



PROCESSING OF POLYMER MATRIX NANOCOMPOSITES USING A HIGH ENERGY MILL

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Abstract

Polymer based nanocomposites are a special class of composite materials which have attracted increased attention due to their potential to significantly improve the polymer properties with a very small amount of nanoparticles added. Due to the strong tendency of nanoparticles to agglomerate, processing techniques able to produce complete particle dispersion in polymer matrix are of great interest.

The goal of this work was to develop and evaluate a processing technique for polymer matrix nanocomposites using a high energy mill. SiO₂/Epoxy nanocomposites with SiO₂ contents of 1-3 wt.% were processed. Transmission Electron Microscopy (TEM) micrographs of the nanocomposites processed indicated good particle dispersion. In addition, agglomerates were not observed on the Scanning Electron Microscopy (SEM) fractographs of the 3 wt.% SiO₂/epoxy nanocomposite. Therefore, according to the preliminary results, the technique holds promise as an efficient method for achieving high levels of particle dispersion within a short period.

1 Introduction

Nanocomposites are a particular class of composite materials where the dispersed phase has dimensions in the range of 1-100 nm. 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 [1-15]. This improvement in properties has been attributed to the very large specific surface area of the nanoparticles [12-15], which greatly affects their interactions with

the polymer chains. Thus, the state of dispersion plays a critical role on the improvement in properties [15,16,17]. Previous investigations have confirmed that, for a given volume fraction, the degree of dispersion and interfacial bonding may be significant to the final properties [15,16,18,19].

The strong tendency of nanoparticles to agglomerate makes the processing of nanocomposites a rather complex task [2,4,15]. Dispersion of nanoparticles is particularly difficult due to their great specific surface area and has been directly related to the preparation of the nanoparticles [16]. Thus, processing techniques able to produce complete particle dispersion in polymer matrix nanocomposites are of great interest [1-3,5-6,12,17]. Various approaches to process nanocomposites have been proposed and evaluated [15,16,17,18,19,20,21].

Previous investigations have shown that SiO₂ nanoparticles may produce a positive effect on the properties of nanocomposites [15,22,23]. In these studies, SiO₂ nanoparticles were added to polymer matrices to enhance strength, modulus, toughness, thermal stability. Therefore, incorporation of SiO₂ nanoparticles may be a promising approach to enhance the thermal and mechanical properties of polymers.

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 [24]. 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 [17] A very homogeneous dispersion of the nanoparticles within the polymer matrix was reported.

In this investigation, a processing technique for thermoset polymer based nanocomposites using a high energy mill is proposed and its effectiveness to produce good particle dispersion is evaluated.

2 Experimental

2.1 Materials

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).

SiO₂ nanoparticles (Aerosil 200) were acquired from Degussa (São Paulo, Brazil). The nanoparticles were added to the epoxy resin in contents of 1-3 wt. %. The particles were analyzed by nitrogen adsorption technique (BET) and a specific surface area of 260 m²/g was obtained. A surfactant (Despulman, Carboflex Produtos Químicos Ltda) was also added to the resin system (10 wt. %) to improve degassing and particle dispersion.

Surfactants have been used in previous studies in the processing of polymer/clay nanocomposites. It has been shown that the clay surfactant solution resists platelet agglomeration, resulting in a dispersed clay/polymer nanocomposite [25]. Their interaction with the surface of the particles improves particle dispersion. However, they might also produce negative effects on the rheology and stability of the dispersion [26].

2.2 Processing

A high energy mill (Fig. 1) was used to disperse the SiO₂ nanoparticles in the polymer matrix. The SiO₂ nanoparticles were first added to the epoxy resin and hand-mixed for about five minutes. The hardener and surfactant were then added to the mixture, which is again hand-mixed for five minutes and placed in the mill. No balls were used in the process to avoid contamination of the nanocomposite produced.



Fig. 1. High energy ball mill.

After 20 minutes in the mill, the material was collected and poured in an aluminum mold. Then, the mold was placed in a desiccator, under vacuum, for 2 hours, 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. Nanocomposites with SiO₂ contents of 1-3 wt. % were processed.

2.3 Characterization

SiO₂ nanoparticles and nanocomposites were characterized by Scanning Electronic Microscopy (SEM) and Transmission Electron Microscopy (TEM).

TEM was first used to analyze the morphology and size of the SiO₂ nanoparticles. Then, it was applied to examine nanoparticles dispersion in the polymer. SEM fractographs were also employed to evaluate the presence of agglomerates.

3 Results and Discussion

3.1 SiO₂ nanoparticles

TEM provides direct evidence of the detailed morphology features of the silica/epoxy nanocomposites. Figure 2 shows the morphology and size of the SiO₂ nanoparticles, while Figures 3, 4 and 5 show size, morphology and distribution of the nanoparticles within the polymer matrix.

Figures 3, 4 and 5 indicate that the nanoparticles were, in general, well dispersed in the epoxy resin, even though some variation of nanoparticles concentration throughout the epoxy matrix was observed. Uniform distribution is very

important for the development of superior technological properties.

TEM images show nanoparticles of various sizes (Fig. 2). Although the SiO₂ particles are not uniform in size, the average particle size observed was under 20 nm.

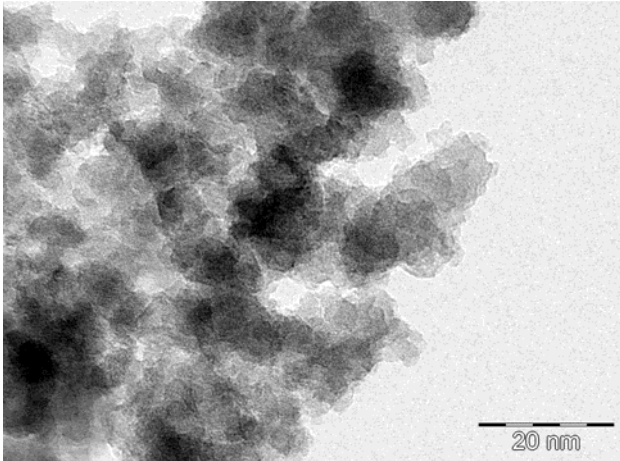


Fig. 2. TEM SiO₂ nanoparticles

3.2 Nanocomposites

TEM of all nanocomposites fabricated are presented in Figs. 3 to 5.

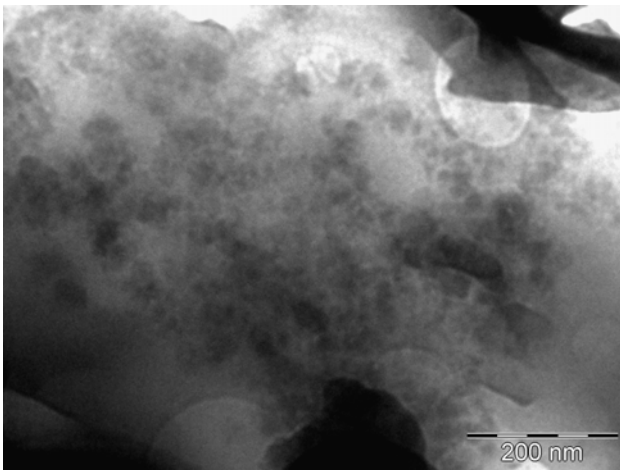


Fig. 3. TEM of the 1 wt.% SiO₂/epoxy nanocomposite.

According to the TEM micrographs (Figs. 3 to 5), the high energy ball mill processing technique employed in this research resulted in good particle dispersion, for 1-3 wt. % SiO₂/epoxy nanocomposites.

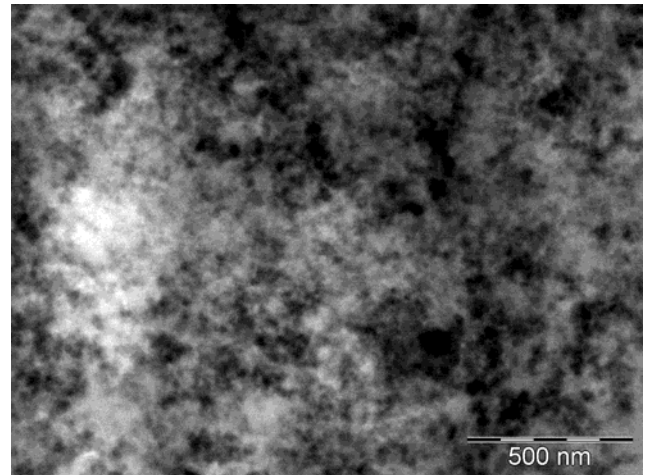


Fig. 4. TEM of the 2 wt.% SiO₂/epoxy nanocomposite.

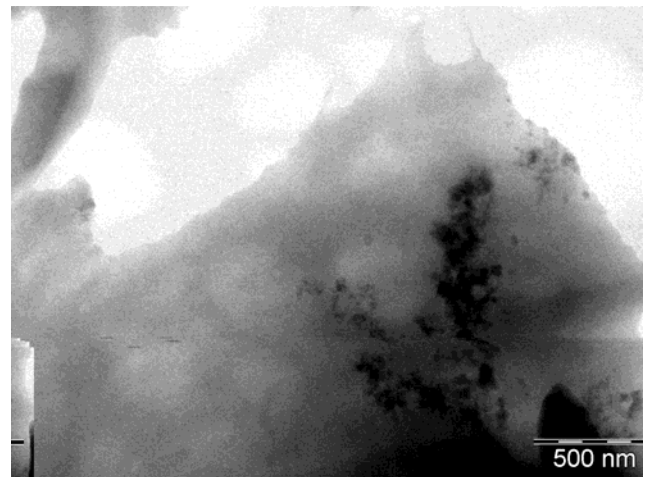


Fig. 5. TEM of the 3 wt.% SiO₂/epoxy nanocomposite.

The SEM fractograph of the 3 wt. % SiO₂/epoxy nanocomposite (Fig. 6) confirms the good dispersion obtained, as agglomerates were not observed on the fracture surface. Backscatter Electron Imaging (BSE) (Fig. 7) of the same fracture surface further confirms this assessment, as spots of different brightness are not observed. Large agglomerates may act as defects in the composite structure and be detrimental to the properties. SEM micrographs were produced only for the nanocomposite of highest nanoparticles content.

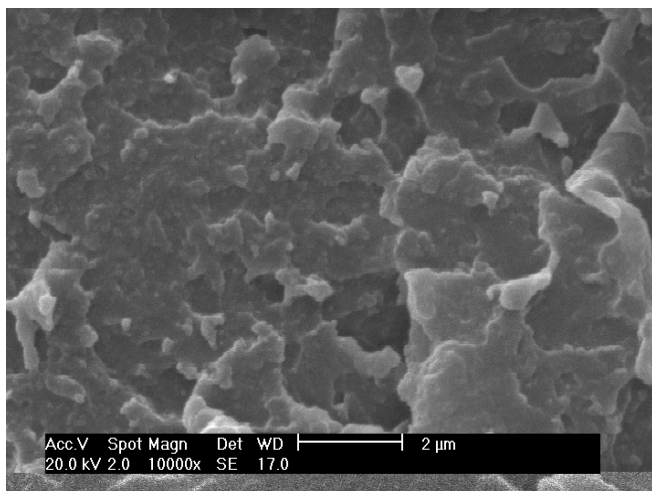


Fig. 6. SEM fractograph of 3 wt.% SiO₂/epoxy nanocomposite.

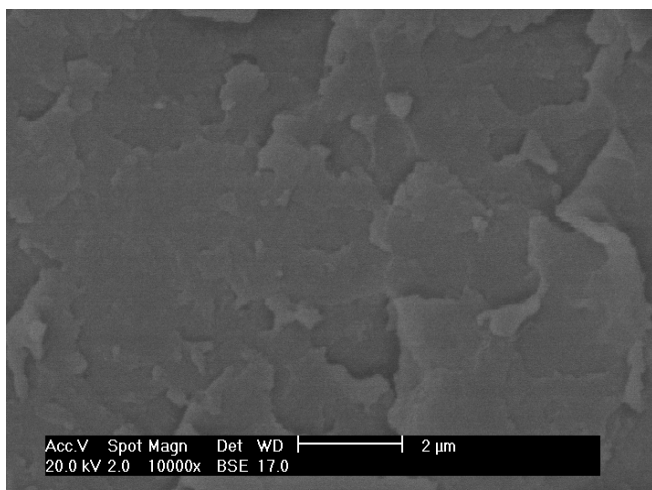


Fig. 7. SEM/BSE fractograph of 3 wt.% SiO₂/epoxy nanocomposite.

Therefore, both TEM and SEM micrographs of the nanocomposites indicates that good particle dispersion was obtained. Thus, the proposed processing technique, using a high energy mill, was found efficient in achieving dispersion of SiO₂ nanoparticles in an epoxy matrix, within a short period.

3 Conclusions

A processing technique for polymer matrix nanocomposites was developed and evaluated. The approach uses a high energy mill to disperse the particles within the polymer matrix. SiO₂/Epoxy nanocomposites with nanoparticles contents of 1-3 wt.% were processed. Dispersion of SiO₂

nanoparticles in the epoxy matrix was obtained within 20 min in the high energy mill.

Therefore, although more studies are still needed, it can be concluded that the technique offers a good potential as efficient method for processing polymer matrix nanocomposites. Based on these preliminary results, further investigations are being carried out to evaluate the mechanical properties of the nanocomposites produced by this technique, as well as to eliminate the need for surfactants, which are known to reduce properties such as glass transition temperature.

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