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PREPARATION, MECHANICAL AND THERMAL CHARACTERIZATION OF ISOPHTHALIC POLYESTER- CLOISITE15A NANOCOMPOSITE

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ABSTRACT

Development of polyester nanocomposites for improved mechanical and thermal performance is the topic of the paper. The mechanical properties such as tensile modulus, impact strength and flexural modulus for different nanofiller content have been determined. All these have been found increased with the addition of nano filler. Dynamic mechanical behavior of the material has been analyzed from -20°C to 120°C. The thermal resistance has been studied by TGA. The study shows that the desirable reinforcement of the polymer occurs mostly in the range of 0.5 to 1.5 wt % clay content.

Key words: nanocomposite, reinforcement, tensile modulus, impact strength, flexural strength, storage modulus, loss modulus, loss weight, derived weight.

1. INTRODUCTION

The right material is necessary for any technological development. Composites represent the most advanced and adaptable of all engineering materials available because of its wide applications. Nanofillers have now emerged as the ultimate reinforcing fillers [1]. Composite materials have been extensively used in areas like aerospace, aircraft, sports and military industries. Advanced composite materials have progressed from a laboratory curiosity to a production reality. Composites have demonstrated weight savings for aircraft structures and outstanding corrosion and fatigue-damage resistance. Commercial aircraft applications have ranged from small flight-control surfaces to more and more primary structures [2].

Polymers filled with Montmorillonite (MMT) clay have attracted significant interest in the past decade. Homogeneous dispersion of the nanoclay in the polymers is the most serious challenge and main step in the synthesis of nanocomposites. Depending on the physical state of the polymer, different processing methods are used, such as in situ polymerization, high shear mixing, three-roll milling, and twin screw extrusion [3]. Mohan et.al.[4] investigated rheology and curing characteristics of epoxy-clay nanocomposites. Improvements in the interlaminar fracture toughness and flexural strength by the addition of nanoclays to polymer have been reported by researchers. About 38% improvement in flexural strength by the addition of 2 phr nanoclay to epoxy matrix had been reported. However, adding more clay (4 phr) leads to a drop in flexural strength. That means adding some clay can enhance the properties but adding more clay may not guarantee improvement. This is due to the increase in viscosity of the epoxy on the addition of the clay and the augmentation of the amount of air bubbles during the mixing process [5].

Studies on clay added polymer indicated that the increase in the fracture surface area due to crack deflection is the major toughening mechanism in the clay/epoxy nanocomposite. When the clay particles are intercalated into the resin the potential toughening effect improved significantly as the fracture surface area becomes larger. It has been suggested

that the exfoliated structure mainly leads to an improved modulus, while the remaining stacked structure of intercalated clay platelets is the key to improve toughness [6-9].

Improvement in the stress intensity factor noticed with nanoclay content for DGEBA- MMT clay composite with modified and un modified MMT. The improvement in the elastic modulus also reported but the failure strength and strain decreased [10]. Improvement of fracture toughness and tensile strength by the addition of clay and reactive functionalized engineering polymer to epoxy resin were also reported by many researchers. But the impact strength has been decreased [11-21].

Studies on epoxy/ABS/ TiO_2 system proved that the impact and tensile strengths of the hybrid having similar TiO_2 content were increased with increasing ABS content to 4% and decreased with higher loadings. For specimens with similar ABS content, the impact and tensile strengths were increased with increasing TiO_2 content up to 6% and decreased at higher loadings. Combination of layered and particulate nanofillers had synergistic effect on impact and tensile strengths of the epoxy polymer [22]. Generally the impact strength may increase by the presence of fibers. The presence of filler can impede crack growth due to the possibility of imposing a greater tendency for plastic deformation in the matrix. [23]

Hence the increasing demand for the high performance materials can be met by the performance improvement of an easily available low cost polymer such as polyester. The goal of this paper is to analyze the mechanical and thermal characteristic of the polyester to suggest the method for the modification of its characteristic. One of the methods to modify is the addition of nanofiller is proposes to provide mechanical and thermal property enhancement.

2. EXPERIMENTAL

2.1 Raw Materials

Isophthalic polyester resin with cobalt naphthanate as the accelerator and methyl ethyl ketone peroxide (MEKP) as the catalyst were used. The clay was made into dispersion with styrene and then the dispersion was added to the polyester resin for modification. Cloisite15A, quaternary ammonium modified montmorillonite was used as the filler.

2.2 Material preparation

Test specimens for mechanical testing as per ASTM standards were prepared by casting in a Teflon mould. Initially the clay was kept in a microwave oven for 24 hours at a temperature of 80 °C to remove the moisture. For the preparation of polyester/clay nanocomposite, the polyester resin was mixed mechanically with desired amount of clay and the mixture was stirred well for 20 to 30 minutes by using mechanical stirrer. Then the mix is sonicated for 10 to 20 minutes by using an ultrasonicator. The mix kept in an ice bath to prevent the overheating during the ultrasonication process. The mixture was degassed and cooled in a water bath. Then a certain amount of reagents such as cobalt naphthanate and methyl ethyl ketone peroxide were added and mixed thoroughly. The mixture was poured in to a Teflon mould prepared for the specimen for tensile test, flexural test and impact test as per the ASTM standards. Then it was kept undisturbed for 24 hrs for proper curing. Specimens have been prepared by varying the clay content from 0 to 2 % by weight of the polyester resin. Similar procedure has been adopted by Mirmohseni et.al. [22].

2.3 Characterization

2.3.1 Mechanical characterization

Tensile test was carried out by a universal testing machine as per ASTM D 638-03. The parameters considered for tensile test were cross head speed (CHS) and percentage composition of the filler. For finding the effect of loading rate three test speeds: 0.5 mm/min, 5mm/min and 50 mm/min were used. The experiment conducted for five specimens of each category viz pure polyester (0% Cloisite 15A), 0.5 %, 1%, 1.5 % and 2 % filler incorporated samples.

The specimen prepared as per ASTM: D6272-02 was used for flexural test. The test was carried out in universal testing machine and done at loading rate, i.e. Cross Head Speed (CHS) 0.5 mm/min, 5 mm/min and 50 mm/min. The experiment conducted for 5 specimens prepared under identical condition for each category.

The impact property was determined by Izod impact test as per ASTM D 4812-99. Here also the specimen prepared from samples with pure polyester, 0.5 % Cloisite15A filled, 1 % Cloisite15A filled, 1.5 % Cloisite15A filled and 2 % Cloisite15A filled. Five samples of each category were experimented.

2.3.2 Thermo mechanical Properties

Dynamic mechanical analysis (DMA) and Thermogravimetric analysis (TGA) have been conducted for the specimen with 0, 0.5, 1, 1.5 and 2 % by weight of Cloisite15A. The DMA was done in the temperature range from -20 °C to 120 °C in dual cantilever configuration at frequency 1 hz. The properties like storage modulus, loss modulus and

damping coefficient $\tan \delta$ were studied with respect to the temperature variation. TGA data obtained are the variation of weight and derived weight with respect to the temperature.

Table 01: Tensile test results

% weight of filler	CHS = 0.5 mm/min		CHS = 0.5 mm/min		CHS = 0.5 mm/min	
	Tensile Strength in MPa	Tensile Modulus in MPa	Tensile Strength in MPa	Tensile Modulus in MPa	Tensile Strength in MPa	Tensile Modulus in MPa
0	37.48	918.99	30.24	1505.59	34.51	2002.67
0.5	27.44	1148.41	29.95	2109.53	33.80	2507.14
1	32.05	1039.53	27.97	2091.86	24.06	2092.19
1.5	34.09	1032.45	37.95	1217.10	29.40	1379.80
2	25.10	932.17	25.60	946.11	24.76	1264.86

3. RESULTS AND DISCUSSION

3.1 Tensile test

Fig-1 shows the tensile test results. The tensile modulus improves with increase in clay content, reaches a maximum value and thereafter decreases. The value of tensile modulus increases by 20 to 30 % at a clay content of 0.5% by weight of resin for all loading rate. The maximum value is noticed with clay content of 0.5 – 1 wt%. Further increment of clay content causes the tensile modulus to decrease. At the lower percentage of filler content, it will disperse properly in the polyester and will act as a reinforcing agent. However at high filler content the proper mixing of the filler in the polyester medium become too cumbersome because of the increase in viscosity of the mix, which will cause agglomeration of the clay platelets and create more voids. Consequently there is the possibility for the decrease in value of tensile modulus at higher filler content. The maximum tensile modulus of the material is obtained at the maximum testing speed as expected. With the addition of clay above 1 wt%, the tensile modulus showed a decrease.

The improved modulus can be directly ascribed to the stiffening effect of clay fillers since the clay has a higher modulus than polyester. However, the limited improvement in some cases may be related to the microstructures formed under the present processing conditions. Also at increased level of clay content the decrease of stiffness can be attributed to the improper dispersion, agglomeration of clay platelets and formation of voids [10]. The tensile modulus showed a higher value at higher loading rate i.e. Cross Head Speed, CHS = 50 mm/min is an indication of the capacity of the material to carry impact load rather than gradually applied load.

Table 02: Impact test results

Wt% of filler	Impact energy in J/m	Impact strength in kJ/m ²
0	44.32	3562.88
0.5	68.70	5522.66
1	81.58	6558.49
1.5	84.93	6827.60
2	79.18	6365.38

The value of tensile modulus obtained is high for CHS 5 mm/min and 50 mm/min as compared to CHS 0.5 mm/min. The effect of the addition of filler in polyester resin for its improvement in tensile modulus is much more evident in high loading rate as compared to low loading rate. The nature of loading at low CHS is gradually applied and leads to the failure mode as ductile for the composite. But a sudden application load during the CHS 5 mm/min and 50 mm/min induce a brittle nature of failure with un due delay in loading. Consequently the tensile modulus found high for high CHS.

Figure 01: Variation of Tensile modulus with wt% of Cloisite15A

Table 03: Flexural Test results

% weight of filler	CHS = 0.5 mm/min		CHS = 5 mm/min		CHS = 50 mm/min	
	Flexural modulus in MPa	Flexural Strength in MPa	Flexural modulus in MPa	Flexural Strength in MPa	Flexural modulus in MPa	Flexural Strength in MPa
0	3829.42	79.28	4032.05	78.68	4715.76	69.45
0.5	4639.18	68.44	4875.72	71.56	4877.10	62.84
1	5116.62	63.77	5123.97	67.74	5265.57	61.99
1.5	5261.28	68.78	5585.54	62.81	5395.61	63.46
2	5833.7	66.39	5934.23	67.49	6135.12	60.64

3.2 Impact test

The impact strength is also found to increase significantly (from 3562.88 kJ/m² for pure polyester resin to 6827.6 kJ/m²) by the incorporation of 1.5 wt% Cloisite15A, while the impact strength decreased for higher filler loading. The impact strength increased to about 50 to 110 % with the addition of 0.5 to 1.5 wt% clay. The increasing trend continues only up to 1.5 wt% filler and further it is decreasing. The reduced strength at higher wt% may be caused due to the weakening of the clay matrix interface because of the improper dispersion and agglomeration. Also with increase of clay content there is the possibility for the formation of voids due to the improper dispersion, which also causes the weakening of interface, makes the crack formation easy and hence the reduction of impact strength[11]. The brittle nature of failure due to impact load also contributed to reduced impact strength at high filler content.

Fig: 02, Variation of impact strength with % weight of Cloisite15A

Fig 03: Variation of Flexural modulus with % weight of Cloisite15A

3.3 Flexural Test

The flexural modulus showed a continues improvement with increase in clay content as in the case of tensile modulus for CHS 0.5 mm/min and 50 mm/min. However there is a short fall of flexural modulus value for 1.5 % filler content when CHS = 5 mm/min. The flexural strength decreased with increase of filler content. A maximum of 79.28 MPa is observed for pure polyester and minimum of 60.64 obtained for 2 % filler content. The flexural modulus increases for smaller filler concentration where at higher filler concentration i.e. to 2% by weight of filler content it does not show as much as increase in its value for 0.5% filler content. At smaller particle content the interaction of the particle with the matrix will be higher and the agglomeration will be less which will be responsible for the high flexural modulus value. However at high filler content the possibility for the agglomeration reduces the strength and stiffness [24]. Indifferent from impact loading the ductile nature of failure during flexural loading may be the reason for the sustainability with the hike of flexural modulus. For a solid conclusion more analysis are required

3.4 Dynamic Mechanical Analysis (DMA)

The comparison of storage modulus shows that by the addition clay there is an increase of storage modulus initially, but the value is decreases with further increase of clay content. The initial increase can be attributed to the property of the clay to act as reinforcement to some extent. But further addition may create agglomeration of clay particles, which reduces the strength. Up to 35 °C there is only a very little change in the storage modulus. After that the rate of decrease in storage modulus is high. This is due to the weakening of intermolecular bonding in the polymeric matrix with the increase of temperature. The $\tan \delta$ value of pure polyester is approximately 0.5 and on increasing the filler $\tan \delta$ values increase up to 0.8 in different cases. Filler can induce damping of vibrations due to scattering and assist in dissipation of energy within the matrix. The temperature at which maximum damping occurs (Glass Transition ' T_g ') also comes down with increase of filler content.

Figure04: Results of Dynamic Mechanical Analysis
 (a) Variation of Storage modulus, (b) Variation of loss modulus and
 (c) variation of $\tan \delta$ with temperature

Thermo gravimetric analysis

The plot of temperature vs. weight% in fig. 05 shows that the degradation starts at 320 °C. There is no remarkable variation of degradation temperature with the addition of clay. The second step portion of all curves extends from 400 °C to 450 °C, which is the degradation of styrene which added with the polyester. The second peak shown in fig:05 (b) corresponds to this, which extends for 10 to 15 % weight loss. Hence the clay particles can be used for the enhancement of mechanical properties without affecting the high temperature properties

Figure 05: Results of Thermo gravimetric analysis, (a) variation of weight loss with temperature, (b) variation of derived weight with temperature.

4. CONCLUSIONS

The following conclusions can be drawn by the study.

1. The tensile modulus appreciably improve by the modification by a small quantity of Cloisite15A
2. The tensile modulus increases with testing speed
3. The impact strength increases with increase in clay content and maximum value is obtained with nearly 1.5% clay content.
4. The flexural modulus improves with clay modification.
5. The storage modulus increases with the addition of clay in the range 0.5 to 1 %.
6. Thermo gravimetric analysis show that the thermal degradation starts at around 320°C for the pure polymer and the composites.

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