Preparation And Characterization Of Epoxy-Clay Nanocomposites Using Butadiene Acrylonitrile-Montmorillonite Intercalates

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ABSTRACT

Epoxy–clay nanocomposites have been prepared by dispersing amine terminated butadiene acrylonitrile grafted montmorillonite(ATBN-MMT) in an epoxy resin (diglycidylether of bisphenol-A, DGEBA) and curing in the presence of polyoxypropylene diamine at 80-120°C. ATBN-MMT was prepared by an ion exchange between the onium salt of butadiene acrylonitrile copolymer and the interlamellar sodium cation of MMT. X-ray diffraction (XRD) data confirms the intercalation of ATBN between the layers. Although XRD data for epoxy nanocomposites reveals the absence of the peak characteristic to d_{001} spacing, transmission electron microscopy, confirms the presence of mineral rich domains with an average size of 150 nm. These domains consist of multiplets and the average spacing between the multiplets was 100 Å. A good wetting of the silicate surface by the epoxy matrix and absence of large mineral aggregates was confirmed using scanning electron microscopy. Epoxy nanocomposites have higher decomposition temperature in comparison with the original epoxy. A significant increase in hardness was observed in composites containing ATBN-MMT up to 6wt%. © 2007 Trade Science Inc. - INDIA

INTRODUCTION

Epoxy resins have considered as one of the most important classes of thermosetting polymers and are extensively used for many applications. They are ex-cellent adhesives for metals, wood, glass and widely used as coating. However, their brittleness, low toughness and poor impact resistance result in limitation of their applications. One of the most successful methods of increasing the toughness of ep-

oxy resin is to incorporate some dispersed particles as second phase into the crosslinked polymer[1]. The impact strength of epoxy resin can be increased when the amount of rubbery material in the system is lower than 10 wt%. Synthetic rubbers containing hydroxyl, carboxyl and anhydride groups that react with epoxy resins are used for toughening thermosets[2].

Polymer layered silicate nanocomposites have attracted great attention world wide from both academic and industrial points of view. The material properties of polymers such as mechanical strength, thermal stability, chemical resistance, gas barrier properties and solvent resistance can be enhanced dramatically by incorporating layered silicates at fairly low concentrations[3,4]. However, the naturally abundant silicate clay is hydrophilic in nature and lacks the affinity for hydrophobic organic polymers. To improve its miscibility with polymers, the layered silicate must be modified to become organophilic. The modification generally involves swelling the layered silicate and exchanging the interlayer metal cations with organic surfactant salts. Previous work on epoxy has demonstrated the feasibility of dispersing layered silicate within a macromolecular matrix which results in significant improvements in the physical properties. The large majority of studies on the synthesis of epoxy-nanocomposite have focused on using organically modified MMT by long chain of alkylammonium ion. It has been reported that montmorillonite layers are dispersed throughout a cured epoxy matrix[5-10]. In one early study epoxy MMT nanocomposites were prepared using MMT modified by polyoxypropylene.[11] The izod impact strength of a nanocomposite was increased as compared with the pristine polymer. The goal of this work is directed to investigate the effect of modified MMT by butadiene acrylonitrile copolymer[12-14] on epoxy resins. The characterization of epoxy clay nanocomposites was performed by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. In addition, the thermal and hardness of the nanocomposites were measured.

EXPERIMENTAL

Materials

Na-montmorillonite(Na-MMT) was received from southern clay products Inc. under the trade name of mineral colloid BP. The cations exchange capacity(CEC) was 114.8 m.eq/100 g and the inter-lamellar spacing(d_{001}) is 9.6A^0. Amine terminated butadiene acrylonitrile(Hycar ATBN) was obtained from BF Goodrich, specialty polymers & chemicals division with acrylonitrile content of 18%, the number average molecular weight was 1.09×10^3 and the weight average molecular weight was 7.34×10^3, which gives rise to a polydispersity (M_w/M_n) of 6.75. Polyoxypropylene diamine (Jeffamine D_{230}) was obtained from huntsman corporation having an average molecular weight of 230 and the primary amine content is 8.2 meq/g. Standard, general purpose epoxy resin D.E.R.331 (epoxy equivalent weight is 186-190) based on diglycidyl ether of bisphenol A (DGEBA) was obtained from dow chemical Japan Ltd. The chemical structure of epoxy and jeffamine are presented in figure 1.

Preparation of epoxy-clay nanocomposites

Clay modified by ATBN was prepared by following the reported procedure[13]. Accordingly, A suspension of 30g of Na-MMT in 750ml of water was stirred overnight. To the stirred suspension, 500ml of dioxane was added, then a solution of 60 g ATBN in 400ml dioxane was added dropwise. After stirring for 1h, 8ml of 4N HCl was added. After stirring overnight at room temperature, the product was precipitated by addition of H_2O, filtered, washed several times with distilled water until no chloride ions were detected by testing with $AgNO_3$ and dried in vacuum at room temperature.
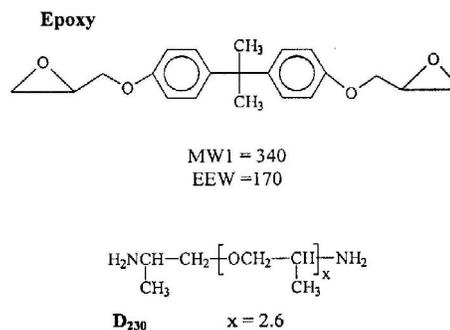
Epoxy

MW1 = 340
EEW =170

$H_2NCH-CH_2-[OCH_2-CH]_x-NH_2$
    CH_3 CH_3

D_{230}   x = 2.6

Figure 1 : Chemical structure of epoxy (DGEBA) and jeffamine D_{230}

Nanocomposites were prepared by first swelling the desired concentration of dry modified MMT by ATBN(2-8 wt%) with epoxide resin for 8 hours at 70°C in order to allow the diffusion of epoxide resin molecules between the layers. The swelled materials were subsequently stirred into the appropriate amount of jeffamine D-230(curing agent) for an additional 15 min and then degassed for approximately 20 min in a vacuum oven until bubble free. Equivalent amount of epoxide resin(25g) and jeffamine D-230(8g) were used for each formulation. This amount was calculated to achieve 1:1 stoichiometry between active hydrogen and epoxide groups. The mixtures were poured into a preheated open rectangular glass mold with dimension 60 mm×80 mm and 5-mm thickness having silicon rubber spacer, followed by removing air bubbles using vacuum pump. The surface of the glass was pretreated by dichlorodimethylsilane. The molds were then cured at 80°C for 2h then 3h at 120°C. All the test results were determined on the same molded specimen.

Measurements

Wide angle X-Ray diffraction (WAXD) measurements were recorded; using a phillips powder-diffractometer equipped with a Ni-filtered Cu-K$_\alpha$ radiation ($\lambda = 1.5418$ A°); at a scanning rate of 0.005°/s and divergent slit 0.3°. Nanocomposites were cut from molded samples with size 20mm x15mm x2mm thick. Bragg´s Law (n$\lambda = 2$dsinθ) was used to compute the crystallographic spacing. IR measurement spectra were carried out on a Perkin-Elmer 1430 spectrophotometer using potassium bromide pressed disc technique in the wavelength range of 4000-600cm^{-1}. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer thermal analyzer system. The temperature range studied was from 30 to 800°C at a heating rate of 10°C/min in the nitrogen atmosphere. A JEOL 5400 Scanning electron microscopy (SEM) was used to observe the particle size of MMT and the particle matrix adhesion in the composites on the fractured surface. The specimens were coated with gold. Transmission electron microscopy (TEM) image was obtained at 100 KV with a JEOL 100CX electron microscope. The sample was ultramicrotomed with a diamond knife on a LKB

8800 ultra microtome at room temperature to give 70 nm-thick section. The section was transferred from water to carbon-coated Cu grids of 200 mesh. The contrast between the layered silicate and the polymer phase was sufficient for imaging, so no heavy metal staining of sections prior to imaging was required. The micro hardness was measured using Matzuzawa MHT-1 machine. In the hardness test, 10 g were applied for 20 sec in a perpendicular direction. For each data point, 10 readings were taken and the average value was calculated.

RESULTS AND DISCUSSION

The initial stage to disperse the clay uniformly into epoxy matrix is the modification of hydrophilic montmorillonite to become hydrophobic. In this study, Na-MMT was intercalated by ATBN through an ion exchange process to prepare organically modified montmorillonite. The synthetic procedure used for nanocomposite preparation is essentially that initially developed by Usuki et al. for nylon-silicate nanocomposites[15]. It involves dispersion of the organically modified montmorillonite in a suitable monomer, followed by polymerization. Under proper conditions delamination of the modified montmorillonite into individual silicate layers occurs, which ultimately become dispersed within the macromolecular matrix. A similar procedure was used which involved mixing of organoclay(ATBN-MMT) and DGEBA at 90°C, followed by addition of curing agent and curing of the network at a prescribed set of temperatures. Initial mixing of clay modified by butadiene acrylonitrile and DGEBA was performed at 90°C to ensure low resin viscosity and in order to allow the diffusion of the epoxy molecules between the silicate layers of the clay. Then curing starts in between the layers.

The IR absorption (Figure 2) at 916cm^{-1} in epoxy resin (I) is attributed to the stretching absorption of C-O in the epoxide ring. This absorption clearly disappeared by curing at 120 °C (II). This confirmed the curing of epoxy and the formation of the network structure. The bands characteristics to secondary amine in rubber that is intercalated to clay by intermolecular interaction are present in the re-
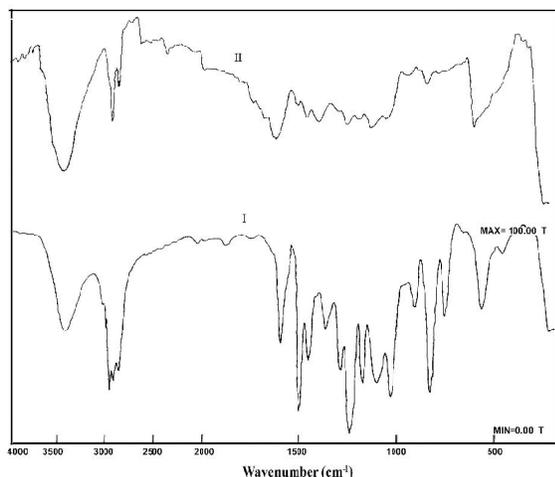
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Figure 2 : IR spectra of pure epoxy before curing (I) and ATBN-MMT/epoxy after curing (II)

Figure 3 : X-ray diffraction pattern of (I) ATBN-MMT and epoxy nano composites with different wt%, of ATBN-MMT, (II$_a$) 2wt%,, (II$_b$) 4wt%,, (II$_c$) 6wt%, (II$_d$) 8wt%,

gion 2700-2400 cm[1-[14]] at 2713, 2620, 2529 cm^{-1}. The characteristic bands corresponding to absorption of inorganic clay is shown in figure 2(II). The peak at 1039 cm^{-1} can be associated with Si-O stretching vibrations and at 582cm^{-1} with stretching of Al-O.

Figure 3 presents the XRD patterns of ATBN-MMT and four nanocomposite samples containing 2, 4, 6, 8 wt% of ATBN-MMT. The main silicate reflection in MMT-ATBN corresponds to a layer d$_{001}$ spacing of 14.1 A°. Subtracting the thickness of the silicate layer (9.3 A°) from the observed d$_{001}$ spacing (14.1 A°) produces the thickness of the polymer layer within the interlamellar span. The corresponding value 4.8 A° is slightly less than bimolecular layer (2x2.8 A°) and might be considered to represent the mean thickness of a buckled and folded macromolecular chain, in which approximately half of the segments of each chain is in contact with the surface. Epoxy-clay nanocomposites does not show a peak characteristics to ATBN-MMT which suggest the presence of delaminated hybrids. This was attributed to the migration of epoxy and curing agent due to the presence of enough hydrophobicity. The results implicate the silicates are well dispersed and possibly exfoliated in the epoxy matrix.

TEM could provide information of real space in a local area on the spatial distribution of the silicate layers. Since the silicate layers are composed of heavier elements Al, Si, O than are the interlayer and surrounding matrix (C, H, N) they appear darker in the bright-field images. The dark lines represent
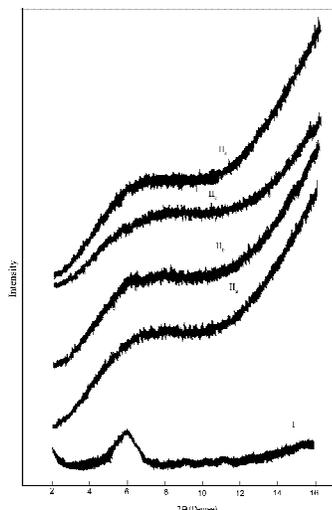
an individual clay layers, whereas the bright area represents the epoxy matrix. TEM micrograph of a thin film of the composite is shown in figure 4a. It is interesting to note that the samples are mostly homogeneous with no phase separation between the silicate layers and the epoxy matrix. The assemblies of nanodomains with thickness take the range from 50 to 250nm reveals the formation of nanocomposites. A closer observation of the micrograph at high magnification (Figure 4b) reveals that each dark line often corresponds to several clay layers. The presence of these multiplets was also observed in ATBN-
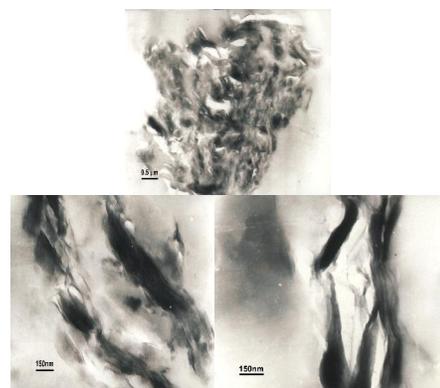

Figure 4 (a and b) : TEM micrograph of thin section of cured epoxy nanocomposite with 6 wt%, of ATBN-MMT (a) low magnification, (b) high magnification

MMT[14]. Some areas of the epoxy matrix contain oriented collections of parallel silicate layers. This interesting detail in the nanocomposites demonstrate that epoxy resin does not diffuse into all the clay galleries during the swelling period. As a consequence, all layers are not separated individually upon polymerization. The average distance between the stacks around 100A°. These data confirm that the absence of 001 reflection may be caused by a wide distribution in layer spacing. The SEM micrograph of the pure epoxy does not show any features. The SEM micrograph of the fractured surface of the composite sample (Figure 5a,b) does not show any aggregation of MMT at the maximum possible magnification that was observed by Kelly et al[16]. This indicates that the mineral domains are submicron in size.

    TGA were recorded for epoxy-clay nanocomposites to monitor the effect of ATBN-MMT on the thermal properties of epoxy resins. As shown in TABLE 1, the improvement in the thermal stability was achieved by the incorporation of only 2% ATBN-MMT. The temperatures at 5 and 10% weight loss indicate that the thermal stability of the epoxy was enhanced by the incorporation of small amount of clay nanolayers. The decomposition temperature of composites containing 2wt% of organoclay became higher for ca. 10°C than the corresponding pristine epoxy. The weight loss reaches 75%at 399°C in pristine epoxy. In contrast, the weight loss of epoxy nanocomposite containing 2wt% of organoclay reaches 75% at 416°C. This behavior is expected because the clay platelets protect and delay the intercalated chains from undergoing a degradation process. As the amount of ATBN-MMT increased, the total weight loss of the nanocomposite decreased. It
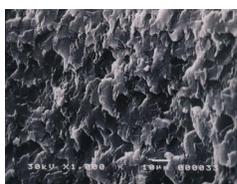

Figure 6 : Effect of ATBN-MMT content on the hardness of pure epoxy

is suggested that for the nanocompo- sites, the silicate layers (nanolayers) with a high aspect ratio (100-1000), are believed to effectively act as barriers, blocking the degradation of epoxy resins located between the interlayer spacing.

    The effect of molecular dispersion of the silicate layers on the hardness properties of the crosslinked polymeric matrix was probed using microhardness. Hardness is increased as the content of organoclay increased by the reinforcing effect of dispersed clay(Figure 6). The shore A hardness is increased in polyurethane as the content of clay is increased[17]. Another publication reported the results of shore A hardness was decreased in PU/clay nanocomposites by the added clay[18].

CONCLUSIONS

    Polymer clay nanocomposites consisting of silicate layers embedded within a crosslinked epoxy matrix have been prepared. The synthetic approach involves dispersion of ATBN-MMT within an epoxy resin,followed by curing of the crosslinked network. A morphological hierarchy based on XRD and TEM observation suggests that multiplets are assembled to form nanodomains. Absence of large mineral aggregates in epoxy matrix was confirmed using SEM. Micro hardness and thermal analysis of the nanocomposites showed significant increases in hardness and thermal stability when only small amounts of ATBN-MMT were added to epoxy resins.

Figure 5 (a)   Figure 5 (b)

Figure 5 (a ,b) : Scanning electron micrograph of fracture surface for Epoxy/ATBN-MMT containing 6wt% of ATBN-MMT (a) low magnification (b) High magnification
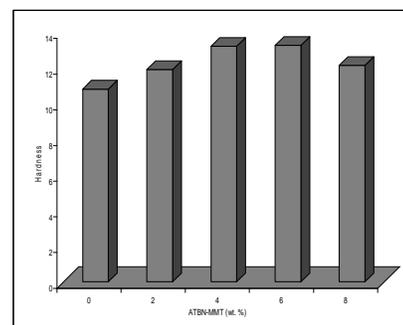
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