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Morphological, thermomechanical and thermal behavior of epoxy/MMT nanocomposites

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ABSTRACT

The present work reports the influence of the MMT content in the dispersing and exfoliating method of the nanofillers on non-isothermal cure behavior, morphology and solid viscoelastic properties of the epoxy resin/MMT systems were determined. The curing kinetics of the polymer systems are controlled by random and diffusion mechanisms. The amount of MMT content does not change the type of mechanism, but it has influence on the reaction enthalpy values and peak. The nanocomposite morphology indicated that the increase in mixing time caused an improvement in the level of dispersion of the clay. The use of ultrasonication decreases the dispersion of MMT in the epoxy matrix. The amount of MMT influences the delamination and uniformity of the matrix and consequently, the systems with 5 wt.% of MMT exhibited greater homogeneity than those containing 3 wt.%. The nanocomposites prepared without ultrasonication showed two peaks in tan δ, which might be related to the consequent formation of regions with different levels of clay distribution and heterogeneities. The storage modulus of the obtained nanocomposites decreased compared to the epoxy matrix. This may be related to the contribution of the interphase region, side reactions, and plasticizing effects of the organic modifier of the clay.

1. Introduction

A strategy to improve the properties of epoxy resin is the use of nanotechnology to obtain epoxy resin nanocomposites (NCPs). This approach has attracted considerable interest in universities and industry because of the notable increase in the mechanical and thermal properties of epoxy resins with the addition of small amounts of nanoparticles [1,2]. In this context, nanoparticles possess the potential to modify significantly the properties of a polymeric matrix. This potential depends greatly on the physical nature of each type of particle. Hybrid [3], metals [4–7] and inorganic particles [8] such as montmorillonite (MMT) [9], fumed silica, and metal-oxide particles affect mostly the mechanical, thermal, and functional properties of thermoset and thermoplastic polymers [10,11]. Polymer–clay nanocomposites are a very promising new class of materials [12]. The intercalated or exfoliated forms of nanolayer silicates in many polymer systems demonstrate improved strength [13], stiffness [14], fracture toughness [15], barrier properties [16], dimensional stability [17], and fire resistance [18] of the polymeric matrices.

The reinforcement capability of nanoclay is due to its high modulus, high strength, and high aspect ratio [19]. The greater the exfoliation of the nanoclays in the polymer matrix is, the greater will be the reinforcing effect [20]. A brief explanation for the improved properties could be based on the much larger aspect ratio of the nanodispersed clay minerals compared with that of conventional short fibers [21]. The conformational degree of freedom of polymer chains is restricted largely by the clay mineral particles and the alteration of the chain dynamics. As the polymer chains in the nanoconfined environment constitute a large volume fraction of the composite, the overall properties are influenced in an unusual way [22].

Epoxy resins have been studied widely to obtain nanocomposites because of their excellent mechanical properties. Messersmith and Giannelis [23] reported a 58% increase in storage modulus in the glassy region, and 450% in the region above the Tg of epoxy resin with the addition of 0.04 volume fraction of clay. Ha et al. [16] investigated the effect of MMT concentration on the fracture behavior of epoxy resin/MMT nanocomposites. The modification of MMT with (3-aminopropyl)triethoxysilane produced better dispersion in the epoxy matrix and also increased the intercalation effect of clay. The authors observed a decrease in toughness with the addition of MMT, but it was not a linear relationship with increasing concentration of MMT.

Riedl et al. [24] modified a commercial MMT by increasing the organophilic character and an increase in the storage modulus of the obtained nanocomposites was observed, especially at temperatures above the glass transition (Tg). Nanocomposites of epoxy-resin/modified-MMT have shown improved thermal stability and

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stiffness, particularly at temperatures above Tg. Mechanical properties have been improved by the addition of modified MMT, and the addition of 1 wt.% of nanoparticles into the epoxy matrix has caused a significant improvement in hardness and impact resistance.

Kaynak et al. [25] studied epoxy-resin/MMT nanocomposite morphology and obtained a mixture of intercalated and exfoliated montmorillonite particles. The improvement in flexural strength and fracture toughness was more significant in those nanocomposites obtained with MMT modified with long-chain quaternary alkyl-ammonium salts. The incorporation of clay, in many cases, increases the thermal stability of the polymer matrix by restricting the output of the volatiles formed by the decomposition of the polymer [18,26–30]. Tan et al. [31] obtained modified MMT/epoxy-resin nanocomposites with high degree of exfoliation of the clay and with improved thermal stability. Wang et al. [32] concluded that processing conditions had a large effect on the thermal and mechanical properties of epoxy-resin/MMT nanocomposites. An increase in stirring was shown to favor an increase in the degree of exfoliation of clay in the epoxy matrix, improving the thermal stability of the nanocomposites. Mohan et al. [33] showed that the presence of MMT facilitates the ring opening polymerization in epoxy resin, affecting the rate of chemical reaction. The amount of clay fillers and their interaction with the epoxy oligomers and curing agents have influenced the properties of epoxy nanocomposites during the cure process. In highly exfoliated systems, epoxy/nanoclay results in the formation of anisotropic solutions, increasing viscosity and surface interactions [34] as well as affecting the mobility of reacting species during the cure. Consequently, this influences the rate of cure, reaction time, enthalpy, vitrification, activation energy, viscoelastic properties, and cross-linking density of the final nanocomposite [35].

Therefore, it is important to understand the influence of nanoclay fillers on the cure behavior of epoxy resin, since the cure process is directly related to the final properties of the nanocomposites. Although several works have been reported the synthesis and characterization of epoxy/MMT nanocomposites, there are only few examples describing the influence of the MMT on the cure of the epoxy resin.

In the current study, the influence of two MMT content values and the method for dispersing and exfoliating the nanofillers on cure behavior of epoxy resin was investigated. Moreover, the cure kinetic parameters were evaluated using non-isothermal studies and the morphological, thermal, and mechanical properties of the systems were characterized by means of dynamic mechanical thermal analysis (DMTA), modulated differential scanning calorimetry (MDSC), transmission electron microscopy (TEM) and wide-angle X-ray diffraction (WAXD) techniques. In this paper we also propose a kinetic approach to random reactions, based on the work of Sánchez-Jiménez and coworkers [36,37].

2. Experimental

2.1. Materials

The epoxy resin used in this work was the commercial bisphenol A diglycidyl ether (DGEBA, CY-2333 from Huntsman-Brazil) with Mw of 1039 g mol^{-1} and polydispersity (M_w/M_n) of 1.5, as determined by gel permeation chromatography. The cross-linking agent used was carboxymethyl tetrahydrophthalic anhydride, which includes in its composition an amount of 1.6 wt.% catalytic agent (HY-2123, Huntsman-Brazil). The MMT nanoclay Cloisite® 30B (Southern Clay

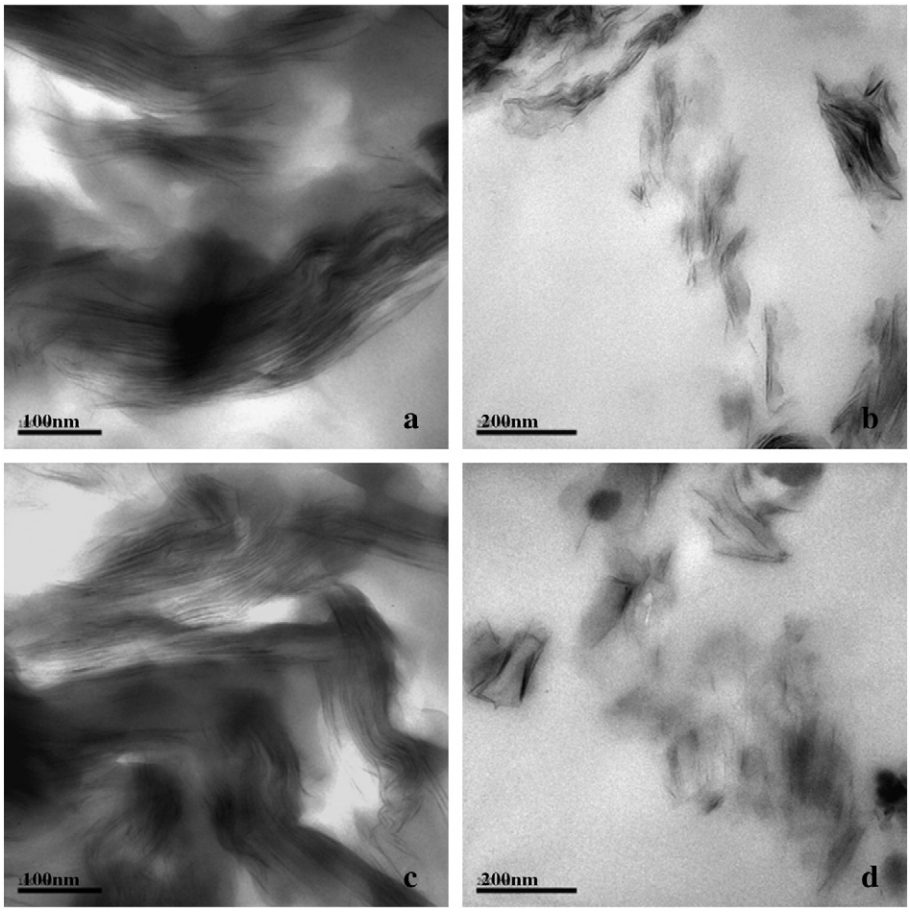

Fig. 1. TEM images of the epoxy/clay nanocomposites with ultrasonication: a) 3 wt.% nanoclay, 3 h; b) 3 wt.% nanoclay, 16 h; c) 5 wt.% nanoclay, 3 h; d) 5 wt.% nanoclay, 16 h. The bars correspond to 100 nm (a, c) and 200 nm (b, d).