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Original Article

Effect of Particulate Fillers on the Mechanical, Thermal, Moisture and Fire Performance of Unsaturated Isophthalic Polyester/Glass Fibre Reinforced Polymer Composites

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Abstract

The fly ash and talc powder produced from the various industrial activities will be hazardous material for the environment. The waste should be used carefully to eliminate environmental pollution. The objective of this research was to investigate the mechanical, thermal, moisture and fire performance of the fly ash and talc dispersed glass fibre reinforced unsaturated polyester composites. The unsaturated polyester composites were made by using a press mold method for 0, 20, 40, 60, 80, and 100 % of fly ash and talc content (w/w). The Vickers hardness showed the maximum hardness value for FCP4 type of composites. The DSC thermo grams illustrated that the increased glass transition temperature (TG) for FCP3 type of composites.

The chemical resistant test was showing the excellent results on all types of fly ash and talc dispersed glass fibre reinforced unsaturated polyester composites. The fire performance test was performed by according to UL-94 standard. The fire resistance increases with the increasing of fly ash content. The longest burning time occurs on the composite containing the highest fly ash content (100% of fly ash content).

Key Words: Unsaturated Polyester, Fly ash, Talc powder and Fire retardancy.

1. Introduction

Fibre reinforced polymer (FRP) composites with particulate fillers have created huge interest basically due to their potential in improving the mechanical, thermal and fire properties and also cost reduction. Although the use of fillers in polymer industry has been known for past several decades, there is still a considerable interest from both industry and academia for the development of composite materials with improved properties. However, to widen the range of applications of the polymer in engineering and structural applications, demands extensive knowledge of all the factors that determine final properties of polymeric composite materials of various applications. Industries are very interest to apply the materials because of their unique characteristics [1-2].

Recently thermosetting resins have received increasing attention from industry. Unsaturated polysters are extremely versatile in properties and applications and have been used as a polymer matrix in composites, such as FRP’s. Unsaturated polyester resins are widely used in a host of application where advantage may be taken of their good range of mechanical properties, low cost, good corrosion resistance and low weight [3-5]. There is an increasing interest to recycle the industrial by-products that have been discarded from the different industries. Coal-burning power stations generate amount of fine powder by-product, famously known as fly ash (FA).
When dry season, the fly ash can be carried by the wind, and when rainy season, it can be carried by water causing soil pollution. As the fly ash is produced in high capacity, the negative effect caused by the fly ash is difficult to be protected. It can also cause the decreasing of some ecosystem. A lot of the fly ash has been been used in other industry, like cement industry. The fly ash is classified into small size powder, containing more than 80% of silicate and alumina oxide. According to the problem, engineers and scientists should have responsible to research the useful of the fly ash for making other engineering product [6-7]. The preservation and managing of FA and Talc are challenging tasks that affect the cost effectiveness of the pertinent industries. The landfill method is mainly used to dispose FA in ash dams and lagoons. Research on recycling and reuse of FA has lately become an interesting field of study in the promising markets for green and eco-friendly manufacturing processes and products [8].

Talc is used as filler at different weight percentages in composite to modify the properties of composites. An important benefit of using fillers is the reduction of cost by replacing portion of polymer with a less expensive material. It has been reported that the fracture surface energies of polyester resin and epoxy resin and their resistance to crack propagation are low [9-11]. But if particulate filler is added to these resins, the particles inhibit crack growth. The resulting mechanical properties of composites generally depend on the filler’s nature, size and distribution, aspect ratio, volume fraction, and the intrinsic adhesion between the surfaces of filler and polymer [12-15].

Review of literature indicated that the increasing interest to recycle the industrial by-products that have been discarded from the different industries. The objective of this current research was to investigate the mechanical, thermal, moisture and fire performance of the fly ash and talc dispersed glass fibre reinforced unsaturated polyester composites.

2. Experimental
2.1 Materials
The unsaturated polyester resin used in this study was supplied by Suntech Fibers Ltd, Vasanth Nagar Bangalore. The curing agents used were cobalt napthenate, di-Methyl acetamide and methyl ethyl ketone peroxide supplied by MP Corporation, Bangalore. The Fly ash and talk powder were collected local industries of Bangalore. The Glass fibre 360 gsm coated with an emulsion based sizing agent, plain-woven fabric type was supplied by Vietrotex, India respectively.

2.1.1 Fly ash
Fly ash is the finely divided mineral residue resulting from the combustion of coal in electric generating plant. Fly ash consists of inorganic matter present in the coal that has been fused during coal combustion. This material is solidified while suspended in the exhaust gases and is collected from the exhaust gases by electrostatic precipitators and is usually of silt sizes (0.074 - 0.005mm). Fly ash is a pozzolanic material and has been classified into two classes F and C based on the chemical composition of fly ash. In the present study class C fly ash was used.

Class C fly ash is produced normally from lignite and sub-bituminous coals. The technical specifications of fly ash used in this work are given below:

- Silicon dioxide (SiO₂) plus aluminum oxide (Al₂O₃) plus iron oxide (Fe₂O₃): 55.0%
- Sulfur trioxide (SO₃): 5.0%
- Moisture content: 3.0% max.
- Loss on ignition: 6.0%

2.1.2 Untreated talc
These purer forms are called steatite talk’s. Commercially important deposits are also found in altered ultra-basic igneous rocks. After purification, the material is ground and screened about 200 to 300 meshes (median diameter: 2.39 μm, density: 2.78 g cm⁻³ and specific area: 10.9 m² g⁻¹).

2.2 Fabrication of Fly ash / Talc powder / Polyester/ Glass composites
The Fly ash / Talc powder was dispersed in polyester resin using tip ultrasonicator. The frequency and duration of ultrasonication were 37 KHz and one hour respectively. The dispersed resin is mixed separately using 2 wt % each of Di-Methyl acetamide as promoter, Cobalt naphthalate as accelerator and methyl ethyl ketone peroxide (MEKP) as catalyst at room temperature. After thorough mixing poured in to the mold and allowed it for curing, after 24 hours the solidified pure resin panels were removed and kept in hot oven at 70°C for 1 hour, later removed from the oven and allowed at room temperature. The FRP composites are fabricated according to wet hand lay-up technique maintaining fibre to resin ratio of 65:35 by wt %. The Specimen prepared with different weight ratios with code mentioned in the below.

2.3 X-Ray Diffraction and Particle Size Studies
X-Ray diffraction study was carried out using a high resolution X-ray Diffractometer (Shimadzu 700 S supplied by Japan) at a scanning rate of 2° min⁻¹ using CuKα radiation operating at 45 KV and 40 mA. Particle Analysis was performed using Model NPA152-31A Zetatrac Supplied by Microtrac, USA. Light scattering particle size technology measurement range size 0.8 to 65 microns, measurement angle 180 degrees Zeta Potential range from -125 to +125 mV.

2.4 DSC of Fly ash and Talc filled polyester composite
The particulate filled polyester specimens were characterized for glass transition temperature, Tg using DSC (Mettler DSC-823, temp range: 25°C to 300°C). A sample of weight 5 mg sealed in a hermetic aluminum crucible was used for the characterization. For obtaining the curing heat flow pattern of the composite, a dynamic scanning experiment was conducted from 25 °C to 200 °C at a heating rate of 20 °C per minute in N₂ atmosphere with a flow rate of 20 ml/min.

2.5 Mechanical Properties of Fly ash and Talc filled polyester glass composites
The specimens were tested for flexural properties as per ASTM D 790. Flexural testing was done in a 3-Point Bending configuration, using specimens 80 mm × 8 mm × 3 mm. The tensile specimens 208 × 12.7 × 3 mm with a gauge length of 90 mm were tested as per ASTM-D 3039 using a cross head speed of 1 mm/min. Tensile and
Flexural tests were performed in a 10-ton capacity computer controlled high precision UTM, supplied by Kalpak Instruments and Controls, Pune, INDIA. Low velocity impact tests were performed as per ASTM D-256 on un-notched specimens 64 × 12.7 × 3 mm at a hammer velocity of 111.4 mm/s using an instrumented impact tester supplied by M/s International Equipment Ltd., Mumbai. The Izod test specimens were clamped in an upright position so that the end of the specimen faced its striking edge and impact energy absorbed for breaking the specimen was directly obtained.

2.6 Fracture Surface studies
The tensile fractured surfaces of specimens were studied using Scanning Electron Microscopy (SEM) (JEOL, Japan, JSM 840A). The interfacial bonding and the modes of failure in the specimens were studied using the SEM micrographs.

2.7 Fire Retardation of Fly ash/Talc/Polyester/glass composites
The GFRP specimens of size 125 mm x 13.3 mm x 3 mm were tested for flammability according to UL 94 VB and UL 94 HB for obtaining horizontal and vertical burning rates respectively. For horizontal direction the test burner is ignited to produce 25.4 mm high blue flame. The specimens are exposed to 6.35 mm deep flame for 30 seconds without changing the position of the burner. Then the specimen is distanced from the burner. If the specimen burns to the 25.4 mm mark before 30 seconds the flame is withdrawn. If the specimen continues to burn after the removal of the flame, the time for the flame front to travel from the 25.4 mm mark to the 101.6 mm mark from the free end is determined and rate of burning is calculated. For vertical burning rate test a small 19.05 mm high blue flame is applied to the bottom of the specimen for 10 sec, withdrawn and then reapplied for an additional 10 sec. The duration of flaming and glowing is noted as soon as the specimen is extinguished. A layer of cotton is placed beneath the specimen to determine whether the dripping material ignites it during the test period.

3. Results and Discussion
3.1 X-Ray Diffraction and Particle Analysis of Fly ash and Talc Powders
Results of the constituent phases of FA obtained by XRD are shown in Fig.1. Comparison with standard reference by search and match method using X-Pert software indicates the contents of FA to be 68.7% orthorhombic mullite (aluminium silicate, 3Al2O3·2SiO2) (essentially a type of glass), 23.2% hexagonal quartz (silicon oxide, SiO2), and 8.1% of hematite (Fe2O3). The QEMSCAN simulation analysis revealed that FA contains 70% aluminium-silicate mullite and 10% silica phase, with various metal oxides constituting the balance. It may be noted that mullite basically, is not a major ingredient in coal. It forms in the process of thermal decomposition of natural mineral kaolinite present in coal by a series of chemical reactions [8, 11]. Results of the constituent phases of Talc obtained by XRD are shown in Fig.2. Utilizing the monoclinic indexing for talc the angular range that was scanned included the reflections. Although the latter three peaks are highly overlapping, choice of this range was partially based...
Fig. 4. Differential Scanning Calorimeter Thermograms of different wt% samples to the presence of silicate leading to better dispersion and exfoliation. Also, the interaction of silicate and the polyester resin network restricted the segmental mobility and thus resulted in higher Tg. Increase in Tg was around 36% for FCP6 sample.

4. Mechanical Properties

4.1. Microhardness or Vickers hardness test

Hardness of a material is defined as the resistance to deformation, particularly permanent deformation, indentation or scratching. As shown in Fig. 5, Vickers hardness increased by 11.8, 12.2, 13.1, 13.7, 14.5 and 15.3 with the addition of 0, 20, 40, 60, 80, and 100% of fly ash and talc content (w/w) respectively to polyester. In order to provide reliable hardness values corresponding to the total hardness of the nanocomposites, the imprints under each load should be larger in size than the dimensions of the dispersed intercalated structures. The maximum Vickers hardness increased by 15.3 in FCP6 sample. This may be because the intercalated/exfoliated silicates formed network like structure with polyester molecules when effectively restricted the indentation and leading to superior microhardness.

Fig. 5. Vickers Hardness No. of different wt% particulate filled polyester composites

4.2. Tensile and Flexural behavior of Fly ash/Talc/Polyester/Glass Composites

The improvements in mechanical properties are attributed to the dispersion of particulate fillers and the interfacial adhesion between polyester matrix and fillers so that the mobility of chain matrix is restricted under loading. The strong interfacial interaction that exists in the composites may also restrict the mobility of the matrix in the interface between the fiber and the matrix or between talc silicates and the matrix allowing better stress transfer to the glass fibers inside the composite. Dispensing beyond 60 wt% of talc in polyester was difficult due to increase in viscosity resulting in the formation of agglomerates, which acted as stress concentration and crack initiation sites. Therefore ultrasonic separation techniques only cannot be effectively used to create good dispersion of fillers when higher levels of loading is to be included in polymers. In general, however, addition of low and medium levels of fillers as reinforcing materials in polymer matrix using this existing method has produced encouraging results. The UTS results shown in Fig. 6. And flexural strength showed in Fig. 7.

Fig. 6. Ultimate Tensile Strength of Different Wt% of samples

Fig. 7. Flexural Strength of Different Wt% of samples

4.3 Impact strength of Fly ash/Talc/Polyester/Glass Composites

The fly ash/talc/polyester/glass composites good increase in impact energy due to the dispersion of fillers by wt% respectively as shown in Fig. 8. The increase in impact energy for FCP4 samples is due to improved interfacial bonding between the fibers and the matrix modified by fly ash and talc. The drop in impact energy at FCP5 and FCP6 samples was mostly due to the voids existed inside the nanocomposites. These might have been created while dispersing fillers in the resin with the hardeners. It was because when the filler loading levels increased, the material itself became too viscous and sluggish. Viscosity of the resin mixture increased with increase in filler loading, once the hardener was added to the premixed filler/polyester, big bubbles were easily created and trapped inside the sluggish mixture, which were permeated to the entire volume increasing the number of voids. Later on,
when it was tested for impact behavior the bubbles inside could not withstand the force and the same might have initiated cracks to propagate throughout the sample.

### 4.4. Morphology study using fractured tensile specimens using SEM

Tensile fractured surfaces were examined using SEM. In Fig.9 all samples shows reasonably good fibre matrix bonding between polyester and glass. The fractured surfaces show fibre breakage and some amount of fibre pull out. FCP3, FCP4 and FCP5 show good dispersion of fillers in polyester without any agglomerates. Fillers are found adhered to the fibre and fibre breakage is dominantly observed in the micrographs. Especially in FCP4 sample pertaining to 60% talc/polyester/glass show good interfacial bonding between polymer and the fibre. These micrographs also evidence fibre breakage and absence of filler agglomerates. Fillers are found uniformly distributed and adhered to polyester and glass. Micrograph pertaining to FCP6 show greater amount of agglomerates causing stress concentration sites resulting in drop in mechanical properties. Clusters of fillers are found everywhere surrounding the fibre and sudden failure of tensile specimens evidenced brittle failure.

### 5. Chemical Resistant Test

The effect of chemical exposure for different weight percent of composites shown in Table.2. and Fig.10. The maximum moisture absorption was found in talc/polyester composites and the least moisture absorption was in the samples of fly ash/polyester based composites, this is because the talc is a type hydrophilic in nature it will absorb more number of moisture content in to it, but the fly ash is hydrophobic in nature it will repels the moisture content prevents the water penetration into the composite. The matrix degradation is more in case of maximum days because of more moisture absorption takes place in case of long duration. This is due to moisture environment aging of polymers may create damage in the form of crazing, micro cracking and other types of morphological changes, thus allowing additional moisture absorption to occur. Especially in the case of organic liquids degrades the more polymer matrix resulting in the negative weight of the composites this is due to the rich number of polar groups present in the liquids. In case of bases of high pH may create damage in the form of crazing, micro cracking and other types of morphological changes, thus allowing additional moisture absorption to occur. On the other hand, immersion time increased, fewer hackles can be seen at the fiber micro cracking and other types of morphological changes, thus allowing additional moisture absorption to occur. The voids present in the matrix are the main reason for moisture diffusion. The micro cracks formed during the composite preparation or by the service condition can store the trapped water.

### 6. Fire Retardation Behavior Using Horizontal and Vertical Burning Rates

The fire retardation of fly ash/talc/polyester/glass improved monotonically with increase in filler loading from FCP1 to FCP6. The results of vertical and horizontal burning rates are presented in Fig. 11. The FCP 6 samples showed maximum decrease in VBR and HBR of compared to that of polyester/glass. The formation of a surface layer during pyrolysis of the nanocomposites was usually considered to be the main reason for improved fire retardancy. This is because the layer acts as a heat barrier which preventing heat from transferring into unpyrolysed material. Also it increases the surface re-radiation heat losses with surface temperature. In this study it was also observed that the FCP, FCP1, FCP2 and FCP3 dripping material ignite the cotton which is placed below the setup and for FCP4, FCP5
Table 1: Specimen prepared with different weight ratios with code

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>% Wt. ratio</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Neat matrix</td>
<td>FCP</td>
</tr>
<tr>
<td>2.</td>
<td>100 FA + 0 TC</td>
<td>FCP1</td>
</tr>
<tr>
<td>3.</td>
<td>80 FA + 20 TC</td>
<td>FCP2</td>
</tr>
<tr>
<td>4.</td>
<td>60 FA + 40 TC</td>
<td>FCP3</td>
</tr>
<tr>
<td>5.</td>
<td>40 FA + 60 TC</td>
<td>FCP4</td>
</tr>
<tr>
<td>6.</td>
<td>20 FA + 80 TC</td>
<td>FCP5</td>
</tr>
<tr>
<td>7.</td>
<td>0 FA + 100 TC</td>
<td>FCP6</td>
</tr>
</tbody>
</table>

Note: FA-Fly ash and TC-Talc

Table 2: The chemical exposure for different weight percent of composites

<table>
<thead>
<tr>
<th>Code</th>
<th>Benzene</th>
<th>Toluene</th>
<th>CCl4</th>
<th>Distilled water</th>
<th>10% NaOH</th>
<th>10% NH4OH</th>
<th>10% HCl</th>
<th>40% HNO3</th>
<th>20% Na2CO3</th>
<th>5% CH3COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCP</td>
<td>-1.3975</td>
<td>-0.5696</td>
<td>0</td>
<td>-0.1565</td>
<td>-0.0515</td>
<td>-0.8785</td>
<td>0</td>
<td>-0.3084</td>
<td>-0.3091</td>
<td>-0.3091</td>
</tr>
<tr>
<td>FCP1</td>
<td>-1.3947</td>
<td>-0.4816</td>
<td>-0.0601</td>
<td>-0.1214</td>
<td>0.4016</td>
<td>-0.8599</td>
<td>0.124</td>
<td>-0.5597</td>
<td>-0.1244</td>
<td>-0.1244</td>
</tr>
<tr>
<td>FCP2</td>
<td>-1.4501</td>
<td>-0.6365</td>
<td>-0.0577</td>
<td>-0.5837</td>
<td>0.2247</td>
<td>-0.7143</td>
<td>0.5069</td>
<td>-0.5736</td>
<td>-0.7677</td>
<td>-0.7677</td>
</tr>
<tr>
<td>FCP3</td>
<td>-0.9718</td>
<td>-0.6786</td>
<td>-0.145</td>
<td>-0.5859</td>
<td>0.1308</td>
<td>-0.6256</td>
<td>0.194</td>
<td>-0.3892</td>
<td>-0.3898</td>
<td>-0.3898</td>
</tr>
<tr>
<td>FCP4</td>
<td>-1.2724</td>
<td>-0.655</td>
<td>-0.1742</td>
<td>-0.1318</td>
<td>0.826</td>
<td>-0.5274</td>
<td>0.0441</td>
<td>-0.3097</td>
<td>-0.177</td>
<td>-0.177</td>
</tr>
<tr>
<td>FCP5</td>
<td>-1.7525</td>
<td>-0.7387</td>
<td>-0.2105</td>
<td>-0.1596</td>
<td>0.4724</td>
<td>-1.0565</td>
<td>0.2131</td>
<td>-0.3205</td>
<td>-0.5347</td>
<td>-0.5347</td>
</tr>
<tr>
<td>FCP6</td>
<td>-1.9351</td>
<td>-0.7046</td>
<td>-0.2158</td>
<td>-0.2744</td>
<td>0.5379</td>
<td>-1.0851</td>
<td>-0.0542</td>
<td>-0.271</td>
<td>-0.3806</td>
<td>-0.3806</td>
</tr>
</tbody>
</table>

Fig.11. Burning Rates of Different Wt% of samples

and FCP6 samples there is no dripping material ignites the cotton. From this we can come into the conclusion that the FCP4, FCP5 and FCP6 are the class of fire retardant grade composites compared to other samples in the study. The fly ash doesn’t showed an significant role in the fire retardation compared to talc. Adding talc to polyester/glass reduces the flammability and hence talc acts as a good flame retardant.

7. Conclusion

Influence of addition of particulate fillers to polyester on the thermal, mechanical, moisture and fire behaviour of polyester and polyester/glass was studied based on dispersion and characterisation experiments.

- XRD and Particle analysis results showed that the particle size of both fly ash and talc are in the rage of micron size.
- Addition of more and more talc in polyester increased the glass transition temperature and microhardness.
- Mechanical properties such as UTS, Flexural strength and impact strength of FCP4 showed improvements up to 60 wt % talc addition to polyester/glass.

- SEM micrographs evidenced that fillers had a tendency to form agglomerates when addition of more concentrations.
- The chemical resistance study revealed that the filler effect is poor when immersed in organic liquids.
- Fire retardation was monotonic with increase in filler concentration. The particulate filled polyester based nanocomposites, with their highly enhanced properties, can find applications in areas such as marine, automotive, aerospace and the like.

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9. References


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