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 (Tg) is generally higher in the samples with nanoparticles; however, the observed Tg showed no variation with nanoparticle concentration. For the final version of this study, analysis of Termogravimetric Analisys (TGA) was performed to confirm the nanoparticle volume fraction and the DSC results.*

Keywords: *Epoxy/Alumina nanocomposites, DSC, TGA.*

1. 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 (Tg), 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 glass transition temperature (Tg), the polymer softens, the modulus drops three orders of magnitude and the polymer becomes rubbery (Sperling, 2006).

2. Experimental

2.1 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^{o}C (cP)[1]	12,000-13,000
Density (kg/m^3)	1160
Heat distortion temperature, HDT (^{o}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. Tha nanoparticle properties are summarized in Table 2.

Table 2. Properties of nanoparticles.

Property	Al_2O_3
Modulus of elasticity, E (GPa)	300
True Density (kg/m^3)	3700
Morphology	Spherical
Particle size (nm)	30-40
Specific surface area, SSA (m^3/kg)	35,000
Purity	$\geq$99.9%

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 calculate 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.

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.

2.2 Experimental setup

The glass transition temperature of the DGEBA/nano-Al_2O_3 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-Al_2O_3/DGEBA 2.5% v/v; nano-Al_2O_3/DGEBA 5% v/v, nano-Al_2O_3/DGEBA 7.5% v/v, nano-Al_2O_3/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 hate of 10°C/min under a nitrogen atmosphere.

3. RESULTS AND DISCUSSION

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-Al_2O_3/ER 10% v/v are given in figure 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.

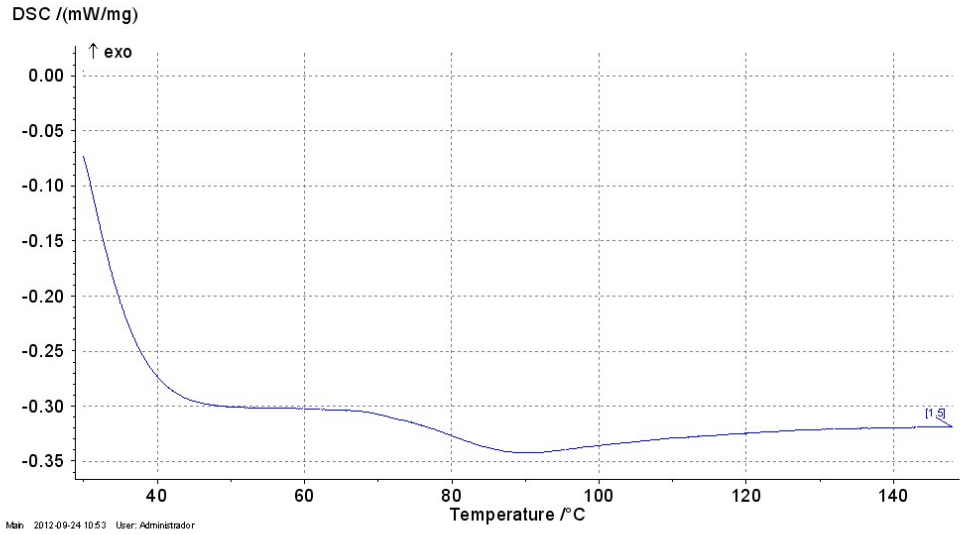

Figure 1. Nano-Al_2O_3/ER 10% v/v DSC curve.

Table 3. DSC results.

Sample	$Tg(^oC)$
Pure ER	72.15
nano-Al_2O_3/ER - 2.5%	86.65
nano-Al_2O_3/ER - 5.0%	71.80
nano-Al_2O_3/ER - 7.5%	77.80
nano-Al_2O_3/ER - 10.0%	80.00

Only the sample nano-Al2O3/ER 5% v/v not presented a result consistent with the literature and the responses of the other samples. During demolding and milling for the manufacture of DSC samples was observed the presence of bubbles inside the nanocomposite. Such bubbles can be regarded as points of concentration of alumina and adversely interfere in the analysis by DSC, were tried to avoid as much that they be added to the DSC samples.

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

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_2O_3/ER Volume Fraction	Nano-Al_2O_3/ER Mass Fraction	Nano-Al_2O_3/ER 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 analisis of the results for samples Nano-Al_2O_3/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. In the figure 3 provides detail about the behavior of the mass fractions used in the preparation of samples and measured by

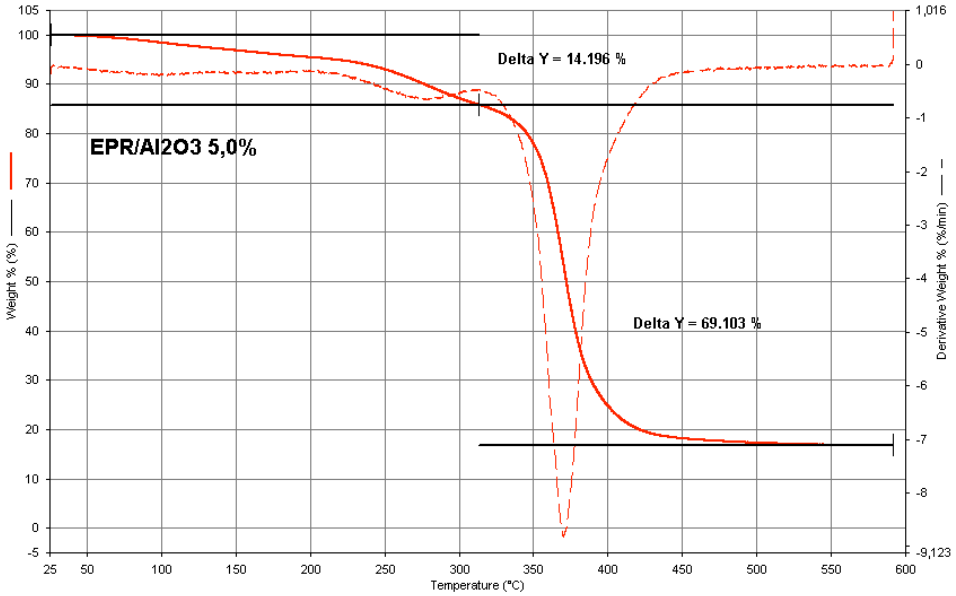

Figure 2. Nano-Al_2O_3/ER 5.0% v/v TGA curve.

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.

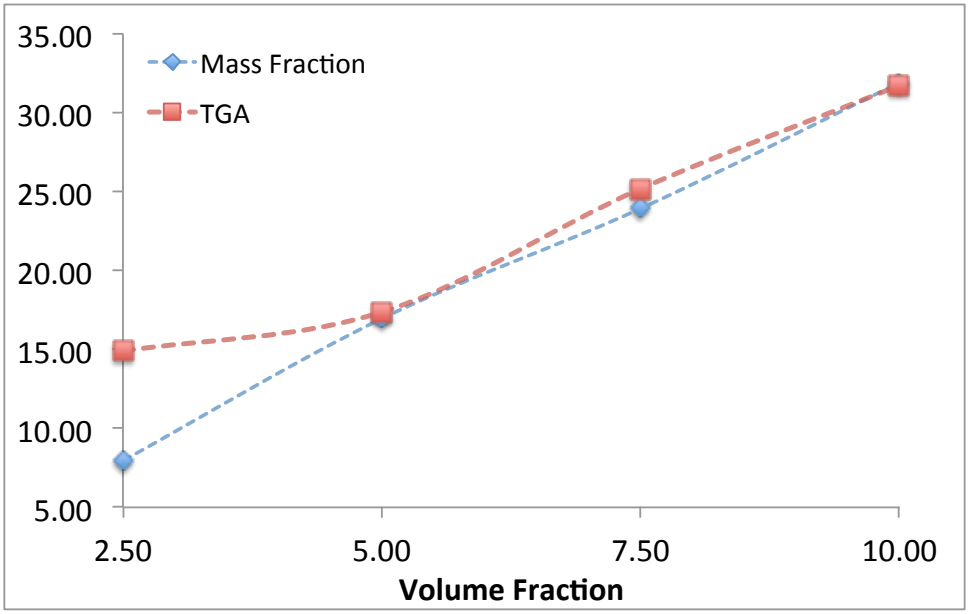

Figure 3. Volume fractions and Mass Fractions relationship.

4. 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-Al_2O_3/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.

5. ACKNOWLEDGEMENTS

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