

# Development of Stearic Acid Coated Fly Ash Reinforced Recycled Polypropylene Matrix Composites and their Thermal Analysis

Shubhalakshmi Sengupta, Pulakesh Maity, Dipa Ray, Anirudhha Mukhopadhyay

**Abstract**—The industrial wastes fly ash (FA) and polypropylene (PP) were used to develop novel green composites using a renewable, cheap coupling agent i.e. stearic acid. The fly ash (FA) particles were coated with stearic acid (SA) in different weight % like 0, 1, 2, 3 and 5. The SA coated fly ash particles were incorporated as filler in recycled polypropylene (RPP) matrix which was obtained from post-consumer plastic products by melt mixing in 1:1 weight ratio. The composites were tested for dynamic mechanical properties (DMA) and thermogravimetric analysis (TGA). The DMA results showed enhancement in mechanical properties indicated by the shift in the glass transition temperature to a higher value. In 1wt% SA coated FA/RPP (RFASA1) composites highest improvement in the dynamic mechanical properties were observed. Increase in thermal stability in the stearic acid treated composites was also witnessed. The RFASA1 composites showed a highest rise in the onset of thermal degradation temperature. The SA treated composites also showed a considerable increase in the activation energy values from that of 0 wt % SA treated FA/RPP (RFASA0) indicating their enhancement in thermal properties in presence of the coupling agent. Thus, an unconventional coupling agent stearic acid could be used in place of commonly used silane coupling agents to develop composite materials FA and RPP with tailor made properties.

**Index Terms** – Composites, Coupling agent, Dynamic Mechanical Analysis, Fly ash, Recycled Polypropylene, Stearic acid, Thermogravimetric analysis.

## 1. INTRODUCTION

Fly ash (FA) and polypropylene (PP) are industrial wastes which affect the environment of our planet. A proper management and commercial utilization of fly ashes will provide alternative value added products and also reduction of environmental and economic impacts from the cost of its disposal. Fly ashes are mainly by-products of the thermal power plants which are produced from the combustion of carbon and fossil fuels and are comprised of primarily of SiO<sub>2</sub> along with lower contents of Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, MgO, K<sub>2</sub>O etc. [1]. Attempts are going on in establishing fly ash as attractive mineral filler in various polymer matrix composites [1-3]. Earlier, a lot of studies were conducted on the mechanical properties of fly ash filled polymer matrix composites [4]. Sridhar et al. reported from the thermogravimetric analysis of fly ash / waste tire powder/ isotactic PP composites that there was a progressive increase in the activation energy of the composites with increase in fly ash loadings [3]. Pardo et al. reported that improved stiffness and strength of materials were observed when silane coupling agents of three types were used in mixing fly ash with isotactic polypropylene matrix along with improved thermal stability. This improvement was greater in the composites containing

vinyl and amino silane treated fly ashes, which showed higher onset temperature and was strongly dependent on filler-matrix adhesion [1]. Das et al reported utilization of recycled polypropylene by forming composites with fly ash in 1:1 weight ratio and using two types of coupling agents (vinyl trimethoxy silane coupling agent, VTMO and maleated polypropylene, Epolene G3003). Thermal stability was found to be much higher in the VTMO treated composites compared to the untreated ones [5]. In our earlier study, the mechanical properties of furfuryl palmitate coated fly ash reinforced recycled polypropylene matrix composites were reported [6]. In that earlier study it was found that the highest enhancement in mechanical properties was observed in 2 wt% FP (FP2) coated fly ash filled composites. In this study, stearic acid (SA) was used to coat the fly ashes and stearic acid coated fly ash was then used as reinforcement in RPP matrix composites. Mechanical and thermal properties of the composites were studied in order to analyze the efficiency of this low cost easily available organic acid as a coupling agent in FA/RPP composites. The composites were tested for their dynamic mechanical behaviour (DMA) and thermogravimetric analysis (TGA).

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## 2. EXPERIMENTAL

### 2.1 Materials

Fly ash used was collected from Kolaghat Thermal Power station, India. This ASTM class 'F' fly ash (as per ASTM-C 618) was found to have different proportions of oxides. The ash particles had a particle size distribution: 42 wt% of the particles had a particle size between 104 and 152  $\mu\text{m}$ , 25 wt% were between 76 and 104  $\mu\text{m}$  and the rests were below the range. Recycled polypropylene (RPP) was obtained from post-consumer plastic products and was used as the matrix material. Stearic acid and the solvents, acetone and toluene, were obtained from Loba chemie.

### 2.2 Surface treatment of fly ash

The fly ash particles (100 gms in each case) were surface coated by immersing them in the solutions of stearic acid (SA) (1, 2, 3, 5 gm of SA in 100 ml of acetone and toluene in the ratio of 3:1) separately under constant stirring for 15 min. It was kept for drying for 2 days at room temperature. Then it was vacuum dried to completely remove the solvents. The surface coated fly ash particles were designated as FASAX, where X denoted the wt% of stearic acid with respect to the weight of fly ash coated.

### 2.3 Fabrication of composites

The surface coated fly ash (FASAX) samples and the recycled polypropylene (RPP) were taken in a 1:1 weight ratio. Uncoated fly ash (designated as FASA0) and RPP were also taken. RPP and FASAX were mixed in an internal mixer (Brabender 30/50 E, Germany) for 20 minutes at a temperature of 170°C. The resultant product was compression moulded at 170°C for 10 minutes to form composite laminates of 1.5 mm thickness. The composites were designated as RFASA0, RFASA1, RFASA2, RFASA3 and RFASA5.

### 2.4. Characterizations

Dynamic Mechanical Analysis of the composite samples was carried out in a DM Q 800 in nitrogen atmosphere in a fixed frequency flexural mode of 1.0 Hz. The samples were evaluated in the temperature range of -

50°C to 150°C with a heating rate of 10°C per minute. The thermal degradation behaviour was studied in a TGA HI Res TGA 2950 Thermogravimetric analyzer. The samples were scanned from 25°C to 600°C at a heating rate of 10°C/min.

## 3. RESULTS AND DISCUSSION

### 3.1 Dynamic mechanical analysis

The Dynamic mechanical analysis of the composite samples was carried out to investigate the properties of the composites under dynamic loading condition with increase in temperature. The glass transition temperature ( $T_g$ ) was measured from the loss modulus data. The values are given in TABLE 1. From this a delay in transition from glassy to rubbery state in all the SA coated FA/RPP composites is visible indicating a restricted chain mobility, which can be attributed to effective interfacial bonding with highest being in the case of RFASA1.

TABLE 1.  $T_g$  values of the composite samples

Composite	$T_g$ (°C)
RFASA0	-1.6
RFASA1	+6.3
RFASA2	+5.61
RFASA3	+5.16
RFASA5	+4.21

### 3.2 Thermogravimetric analysis

From TGA analysis the temperatures for onset of degradation was obtained. The temperature at which the rate of degradation was highest was also derived. These values are indicative of the thermal stability of the composites. The values are given in TABLE 2.

TABLE 2. Data from TGA analysis

Composite	Onset of thermal degradation (°C)	Temperature at highest rate of thermal degradation (°C)
RFASA0	241	443
RFASA1	269	425, 444
RFASA2	268	415, 436
RFASA3	250	410, 442

RFASA5	190	411, 440
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From the data, it could be understood that RFASA1, RFASA2 and RFASA3 were thermally more stable than RFASA0. This could be attributed to their mechanical properties which were studied in earlier. In our earlier study both RFASA1 and RFASA2 had shown enhancement in mechanical properties due to better interfacial bonding between the filler and matrix. In case of RFASA5 which showed the lower onset of thermal degradation, higher concentration of coupling agent might have facilitated thermal degradation and consequently lowered its thermal stability. In RFASA0 the rate of degradation reached its peak at 443°C but in all the SA coated FA/RPP composites two degradation peaks were observed. This could be due to the thermal degradation of the less compact RPP chains at a lower temperature followed by the degradation of closely packed RPP chains at a higher temperature. In an earlier study by Manna et al, the DTGA curve showed the degradation peak over a range of temperature for silane treated clay reinforced epoxidized natural rubber (ENR) matrix composites and it was reported to be due to breaking of bonds between filler and the coupling agent and then breaking of the matrix bonds [7]. In our case strong physical interaction between the filler and the coupling agent and the matrix was discussed earlier. Thus, breaking of such interactions and then the RPP chains might have resulted in such multistep higher rate of degradation. However, RFASA1 showed delayed onset of this degradation peak among all the composites rendering it to be the most stable among all the composites.

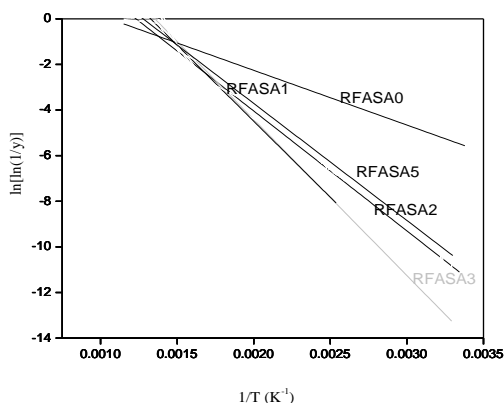


Fig.1. Plot of  $\ln[\ln(1/y)]$  vs  $1/T$  for the composite samples

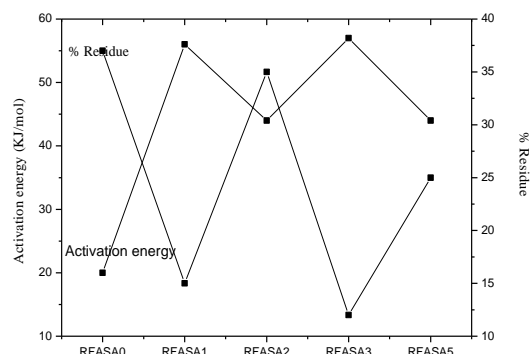


Fig.2. The activation energy and % residue left in the composite samples

The activation energy of the composites were also studied which revealed information about the thermal degradation behavior of the composites. The present calculation is based on the equation derived by Broido [8],

$$\ln[\ln(1/y)] = E/R [1/T+K],$$

where,  $y = W_t/W_0$ ,  $W_t$  = weight remaining at time  $t$ ,  $W_0$  = initial weight,  $T$  = temperature in Kelvin. From the residual weight of the samples,  $\ln[\ln(1/y)]$  was plotted against  $1/T$  (Fig.1.). From the slope of the linear plot, which was  $-E/R$  ( $R$ =universal gas constant), the activation energy  $E$  was calculated.

The variation of the activation energy of the composites and the % residual weight derived from TGA analysis are shown in Fig.2. The activation energy was found to be 20 KJ/mol, 56 KJ/mol, 44 KJ/mol, 57 KJ/mol and 43 KJ/mol in case of RFASA0, RFASA1, RFASA2, RFASA3 and RFASA5 respectively. Thus the SA coated FA/RPP composites required higher amount of activation energy for their degradation. Thus, they are thermally more stable. Increase in activation energy was marked with a decrease in percent residue of the thermally degraded composite. In SA treated FA/ RPP composites the percent residue was found to be much less. Thus, they thermally degrade well

but require more energy for their degradation as a result of strong interfacial bonding between the filler and the matrix.

#### 4. CONCLUSION

Stearic acid was used as a coupling agent between recycled polypropylene and fly ash particles. The concentration of the coupling agent was varied from 1 wt% to 5 wt% with respect to the fly ash weight. The glass transition shifted to a higher temperature in all the treated composites, the highest being in RFASA1 at + 6.3°C from that of -1.6°C in RFASA0. This reflects restricted chain mobility in the treated composites due to enhanced interfacial interaction. The thermal stability also increased with maximum delay in the onset of degradation in RFASA1 at 269° C due to better interfacial bonding between the filler and matrix. The coupling agent also increased the activation energy of the composites. Thus, a renewable, low cost chemical like stearic acid can be used as an effective coupling agent for fly ash in place of expensive synthetic coupling agents which are more commonly used in order to make materials from recycled plastics (here RPP) with tailor made properties specially in case of better thermal stability.

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