circ}{\rm C})$
Neat epoxy	154	314	111	111
30% BN	155	232	115	112
40% BN	156	191	113	114
50% BN	156	174	117	113

^a Temperature of the maximum of the curing exotherm.

^b Enthalpy of the curing process by gram of mixture.

^c Enthalpy of the curing process by epoxy equivalent.

^d Glass transition temperature of samples cured in an oven determined by a dynamic scan.

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Table 2. Thermomechanical data extracted from TGA, DMTA and thermal conductivity measurements.

Sample	<i>T</i> _{5%} ^a (°C)	Char residue ^a (%)	Young's Modulus ^b (GPa)	$T_{tan \delta}^{c} (°C)$	Thermal conductivity (W/m·K)
Neat epoxy	364	5.7	2.67 ± 0.03	163	0.17 ± 0.001
30% BN	374	36.2	4.32 ± 0.15	165	0.89 ± 0.003
40% BN	377	45.1	3.28 ± 0.19	167	1.41 ± 0.028
50% BN	368	53.4	2.6 ± 0.11	170	1.58 ± 0.034
60% BN	374	62.6	-	-	2.03 ± 0.023
70% BN	384	72.3	-	-	2.83 ± 0.056
80% BN	392	81.3	-	-	3.06 ± 0.051

esidue MTA wit. d at 1 Hz in a. ^a Temperature of 5 wt. % loss and final residue in TGA tests at 10 °C/min under N₂ atmosphere.

^b Young's modulus tested at 30 °C in DMTA with a controlled force experiment.

^c Temperature of *tan* δ peak determined at 1 Hz in an oscillatory experiment by DMTA.



Figure 1. DSC dynamic exotherms of epoxy mixtures with BN agglomerates

146x110mm (120 x 120 DPI)





Figure 2. Plots of G' (filled symbols) and G" (open symbols) against angular frequency (ω) of each formulation at 30 °C.

147x98mm (120 x 120 DPI)



Figure 3. Thermal degradation curves obtained by TGA under N2 atmosphere at 10 °C/min. 149x106mm (120 x 120 DPI)



Figure 4. Microscopic images of fracture surfaces at 800 magnifications (Neat epoxy and 30% of BN) and 200 magnifications (50 and 70% of BN).

150x127mm (96 x 96 DPI)



