

## Stearic Acid as Coupling Agent in Fly Ash Reinforced Recycled Polypropylene Matrix Composites: Structural, Mechanical, and Thermal Characterizations

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**ABSTRACT:** Two industrial wastes, fly ash (FA) and recycled polypropylene (RPP) were used to prepare a value-added, sustainable, low cost composite material. Improving the interfacial interaction between the hydrophobic RPP matrix and the hydrophilic FA particles is important to get a good combination of properties. In order to tailor the interface, stearic acid was used as the coupling agent. The FA particles were coated with a saturated fatty acid, stearic acid (SA), in different weight % like 1, 2, 3, and 5. The SA coated fly ash particles were incorporated as filler in RPP matrix composites by melt mixing in 1 : 1 weight ratio. The composites were tested for their flexural properties, impact behavior, dynamic mechanical properties, fracture surface analysis, X-ray diffraction (XRD) study, and differential scanning calorimetry (DSC). An increase in flexural modulus and impact strength was observed in the stearic acid coated FA/RPP composites. In 1 wt % SA treated FA/RPP (RFASA1) composites, a significant increase in glass transition temperature was observed along with an increase in crystallinity. A green, renewable, inexpensive chemical like stearic acid was thus found to be an effective coupling agent in fabrication of a composite with 50 wt % filler loading. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1996–2004, 2013

**KEYWORDS:** composites; crystallization; glass transition

Received 19 January 2013; accepted 4 April 2013; Published online 14 May 2013

**DOI:** 10.1002/app.39413

### INTRODUCTION

The industrial wastes like fly ash (FA) and polypropylene (PP) are known to be detrimental to our planet's environment. Recycling of these wastes in economically viable technique is now being attempted in order to reduce their harmful effects and to develop value-added products from them.<sup>1,2</sup> Fly ashes are by-products of thermal power plants and constitute about 85% of the total residue generated from coal combustion process.<sup>3</sup> The composition of fly ash vary depending upon the source of coal and comprises 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.<sup>3,4</sup> Utilization of fly ash in producing energy and cost efficient materials like fly ash based cements and clay/fly ash bricks have been attempted in the recent past.<sup>5</sup> Nowadays, attempts are going on in establishing fly ash as attractive mineral filler in various polymer matrix composites.<sup>4,6–8</sup> Ramakrishna et al.<sup>9</sup> and Gupta et al.<sup>10</sup> studied the mechanical properties of fly ash filled polymer matrix composites. Gupta et al.<sup>10</sup> reported an increase in the impact properties on addition of fly ash in glass fiber/epoxy composites. Menon et al.<sup>11</sup> investigated the use of fly ash as a filler in

natural rubber in presence of 5–10 phr of phosphorylated cardanol prepolymer (PCP) and hexamethylenetetramine cured PCP which resulted in higher thermal stability along with improvement in mechanical properties. Sridhar et al.<sup>7</sup> reported an increase in thermal stability with increasing fly ash content in fly ash/waste tire powder/isotactic PP composites. Ray et al. studied the changes in the mechanical properties of the vinyl-ester resin matrix composites which were fabricated with 30, 40, 50, and 60% fly ash loading by room temperature casting method. The study reported that fly ash can be used effectively to increase the rigidity and stiffness of the vinyl-ester resin matrix, however there was a lowering in the value above 50 wt % of fly ash loading.<sup>5</sup> In a separate study, these composites showed faster thermal degradation at a lower temperature, particularly in case of the 30 and 60 wt % composites and a higher onset temperature for the 40 and 50 wt % composites.<sup>12</sup>

However, according to Yu-fen et al.<sup>13</sup> improvement of composite strength by using fly ash as filler has problems regarding the weak interfacial bonding between untreated fly ash and polymer due to low friction of the fly ash surface. Therefore,

modification of fly ashes is done by various techniques where either coupling agents or surfactants have been used followed by mechanical mixing.<sup>13</sup> Bose et al.<sup>14</sup> and Nath et al.<sup>15</sup> reported the usage of coupling agent resulted in better level of physical bonding with improvement in mechanical properties in fly ash filled Nylon 6 and PVA composites respectively. Pardo et al. reported an improved stiffness, strength and thermal stability of fly ash/isotactic polypropylene composites where silane coupling agents containing three different reactive functional groups like amine (GF96), vinyl (XL10), and vinyl-benzylamine (Z-6032) were used. The vinyl and amino silane treated fly ashes, showed better results owing to strong filler–matrix adhesion.<sup>4</sup> Das et al.<sup>16</sup> 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). Mechanical properties and thermal stability was found to be much higher in the VTMO treated composites compared to the untreated ones which were due to the enhanced chemical bonding at the matrix–filler interface in presence of the coupling agent VTMO.<sup>16</sup> Stearic acid has been used as a surface modifier for fillers such as nano alumina in EPDM composites and for calcium carbonate nanoparticles in polypropylene matrix.<sup>17,18</sup>

In our earlier study, the mechanical properties of furfuryl palmitate (FP) coated fly ash reinforced recycled polypropylene (RPP) matrix composites were reported, where the highest enhancement in mechanical properties was observed in 2 wt % FP (FP2) coated fly ash filled composites and the highest impact strength was observed in 1 wt % FP coated fly ash filled composites. Therefore, a renewable chemical like furfuryl palmitate was first time shown to be an effective coupling agent for fly ash in place of expensive silane coupling agents which are more commonly used.<sup>19</sup>

In our earlier study, thermal properties of stearic acid (SA) coated fly ash (FA) reinforced recycled polypropylene (RPP) composites were evaluated by thermogravimetric analysis (TGA).<sup>20</sup> The stearic acid coated composites in this initial study showed an improvement in thermal stability. To evaluate these composites comprehensively and to compare the efficacies of stearic acid as a coupling agent over other conventionally used coupling agents, an in-depth study has been carried out in this study on structural, mechanical, and thermal properties of these composites. The composites have been subjected to X-ray diffraction (XRD) analysis, tested for their flexural properties, impact properties, dynamic mechanical behavior (DMA), fracture surface analysis (SEM), and differential scanning calorimetric (DSC) analysis.

## EXPERIMENTAL

### 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 (59% SiO<sub>2</sub>, 21% Al<sub>2</sub>O<sub>3</sub>, 8% Fe<sub>2</sub>O<sub>3</sub>, and rest other oxides).<sup>12</sup> The ash particles had the following particle size distribution: 10% of the samples had a particle size below 2.38 μm, 50% of the samples had a particle sizes below 13.58 μm, and 90% of the samples

were below 111.16 μm. Recycled polypropylene (RPP) was obtained from recycling of post-consumer plastic products and was used as the matrix material. Stearic acid and the solvents, acetone and toluene, were obtained from Loba Chemie.

### Surface Treatment of Fly Ash

The fly ash particles (100 gm in each case) were surface coated by immersing them in the solutions of stearic acid (SA; 1, 2, 3, and 5 gm of SA in 100 mL of acetone and toluene mix in the ratio of 3 : 1 by volume) 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.

### 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. The recycled polypropylene (RPP) in chips and fly ash (FA) particles were mixed in the internal melt mixer (Brabender) for 20 min at a temperature of 170°C in separate sets. The melt mixed dough was further compression molded into sheet form. The composites were designated as RFASA0, RFASA1, RFASA2, RFASA3, and RFASA5.

### Mechanical Testing

The composite samples were tested for their flexural properties under three point bending in an Instron 4303 machine in accordance with ASTM D790. Five samples of each set was taken to get the mean value and the standard deviation was also calculated. Impact strength of the samples was tested in a CEAST Izod tester following ASTM D 256. Five samples of each set were taken to get the mean value and the standard deviation was also calculated.

### Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis of the composite samples was carried out in a DM Q 800 in nitrogen atmosphere at a fixed frequency flexural mode of 1.0 Hz. The samples were evaluated in the temperature range of –50–150°C with a heating rate of 10°C min<sup>-1</sup>.

### Scanning Electron Microscopy

The fracture surface of the composite samples were coated with Au–Pd alloy and investigated under SEM (Hitachi S-3400N).

### X-ray Diffraction Analysis

XRD analysis was done using X-ray diffractometer (X Pert Pro) with Cu K $\alpha$  radiation operating at 40 kV and 30 mA, at a scanning rate of 2° min<sup>-1</sup> in the range of diffraction angle  $2\theta = 5^\circ\text{--}90^\circ$ .

### Differential Scanning Calorimetry

DSC analysis of all the composite samples was done using Perkin Elmer Pyris Diamond Calorimeter at a heating rate of 10°C min<sup>-1</sup> in nitrogen atmosphere in the temperature range between –50°C to 200°C. Heating, cooling, and heating cycles were used. The sample was held for 2 min at 200°C after the first heating cycle to remove all the thermal history. The cooling

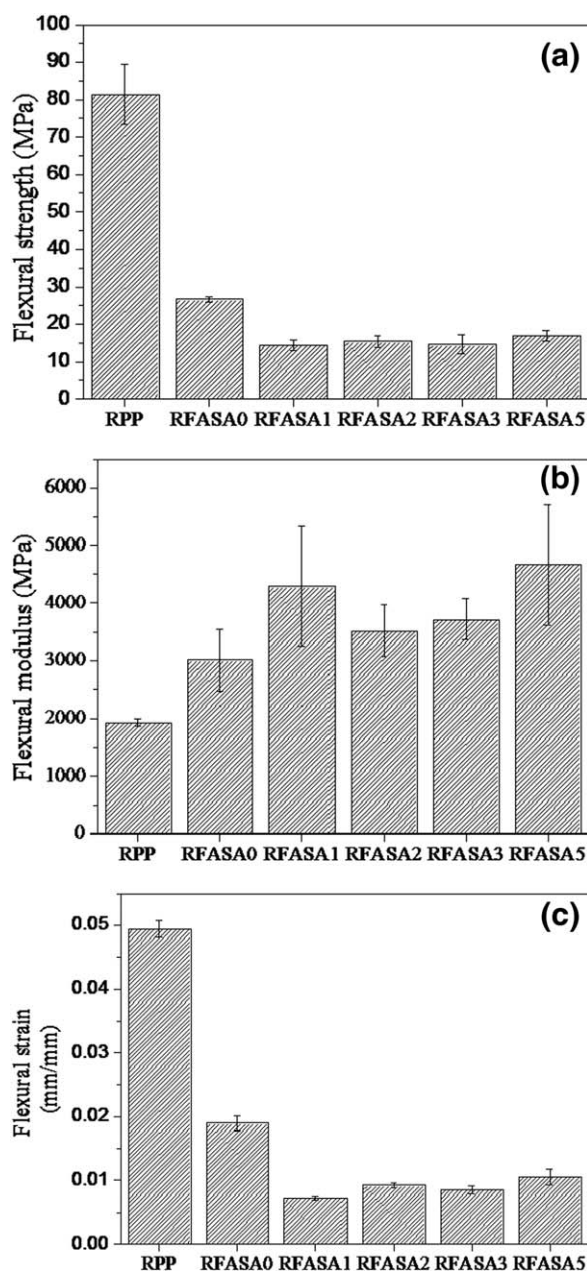
and second heating were then done to evaluate the thermal transition behavior of the composites.

## RESULTS AND DISCUSSION

The FA/RPP composites were tested for various properties.

### Mechanical Testing

The flexural strength, modulus, and strain of the matrix material RPP and different SA treated FA/RPP composite samples were measured. The flexural strength, modulus, and strain of RPP up to 5% strain level were found to be 81 MPa ( $\pm 8$ ), 1928 MPa ( $\pm 59$ ), and 0.05 mm/mm ( $\pm 0.001$ ), respectively.<sup>21</sup> The flexural properties of the composite samples are shown in



**Figure 1.** Variation in (a) flexural strength, (b) flexural modulus, (c) strain of the composite samples.

Figure 1(a–c). FA incorporation increased the flexural modulus to 3012 MPa ( $\pm 542$ ) and decreased the flexural strength to 27 MPa ( $\pm 0.6$ ).

There was a drop in the flexural strength values in SA treated composites. The flexural strength decreased by 45% in RFASA1, 42% in RFASA2, 45% in RFASA3, and 36% in RFASA5, respectively, with respect to RFASA0. This decrease can be attributed to the reduced mechanical interlocking between RPP chains and FA due to smoothening of the fly ash particle surface which lowered the stress transfer at the interface.

When the fly ash particles have rough surface, there is a possibility of some mechanical anchorage, although there may not be any physical interaction between the matrix and the filler. Similarly, in earlier works, in a similar hydrophobic polymer (HDPE) and particulate filler (glass beads) system with titanate and silane coupling agents, mechanical anchorage of the matrix onto the filler surface was reported in case of uncoated filler matrix composites. In presence of the titanate, coupling agent physical entanglement was stated as the interfacial bonding state between the coated filler and the matrix.<sup>22</sup> Hence in our study, there is a strong possibility that uncoated, rough fly ash particles rendered mechanical anchorage to the RPP chains and when stearic acid was used, physical interaction was achieved with a reduction in mechanical anchorage.

Therefore, when a surface modifier like stearic acid is present on the surface of the fly ash particles, two opposite phenomenon were operative. First, there was a chance of lowering in the mechanical anchorage of the polymer chains onto the fly ash particle surface due to smoothening of the surface, and on the other hand, there was a physical interaction and entanglement between the long hydrophobic chains of stearic moiety present on the fly ash particles and the hydrophobic RPP chains. The overall predominance of one factor over another might have controlled the change in properties.

However, the presence of stearic acid at the interface increased the rigidity of the composites. The modulus increased by 43, 17, 23, and 55% in RFASA1, RFASA2, RFASA3, and RFASA5, respectively, in comparison to that of RFASA0. The strain values of RFASA1, RFASA2, RFASA3, and RFASA5 decreased by 61, 51, 55, and 45%, respectively, in comparison with the value of RFASA0. However, an increase in flexural modulus values indicated an enhancement in rigidity of the composites, especially in case of RFASA1 and RFASA5. Thus incorporation of filler increased the flexural modulus due to restriction in chain mobility which was more pronounced when the fly ash particles were surface treated with stearic acid. Thus, a decrease in flexural strength along with an increase in flexural modulus was observed in the treated composites. Such increase in flexural modulus with decrease in flexural strength in polymer matrix on incorporation of filler has been reported earlier.<sup>23</sup>

### Comparison of Present Results with Previously Reported Commercial Coupling Agents

In an earlier work by Das et al.,<sup>16</sup> a silane coupling agent (Dynasylan VTMO) and maleated polypropylene (Epolene G3003) were used as surface coating agent for fly ash and the

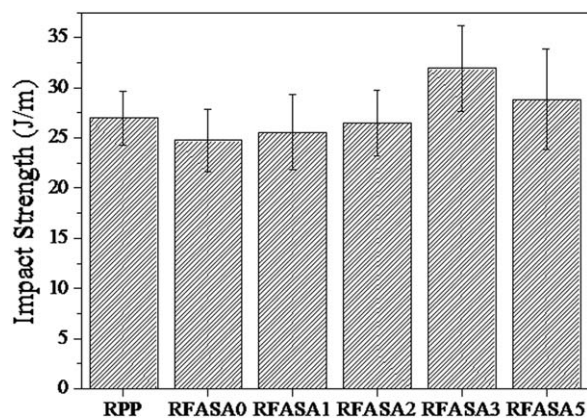


Figure 2. Variation in impact strength of the composite samples.

surface coated FA was incorporated in RPP (1 : 1 wt %) by solvent impregnation method followed by compression molding. With 6 wt % Dynasylan VTMO coating on FA surface, the flexural modulus of the composite changed to 3.8 GPa from 3.2 GPa (untreated composite) and the flexural strength changed to 23 MPa compared to 21 MPa observed for the untreated RPP/FA composites. Consequently, 2 wt % Dynasylan VTMO and 2, 5, and 10 wt % Epolene G3003 coated FA/RPP composites exhibited a decrease in flexural modulus to 3.1, 2.1, 2.2, and 2.3 GPa respectively, and the flexural strength values also decreased to 14, 14, 18, and 15 MPa, respectively.

In a work by Pardo et al.<sup>4</sup> three organosilanes containing different reactive functional groups like amine (GF96), vinyl (XL10), and benzyl amine (Z-6032) were used as coupling agents in FA/PP composites (60 : 40 ratio). An increase in Young's modulus to 1317 MPa ( $\pm 11$ ) from that of virgin PP [527 MPa ( $\pm 11$ )] was reported on incorporation of filler with a decrease in tensile strength from 29.31 MPa ( $\pm 1.4$ ) to 17.8 MPa ( $\pm 1$ ). The modulus value decreased to 1205 MPa ( $\pm 61$ ) in the presence of silane Z-6032 and the tensile strength decreased to 17.3 MPa ( $\pm 1.1$ ). However, the other two organosilanes GF96 and XL10 resulted in an increase of tensile modulus to 2136 MPa ( $\pm 131$ ) and 2517 MPa ( $\pm 76$ ) and tensile strength to 20.6 MPa ( $\pm 0.6$ ) and 24.7 MPa ( $\pm 3.4$ ), respectively. Iraola-Arregui et al.<sup>3</sup> used three commercially available coupling agents, Lubrizol solplus C800 (an unsaturated carboxylic type coupling agent), N,N'-(1,3-phenylene) dimaleimide (BMI),  $\gamma$ -methacryloxypropyltrimethoxysilane (MPS), and maleic anhydride grafted PP (MAPP) in their work on PP/FA composites with 50 wt % fly ash loading. They reported an increase in flexural modulus from 1.7 GPa of virgin PP to 2.9 GPa ( $\pm 1$ ) and decrease in flexural strength from 51.3 MPa to 35.7 MPa ( $\pm 0.4$ ) in PP/FA composites with 50 wt % fly ash loading. In presence of the coupling agents C800, BMI, MPS, and MAPP, the flexural moduli values increased to 3.6 GPa ( $\pm 0.2$ ), 3.6 GPa ( $\pm 0.2$ ), 3.4 GPa ( $\pm 0.1$ ), and 3.0 GPa ( $\pm 0.2$ ), respectively, and the flexural strength increased to 65.7 MPa ( $\pm 3.1$ ), 58.8 MPa ( $\pm 2.8$ ), 58.8 MPa ( $\pm 2.8$ ), and 64.4 MPa ( $\pm 6.2$ ), respectively.

It is noteworthy to mention here that in comparison to the flexural modulus values observed in the earlier works, use of stearic

acid as a surface coating agent in this similar composite system with different fabrication technique resulted in an improved flexural modulus value of 4295 MPa ( $\pm 1042$ ) in RFASA1 and 4662 MPa ( $\pm 1047$ ) in RFASA5 which were significantly higher than the flexural modulus values reported earlier.

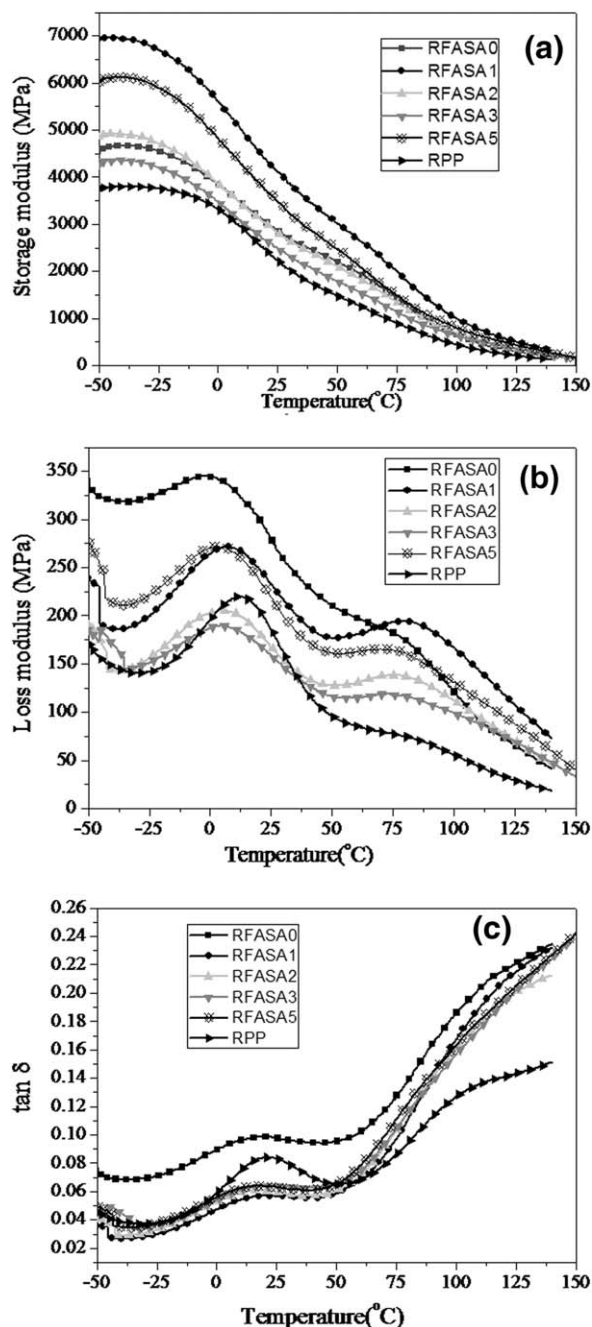
In comparison to the above discussed commercially available expensive coupling agents, stearic acid seems to have a potential as an effective coupling agent in FA/RPP composites. Another important aspect of this study was that the filler loading was significantly high, 50 wt % and recycled, waste polypropylene was used as the matrix material in place of virgin ones.

### Impact Tests

An increase in impact strength was evident in all the treated composites (Figure 2). The impact strength increased by 3, 7, 29, and 17% in RFASA1, RFASA2, RFASA3, and RFASA5, respectively, compared to that of RFASA0. The impact strength of the RPP matrix was found to be 27 J/m ( $\pm 5$ ). Incorporation of filler (RFASA0) reduced the impact strength to 24 J/m ( $\pm 3$ ), but in the presence of stearic acid it increased, particularly in case of RFASA3 and RFASA5 it increased to 32 J/m ( $\pm 4$ ) and 29 J/m ( $\pm 5$ ), respectively. Thus stearic acid aided in enhancing the impact strength of the composites.

### 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, shown in Figure 3(a–c). For RPP, the highest storage modulus value was found to be 3778 MPa,  $T_g$  (from loss modulus peak) was 12°C and damping values at the transition temperature was 0.1. The variation of the storage modulus as a function of temperature is shown in Figure 3(a). FA reinforcement did increase the storage modulus values (4650 MPa) and surface coating of FA by SA enhanced it further to 7000 MPa for RFASA1, indicating an improvement in interfacial bonding. The storage modulus also increased in case of RFASA5 and RFASA2 and decreased in RFASA3 with respect to RFASA0. The variation of loss modulus as a function of temperature is shown in Figure 3(b). The loss modulus of all the surface coated FA filled composites decreased. The loss modulus curves of RFASA1 and RFASA2 composites exhibited a second prominent peak at 78 and 76°C respectively, and a smaller second hump was observed at 75°C in both RFASA3 and RFASA5 unlike RFASA0 and RPP. The appearance of two loss modulus peaks at a lower and a higher temperature might be attributed to the mobility of the polymer molecules in the bulk and near the interface, respectively. This type of loss modulus spectra have been reported earlier in case of kenaf fiber filled polypropylene composites where two transitions were seen due to relaxation of unrestricted PP chains and restricted PP chains at lower and higher temperatures, respectively.<sup>24</sup> The glass transition temperatures ( $T_g$ ) measured from the loss modulus curves were -2°C, +6°C, +6°C, +5°C, and +4°C for RFASA0, RFASA1, RFASA2, RFASA3, and RFASA5, respectively. This shows a delayed transition from glassy to rubbery state in all the SA coated FA/RPP composites, indicating a restricted chain mobility, which can be attributed to an effective entanglement of the hydrophobic chains of SA with the RPP



**Figure 3.** Variation of (a) storage modulus, (b) loss modulus, and (c)  $\tan \delta$  of the composite samples.

chains, with highest being in the case of RFASA1 and RFASA2. The variation of the damping parameter ( $\tan \delta$ ) as a function of temperature is given in Figure 3(c). The curves showed an overall increase in  $\tan \delta$  with temperature and presence of SA coating reduced the damping parameter compared to RPP and RFASA0. The damping ( $\tan \delta$ ) values of RFASA0, RFASA1, RFASA2, RFASA3, and RFASA5 at the transition temperature were 0.1, 0.06, 0.06, 0.06, and 0.06, respectively. Thus, from DMA analysis stearic acid as a coupling agent was found to improve the interfacial bonding at the filler–matrix interface.

### Fracture Surface Analysis

To clearly visualize the filler–matrix interactions, the fracture behavior of the composites was investigated under SEM (Figure 4). In RFASA0 [Figure 4(b)], the adhesion of the fly ash particles with the matrix was poor when compared with the rest of the composite samples. In the composites where surface coated fly ash particles were present, improved interfacial bonding was evident, most significant being in case of RFASA1 and RFASA2. In presence of stearic acid as a coupling agent, better filler incorporation and filler–matrix interactions were visible. This filler–matrix interaction in the presence of coupling agent was discussed in our earlier work.<sup>19</sup> In this case, it could also be said that the hydrophilic ends of the long chain stearic acid might have interacted with the fly ash particles and their long hydrophobic chains might have formed compatible interfaces with the polymer. However, the extent of entanglement between stearic acid molecules and the RPP chains and the amount of stearic acid present at the interface controlled the extent of compatible interface produced or resulted into an agglomeration effect.

### X-ray Diffraction Analysis

To corroborate the mechanical properties with the structural changes incurred by the composite in the presence of the coupling agent SA, XRD analysis was carried out. The X-ray diffractograms of RPP, FA, and FASA5 are shown in Figure 5(a) and of the composites (RFASA0, RFASA1, RFASA2, RFASA3, and RFASA5) are shown in Figure 5(b). The % crystallinity and the crystallite size of RPP and of RPP in the composites were calculated and given in Table I. The crystallite size was calculated using the Schquation,

$$L_{h,k,l} = K\lambda / \beta \cos \theta$$

where  $K = 0.94$ , where  $\beta$  is the full width half maxima perpendicular to each plane, and  $\theta$  is the Bragg's angle.<sup>25</sup> The % crystallinity was also calculated as per the formula,

$$\% \text{ Crystallinity} = (I_{h,k,l} - I_{\text{amp}}) / I_{h,k,l} \times 100$$

for each crystalline plane of the matrix.<sup>25</sup>

In Figure 5(a), RPP showed a diffraction pattern similar to a semicrystalline polymer with sharp peaks and an amorphous halo underneath. The Bragg reflections were observed at around  $2\theta = 14.1, 16.8, 18.5, 21,$  and  $22^\circ$ , respectively, which were similar to that of PP and these positions corresponded to the indexed planes of  $\alpha$  monoclinic planes of (110), (040), (130), (111), and (131), respectively.<sup>26,27</sup> The characteristic peaks of fly ash, both in surface coated and uncoated forms, were similar with a sharp peak at  $2\theta = 26.6^\circ$ . In the composites, a reduction in peak intensity and sharpness could be seen as a result of lessening in the amount of the polymer matrix. Incorporation of the crystalline fly ashes was also evident. However, surface coating of fly ashes and their incorporation into the matrix resulted in changes in the crystalline nature of the polymer. The change in polymer crystallinity due to incorporation of FA cenospheres in PP matrix was also reported earlier.<sup>28</sup>

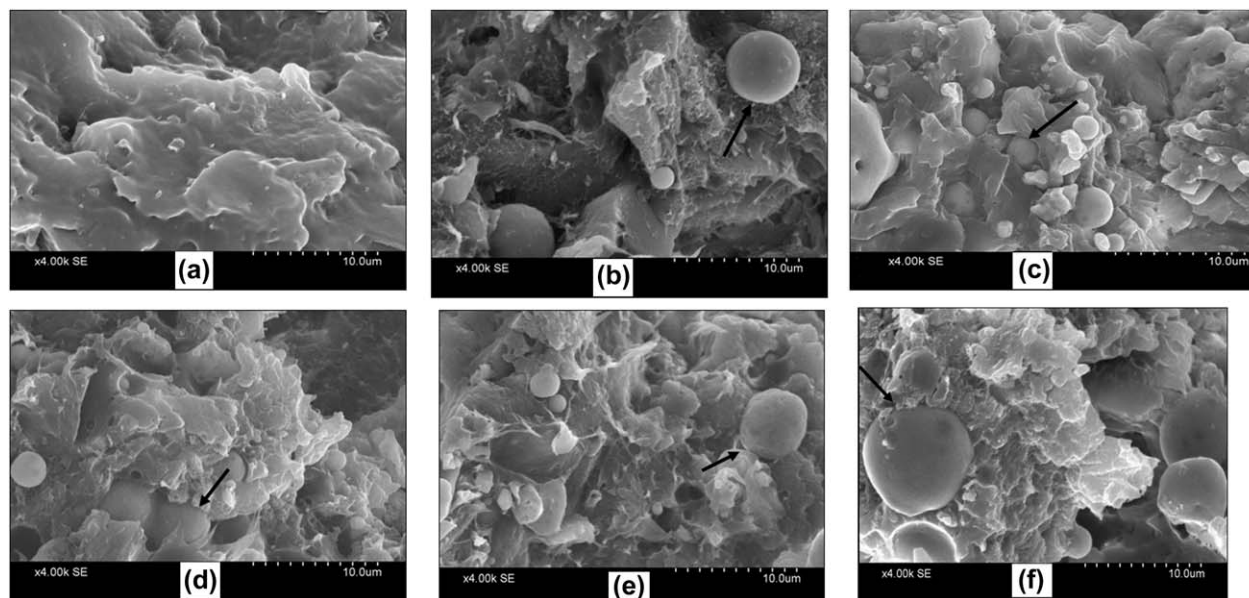


Figure 4. SEM micrograph of composite samples: (a) RPP, (b) RFASA0, (c) RFASA1, (d) RFASA2, (e) RFASA3, and (f) RFASA5.

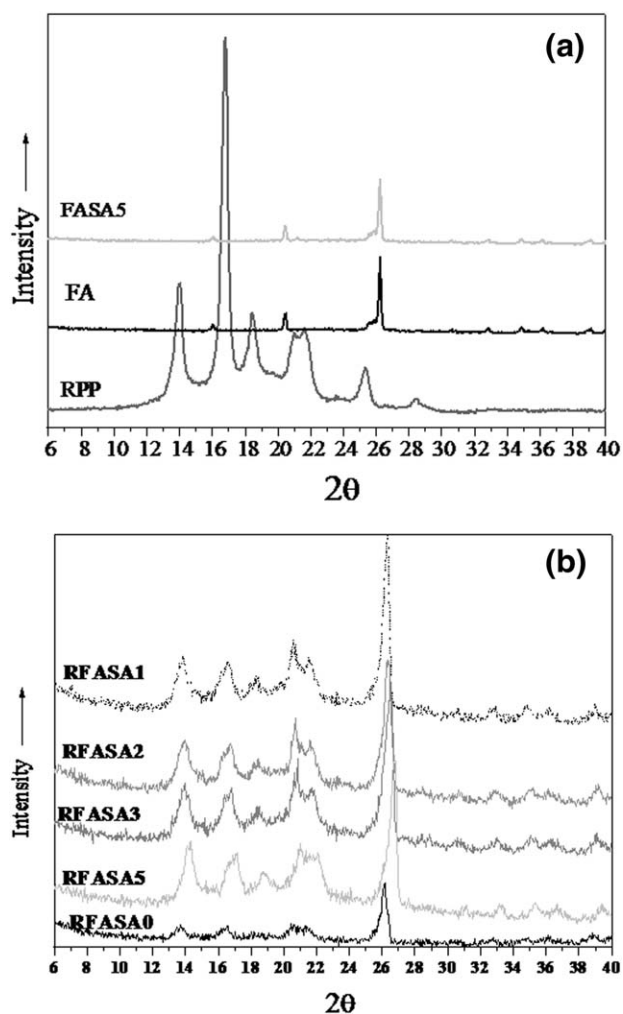
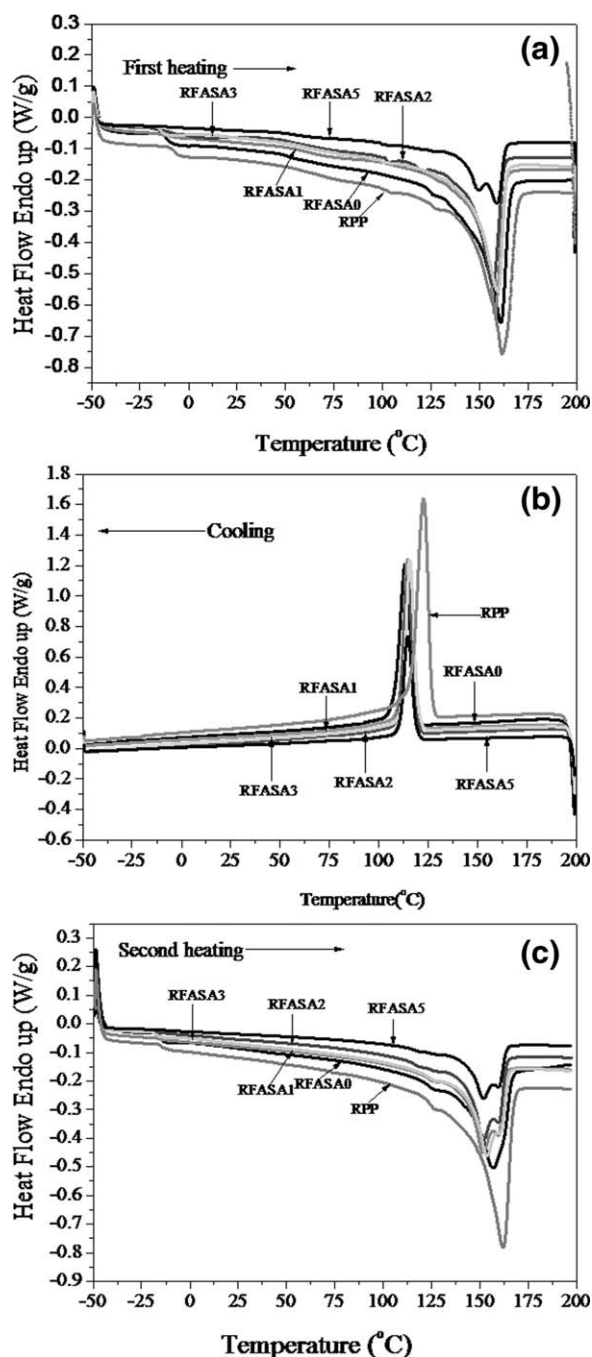


Figure 5. XRD analysis of (a) RPP, FA, and FASA5 (b) the composite samples.

The composites showed the characteristic peaks of mainly (110), (040), (111), and (131) monoclinic planes. In the composites, only 50% RPP was present; so a decrease in both the non-

Table I. Percentage Crystallinity and Crystallite Size of RPP, RFASA0, RFASA1, RFASA2, RFASA3, and RFASA5

	Peak position ( $2\theta$ )	% Crystallinity	Crystallite size (nm)
RPP	13.9	80	52
	16.8	95	47
	18.4	65	52
	20.9	65	47
	21.6	68	37
RFASA0	13.7	80	21
	16.5	81	21
	20.6	84	11
RFASA1	14.04	88	33
	16.7	81	26
	20.7	74	33
	21.7	64	33
RFASA2	14.1	87	29
	16.7	77	22
	20.7	75	53
RFASA3	14.07	86	26
	16.8	68	26
	20.86	72	22
	21.9	55	22
RFASA5	14.1	88	36
	17.08	76	18
	18.8	57	22
	22.1	73	33



**Figure 6.** DSC plot (a) first heating cycle, (b) cooling cycle, and (c) second heating cycle of the composite samples.

crystalline and crystalline portions had occurred which resulted in reduction of the peak intensities, as evident in Figure 5(b). Among all the SA treated composites, the highest increase in % crystallinity and crystallite size was observed in case of RFASA1. In the (111 $\alpha$ ) an increase in % crystallinity in comparison with the RPP matrix was evident. RFASA1 showed a shift in the peak positions with highest crystallinity and also greater average crystallite sizes. This fully supported our DMA results where the highest storage modulus and higher shift of  $T_g$  were observed in RFASA1.

Thus, the filler–matrix interaction in presence of the coupling agent changed the molecular packing order and the crystalline morphology of the composites.

#### Differential Scanning Calorimetry

The thermal properties of the composites were revealed through differential scanning calorimetric analysis. The DSC plots for the first heating, cooling, and second heating cycles are given in Figure 6(a–c) respectively. The melting point ( $T_m$ ), crystallization temperature ( $T_c$ ), and melting enthalpy ( $\Delta H$ ) values of the second heating and cooling cycles of the composites and the matrix material RPP are given in Table II. The RPP matrix showed higher single melting peak and cooling peaks with higher enthalpy values than the composites. In RFASA0, a single sharp melting peak ( $T_m$ ) was observed at 157°C along with a distinct  $T_g$  at –16°C and an endothermic peak at 126°C [Figure 6(c)]. Whereas for the treated composites, melting occurred in a temperature range between 150°C to 160°C with bimodal melting peaks with two distinct melting points along with a small endothermic peak at 128°C. Thus incorporation of filler lead to changes in the polymer chain alignments reflected in their thermal transitions.

Somnuk et al.<sup>29</sup> reported the presence of similar broad melting peaks in the core layer of vetiver grass fiber–PP composites. They had attributed the existence of those multiple and broad endotherms to the presence of several crystallographic forms of PP. It is known that the semicrystalline PP generally forms three crystallographic phases, i.e.,  $\alpha$ -monoclinic phase,  $\beta$ -pseudohexagonal phase, and  $\gamma$ -orthorhombic phase.<sup>25</sup> The  $\alpha$ -monoclinic phase is thermodynamically more stable with radial and tangential lamellae and the sporadically occurring  $\beta$ -pseudohexagonal phase with parallel stacked lamellae.<sup>24</sup> Bhattacharya et al.<sup>30</sup> in their PP/SWNT composites designated the melting peak at 165°C to the melting of the  $\alpha$  crystals and the broad peak in the range of 145–160°C to the melting of  $\beta$ -crystals or imperfect  $\alpha$  crystals. Therefore, the presence of these different crystallographic forms might have resulted in the appearance of such melting peaks. In the SA treated FA/RPP composites, two distinct melting peaks were seen, decrease in enthalpy had occurred in comparison to RFASA0 and melting occurred over a wide range of temperature. The melt crystallization peak during the cooling cycle ( $T_c$ ) appeared at a slightly higher temperature in the surface coated FA/RPP composites than that in untreated composite (RFASA0) exhibiting the ease of crystallization in presence of SA coupling agent. The RFASA1 showed highest exothermic  $\Delta H$  value during melt crystallization compared to other treated composites. Also, RFASA1 showed highest melting enthalpy value indicating highest crystallinity among the treated composites and this supported the XRD results also. Thus, stearic acid as a coupling agent was found to influence the structural properties of RPP/FA composites significantly with distinct indications of polymer chain reorientation and the most predominant effect was observed in case of RFASA1.

#### Correlating the Mechanical Properties with the Structural Properties

The changes in the structural properties of the composites could be correlated with the previously obtained results of the

**Table II.**  $T_c$ ,  $T_m$ , and the Enthalpies ( $\Delta H$ ) of the Composites During the DSC Cooling and Second Heating Cycles

Composite samples	DSC cooling cycle		DSC 2nd heating cycle		$\Delta H$ (J/g) (Melting enthalpy values from the major peak)
	$T_c$ ( $^{\circ}\text{C}$ ) (Melt crystallization temperature from cooling cycle)	$\Delta H$ (J/g) (Melt Crystallization enthalpy)	$T_m$ ( $^{\circ}\text{C}$ ) (Melting Temperature from second heating cycle) Major peak	Minor peak	
RPP	123	87	162	-	57
RFASA0	113	55	157	-	45
RFASA1	115	50	152	160	25
RFASA2	115	41	153	160	23
RFASA3	116	42	154	161	24
RFASA5	115	26	152	160	19

mechanical characterizations. RPP matrix, having very high % crystallinity (95% at  $2\theta = 16.8^{\circ}$ ), larger crystallite size (52 nm) and higher melting enthalpy (57 J/g), exhibited higher  $T_g$  in the loss modulus curve at  $12^{\circ}\text{C}$  implying that the rigid crystalline regions restricted the chain mobility and delayed the onset of  $T_g$ . But when FA particles were incorporated, RFASA0 showed  $T_g$  at a lower temperature of  $-2^{\circ}\text{C}$ . This indicates that the uncoated FA particles influenced the crystalline morphology resulting in decreased % crystallinity, reduced crystallite size and lowered melting enthalpy value implying easier mobility of the amorphous phase. A similar decrease in  $T_g$  observed from DMA on incorporation of filler talc in polypropylene matrix has been reported earlier.<sup>31</sup> In presence of SA coated fillers further reorientation of the RPP chains occurred with a significant change in crystalline morphology as evident from XRD and DSC analysis which might have resulted in a higher  $T_g$  in all the SA coated RPP/FA composites and specially in RFASA1 as mentioned earlier.

This delay in onset of  $T_g$  in SA coated RPP/FA composites implied that the changed crystalline morphology enhanced the rigidity of the composites as reflected in enhanced flexural modulus and storage modulus values. The results indicated that the improvement in mechanical properties was a resultant of two phenomena (i) improved interfacial interaction in presence of stearic acid and (ii) crystalline reorientation in the RPP matrix.

Analyzing the mechanical, structural, and morphological properties a clear trend was seen where the lower SA wt % coated FA/RPP composites, especially RFASA1, showed improved interfacial interaction, higher % crystallinity, larger crystallite size, and higher melting enthalpy among all SA coated composites which resulted in an enhanced flexural and storage modulus values, higher  $T_g$  value in comparison to RFASA0. With further increase in SA wt %, interfacial interaction was hampered due to agglomeration of the FA particles. But these FA agglomerates did provide higher rigidity to the RPP matrix as depicted by the flexural modulus and storage modulus values of RFASA5. Thus, an optimum SA amount is required to achieve an effective filler/matrix interaction and minimum agglomeration. In our study, RFASA1 was proved to be the optimum one.

## CONCLUSIONS

Stearic acid was used as a coupling agent between recycled polypropylene and fly ash particles where filler and matrix were present in 1 : 1 weight ratio. The concentration of the coupling agent was varied from 1 wt % to 5 wt % with respect to the fly ash weight. There was a decrease in the flexural strength of the treated composites. This could be attributed to the reduced mechanical interlocking between RPP chains and FA due to smoothening of the fly ash particle surface which lowered the stress transfer at the interface. But the presence of stearic acid at the interface increased the rigidity of the composites and modulus increased by 43, 17, 23, and 55% in case of RFASA1, RFASA2, RFASA3, and RFASA5, respectively in comparison to that of RFASA0. An increase in the impact strength of the composites in presence of stearic acid was also found. The glass transition shifted to a higher temperature in all the treated composites, the highest being in RFASA1 and RFASA2 at  $+6^{\circ}\text{C}$  from that of  $-2^{\circ}\text{C}$  in RFASA0. This reflects restricted chain mobility in the treated composites due to enhanced interfacial interaction. Stearic acid as a coupling agent influenced the structural properties of the composites with increase in crystallinity along with evidence of polymer chain reorientation as sufficed from XRD and DSC analyses. Thus, a renewable, low cost chemical like stearic acid was found to be an effective coupling agent for FA/RPP composites and the improvement in properties was quite visible when compared to that observed for conventional expensive coupling agents.

## ACKNOWLEDGEMENT

Dipa Ray is thankful to Department of Science and Technology (DST), Government of India, for granting her the project. Shubhalakshmi Sengupta is thankful to DST for her fellowship.

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