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Effect of Clay on Chemical and Mechanical Properties of Blended Nanocomposites

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ABSTRACT

Epoxy/Unsaturated polyester (UP) blend is prepared with varying montmorillonite (MMT) clay (viz. 0%, 1%, 2%, 3%, 4% and 5% by weight) content. The chemical resistance of these nanocomposites to some acids, alkalis and solvents is studied. The hardness property of these nanocomposites is determined. The nanocomposites showed good resistance to acids and alkalis, but showed minimal resistance to solvents. The nanocomposite blend indicated better hardness at 3% clay when compared to other combinations considered in this study. The homogeneous morphologies of the UP toughened epoxy and epoxy/UP/clay nanocomposite systems are ascertained using scanning electron microscope (SEM) and transmission electron microscope (TEM) studies. The above studies indicate that the Epoxy/UP/MMT clay nanocomposite can be used in applications like aerospace, automobiles and marine systems. The main objective of the study is to identify a low-cost, light-weight, eco-friendly and high-strength composite material that can be used for various engineering and commercial applications.

Introduction

In recent years, from the point of view of developing high-strength, light-weight, environment friendly and economically viable composites; different blends of polymer resins with various combinations of organic nanomaterials like clay as reinforcements has increased. Several studies on the above mentioned composite blends and nanocomposites are reported in the literature [1-12]. Thus, in order to develop better nanocomposites blends, it is customary to test the miscibility and performance of the nanocomposite blends that are developed and if they show better properties, then they can be recommended for production. Varadarajulu et al. [1] in 2003 and Benny Cherian et al. [2] in 2007 have conducted miscibility study on the blend of epoxy with unsaturated polyester resin and confirmed that the blend is miscible. Varadarajulu et al. [3] in 2002 conducted studies on chemical resistance and tensile properties of epoxy/unsaturated polyester (UP) blend coated bamboo fibers and suggested that these materials are suitable for making composites. Kedzierski et al. [4] in 2004 have investigated the hardness properties of unsaturated polyester/clay nanocomposites and indicated that they exhibit better properties than most other composites.

The primary goal of this study is to characterize the chemical resistance and hardness properties of the epoxy/UP/ clay nanocomposite. For this purpose a blend of epoxy/polyester (85/15 %w/w) [1,2] polymers is prepared as a function of Montmorillonite (MMT) clay in different weight ratios such as 0%, 1%, 2%, 3%, 4% and 5%. The final objective is to identify a suitable nanocomposite which offers low-cost, high strength material, which can be applied in making light-weight components for automobile parts, transportation systems and consumer products.

Materials and Methods

Resins and Nanoclay

The resins used in this study are (i) Epoxy (Ciba-Geigy, Araldite-LY 556 and Amine hardener HY-951) with the resin-hardener ratio as 100:10 and (ii) Unsaturated Polyester (Ecmalon 9911, Ecmas Hyderabad), with 2% cobalt naphthanate as accelerator, 2% Methyl ethyl ketone peroxide (MEKP) as catalyst in 10% Dimethylaniline (DMA) solution as promoter, in the ratio of the resin/ accelerator/ catalyst/ promoter:100/2/2/2. In addition, exfoliated montmorillonite clay (MMT) (product No.:682659; brand: Aldrich, USA; product name: Nanoclay, hydrophilic bentonite; formula: $H_2Al_2O_6Si$; size: $\leq$ 25 microns), surface modified with 25-30% trimethyl stearyl ammonium, is used as filler material.

Chemicals

In the present work, chemical resistance test on epoxy/unsaturated polyester/clay nanocomposite is conducted by using the chemical reagents mentioned below:

Acids: Acetic acid (CH_3COOH), Nitric acid (HNO_3) and Hydrochloric acid (HCl)

Alkalis: Sodium hydroxide (NaOH), Sodium carbonate (Na_2CO_3) and Ammonium hydroxide (NH_4OH)

Solvents: Benzene, Toluene, Carbon tetrachloride (CCl_4) and Distilled water

Sample Preparation

Firstly, clay is dried in an oven at a temperature of 80 °C for 24hrs. Then pre-calculated amount of clay and epoxy/polyester (i.e. 85/15 %w/w ratio) are mixed together in a suitable beaker. Clay is mixed in stipulated quantity to the epoxy/polyester blend and is mixed thoroughly with mechanical shear stirrer for about 1 hour at ambient temperature conditions. Then the mixture is placed in a high intensity ultra-sonicator for one and half hour with pulse mode (15sec on / 15sec off). External cooling system

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is employed by submerging the beaker containing the mixture in an ice bath to avoid temperature rise during the sonication process. Once the process is completed, hardener/ accelerator/ catalyst/promoter (100:10/2/2/2) parts by weight is added to the modified epoxy/polyester mixture. A glass mould with required dimensions is used for making samples on par with ASTM standards. The glass mould is coated with mould releasing agent to enable easy removal of the sample. The nanocomposite mixture is poured over the glass mould. Brush and roller is used to impregnate the nanocomposite. The closed mould is kept under pressure for 24 hours at room temperature. To ensure complete curing the blended nanocomposite samples are post cured at 70ºC for 1 hour and the test specimens of required sizes are cut out from the sample sheet.

Rockwell Hardness Measurement

Hardness of the blended nanocomposites is measured using Rockwell hardness tester (Model-2000R). The specimens are made according to ASTM D 785 [5] specifications (10 mm x 10 mm x 6 mm). The diameter of the indenter ball used is 1/16-inches and the maximum load applied is 60 kgs. Here, five specimens are tested and their average values are tabulated as shown in Table 1.

Chemical Resistance Measurement

To study the chemical resistance of the nanocomposites, the test method ASTM D 543-87 [5] is employed. Three acids, three alkalis and four solvents are used for this purpose. Acetic acid, nitric acid, hydrochloric acid, ammonium hydroxide, aqueous sodium carbonate, aqueous sodium hydroxide, carbon tetrachloride, benzene, toluene, and distilled water are used after purification. In each case, ten specimens (5mm x 5mm x 3 mm) are pre-weighed in a precision electrical balance and dipped in the respective chemical reagents for 24 hrs. They are then removed and immediately washed in distilled water and dried by pressing them on both sides with a filter paper at room temperature as described elsewhere. The treated specimens are then re-weighed and the percentage loss or gain is determined using the equation:

$$\text{\% gain/loss in weight of the specimens} = \frac{\text{Original weight} - \text{Final weight}}{\text{Original weight}} \times 100$$

Results And Discussion

Hardness test

On comparing the neat blend with other modifications the following observations are noted. Hardness number measured for pure blend is 101. Hardness is improved by 3.9%, when 1wt. % clay content is added to the blend. And again, hardness is improved by 6.9%, when clay content is increased by 2 wt. %. Hardness is improved by 13.8%, when 3 wt. % of clay content is added to the blend. Hardness is decreased by 13.8% when clay content is further increased by 5 wt. %. In the literature, it has been indicated that adding small amounts of nanoclay into polymer-based materials could potentially enhance their strength, like hardness of the current samples with the clay contents less than 4 and 5 wt %. This substantiates the existence of an optimal limit, since the physical properties between these nano-structural materials and matrix are different. It is noticed for nanoclay beyond 3 wt% that the drop in hardness is due to the fact that longer time is required for solidification and relatively softer surface when compared with other samples of lower clay contents.

Chemical resistance test

From Table 2 it is clearly evident that nanocomposites are resistant to all chemicals considered except for the solvents. In each case, ten pre-weighed samples are dipped in the chemicals under study for 24hr, removed and washed thoroughly in distilled and dried immediately by pressing between filter papers. The nanocomposite blend specimens show a weight reduction on treatment with solvents. This is understandable as UP, that is present in the blend, dissolves in the solvents under study. These nanocomposites prove to be having good resistance to attack from chemicals except solvents. The increase in weight of the nanocomposites in other cases is understandable as the matrix is well cross linked and as a result swelling takes place instead of dissolution.

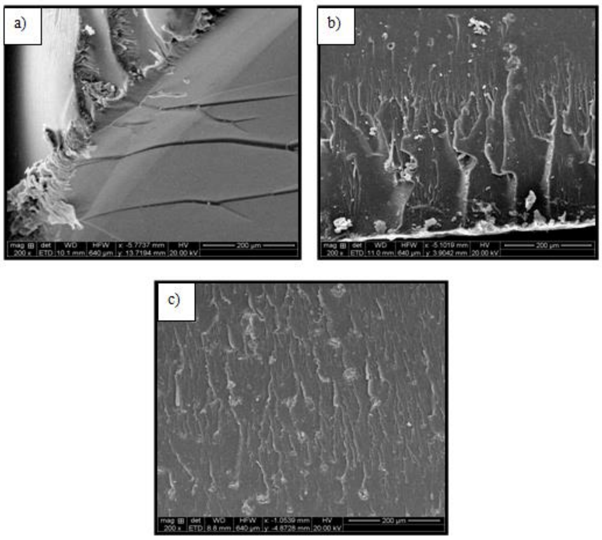
Table 1 Hardness test results of epoxy/polyester blend as a function of nanoclay

Name of the sample	Hardness (Rockwell)
Epoxy/UP + 0wt.% clay (neat blend)	105
Epoxy/UP + 1wt. % clay	108
Epoxy/UP + 2wt.% clay	115
Epoxy/UP + 3wt.% clay	120
Epoxy/UP + 4wt.% clay	115
Epoxy/UP + 5wt.% clay	95

Table 2 Experimental values showing % change in weight of epoxy/UP/clay nanocomposite after dipping in chemicals for 24 hours

Name of the chemical	Clay content (in wt. %)					
	0 wt.%	1 wt.%	2 wt.%	3 wt.%	4 wt.%	5 wt.%
HCl (10%)	+1.327	+0.925	+0.845	+0.455	+0.535	+0.576
CH_3COOH (5%)	+1.256	+0.287	+1.348	+0.934	+0.457	+0.223
HNO_3 (40%)	+1.978	+1.546	+1.656	+1.645	+1.698	+1.728
NaOH (10%)	+1.323	+1.625	+0.302	+0.785	+0.645	+0.575
Na_2CO_3 (20%)	+0.326	+0.320	+0.250	+0.167	+0.152	+0.144
NH_4OH (10%)	+0.825	+0.676	+0.532	+0.440	+0.487	+0.532
Benzene	-2.450	-5.247	-5.420	-7.575	-7.897	-8.352
Toluene	-1.054	-2.926	-8.265	-14.956	-10.567	-8.345
CCl_4	-0.364	-0.956	-3.958	-17.256	-12.345	-8.745
Distilled Water	+0.909	+1.325	+9.352	+11.526	+10.457	+9.348

Scanning electron microscope (SEM) and Transmission electron microscopy (TEM) analysis



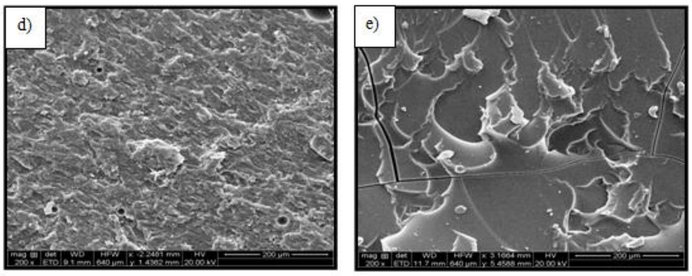


Figure 1 SEM analysis of epoxy/polyester blend as a function of nanoclay at (a) 0 wt% clay (b) 1wt% clay (c) 2 wt% clay (d) 3 wt% clay (e) 5 wt% clay.

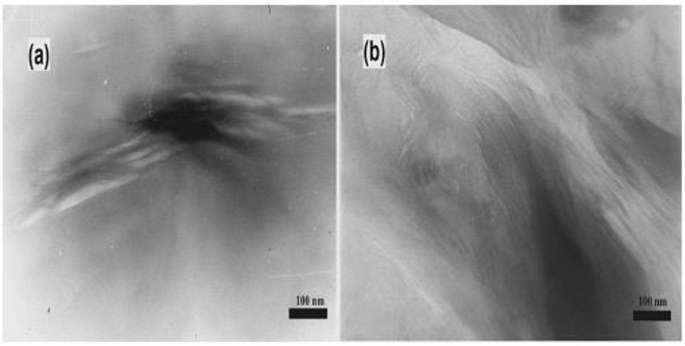


Figure 2 TEM analyses of epoxy/polyester blend as a function of nanoclay at 3 wt% clay.

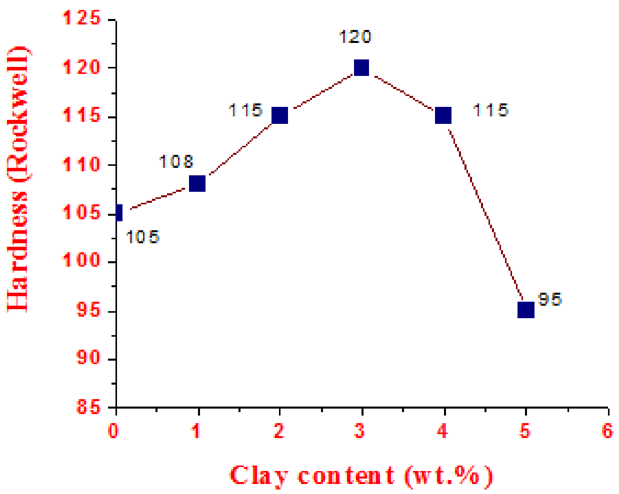


Figure 3 Hardness test results of epoxy/polyester blend as a function of nanoclay

Examination of impact-fractured surfaces can provide information related to interfacial property and mode of involved dissipation of materials. SEM micrographs of various epoxy/polyester blends containing varying clay concentration are shown in Figures 1(a)-(e). The neat blend sample shows brittle fracture surface, indicative of miscible characteristics between the epoxy and polyester as in the Figure 1(a). Varada Rajulu at al [1] has successfully proved that epoxy and polyester have good miscibility. In Figure 1(b) it is observed that brittle fracture is turned to ductile fracture due to addition of clay particles. In Figure 1(c) brittle fracture can no longer be seen as the clay content is gradually increased from 1 to 2wt. % as a result of which strong ductile nature of the composite is observed. In the Figure 1(d), another strong ductile fractured surface can be observed. This is yet an indication of good dispersion of nanoparticles that brought out maximum improvement of hardness property at 3 wt. % clay. On the other hand agglomeration of several clay particles, poor adhesion and bonding are observed in the Figure 1(e). Increase in clay particles correspondingly increases viscosity of the modified polymer that might be the reason for the failure at 5wt% of clay. With the increase of clay loadings, the well-dispersed layers or lines also increased in the matrix as are observed in earlier studies [7, 8]. The crack initiation is caused by the stress concentrations caused by the agglomerated clay. The high stress concentrations caused by the agglomerated particles might affect the mechanical properties, which is low deformation property and reduced strength by initiating early failure in the epoxy/UP blends.

The morphology and the actual structure or pattern of the clay layer dispersion in the polyester/epoxy blends are further analyzed by TEM. It has been reported in the literature that increased clay loading enhances the ordering of clay platelets and gradually degrades the exfoliation potential of the polymer. Figures 2a & 2b show a homogeneous dispersion of clay platelets for 3wt% clay loading.

Upon nanocomposite formation, the individual clay layers are found to be disintegrated or partially exfoliated and well dispersed in the polymer matrix. Also, the individual clay layers and zones with more than one clay layer are noted in the TEM images. The reason for this excellent distribution is the strong interactions between the polar carboxylic ester groups of the polymer and the -OH group of clay.

Conclusions

In this study, the hardness and chemical resistance properties of epoxy / polyester blend reinforced with MMT clay are studied.

The following conclusions can be drawn:

1. It is observed from Figure 3, the hardness property is optimized at 3 wt% clay content. When compared with neat blend specimens, 3 wt% clay filled blend specimen samples show a 14% increase in hardness.
2. It is clearly evident, that these nanocomposites are resistant to all chemicals considered for study except in case of the solvents.
3. The above results suggest that they can be used for making water and chemical storage tanks in applications like transportation, aerospace and marine systems.
4. SEM & TEM analysis revealed that excellent adhesion and interfacing between the matrices and clay is the main reason for optimum improvement of properties. This nanocomposite can be applied in making light weight components as automobile parts, transportation systems and consumer products.

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