# CHARACTERIZATION OF POLYMER MATRIX NANOCOMPOSITES PROCESSED IN A HIGH ENERGY MILL

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***Abstract.*** *Nanocomposites are a particular class of composite materials where the dispersed phase has dimensions in the range of 1-100 nm. It has been proven that small amounts of nanosize particles may significantly improve the mechanical and thermal properties of the pure polymer matrix. However, the improvement of properties is believed to be related to the complete dispersion of the nanoparticles in the polymer matrix and, due to their enormous specific surface area, nanoparticles tend to agglomerate. In this work, a simple processing technique using a high energy mill was demonstrated as an effective means to disperse ceramic nanoparticles in a polymer matrix. The process was carried out using various contents of nanoparticles. SEM micrographs of the nanocomposites indicated good particle dispersion. Further, the viscoelastic properties of the nanocomposites produced were measured using a Dynamic Mechanical Analyzer and related to the content of nanoparticles . In summary, the technique was found very efficient in achieving high levels of dispersion within a short period of time.*

***Keywords****: nanocomposites, processing, high energy mill.*

## 1. INTRODUCTION

Nanocomposites are a distinct class of composite materials where the dispersed phase has at least one dimension in the range of 1–100 nm (Kalaitzidou et al., 2007). Many studies have indicated that the mechanical, thermal, and other properties of a polymer matrix, such as dimensional stability, may be significantly improved by the incorporation of nanoparticles (Zerda and Lesser, 2001; Yasmin et al., 2003; Luo and Daniel, 2003; Wei et al., 2002; Liu and Wu, 2001; Gu and Chang, 2001; Yoon et al., 2002; Magaraphan et al, 2001; Agag et al., 2001; Becker et al., 2002; Chen et al., 2002; Yasmin et al., 2006; Viculis et al., 2003; Zheng et al., 2003). This improvement in properties has been attributed to the very large specific surface area of the nanoparticles (Yasmin et al., 2006; Luo and Daniel, 2003; Viculis et al., 2003; Zheng et a., 2003), which greatly affects their interactions with the polymer chains. Thus, the state of dispersion plays a critical role on the improvement in properties (Yasmin et al., 2006; Zheng et al., 2003; Yong and Hahn, 2004; Castrillo et al., 2007). Previous investigations have confirmed that, for a given volume fraction, the degree of dispersion and interfacial bonding may be significant to the final properties (Zheng et al., 2003; Yong and Hahn, 2004; Yong and Hahn, 2005; Singh et al., 2002; Sun et al., 2005).

The strong tendency of nanoparticles to agglomerate makes the processing of nanocomposites a rather complex task (Yasmin et al., 2003a; Wei et al., 2002; Zheng et al., 2003; Zhang et al., 2006). Dispersion of nanoparticles is particularly difficult due to their great specific surface area and has been directly related to the preparation of the nanoparticles (Yong and Hahn, 2004). Thus, processing techniques able to produce complete particle dispersion in polymer matrix nanocomposites are of great interest (Zerda and Lesser, 2001; Yasmin et al., 2003; Luo and Daniel, 2003; Liu and Wu, 2001; Gu and Chang, 2001; Yasmin et al., 2006a; Castrillo et al., 2007). Various approaches to process nanocomposites have been proposed and evaluated (Zheng et al., 2003; Yong and Hahn, 2004; Castrillo et al., 2007; Yong and Hahn, 2005; Singh et al., 2002; Yasmin et al., 2006a; Chan et al., 2002).

Inorganic particles have been employed to improve the mechanical performances of polymers for engineering applications (Zhang et al., 2006). Previous investigations have shown that $SiO_2$ nanoparticles may produce a positive effect on the properties of nanocomposites (Zheng et al., 2003; Peng et al., 2005; Ou et al., 1998; Sun et al., 2005). In these studies, $SiO_2$ nanoparticles were added to polymer matrices to enhance strength, modulus, toughness, thermal stability. Therefore, incorporation of $SiO_2$ nanoparticles may be a promising approach to enhance the thermal and mechanical properties of polymers.

Dynamic Mechanical Analysis (DMA) is a widely accepted research technique in the polymer industry to perform viscoelastic material characterization through sinusoidal excitation, over a wide range of frequency and temperature, and providing important information about the cure of thermoset resins and the aging of thermoplastics (Menard, 1999). The method provides fast and reliable results using a very small amount of material, which can, in many cases, be taken directly from the part. In addition, DMA test equipment allows accurate temperature and atmosphere control. Therefore, it is an appropriate method to study the viscoelastic properties of polymer-based nanocomposites.

High energy ball milling is an important alternative for the processing of powder materials. It is an efficient method to perform particle size reduction of hard, brittle materials, to adjust particle size distribution, to promote chemical reaction in solid state, to produce phase amorphization and to the synthesis of nanoparticles. Mills have been used for blending powders, making emulsions, and performing mechanical alloying. Under the technological point of view, this technique offers the advantages of versatility, scalability and cost-effectiveness (Gacitua et al., 2005). In general, a vial, which contains the sample material and one or more balls, is shaken in a complex and vigorous motion that may combine back-and-forth and lateral movements. Recently, thermoplastic-based nanocomposites have been prepared using high energy ball milling process (Castrillo et al., 2007). A very homogeneous dispersion of the nanoparticles within the polymer matrix was reported.

Recent work (Melo et al., 2007) has demonstrated the feasibility of processing thermoset polymer matrix nanocomposites using a high energy mill. $SiO_2$/Epoxy nanocomposites with nanoparticles contents of 1-3 wt.% were processed and a good dispersion of the $SiO_2$ nanoparticles in the epoxy matrix was obtained within 20 min in the high energy mill. However, the use of surfactants, which are known to reduce properties such as glass transition temperature, was necessary to improve degassing and particle dispersion.

Based on this previous work, in the present investigation, the processing technique using a high energy mill was carried out to process $SiO_2$/epoxy nanocomposites, with various contents of nanoparticles and without the use of surfactants. The fracture surface of the nanocomposites was investigated by scanning electron microscopy (SEM). In addition, the dynamic mechanical properties of the nanocomposites produced were measured and the effect of nanoparticles content on the measured properties was evaluated.


## 2. EXPERIMENTAL

### 2.1. Materials and Processing

The matrix material used in the present study was the epoxy resin system Araldite LY 1564 / Aradur 2954 (Huntsman Advanced Materials) combined in proportions of 100:35 wt. (resin/hardener).

$SiO_2$ nanoparticles (Aerosil 200) were acquired from Degussa (São Paulo, Brazil). The nanoparticles were added to the epoxy resin in contents of 2, 4 and 8 wt. %. The particles were analyzed by nitrogen adsorption technique (BET) and a specific surface area of 260 $m^2$/g was obtained.

A high energy mill (Fig. 1) was used to disperse the $SiO_2$ nanoparticles in the polymer matrix. The $SiO_2$ nanoparticles were first added to the epoxy resin, poured into a polyamide vial and hand-mixed for about five minutes. One alumina ball was placed in the vial to improve particle dispersion, thus reducing agglomerates. The use of more than one ball was avoided, as internal collisions could contaminate the nanocomposite.

After 20 minutes in the mill, the process was interrupted and the hardener was added to the mixture, which was again placed in the mill for 20 more minutes. After that, the material was collected and poured in an aluminum mold, previously prepared with a PVA (Polyvinyl Alcohol) based mold release (Fig. 2). Then, the mold was placed in a desiccator, under vacuum, for about 5 minutes, for degassing. After degassing, air bubbles were not observed and the mixture was oven cured. The two-step cure was carried out at temperatures of 80°C for 1 h, and 140 °C, for 8 hs.

Upon cool-down, 105 x 70 mm nanocomposite plates were removed from the mold. Beam specimens were cut from the processed material using a diamond abrasive saw. After the cutting procedure, the specimens edges were sanded flat for better dimensional precision. The specimens final dimensions were nominally, 60 x 15 x 3 mm (L x W x H), as suggested by ASTM D 5023 – 01. Five test specimens were fabricated from each plate for the dynamic mechanical analysis (Fig. 3).

Figure 1. High energy ball mill.



Figure 2. Aluminum mold.



Figure 3. Flexure Beam.

## 2.2. Dynamic Mechanical Analysis

Sub scale dynamic measurements were carried out using a TA Dynamic Mechanical Analyzer – DMA Q800 (Fig. 4), in a 3-point bending testing mode, with a 50.0 mm span between the supports. Temperature scan measurements were performed over the temperature range of 30 ℃ to 200 ℃, with a heating rate of 2.0 ℃/min, and under a constant frequency of 1.0 Hz. All tests were carried out under a sinusoidal strain controlled mode. A very small strain amplitude (0.1%) was used throughout the measurements to ensure that linear viscoelastic material properties was a valid assumption. The beam specimens were pre-stressed with an applied force 10 % larger than the force necessary to produce the desired strain amplitude. This procedure guarantees that the center probe is always in contact with the beam. The force necessary to pre-stress the beam is automatically calculated throughout the experimental procedure.

Figure 4. DMA Q800 Dynamic Mechanical Analyzer.

## 2.3. Microscopic Characterization

The nanocomposites were characterized by Scanning Electronic Microscopy (SEM). .SEM fractographs were employed to evaluate the presence of agglomerates on fracture surfaces.

## 3. RESULTS AND DISCUSSION

### 3.1. Dynamic Mechanical Properties

The variation of storage modulus and *tan δ* with temperature is presented in Figs. 5 and 6, respectively, for the $SiO_2$/epoxy nanocomposites.  Over the entire temperature range studied, an increase of storage modulus with the $SiO_2$ content is observed.  At 30 ºC, the increase in storage modulus over the neat resin was of 3, 10, and 13 %, for $SiO_2$ contents of 2, 4, and 8 wt.%, respectively.

As the temperature increases, a gradual drop in storage modulus up to the onset of the glass transition temperature (Tg) is observed, for both the pristine epoxy and the nanocomposites. At the onset of Tg, a sudden drop in the storage modulus is shown. This improvement in elastic modulus with the addition of inorganic nanoparticles has been attributed to the good dispersion of the particles and good interfacial adhesion between the particles and the epoxy matrix, so that the mobility of polymer chains is restricted under loading (Yasmin et al., 2006).
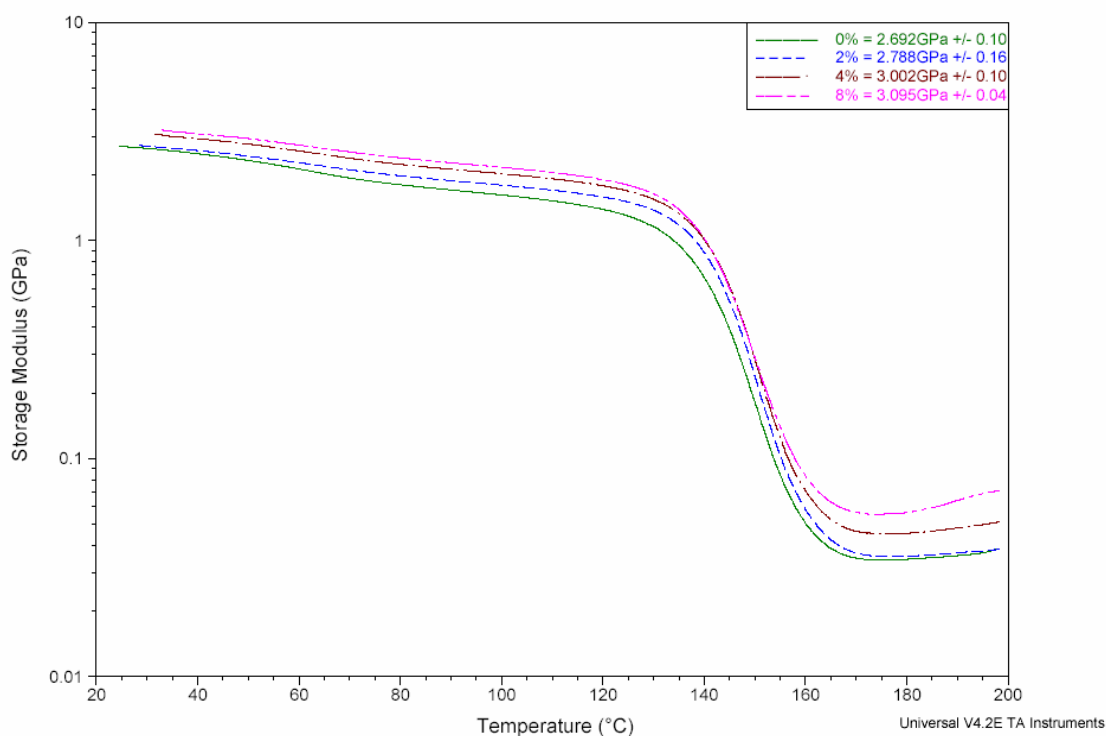


Figure 5. Storage modulus of pristine epoxy and $SiO_2$/epoxy nanocomposites.

The effect of $SiO_2$ content on the Tg of the nanocomposites, based on the *tan δ* peak, is presented in Fig. 6. It can be seen that the addition of silica nanoparticles did not produce any significant changes in the Tg, which was about 154 ºC for all materials tested.  Thus, the untreated $SiO_2$ nanometer size particles used in this work were not able to restrict the segmental motion of cross-links near the organic–inorganic interface (Agag et al., 2001).  In addition, the interaction of the polymer chains with the surface of the inorganic particles can alter the chain kinetics in the regions surrounding them and lead to changes in cross-link density and in Tg (Yasmin et al., 2006).  Surface modification treatments of the particles and the level of particle dispersion have been reported as important factors that can affect Tg (Yasmin et al., 2006).
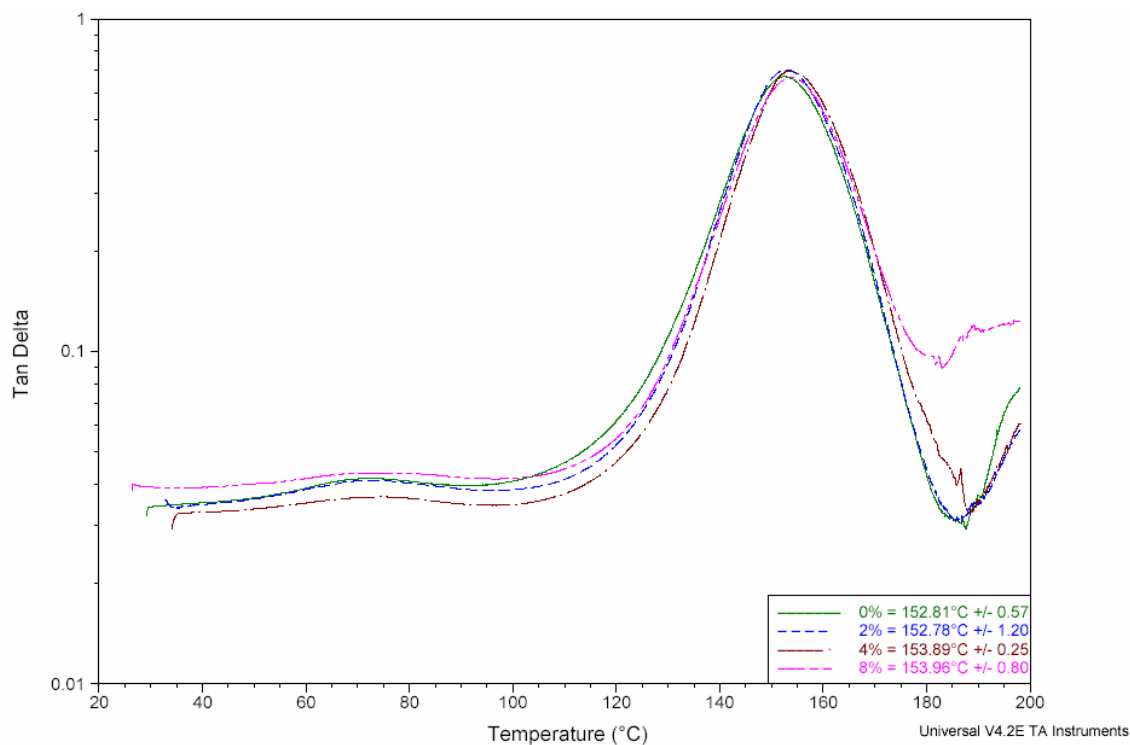


Figure 6. Tan delta of pristine epoxy and $SiO_2$/epoxy nanocomposites.

## 3.2. Microstructural Analysis

The SEM fractographs of the 2, 4, and 8 wt. % $SiO_2$/epoxy nanocomposites are presented in Figs. 7 to 9, respectively.  In general, the fractographs indicate good particle dispersion.  However, some bright spots observed on the fracture surfaces correspond to agglomerates finely dispersed in the material.  Yasmin et al. (2003a) have reported similar agglomerations in clay/epoxy nanocomposites. These agglomerations of nanoparticles in the matrix are known to be detrimental since they may act as additional crack initiation sites by splitting up easily under applied load (Zerda and Lesser, 2001).  The agglomerates concentration observed by SEM increased with silica content.
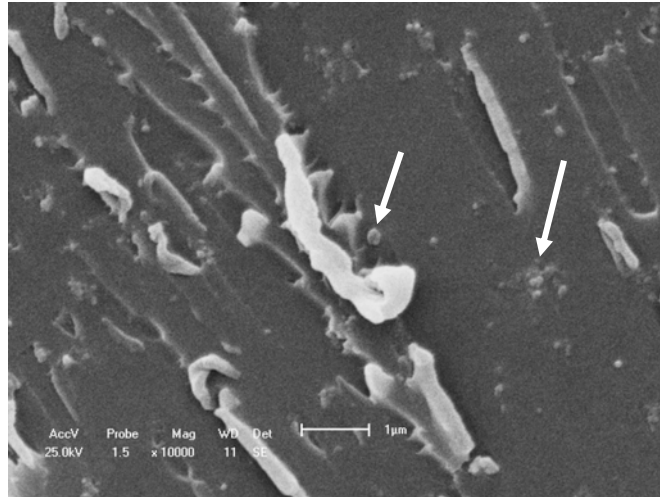
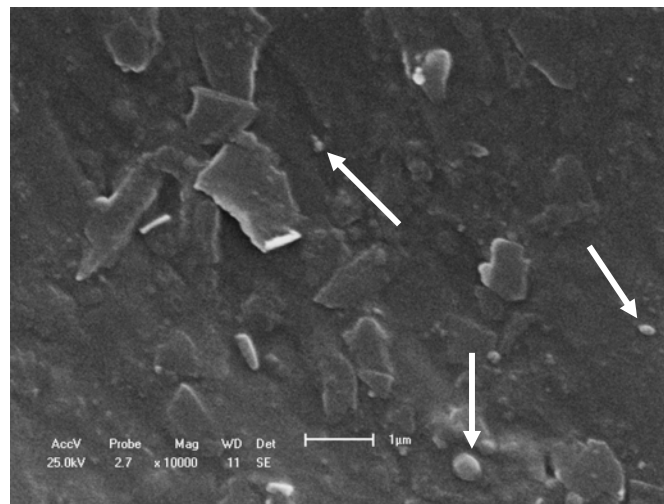Figure 7. SEM fractograph of 2 wt.% SiO$_2$/epoxy nanocomposite.



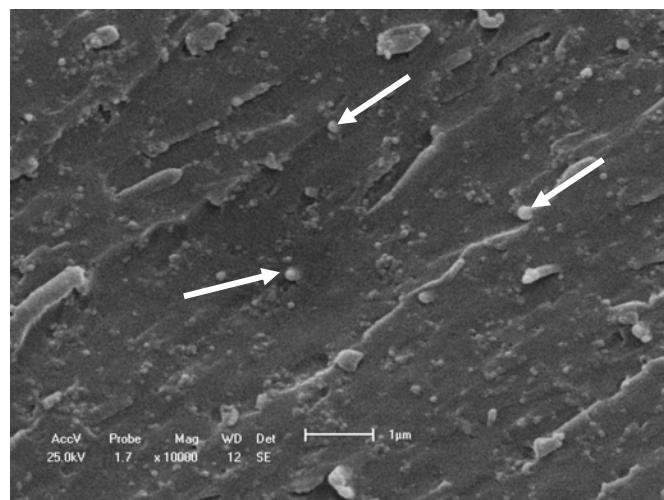Figure 8. SEM fractograph of 4 wt.% SiO$_2$/epoxy nanocomposite.



Figure 9. SEM fractograph of 8 wt.% SiO$_2$/epoxy nanocomposite.

## 4. CONCLUSIONS

A processing technique for polymer matrix nanocomposites was studied and evaluated. The approach uses a high energy mill to disperse the particles within the polymer matrix. $SiO_2$/epoxy nanocomposites with nanoparticles contents of 2, 4, and 8 wt.% were processed. Dispersion of $SiO_2$ nanoparticles in the epoxy matrix was obtained within 40 min in the high energy mill. Although, in general, a good dispersion of nanoparticles was observed, SEM fractographs indicate the presence of agglomerates, which increased with the silica content.

Dynamic mechanical properties of the nanocomposites produced were measured. An increase of storage modulus with the $SiO_2$ content was observed. This improvement in elastic modulus was attributed to the good particle dispersion. The addition of silica nanoparticles did not produce any significant changes on the Tg of the polymer.

In summary, the addition of $SiO_2$ nanoparticles to an epoxy matrix produced only a modest effect on the polymer properties measured. This observation may be related to the level of particle dispersion and interactions between the nanoparticles and the polymer chains. Further investigations are currently being carried out to improve the level of particle dispersion. In addition, mechanical properties of nanocomposites produced by this technique, using surface modified nanoparticles are being conducted.

## 5. ACKNOWLEDGEMENTS

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