



Research paper

Synthesis and properties of new epoxy-organolayered silicate nanocomposites



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ABSTRACT

In this research, both commercially available (Cloisite 93A) and advanced functionalized clay mineral were used to obtain clay-epoxy nanocomposites. Cloisite 93A was modified with three different alkoxysilanes and was incorporated in Epon 862 epoxy resin which was crosslinked using tetraethylenepentamine as a curing agent. The determination of color grades of the composite samples was followed. The morphology of the composites was analyzed using X-ray diffraction and ESEM micrographs which provided insight into the fracture mechanism. Thermal behavior was evaluated by TGA and DSC and thermo-mechanical properties of the cured samples have been evaluated by DMA technique. The data indicated that intercalated or agglomerated silylated Cloisite-epoxy nanocomposites were obtained. The silylated Cloisite samples are more compatible with the polymer matrix due to their enhanced hydrophobic behavior leading to an improvement in storage modulus and stiffness but also to the increase of glass transition temperature up to 30 °C.

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1. Introduction

Clay-epoxy nanocomposites have attracted worldwide attention due to their enhanced properties such as tensile and thermal properties, flame retardant properties and reduced permeability to small molecules and solvent uptake, with respect to the pristine polymeric matrix (Azeez et al., 2013; Kango et al., 2013; Cortes et al., 2014). Their application could be found in: engineering components in aeronautics, adhesives for almost all types of substrates, protective coatings, electronic and electrical components, high tension electrical insulators, body solders and caulking compounds, flooring tooling, compounds for molds, stamping dies and patterns, potting and encapsulation compounds, low pressure molding resins, and matrix for fiber-reinforced composites (Khanbabaie et al., 2007; Qian et al., 2009; Saadati et al., 2013; Unuabonah and Tauber, 2014). Different studies demonstrated that their behavior is related to the extremely large particle surface area available for interaction with the polymeric matrix coupled with clay mineral layers' high aspect ratio (Pinnavaia and Beall, 2000; Utracki, 2004; Bergaya and Lagaly, 2006; Kusmono et al., 2013; Corobea et al., 2014). The main

advantages of using inorganic fillers extend also to the fabrication of inexpensive and lightweight materials (Le Pluart et al., 2004). The most widespread clay mineral used to obtain polymer clay mineral nanocomposites is montmorillonite. Its hydrophilic nature makes it incompatible with most of the hydrophobic polymeric matrices (Ianchis et al., 2009, 2010; Mohd et al., 2010). Due to functionalization, the organomodified clay minerals become compatible with hydrophobic epoxy resins making them suitable to be transformed after curing into nanocomposites (Lin et al., 2010). The most common method to functionalize the clay mineral surface is by reaction with a quaternary ammonium or phosphonium salt through cation exchange reactions in the interlayer space. Another method is the covalent bonding with organosilanes at the hydroxyl edge groups (Herrera et al., 2004, 2006). In order to ensure an advanced dispersion of clay mineral inside monomer/polymer matrices, some of our studies combined the interlayer modification with the edge covalent bonding functionalization (Ianchis et al., 2012, 2014).

In the present study we examine the possibility to obtain clay mineral-epoxy nanocomposites using a commercial organomodified montmorillonite (CI 93A) and some others obtained by us from the same clay mineral modified by edge covalent bonding with three different alkoxysilanes (phenyl dimethylethoxysilane, octyl

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dimethylmethoxysilane and octadecyl dimethylmethoxysilane). The goal was to follow how the clay mineral structure affects the properties of the final material.

From our knowledge, it is the first attempt which provides new insights of the synthesis of silylated organomodified CI 93A montmorillonite and its implication in the obtaining of clay–epoxy nanocomposites.

2. Experimental

Commercial organoclay mineral (Cloisite 93A) modified with (methyl, dehydrogenated tallow)-(90 meg/100 g) ammonium salt was provided from Southern Clay Products Inc., USA.

Dichloromethane (DCM) was acquired from Chimreactiv, Romania and the alkoxy silanes (phenyl dimethylethoxysilane, octyl dimethylmethoxysilane and octadecyl dimethylmethoxysilane) from Aldrich, USA and was used without further treatment.

The epoxy resin, diglycidyl ether of bisphenol F (Epon 862, epoxide equivalent weight 165–173 g/eq, viscosity at 25 °C = 25–45 Pa) was purchased from Miller-Stephenson, USA. The Hardener, tetraethylenepentamine was provided from Sigma-Aldrich, USA and used as such.

2.1. Analyses

Dynamic light scattering (DLS) was used to determine the particles size distribution (Zetasizer NanoZS instrument, Malvern Instruments Ltd.). The commercial and silylated Cloisites were redispersed in DCM (0.02 wt.%), ultrasonicated for 1 min in an ice bath and then analyzed.

TGA analyses were performed with a SDT Q600 instrument. The clay mineral samples were heated, in nitrogen atmosphere with a rate of 20 °C/min, while the clay–epoxy samples were heated in the same atmosphere with a rate of 10 °C/min. Differential scanning calorimetry (DSC) thermographs were recorded with the same instrument at a heating rate of 10 °C/min, helium atmosphere.

The tiles were broken manually for a better observation inside the sample. The broken tiles were analyzed by environmental scanning electron microscopy (ESEM-FEI Quanta 200).

X-ray fluorescence (XRF) analysis was performed on a PW4025-MiniPal-Panalytical type EDXRF Spectrometer. The determinations have been carried out in helium atmosphere, Kapton filter, for a period of 300 s, at a voltage of 20 kV and by automatically adjusting the current intensity; for the construction of the cap a 3.6 µm Mylar film was used.

XRD diffraction patterns were obtained using a RIGAKU Ultima IV Instrument with Parallel Beam geometry and Ultima IV In-plane Goniometer operating at 40 kV/30 mA (Cu K α), in 2 θ range: 1°–30° and with a scanning speed of 5°.

Total color differences in CIELAB system, using a 10 degree standard observer and illuminant D65 were measured with a JASCO V570 UV–VIS–NIR spectrophotometer equipped with a JASCO ILN-472 (150 mm) integrating sphere, at room temperature, using Spectralon as reference.

The dynamic mechanical analysis (DMA) experiments were performed using a Q 800 Dynamic Mechanical Analyser from TA Instruments using a dual cantilever clamp and operating in bending mode. The experimental parameters employed in this study were: dynamic displacement amplitude of 20 µm under a frequency of 1 Hz and a heating rate of 2 °C/min, from RT to 200 °C, in air atmosphere. The temperature was stabilized for 5 min before starting measurements.

2.2. Method

2.2.1. Modification of clay mineral surfaces

Cloisite 93A was modified by a similar procedure described elsewhere (Donescu et al., 2012). For example, 4 g of dried CI 93A in 250 ml CH₂Cl₂ was sonicated for 10 min, on an ice bath, using a tip

sonicator and then the suspension was introduced in a three-neck round bottom flask. The mixture was stirred at 300 rpm and kept under purified nitrogen gas for 30 min, while the alkoxy silanes were added drop wise. Then the reaction mixture was heated to 40 °C and refluxed for 24 h. The reaction product was centrifuged and washed with 300 ml CH₂Cl₂, then was dried in a vacuum oven at 60 °C for 12 h before being analyzed.

2.2.2. Preparation of clay–epoxy nanocomposites

In order to disperse the clay mineral (4 wt.%) in the epoxy matrix, a three-roll mill (EXACT E series) was used. Firstly, the epoxy resin (DGEBA) and the clay mineral were placed between the feed and the center rolls. The distance between cylinders was set on turn to 50, 20, 10 and 5 mm. The mixture was passed once at 200 rpm for each distance established between cylinders. Then the mixture was passed four times at a distance of 5 mm and at a rotational rate of 500 rpm. After homogenization, the mixture was degassed 10 min under a vacuum (Planetary Centrifugal Vacuum Mixer “THINKY MIXER” ARV-310/ARV-310LED) in order to remove trapped bubbles. The curing agent was added to the mixture; the sample was degassed again 2 min under a vacuum and then was poured into an alumina mold previously treated at the surface with a mold-releasing agent. The mold was stored at room temperature for 24 h. On the next day, the mold was placed in an oven at 100 °C for 1 h. The resulting plates of neat epoxy and clay–epoxy nanocomposites samples were 1.6 mm thick.

3. Results and discussion

3.1. Functionalization of clay mineral

DLS analysis of the silylated Cloisite dispersed in the reaction solvent (0.02 wt.% in DCM), showed a different behavior comparatively with the commercial clay mineral. The average aggregate diameter decreased from 940 nm for commercial Cloisite to 500–600 nm in the case of modified clay mineral. From DLS size distribution by intensity (Fig. 1), it can be observed that the modified Cloisite exhibited broader peaks compared to the commercial CI 93A, which presented a single narrow peak. Moreover, besides increasing polydispersity, the clay mineral modified with phenyl and octyl groups displayed a bimodal distribution. This behavior could indicate the modification of clay mineral morphology, and the aggregates formed are the result of hydrophobic assembling phenomenon of hydrocarbon chains (Herrera et al., 2006; Donescu et al., 2012; Ianchis et al., 2012).

TGA curves, presented in Fig. 2, showed three steps of weight loss. The first step situated in the range of 100–250 °C is due to the volatile organic compounds that remained in the sample at the end of the reaction. The second step at 250–550 °C is associated with amine and to the grafted silane chains in the case of silylated samples (Zhang et al., 2006; Qian et al., 2009). The last step is recorded in the range of 550–800 °C, and is attributable to the loss of structural hydroxyl groups (Voorn et al., 2006; Ianchis et al., 2012). For the silylated samples, some modifications occurred in the range of 250–550 °C, and the maximum decomposition temperature increased to about 10 °C by comparison

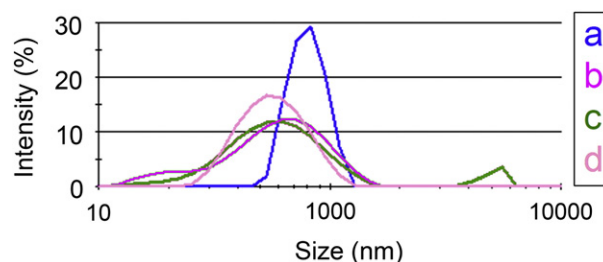


Fig. 1. DLS size distribution by intensity of the modified samples redispersed in the reaction solvent (a – CI 93A; b – CI 93A-Ph; c – CI 93A-C₈; d – CI 93A-C₁₈).

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