

A PRELIMINARY STUDY OF GLASS TRANSITION TEMPERATURE ON EPOXY/ALUMINA NANOCOMPOSITES

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ABSTRACT

The modification of polymer properties through the addition of nanoparticles has lead to the development of the so-called nanocomposites. The purpose of this study was to observe the glass transition temperature by Differential Scanning Calorimetry (DSC) in epoxy/alumina nanocomposites. Analysis was carried-out for different volume fractions, ranging from 2.5% to 10%. The results showed that the glass transition temperature (T_g) is generally higher in the samples with nanoparticles; however, the observed T_g showed no variation with nanoparticle concentration. For the final version of this study, analysis of Thermogravimetric Analysis (TGA) was performed to confirm the nanoparticle volume fraction and the DSC results.

Keywords: Epoxy/Alumina nanocomposites, DSC, TGA.

NOMENCLATURE

T_g Glass Transition Temperature, °C

INTRODUCTION

With the recent increase in nanoscience researches, it was observed a promoting interest in nano-sized reinforced polymers for high technological applications, as coatings, electronic devices, adhesives, automotive and aerospace industries (Jiang *et al.*, 2012; McGrath *et al.*, 2008; Omrani and Rostami, 2009).

Polymer nanocomposites are usually defined as a combination of a polymer matrix and nano-sized particles (Moreira *et al.*, 2011). The possibilities to improve mechanical or thermal properties, developing a new material, by nanoparticles, have found applications in both academia and industry. Were performed several experimental and theoretical studies about micro and nanocomposites mechanical properties but there have been few studies on the thermo-mechanical properties of these materials.

A property that has been widely used to predict the change in mechanical properties of these materials as a function of temperature is the glass transition temperature (T_g), a second-order pseudo transition which constitutes a high interesting parameter of amorphous and semi-crystalline materials (Gracia-Fernández *et al.*, 2010). The glass transition temperature basis is the onset of coordinated molecular motion is the polymer chain.

In the region of T_g , the polymer softens, the modulus drops three orders of magnitude and the polymer becomes rubbery (Sperling, 2006).

EXPERIMENTAL

Nanocomposites fabrication

The nanocomposite materials used in this study are composed of a polymeric matrix and metal oxides (Al_2O_3) nanoparticles used separately as fillers. The properties and sources of the composite material components are described as follows.

The employed polymer was RR515 (provided by SILAEX), an epoxy resin (ER) based on diglycidylether of bisphenol A. This resin was polymerized by the addition of an aliphatic amine hardener in a portion of 25 phr by weight.

The ER properties are presented in Table 1.

Table 1. Properties of epoxy resins.

Property	Epoxy
Viscosity at 25°C (cP)	12,000-13,000
Density (kg/m^3)	1160
Heat distortion temperature, HDT (°C)	50
Modulus of elasticity, E (GPa)	2.4-5.0
Flexural strength (MPa)	60
Tensile strength (MPa)	73
Maximum elongation (%)	4

The nano-particles, spherical alpha aluminum oxide nanoparticles with mean diameter of 35nm, provided by NanoAmor (www.nanoamor.com), containing 5-10% theta, were employed as filler. The nanoparticle properties are summarized in Table 2.

The samples were manufactured by adding different amounts of nanoparticles from 0% to 10% in volume of the total mixture to the liquid resin. The nanoparticles volume fractions were calculating based on true densities data provide by the manufactures and the rule of mixtures. The nanoparticles drying process was performed at 120°C for 24 hours before added to the liquid resin. Homogenization by a planetary ball milling was performed during 1h at 200rpm. After mixing, the hardener has added and the resulting blends were manually homogenized and poured into the mold.

Table 2. Properties of nanoparticles.

Property	Al ₂ O ₃
Particle size (nm)	30-40
Modulus of elasticity, E (GPa)	300
True Density (kg/m ³)	3700
Morphology	Spherical
Specific surface area, SSA (m ² /kg)	35,000

The mold was composed of a metal frame with tree channels between two glass plates. The specimens were cured at room temperature for 24 hours. The demolding of the samples occurred after the first 24 hours, and the samples remaining in a post cure process at room temperature for at least 7 days. After this time, the samples were grounded for DSC and TGA analyses.

Experimental setup

The glass transition temperature of the DGEBA/nano-Al₂O₃ composites was measured by DSC (NETZSCH, DSC 200 MAIA) at temperature ranging from 30 to 150°C at a heating rate of 10°C/min under a nitrogen atmosphere. Two analyses

were performed for each sample (pure epoxy resin, nano-Al₂O₃/DGEBA 2.5% v/v; nano-Al₂O₃/DGEBA 5% v/v, nano-Al₂O₃/DGEBA 7.5% v/v, nano-Al₂O₃/DGEBA 10% v/v).

After the DSC analyses, TGA studies were performed to corroborate the volume fraction and quality of the samples. The TGA were conducted from room temperature until 600°C at a heating rate of 10°C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

DSC results

As observed by Tanaka et al. (2005), organic-inorganic bonding force seems to be relatively week in epoxy/alumina nanocomposites. Some authors, as Zhang and Singh (2004), are studying the addition of silane as a treatment to improve the particle (inorganic)/matrix (organic) adhesion. The second heating DSC curve for nano-Al₂O₃/ER 10% v/v are given in Fig. 1, revealing an well-marked change of base line. Glass transition data show in Table 3 are apparently according to what have been obtained recently for nanocomposites without silane treatment.

Table 3. DSC Results.

Sample	T _g (°C)
Pure ER	70.3
nano- Al ₂ O ₃ /ER - 2.5%	78.1
nano- Al ₂ O ₃ /ER – 5.0%	70.9
nano- Al ₂ O ₃ /ER – 7.5%	75.9
nano- Al ₂ O ₃ /ER - 10%	76.8

The TGA confirm that hypothesis and show a lower volume fraction of alumina as can be seen in Fig. 2.

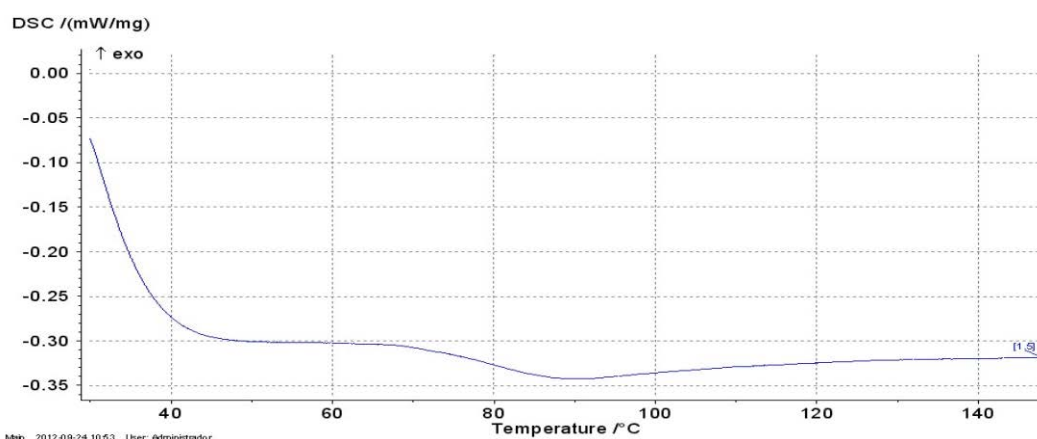
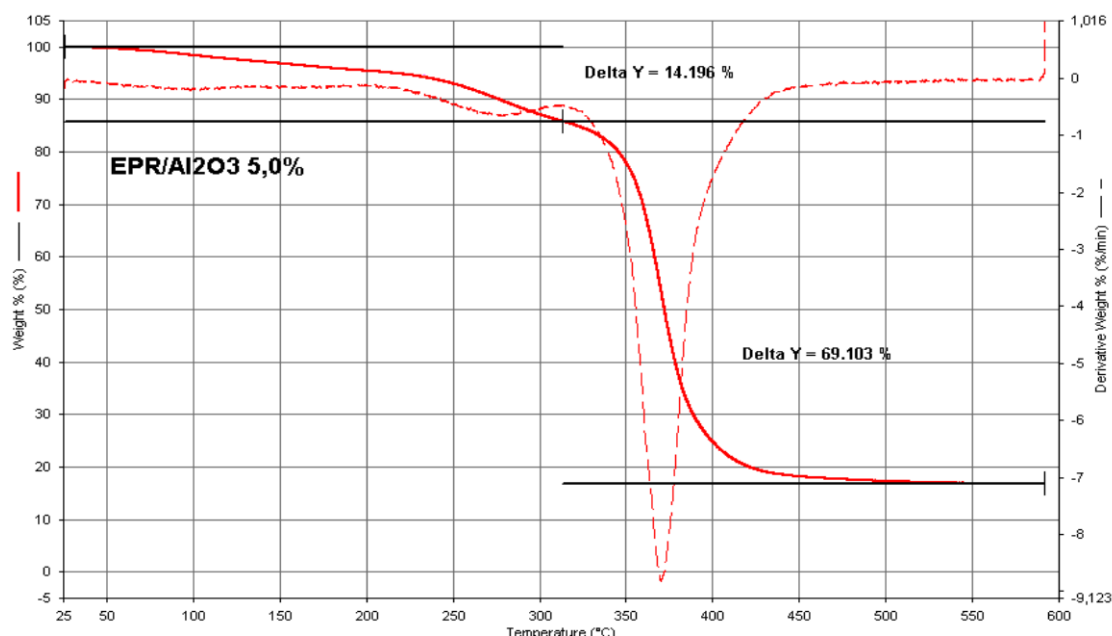


Figure 1. Nano-Al₂O₃/ER 10% v/v DSC curve.

Figure 2. Nano-Al₂O₃/ER 5.0% v/v TGA curve.

The first loss of weight corresponds to ER's melting e liberation of the air inside the observed bubbles, which is considered like one part of the composite material. Only the second degradation step is related to the matrix decomposing and the residual mass corresponds to the nano-alumina.

Table 4 shows the mass fractions for each sample analyzed.

Table 4. Comparison between the samples.

Nano-Al ₂ O ₃ /ER		
Volume Fraction	Mass Fraction (Calculated)	Mass Fraction (TGA)
2.5%	7.97%	14.87%
5.0%	15.95%	17.36%
7.5%	23.92%	25.17%
10.0%	31.89%	31.71%

By a simple statistical analysis of the results for samples Nano- Al₂O₃/ER 2.5, 7.5, and 10% v/v, it is possible to notice that the sample of Nano- Al₂O₃/ER 5.0% v/v actually presents a reduction of approximately 10% between the expected and measured mass fraction by TGA. Justifying, thereby, the contradictory results in the DSC analysis for this sample. The Fig. 3 provides detail about the behavior of the mass fractions used in the preparation of samples and measured by TGA in relation to volume fraction. Whereas for the mass fraction used in the preparation of the samples shows linear variation with the volume fraction, TGA results appear to have a third-order polynomial relation with the volume fraction.

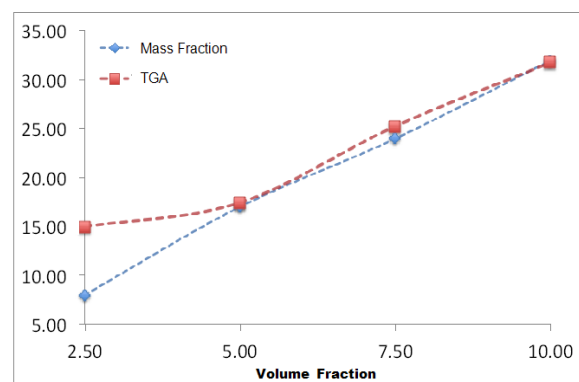


Figure 3. Volume fractions and Mass Fractions relationship.

CONCLUSIONS

The purpose of this study was to observe the glass transition temperature by Differential Scanning Calorimetry (DSC) in epoxy/alumina nanocomposites. Analysis of DSC and TGA was carried-out for different Nano- Al₂O₃/epoxy volume fractions. Was observed that the glass transition is unchanged between different volume fractions. These results are in accordance to the literature and posterior studies varying the diameter of the nano-alumina particles will be done to confirm this behavior for others particles sizes.

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