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Research paper

Assessing the nanoscale structure of clay epoxy nanocomposites by tuning the physicochemical and processing conditions

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ABSTRACT

Organoclay/polymer nanocomposites are known to present improved mechanical properties, mainly when the organoclay is well dispersed or completely exfoliated in the polymer matrix. The objective of this work was to systematically evaluate the effect of different parameters, such as premixing procedure, role of the intercalating agent as well as the influence of the curing agent on the dispersion and intercalation/exfoliation state of organoclay in epoxy nanocomposites and how the extent of the dispersion affects the mechanical properties. For this purpose, two commercial organically modified montmorillonite (Cloisite 20A and Cloisite 30B) were dispersed within diglycidyl ether of bisphenol A (DGEBA) using different mixing approaches, namely conventional mechanical stirring followed by high-speed homogenization and/or ultrasonication. The dispersion state was evaluated before curing by means of X-ray diffraction (XRD), small-angle X-ray scattering (SAXS) and rheological measurements and after curing by SAXS, transmission electron microscopy (TEM), dynamic mechanical analysis (DMA) and mechanical properties. High-speed mixing combined with ultra-sonication resulted in better dynamic mechanical properties. The DGEBA/Cloisite 30B system cured with 4-methyl-tetrahydro-phthalic anhydride presented a better clay mineral dispersion in comparison with triethylene-tetramine (TETA)-cured systems. When the clay mineral was previously dispersed in acetone and submitted to high-speed mixing and sonication the dispersion of the clay mineral was even better.

Epoxy networks containing Cloisite 30B and cured with anhydride presented both elongation at break and modulus significantly higher than those got with the other systems, including neat epoxy network. The previous treatment of clay mineral with solvent resulted in a marginal increase in tensile strength of the epoxy network and a decrease in modulus.

1. Introduction

Epoxy networks are considered among the most versatile thermosetting materials, that find many industrial applications as adhesives and coatings for the electronic packaging and as matrices of carbon or aromatic fibers reinforced structural composites. These epoxy based composites very used in the aerospace industry display high performance in terms of high modulus and thermal stability. However, they are usually very brittle due to their high crosslink density. They are also sensitive to moisture absorption that can alter their performance. Nanocomposite technology using layered silicates as nanoscale reinforcements offers an alternative for the modification of epoxy based nanocomposite properties. The synthesis of this material that involves nanoscale dispersion of silicate layers within epoxy pre-polymer is rather easy because of the low viscosity of prepolymer before curing, facilitating the diffusion of the epoxy chains into the interlayer space of the clay mineral (Hackman and Hollaway, 2006; Le Baron et al., 1999; Tjong, 2006). Significant improvements of important properties such as mechanical performance, barrier characteristics, thermal stability, etc., are usually achieved with the addition of low amounts of organo-modified clay (Wang et al., 2000). The unique characteristics of organoclay–epoxy nanocomposites are due to the nanometer size of the clay mineral, its high aspect ratio, its extraordinarily high surface area and the extent of filler adhesion to the epoxy matrix.

The dispersion of the clay mineral inside the epoxy matrix can result in aggregated, intercalated and/or exfoliated structures. Generally, the best physical–mechanical performance is achieved with intercalated/exfoliated structures. However to attain appropriate dispersion, it is important to establish some experimental conditions to provide a balance between the prepolymer intercalation within the clay interlayer spaces and the curing reaction in or out of the clay interlayer spaces (Messersmith and Giannellis, 1994; Wang et al., 2003). Such features are strongly dependent on the nature of the intercalant in the organoclay, the nature of the curing agent, the curing conditions and the processing conditions used to disperse the clay mineral. The influence of these parameters on the properties of clay/epoxy nanocomposites has been investigated by different

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authors. For example, Kornmann et al. (2001a) employed different aliphatic amine-based curing agents and concluded that exfoliated structures were favored by using curing agents with low reactivity and/or high curing temperature. Similar behavior was also reported by Kong and Park (2003) when using aromatic diamines with different reactivities. Anhydride-based cured systems were reported to promote a higher degree of exfoliation of organoclays in epoxy networks, compared to amine-based hardeners (Jiankun et al., 2001; Messersmith and Giannellis, 1994; Miyagawa et al., 2006; Xu et al., 2002). According to Bao et al. (2004), the high curing temperature used in the anhydride systems decreases the viscosity of the epoxy pre-polymer and favors its penetration in the clay interlayer spaces, giving rise to more exfoliated clay mineral. The amount of the curing agent also affects the dispersion of clay mineral inside the epoxy matrix. Chin et al. (2001) found a high degree of exfoliation by using a lower hardener/epoxy molar ratio.

The dispersion of the clay mineral also depends on the nature of the intercalant moiety. Zilg et al. (2000) studied the influence of different alkylammonium cations as intercalating agents on the dispersion degree of organoclays in epoxy–anhydride systems and observed a significant increase of the interlayer distance with the increase of the alkyl group beared by the ammonium cation. Clays modified with primary and secondary onium ions were also reported to be more easily exfoliated than those containing quaternary onium ions (Jiankun et al., 2001; Lan et al., 1995; Ngo et al., 2007; Xida and Triantafyllidis, 2010). This behavior was attributed to the catalytic function of the acidic proton of the primary or secondary onium ions, which promotes the polymerization inside the interlayer spaces of the clay mineral in high extent. Other authors have observed that clay mineral modified with intercalating agents containing hydroxyethyl groups may be more easily dispersed inside the epoxy matrix (Brown et al., 2004; Chen et al., 2002; Miyagawa et al., 2004a, 2005; Shen et al., 2005; Zhang et al., 2004).

Besides the parameters discussed above, the processing conditions play an important role in the extent of the clay mineral dispersion. Conventional shearing tools as high-speed mixing (Ngo et al., 2009a, 2012; Thelakkadan et al., 2013), sonication (Boukerrou et al., 2007a,b,c; Brnardic et al., 2006; Brown et al., 2004; Chin et al., 2001; Kornmann et al., 2001b; Lam et al., 1995; Miyagawa et al., 2004b, 2006; Ratna et al., 2003; Wang and Qin, 2007), three roll-mill (Yasmin et al., 2003, 2006), and the combination of high shear mixing and ultrasonication in the presence of solvent or not (Chen and Tolle, 2004; Chen et al., 2008; Dean et al., 2007; Hutchinson et al., 2006; Kotsilkova, 2005; Miyagawa et al., 2004a, 2005, 2006; Nuhiji et al., 2011) are some examples. Although the clay-epoxy systems have been extensively studied since the first paper by Wang and Pinnavaia (1994), there are few reports on systematic studies related to different mixing procedures and other important parameters involved in the development of clay–epoxy nanocomposites (CEN).

This work aims to investigate by combining small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) how the nanoscale morphology of the corresponding CEN tuned by different processing conditions (mechanical mixing *vs.* sonication) as well as by varying the nature of intercalant (Cloisite 30B *vs.* Cloisite 20A) and curing agents (triethylene-tetramine (TETA) *vs.* 4-methyl-tetrahydro-phthalic anhydride (MTHPA)) affects the macroscopic properties (rheological, mechanical and dynamical-mechanical properties) of the filled epoxy nanocomposite.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA)-based epoxy prepolymer (EPON 828) was purchased from Shell Química do Brasil and has the following characteristics: viscosity = 110–150 P, epoxide equivalent = 185–192 g/equiv, and hydroxyl groups around 0.05 mol/100 g. The hardeners used for the curing were triethylene-tetramine (TETA), supplied by Vetec Ind. Quim. Ltda. and 4-methyl-tetrahydro-phthalic anhydride (MTHPA) (Aradur HY 2123) supplied by Huntsman. The organoclays used in this study were supplied by Southern Clay Products: Cloisite® 30B (OC30B) (a natural montmorillonite modified with methyl tallow bis(2-hydroxyethyl)quaternary ammonium with a cationic exchange capacity (CEC) of 90 mequiv/100 g clay mineral and a basal

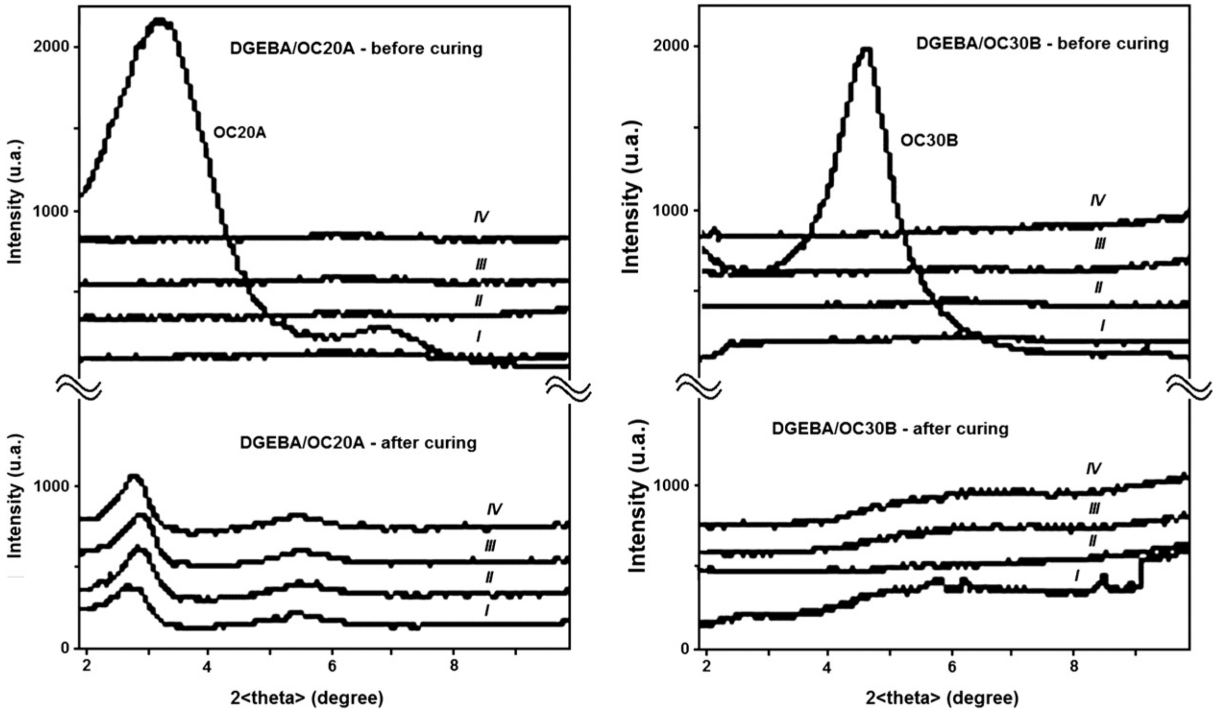

Fig. 1. XRD patterns of clay–DGEBA systems (before curing and after curing with TETA) containing 2.5 phr of OC20A or OC30B, as a function of the pre-mixing procedure.