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THERMOMECHANICAL BEHAVIOR OF EPOXY MATRIX REINFORCED BY TITANIUN OXIDE NANOPARTICLES

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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 investigate the effect of TiO2 nanoparticles on the thermomechanical properties epoxy (ER) based nanocomposites. Analysis was carried-out for different volume fractions of nanoparticles, ranging from 2.5% to 10%. The results showed that the TiO2/ER nanocomposites presented a decrease in all thermomechanical properties studied. In addition, the obtained Glass Transitions Tempereture (Tg) showed no significant change with nanoparticle concentration. The cross-link density studied by DMA for each nanocomposite shows that the fillers are responsible for the decrease in cross-link density. A significant decrease in thermal stability of epoxy resin containing nanoparticles was observed.*

Keywords: *nanoparticles, nanocomposites, Tg, DSC, DMA.*

1. INTRODUCTION

Nanocomposite materials can be described as materials consisting of embedded nanoparticles or nanopores in a solid matrix, polymers for example. They are considered for various applications as their properties can be tuned by varying the particle material, shape, size, and concentration. Also, it was observed a promoting interest in nano-sized reinforced polymers for high technological applications, as coatings, electronic devices and adhesives, automotive and aerospace industries (Jiang, *et al*., 2012; McGrath, *et al.* 2008; Omrani and Rostami, 2009).

The advantage of nanofillers is that they are miscible with the polymer matrix exploiting unique synergisms between the combined materials. Polymer nanocomposites are usually defined as a combination of a polymer matrix and nano-sized particles (Moreira, *et al.*, 2012). The possibilities to improve mechanical or thermal properties, developing a new material, by nanoparticles, have found applications in both academia and industry. The thermal stability of polymer nanocomposites is considered an important factor and its study provides the required information about the period of the applicability for such nanocomposites (ShA Mansour, 2013).

The quantitative study of solid state transformation in various kinds of materials by means of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) has been widely discussed (ShiqiangDenga, *et al.*, 2007; Peterson, *et al.*, 2001; Lu, *et al*, 2005; Kotkata and ShA Mansour, 2011a; Kotkata and ShA Mansour, 2011b). While, DSC elucidates the kinetics of physical and/or chemical changes of the polymers such as crystallization and degradation (Kotkata and ShA Mansour, 2011b), DMA provide a sensitive testing system for rapid determination of thermo-mechanical properties as a function of frequency, temperature or time (ShiqiangDenga, *et al.*, 2007). One of the main ideas of modifying polymers with oxide nanoparticles is to enhance the material's thermal and mechanical properties. DMA was frequently used in nanocomposites characterization since it allows the measurement of two different modulus of the nanocomposites, a storage modulus (E') and a loss modulus (E''). The first is related to the ability of the material to return or store mechanical energy and the second is related to the ability of the material to dissipate energy a function of temperature.

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 pseudo-second order pseudo transition which constitutes a high interesting parameter of amorphous and semi-crystalline materials (García-Fernandez, *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). In essence, if the addition of a particle to an amorphous polymer leads to a change in the Tg, the resultant effect on the composite properties would be considered a ''nano-effect''. Also, the temperature-dependent elastic modulus of a composite material isan important material parameter in structural analysis and design, especially

for stiffness-based design. Elastic modulus represents the material stiffness and in polymer based composites, the temperature will significantly influence materials rigidity.

Epoxies are thermosetting polymers that exhibit a high glass transition temperature compared with other polymers that can be used as a nanocomposite matrix (Tanaka, *et al.*, 2005). In addition, nanoparticles presented better interfacial interactions with the matrix compared with conventional microparticles (Zhang and Singh, 2004). There are many studies that investigate the influence of nano-sized fillers to solid polymeric materials (Moreira, *et al.*, 2012; Etienne, *et al.*, 2007; Arunkumar, *et al.*, 2010; Banerjee, *et al.*, 2011; Zabihi, *et al.*, 2012a; Małecka and Rajska, 2010; Guo, *et al.*, 2009; Guo, *et al.*, 2007; Surdiman, *et al.*, 2012).

Because of their high mechanical properties, thermosetting polymers are well applied as the matrix of nanocomposites. The two most used thermosetting polymers in nanocomposites researches are epoxy and polyester resins.

Epoxy networks are largely applied in industry as adhesives, as electronic coatings and as matrices on structural composites reinforced with fibres. These polymers have high modulus and thermal stability. On the other hand, their high value of crosslink density causes the material to become very brittle (Banerjee, *et al.*, 2011).

Since the high level of crosslink of these polymers results in poor crack initiation and propagation resistance, an improvement in damage tolerance and durability of these materials are required (Peterson, *et al.*, 2001) . So, the addition of nanoparticles, as Al2O3 and TiO2, have been applied and studied for a better enhancement in wear resistance (Jawahar, *et al.*, 2006). However, the improvement in thermal and mechanical properties of thermosetting matrices by the addition of inorganic fillers is only effective when the composite materials presented strong interfacial adhesion between the polymer matrix and the reinforcement material. This adhesion is affected by two important factors that will be discussed in this work: the interfacial area between the matrix and the filler and relative incompatibility that exists in organic (matrix) / inorganic (nanoparticle) systems (Guo, *et al.*, 2007).

It is well known that nano-structured materials presented much large surface interaction area than conventional materials. This higher surface area permits an increase in van der Waals forces and physical interactions, which promotes an improvement in adhesion forces when the nanoparticles are well dispersed in the polymer matrices (Małecka and Rajska, 2010; Luo and Daniel, 2003; Hanemman, 2006).

In order to improve the particle-matrix adhesion and consequently the thermomechanical properties and stability of inorganic/organic composites, many investigators have studied the adhesion phenomena in these materials, such as the possibilities to use the surface modification of nanofillers by chemical treatments to improve the homogeneous dispersion of the nanoparticles in the polymer matrix and chemical interactions between the polymer and the nano-reinforcement (Moreira, *et al.*, 2012; Zabihi, *et al.*, 2012).

Titanium dioxide nanocomposites are highly used for their high mechanical, electrical, thermal and insulating properties. On the other hand, nanocomposites based on thermosetting polymers reinforced with TiO2 are not well studied. The thermomechanical behavior and the mechanical properties of this kind of nanocomposites have been studied more extensively in the past decade with a focus in characterization of this material (Chatterjee and Islam, 2008; Ng, *et al.*, 1999; Al-Turaif, 2010; Shi, *et al.*, 2008; Yinghong, *et al.*, 2002; Evor and Shukla, 2003).

Chatterjee and Islam (2008) studied the mechanical performance and the thermomechanical behavior of TiO2/epoxy nanocomposites. The addition of 1% by weight of these nanofiller presented the best results for tensile modulus, flexural modulus, glass transition temperature and thermal stability.

The effect of nano-TiO2 particle size in mechanical properties of epoxy based nanocomposites was studied by Al-Turaif (2010). Also, the best results were measured for an addition of 1% of nanoparticles. The better resistance to weight loss was measured for the lower nanoparticles sizes suggesting that the amount of reinforcement added affected the the matrix deformation. The particle size also presented this same effect, with consequences to the quality of the matrix/nanoparticles adhesion.

For polyester based nanocomposites, Yinghong et al. (2002) observed an excellent interface adhesion for the UPR/TiO2 nanocomposite, resulting in good improvement in mechanical properties for an addition of 4 wt% of the titanium dioxide.

The goal of this study is to experimentally determine how the effective thermal-physical properties are influenced by the addition of TiO2 nanoparticles to an epoxy resin matrix.

2. EXPERIMENTAL

2.1 Nanocomposites Fabrication

Epoxy and metal oxide TiO_2 nanoparticles used as filler compose the nanocomposite materials used in this study. The properties and sources of the composite material components are described as follows.

The employed polymers were RR515 (provided by SILAEX®). The epoxy resin (ER) is 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 characteristics physical properties of the used neat epoxy and unsaturated epoxy matrices are presented in Table 1.

Table 1. Properties of thermosetting polymer

Property	Epoxy
Viscosity at 25°C, μ /cP	12000-13000
Density, ρ /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 nanoparticles employed as filler were titanium dioxide nanoparticles, provided by NanoAmor®. The nanoparticle properties are summarized in Table 2.

Table 2. TiO_2 nanoparticles properties

Property	TiO_2
Modulus of elasticity, E (GPa)	259
True Density, ρ (kg/m³)	3,900
Morphology	Spherical
Particle size (nm)	10 x 40
Specific surface area, SSA (103 m²/kg)	240
Purity	99%

The samples were manufactured by adding different quantities of nanoparticles from 0% to 10% in volume of the total mixture to the liquid resin. The nanoparticles volume fractions were calculated based on true densities data provide by the manufactures and the rule of mixtures. The nanoparticles were previously dried at 120ºC for 24 h before added to the liquid resin. Homogenization by a planetary ball milling was performed during 1h at 200rpm. After mixing, the hardener was added and the resulting blends were manually homogenized and poured into the mold. The mold was composed of a metal frame. The specimens were cured at room temperature for 24 h. The demolding of the samples occurred after the first 24 hours, and the samples remaining in a post cure process at room temperature for 7 days.

2.2 Experimental Setup

The glass transition temperature, as defined by the endothermic change in the DSC trace, indicates a large change of viscosity, marking an alteration from glassy solid phase to super-cooled liquid state. In DSC measurements, Tg is recognized from the baseline change in the DSC signal.

The glass transition temperature of the manufactured nanocomposites was measured by DSC (DSC F3 MAIA, NETZSCH, Germany) at temperatures ranging from 30 to 150ºC, at a heating rate of 10ºC/min under a nitrogen atmosphere according to ASTM D3418 (ASTM D 3418, 2008). The temperature range was chosen after a previous scan up to 500°C to observe the thermal stability and decomposition for each nanocomposite. Three sample crucibles were prepared and tested for each composite. Each pan was filled out with, approximately, 12mg of the material, sliced in homogeneous small pieces.

The glass transition temperature as defined by the endothermic change in the DSC trace indicates a large change of viscosity, marking an alteration from glassy solid phase to super-cooled liquid state. In DSC measurements, Tg is recognized from the baseline change in the DSC signal.

A dynamic mechanical analyzer (DMA 242D, NETZSCH, Germany) was used for measuring the temperature dependent elastic modulus of the all studied formulations of the nanocomposites. Three samples with mean dimensions of 50 x 10 x 4 mm were tested in three-point bending mode and the support span was 40 mm, according to ASTM D7028 (ASTM D 7028, 2007). Temperatures scanning from low to high was performed with a heating rate of 10ºC min-1, within temperature range 30-500 °C at an oscillation frequency of 1 Hz.

The termogravimetric analysis (TG) were carried out using TG/DTG equipment (TGA – 50, SHIMADZU, Japan) under N_2 atmosphereand gas flow of 50 ml/min. All experiments were conducted from room temperature to 500°C with a heating rate 5 ºC/min.

3. RESULTS AND DISCUSSION

Scanning calorimetry and dynamical mechanical tests over a wide range of temperature were performed to observe

the physical and mechanical structural changes of the epoxy resin and the nanocomposites.

The glass transition temperature measured by DSC showed that with the increase of nanoparticles loading, the *Tg* of the nanocomposites also increases quite linearly until the highest *Tg* observed for 5% of TiO_2 in volume. After this point, it starts to decrease, with values still higher than the measured for neat epoxy. This observation is a result of the restriction effect in segmental motion caused by the nanoparticles/matrix interactions. Table 3 provides the glass transition measured by DSC.

Table 3. TiO_2/ER Nanocomposites DSC results

TiO_2 Volume Fraction (%)	0	2.5	5.0	7.5	10.0
Average *Tg* (^oC)	70	72	75	71	71
Standard Deviation	1.5	0.4	4.3	0.7	0.9

The effect of nanofillers in epoxy resin on dynamic mechanical properties and the glass transition temperature of the nanocomposite and neat matrix were observed by a DMA analyzer.

As observed for Zabihi *et al*. (2013), a strong compositional effect on *Tg* measured by DMA was observed as a result of the nanoparticle addition in epoxy polymer, resulting in higher *Tg* values than that obtained in DSC analyzes. The same adverse behavior was observed for polyester matrix.

The effect of the nanoparticles on the viscoelastic properties of cross-linked nanocomposites has been investigated by DMA estimating the effect of each nanoparticle in each matrix calculating the cross-link density using the equation below (Zabihi, *et al*, 2012b).

$$\upsilon_e = \frac{E_r}{3RT_r} \tag{1}$$

Were υ_e is the cross-link density, $E_r$is equal to the rubber modulus at T_r (rubbery temperature), R is the universal gas constant and $T_r = Tg + 30$.

Figure 6 shows the temperature dependence of storage modulus and this effect seems to be distinct in magnitude for each sample analyzed. The storage modulus in rubbery region presented significant variation with nanoparticle addition, implying variations in cross-link density. Table 7 also shows the υ_e for each nanocomposite produced.

Chatterjee and Islam [26] reported the volume fraction of 1% as the best result for this nanocomposite. In this way, the effect of the volume fraction of nanoparticles addition seems to be a consequence of nanoparticle agglomeration. The physicochemical interactions in nano-filler/polymer system decrease since the interfacial interactions between epoxy and titanium oxide decrease with the van der Waals forces that attract the nanoparticles. Table 4 shows the storage modulus and also the rubbery modulus and crosslink density of the nanocomposites.

Table 4. TiO_2 Nanocomposites DMA results.

Sample	TiO_2/ER			
	E' (MPa)	*Er* (MPa)	T_r (^oC)	υ_e (mol/m^3)
Pure matrix	2724.3	57.6	114	6784
nano- TiO_2 - 2.5%	1919.7	35.0	108	3639
nano- TiO_2 – 5.0%	1754.7	33.8	103	3608
nano- TiO_2 – 7.5%	1989.0	50.7	105	5376
nano- TiO_2 - 10%	2197.3	64.5	102	6882

Also, the decrease in thermal stability of the material is expected because of the low quality of adhesion forces that is responsible for retard the polymer chain degradation. The high residue value is a consequence of the nanoparticle addition, since TiO_2 did not present degradation temperature under the temperature range studied. Table 5 shows the temperature of thermal stability and the residual mass at the end of the TG.

Table 5. TiO_2 Nanocomposites TGA results.

Sample	TiO_2/ER	
	T_{sb} (°C)	Residue (%)
Pure Matrix	262	4.2
nano- TiO_2 - 2.5%	248	28.1
nano- TiO_2 – 5.0%	240	28.8
nano- TiO_2 – 7.5%	248	33.4
nano- TiO_2 - 10%	248	38.6

The ANOVA applied for the glass transition temperature showed that the addition of titanium dioxide nanoparticles did not produced any effect in this property, increasing or decreasing it (Fig. 1).

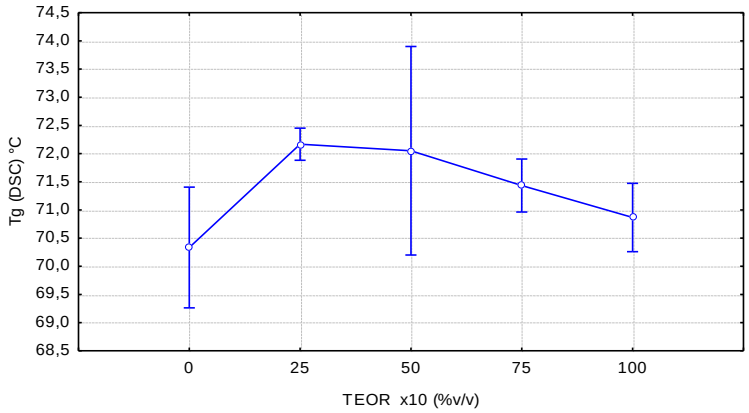

Figure 1. Statistical analysis of DSC results

The second dependent variable analyzed by ANOVA was the storage modulus of the nanocomposites manufactured. This depend variable presented normality distribution and homogeneity of variances by Shapiro-Wilks, Lilliefors, Cochran-Bartlet and Levene's tests. LSD analysis and the figure 2 did not show influence of the volume fraction, only the adverse effect of the nanoparticle in the storage modulus of the neat epoxy resin.

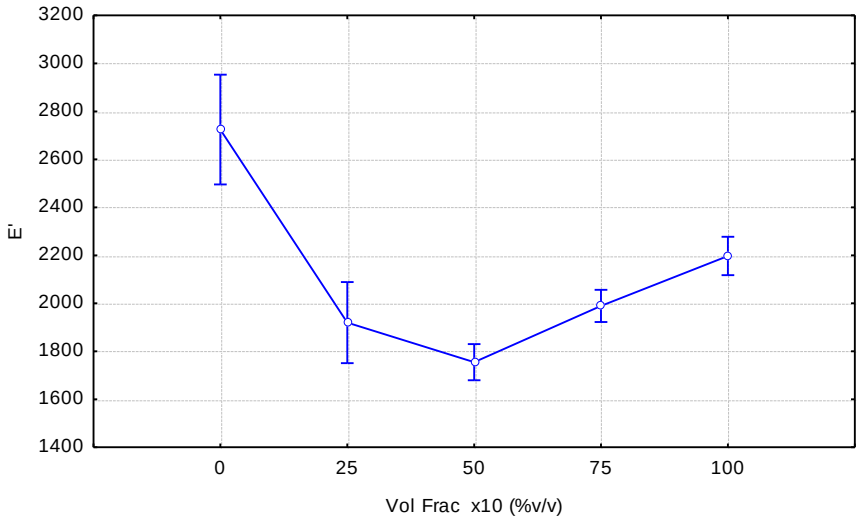

Figure 2. Statistical analysis of *E'* measured by DMA.

Finally, for T_{sb}, statistical analysis showed, in figure 5.13, no significant influence of the reinforcement, as observed for the glass transition temperature.

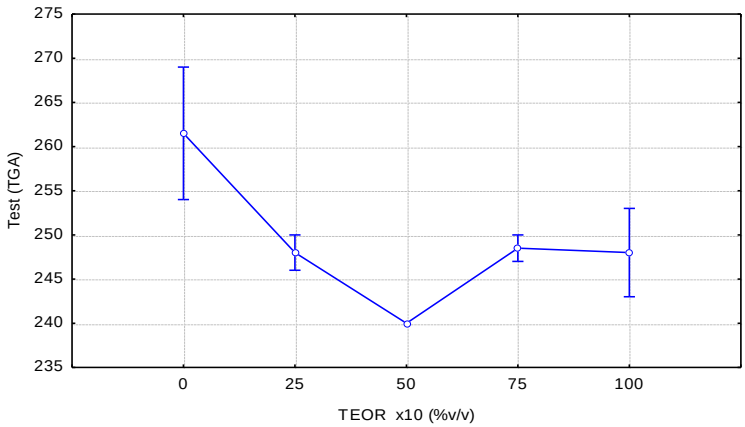

Figure 3. Statistical analysis of TGA results

4. CONCLUSIONS

Polymer nanocomposites are usually defined as a combination of a polymer matrix and nano-sized particles. The possibilities to improve mechanical or thermal properties, developing a new material, by nanoparticles, have found applications in both academia and industry. Several experimental and theoretical studies about micro and nanocomposites mechanical properties were performed but there have been few studies on the thermo-mechanical properties of these materials. The study of the nanoparticles influence in thermomechanical properties of nanocomposites was the aim of this work.

In order to observe this influence, DSC, DMA, TGA, SEM and statistical analysis were performed permiting an evaluation about the influence of the nature of the matrix and the nanoparticles, the influence of the nanoparticle size and also showed how the thermomechanical properties can vary with the volume fraction of nanoparticles.

The most important conclusion that can be obtained by this work is related to the bonding forces between the nanoparticle and the matrix. These interactions are related to a great number of factors and are also responsible for the degree of the polymer chain motion which is directly responsible for an increase or decrease in thermomechanical properties of polymeric nanocomposites.

TiO2/ER nanocomposites presented a decrease in all thermomechanical properties studied, as an effect of the poor inorganic/organic adhesion forces, probably because of the high volume fraction studied. In the way to complete this work, a new group of nanocomposites, with volume fractions of 1%, 2%, 3%, 4% and 5% will be study briefly.

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