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Reinforcement of Montmorillonite Clay in Epoxy/Unsaturated Polyester Blended Composite: Effect on Composite Properties

Chakradhar V.P. Komanduri

Abstract

Montmorillonite (MMT) clay was disseminated into Unsaturated Polyester (UP) and Epoxy blend systems in diverse weight ratios namely, 0, 1, 2, 3, and 5% to prepare Epoxy/UP/MMT clay composite. The specimen was characterized by thermal and chemical analysis. Homogeneous mixture of blended composites is obtained through mechanical stirring and ultrasonication processes. The testing of thermal and chemical properties was performed. Evidence acquired from the above tests indicate that Epoxy reinforced with UP and further strengthened with MMT clay enhanced the thermal and chemical properties of the composite to a considerable extent. The purpose of this study was to recognize an appropriate composite offering a stronger material with enhanced performance; that is suitable for diverse industrial uses.

Keywords: montmorillonite clay, epoxy, unsaturated polyester, thermal properties, chemical properties

1. Introduction

Polymer blending attained an appreciable market, since they save by weight approximately 36–40% of polymer consumption. Epoxy is a flexible, popular resin used for manufacturing state-of-art composites since it has superior binding, thermal, mechanical and aging characteristics [1, 2]. But for enhancement of impact attribute in state-of-art engineering uses, reinforcing epoxy is required. It can be improved through mixing with adaptable polymers and elastomers. Nevertheless, alteration of epoxy with elastomers enhances its toughness property besides drop in few properties of epoxy at elevated temperatures [3–5]. Hence, an apt polymer is needed to improve the toughness of epoxy, by preserving stiffness, glass transition temperature, and heat stability. It is accomplished by an inter cross-linked polymer network of thermoset-thermoset blends [6–10].

A good range of commercial relevance to polyester resins is identified in areas like paints and surface coatings. Several merits of polyester are observed with inclusion of flexibility in properties, reasonable cost and ease of use. But polyester possesses some demerits such as inferior resistance to alkalis and hardness. For overcoming the above-mentioned demerits, blending of polyester with suitable

resins can be performed as it exhibits better compatibility with diverse resins. The technique of blending can be productively applied to eliminate the substandard properties of both components. Blended polymers provide superior composite from lesser superior components.

The merits of nano-particles over conventional macro or micro particles are improved surface area and aspect ratio which could improve binding of nano-particles and polymers. Presently the most popular clay used for polymer-clay composites is MMT. Various studies were conducted on epoxy-clay composites (ECN) under different curing conditions. The exfoliated clay provides superior properties and offers advantages over other nanofillers in terms of cost and biodegradability [8, 9]. This paper furnishes facts on the property's analysis of the MMT clay reinforced polymer blended composites. The intention of this study was to recognize a composite that offers better strength, providing better performance at minimum cost; applicable for diverse applications.

Composites are influenced by chemical and thermal properties. Thermal and chemical properties of materials play an equally important role as mechanical properties. Polymers are very vulnerable to changes in temperature. Plastics tend to become rigid and brittle at minimal temperatures. The portability of the polymer chain is greatly reduced at low temperatures, which is the reason for the above. The temperature and dimensions of solid increases as it absorbs heat. Further heating melts the solid. Thus, knowledge of heat properties of materials becomes crucial for assessing the performance of polymers and their reaction to thermal changes.

2. Experimental procedure

2.1 Materials and methods

- i. **Epoxy** (Araldite-LY 556 and Amine hardener HY-951; ratio-100:10)
- ii. **Unsaturated polyester** (Ecmalon 9911; accelerator: 2% cobalt naphthenate, catalyst: 2% methyl ethyl ketone peroxide (MEKP) and promoter: 10% dimethylaniline (DMA) solution), are the resin materials. Exfoliated MMT clay treated with 25% trimethyl stearyl ammonium is the reinforcement material (**product name:** hydrophilic bentonite powder; **Density:** 600–1100 kg/m³; **Size:** 25 µm).

Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC-2010 TA Instrument) are employed to assess the heat attributes of the epoxy/polyester/MMT clay blended composites [11]. The thermal degradation behavior of the composite blend is investigated using TGA. TGA is performed on a 10 mg powdered sample to identify changes in weight to corresponding changes in temperature. The sample is placed in a thermocouple fitted oven for precise temperature measurement. An inert gas atmosphere is used to suppress unwanted reactions. A computer monitors and controls the entire process. Steadily enhancing sample temperature until 1200°C, evaluation is performed. A graph of percentage weight Vs temperature is plotted [12].

Evaluation of Glass transition temperature (T_g) of the material and assessment of thermal deterioration of polymers is carried out using DSC [13]. Studies are performed under an inert atmosphere at 10°C/min scan rate and a temperature ranging from 30°C up to 600°C. A 10 mg powdered specimen is used for each run. Thermograms are plotted recording weight change with respect to temperature change. Weight change results from bond-forming or breaking at elevated

temperatures. Throughout the experiment identical temperatures are maintained for the sample and reference. Heat capacity over a span of temperatures was examined. When the sample undergoes phase transition, heat is required to flow to it and the reference to sustain them at similar temperatures. Suppose as a solid sample changes phase to liquid it needs more heat flow to enhance its temperature at the same pace as the reference. DSC can estimate quantity of heat taken in and discharged in sample and reference by perceiving variation in heat flow. DSC can also perceive precise change of state, like glass transitions. It is extensively applied in industries as a quality checking instrument to estimate sample clarity and to observe curing of polymers.

To analyze the chemical resistance of the composites, ASTM 543–87 test methodology is employed. Standard reagents are applied to confirm outcomes. In the existing work, tests on epoxy/UP/clay composites are conducted to identify the resistivity to chemicals. The reaction of acids, alkalis and solvents on the composite are studied. In each case, pre-weighed specimens (5 x 5 x 3 mm) of 10 numbers were dipped into the respective chemical reagents for twenty-four-hour duration.

2.2 Thermal properties

The thermal properties analysis like TGA and DSC are performed on clay-filled epoxy/UP blended composite as per ASTM E1131 and ASTM D3418 respectively. The properties like degradation temperature and glass transition temperature are studied. In TGA, the heat stability of composite is studied as % weight loss v_s temperature.

2.3 Resistivity to chemicals

ASTM 543–87 is employed to evaluate the chemical resistivity of the composite. In the present work, chemical resistivity tests on epoxy/UP/clay composites are conducted. In each case, ten specimens are tested. Pre-weighed specimens are dipped in chemical reagents for 24 hours. They are then removed from the chemicals, cleaned in distilled water, and completely dried at room temperature using filter paper. The specimens are again weighed and the % gain/decrease in weight is ascertained as shown below.

$$\% \text{gain / decrease in specimen weight} = \frac{\text{Original weight} - \text{Final weight}}{\text{Original weight}} \times 100 \quad (1)$$

The chemical reagents used in the study are mentioned below:

Acids: Acetic acid, Nitric acid and Hydrochloric acid.

Alkalis: Sodium hydroxide, Sodium carbonate and Ammonium hydroxide.

Solvents: Benzene, Toluene, Carbon tetrachloride and Water.

2.4 Results and discussions

2.4.1 Thermogravimetric analysis

Heat stability of composites is analyzed using TGA. **Figure 1** indicates the weight loss of five different samples. In pure blend, loss in weight is constant up to 200°C and degradation starts at 400°C. As clay content is increased to 5 wt. % degradation temperature of the composite shifts upwards to higher temperatures. Until 350°C Weight loss is constant for 5 wt. %. Presence of moisture is the cause

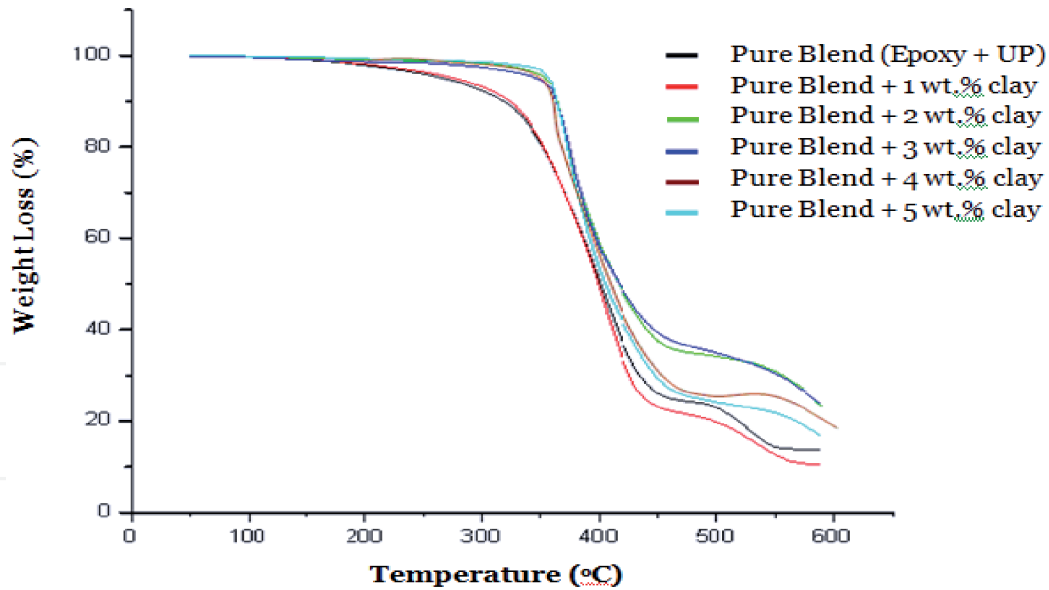


Figure 1.
Epoxy/polyester as a function of MMT clay-TGA.

for drop in weight for 1 wt. % sample. Evidently, the degradation temperature of the composite shifts upwards to elevated temperatures, demonstrating enhanced heat stability for 5 wt. % clay [12, 13]. Presence of inorganic materials like clay is the cause for improved heat stability.

In comparison to pure blend 15% weight loss and a 10° C rise in degradation temperature are observed for 5 wt. % sample. The results indicate that better dispersion of polymer and clay are the reasons for higher heat stability [13].

2.4.2 Differential scanning calorimetry

DSC investigates the thermal transitions of the pure polymer and the composites. A graph indicating glass transition temperatures for diverse clay weight percentages viz. for 0, 1, 2, 3, 4 and 5 wt.% at 430, 432, 433, 433, 431 and 429°C respectively of the composite is presented in **Figure 2**. A fall of 2°C glass transition temperature is noticed for 4 wt%., whereas a fall of 4°C is observed for 5 wt.% in comparison to 3 wt.%. Nil change is perceived for 2 and 3 wt. % samples. Similar changes in T_g are due to: (i) better surface interaction strengthening the interface (ii) enhanced interfacial free volume due to the lower bulk crystallinity of polymer chains. It is also found that the T_g of the Epoxy/UP composite decreases at higher montmorillonite loading.

2.4.3 Chemical resistance measurement

From **Table 1** it is evident that the Epoxy/UP/MMT clay composite exhibits better resistivity to all chemicals considered for the study, except the solvents. In each case, the pre-weighed specimens are immersed in the chemicals, cleaned in distilled water and then dried. 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 composites prove to be having good resistance to attack from chemicals except solvents. The highly expandable montmorillonite clay has caused maximum swelling in nitric acid in contrast to maximum weight loss in benzene due to its high cation exchange capacity. The increase in weight of the composite is due to the penetration of the liquid chemical resulting due to swelling of composite [14].

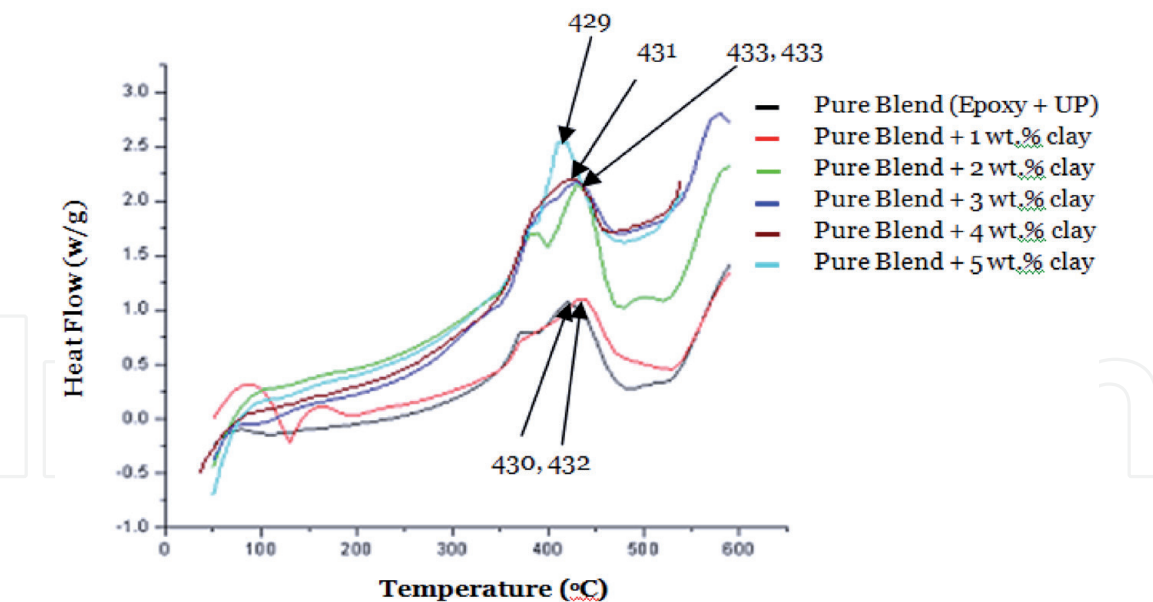


Figure 2.
Epoxy/polyester blend as a function of MMT clay-DSC analysis.

Chemical used	Clay (wt. %)					
	0%	1%	2%	3%	4%	5%
HCl (10%)	+1.327	+0.925	+0.845	+0.455	+0.535	+0.576
CH ₃ COOH (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 ₂ CO ₃ (20%)	+0.326	+0.320	+0.250	+0.167	+0.152	+0.144
NH ₄ OH (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
Water	+0.909	+1.325	+9.352	+11.526	+10.457	+9.348

Table 1.
Experimental values, showing percentage change in weight of epoxy/UP/MMT clay composite

2.5 Conclusions

In the experimental analysis of thermal and chemical resistivity of MMT clay strengthened composite, the following conclusions were made.

From TGA it was observed that clay content does not affect the heat stability at 5 wt.% in comparison to pure and other combinations blends. A weight loss of 15% and rise of 10°C in degradation temperature were noticed in the TGA analysis, while 4°C fall in *T_g* is noticed in differential scanning calorimetry analysis for 5 wt.% clay combinations. The heat properties of the clay-filled composite are perceived to increase gradually and are observed to be the highest at 5 wt.% in comparison to other variants. The presence of clay, in the composite, improves the heat stability of the composites [11–13].

From DSC analysis it was observed that the glass transition temperature (*T_g*) of blended nanocomposites varied for 0, 1, 2, 3, 4 and 5 wt% clay contents at 430, 432,

433, 433, 432 and 429°C respectively. A 2°C decrease in glass transition temperature is observed for 4 wt% clay filled samples while 4°C decrease in glass transition temperature is observed for 5 wt% clay filled samples when compared with 3 wt% clay samples, where as no change is observed between the 2 and 3 wt. % clay samples. A 4°C decrease in glass transition temperature is observed for 5 wt% clay when compared with 3 wt% clay samples, where as no change is observed between the 2 and 3 wt% clay samples. The reduction in the values of T_g for unsaturated polyester toughened epoxy system may be due to the flexibility imparted by unsaturated polyester to the epoxy matrix [15].


The composite blend specimens show a weight reduction on treatment with solvents. This is understandable as Unsaturated Polyester (UP), that is present in the blend, dissolves in the solvents under study. The composite has good resistance to attack from acids and alkalis. The highly expandable montmorillonite clay has caused maximum swelling in nitric acid in contrast to maximum weight loss in benzene due to its high cation exchange capacity. The enhancement in weight of the composite is due to the penetration of the liquid chemical in the composite; resulting in swelling [14]. The epoxy/UP/clay composite can be used for applications like a) charge storage containers in vehicles (Nanoclay limits the diffusion of solvents into polymer) b) chemical containers (as the composite has good resistance to chemicals) and c) fire proof cables.

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