Chapter 3

Lauric acid coated fly ash reinforced recycled polypropylene matrix composites

3.1 Introduction

This chapter deals with the surface coating of fly ash particles with lauric acid (1, 2, 3 and 5 wt % lauric acid w.r.t fly ash) and subsequent characterization of the fabricated composites. The fly ash (FA) particles and 1 wt%, 5 wt% lauric acid coated fly ashes (FALA1 and FALA5) were analyzed by transmission electron microscopy (TEM) and Fourier Transform Infra Red (FTIR) spectroscopy. The fabricated composites (RFALA0, RFALA1, RFALA2, RFALA3 and RFALA5) and the recycled polypropylene (R) were tested for mechanical properties like flexural strength, impact properties, dynamic mechanical analysis (DMA); fracture surface analysis was done by scanning electron microscopy (SEM), structural properties were characterized through X-ray diffraction (XRD) analysis, differential scanning calorimetry (DSC) and thermal properties were characterized through thermogravimetric analysis (TGA). The details of the materials required, composite fabrication technique and test parameters used in characterization along with the instrumental details are given in Chapter 2.
The objective of this study was to evaluate the efficacy of lauric acid (LA) as coupling agent in fly ash (FA) reinforced polymer composites for the first time where the filler (FA) and matrix (R) are present in equal proportion.

3.2 Results and Discussion

The coated and uncoated fly ash particles were examined with TEM and FTIR. The data for FA, FALA1 and FALA5 are given here.

3.2.1 Transmission electron microscopy (TEM)

The TEM images of FA, FALA1 and FALA5 are shown in Figure 3.1.

![Figure 3.1: TEM analysis of FA, FALA1 and FALA5 particles and the EDS data of the fly ash surfaces](image-url)
A greater agglomeration effect was evident with the uncoated fly ash particles which seem to reduce in FALA1 and FALA5 on surface coating. This type of phenomenon was earlier witnessed in sodium lauryl sulphate (SLS) coated fly ash particles where surface coating of fly ashes reduced interfacial interactions between the uncoated particles leading to reduction of agglomeration of the filler particles in composites [Nath et al., 2010b]. In FALA1 and FALA5 cluster of particles were seen on the surface which could be inferred due to the presence of fatty acid. The EDS spectra of those regions on the fly ash surfaces were analyzed and high percentage of carbon content was present (54 wt% in FALA5) with respect to the regions in FA having no clusters (Figure 3.1).

This indicated that those regions were rich in carbon due to the presence of fatty acids. An increase in the amount of carbon content on carbonaceous clusters present on fly ash surfaces was witnessed for SLS surface modified coal fly ashes in an earlier study [Vander Merwe, 2011]. Thus, surface coating of the fly ash particles were witnessed. The chemical evaluation of the surface coated fly ash particles were further carried out with FTIR.

3.2.2 Fourier Transform Infra Red (FTIR) spectroscopy

The FTIR spectra of FA, FALA1 and FALA5 are shown in Figure 3.2.
The stretching bands of Si-O-Al bands mainly appeared in the ranges of 1200-600 cm\(^{-1}\) for the vibrations of Si-O and Al-O bands in FA [Nath et al., 2010b]. The broad band at 1082 cm\(^{-1}\) was attributed to Si-O stretching and the absorption bands at 1625 cm\(^{-1}\) and 3436 cm\(^{-1}\) could be attributed to the \(-\text{OH}\) absorption bands [Çelik et al., 2008; Yao et al., 2013]. In surface coated FA particles, especially in FALA5, the bands at 2851 cm\(^{-1}\) and 2918 cm\(^{-1}\) could be related to the C-H band asymmetric stretching vibrations and symmetric stretching vibration respectively which help to identify -CH\(_2\) group of the fatty acid. The –CH\(_3\) group was also visualized by a small asymmetric stretching vibration of –C-H bond which occurred at 2961 cm\(^{-1}\). These observations proved the presence of lauric acid on the FA surface. Similar FTIR absorption peaks of stearic acid coated coal fly ash were reported earlier [Yao et al., 2013]. Carboxylic acid –C=O peak at 1705 cm\(^{-1}\) [Lima et al., 2004] also indicated
presence of the fatty acid. Thus from earlier reports, [Yao et al., 2013, Iraola-Arregui et al., 2011] and present observations it could be inferred that the surface coating of FA particles by lauric acid occurred as a result of physical interactions between the metal-OH groups of FA and the polar part of the fatty acid and the non-polar part was available for compatibilization with the polymer chains. These coated fly ash particles were incorporated into composites in high proportion (50 weight %) and the efficacy of lauric acid as a coupling agent was studied. The fabricated composites were tested to determine their mechanical, structural and thermal properties.

3.2.3 Flexural and Impact Testing

The variations of the flexural strength, strain and modulus of the recycled polypropylene (R) and the composites (RFALA0, RFALA1, RFALA2, RFALA3 and RFALA5) are given in Figures 3.3a-c.

![Flexural Strength Chart](image.png)

**Figure 3.3a:** Flexural strength of the recycled polypropylene (R) and the composite samples
Figure 3.3b: Flexural strain of recycled polypropylene (R) and the composite samples

Figure 3.3c: Flexural modulus of recycled polypropylene (R) and the composite samples
It was observed that the flexural strength decreased on addition of fly ash by 68% in RFALA0 in comparison to that of R. A decrease in flexural strength of vinylester resin matrix composites in presence of organoclay was reported earlier [Ray et al., 2006c]. Incorporation of filler by 50 wt% in R matrix reduced the polymer chain entanglements as fly ash particles entered in-between the R chains. Among the coated composites, flexural strength increased in RFALA2 by 6% but decreased by 22%, 3% and 20% in RFALA1, RFALA3 and RFALA5 respectively in comparison to that observed in RFALA0. This nominal increase in flexural strength could be attributed to the enhancement in stress transfer at the interface between the 2 wt% LA coated FA particles and the polymer matrix. The decrease in flexural strength in RFALA1, RFALA3 and RFALA5 could be attributed to the reduced mechanical interlocking between the R chains and FA as a result of smoothening of the FA particle surface which could not provide mechanical anchorage to the polymer chains. The flexural strain values were decreased by 36%, 26%, 58% and 71% in RFALA1, RFALA2, RFALA3 and RFALA5 respectively in comparison to that of RFALA0 indicating reduced mobility of the polymer chains. The modulus values of RFALA0 increased by 67% from that of R. The incorporation of filler increases the flexural modulus of a composite due to restriction in chain mobility and such increase in flexural modulus with decrease in flexural strength in polypropylene on incorporation of filler was reported in a previous study [Ray et al., 2006c]. The modulus values increased by 50%, 16% and 10% in RFALA2, RFALA3 and RFALA5 respectively and decreased by 6 % in RFALA1 respectively when compared to that of RFALA0. This indicates that with 1 wt% LA, physical entanglement of the filler with the matrix was not adequate enough to achieve enhanced modulus values. RFALA2 showed highest enhancement in both flexural strength and modulus among
the composites. As discussed earlier, the presence of coupling agent influenced the interfacial bonding and the mechanical properties of the composites. Use of conventional silane coupling agent in fly ash/R matrix was studied earlier where 6 wt% Dynasylan vinyltrimethoxysilane (VTMO) treated composite showed an increase of 4% (21 MPa to 23 MPa) and 15% (3.2 GPa to 3.8 GPa) in flexural strength and modulus respectively in comparison with the untreated ones [Das et al., 2009]. When compared with silane coupling agents, lauric acid has been found to render efficient coupling action at a lower percentage i.e. at 2 wt%. LA (RFALA2) which showed high enhancement in flexural modulus values of 4535 MPa.

The impact strengths of R and the composites were also studied (Figure 3.4).

Figure 3.4: Impact strength of recycled polypropylene (R) and the composite samples

Impact strength decreased in RFALA0 (25 J/m) from that of R (27 J/m). The impact strength was increased by 119%, 80%, and 33% in RFALA1, RFALA2 and RFALA3 respectively when compared to that of RFALA0 and decreased by 66% in
RFALA5. Thus lauric acid aided in enhancing the impact strength of the composites. This observation indicates that the alignment of the R molecules in presence of LA at the interface lead to different structural orientation and the impact strength was influenced accordingly.

3.2.4 Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis of the composite samples was carried out to investigate the properties of the composites under dynamic loading conditions with increase in temperature. The variations of the storage modulus, loss modulus and damping parameter (tan δ) of R and the composites (RFALA0, RFALA1, RFALA2, RFALA3 and RFALA5) are given in Figures 3.5a, 3.5b and 3.5c respectively.

![Figure 3.5a](image)

**Figure 3.5a**: Storage modulus values of recycled polypropylene (R) and the composite samples
The storage modulus value increased from 3778 MPa in R to 4650 MPa in RFALA0. Presence of LA enhanced it further to 4704 MPa in RFALA2 but had a little decrease in RFALA1 (4582 MPa) and decreased further in RFALA3 (4353 MPa) and RFALA5 (4166 MPa). Thus, presence of 2 wt% LA at interface facilitated better interfacial interaction resulting in increase in the storage modulus values.

![Figure 3.5b Loss modulus values of recycled polypropylene (R) and the composite samples](image)

The glass transition temperatures ($T_g$) were determined from the loss modulus curves. The recycled polypropylene (R) had a $T_g$ value of 12°C which on filler incorporation (RFALA0) shifted to -2°C but in presence of LA increased to +1.4°C, +3°C, 0°C and 0°C in RFALA1, RFALA2 RFALA3 and RFALA5 respectively. This delay in transition from glassy to rubbery state in the composites in comparison to RFALA0 indicated a restricted chain mobility which could be attributed to an
effective entanglement of the hydrophobic chains of LA with the R chains, with the highest being in case of RFALA2.

Figure 3.5c: tan δ values of recycled polypropylene (R) and the composite samples

The damping parameter of R and the composites are given in Table 3.1.
Table 3.1: Damping parameter (tanδ) of recycled polypropylene (R) and the composites

<table>
<thead>
<tr>
<th>Composites</th>
<th>tan δ at RT (30°C)</th>
<th>tan δ at 125 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>0.08</td>
<td>0.14</td>
</tr>
<tr>
<td>RFALA0</td>
<td>0.09</td>
<td>0.22</td>
</tr>
<tr>
<td>RFALA1</td>
<td>0.11</td>
<td>0.26</td>
</tr>
<tr>
<td>RFALA2</td>
<td>0.1</td>
<td>0.21</td>
</tr>
<tr>
<td>RFALA3</td>
<td>0.08</td>
<td>0.15</td>
</tr>
<tr>
<td>RFALA5</td>
<td>0.07</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The damping parameter, which is the ratio of loss to storage modulus values, clearly indicate a difference in the viscous and elastic response of the polymer in dynamic mode at room temperature as well as at high temperature (125°C) which may be attributed to the effect of the coupling agent at the interface. Thus, from DMA analysis, LA as a coupling agent was found to influence the interfacial bonding at the filler-matrix interface.

3.2.5 Scanning electron microscopy (SEM)

The fracture surfaces of the composites were investigated under SEM (Figure 3.6a and b).
Figure 3.6a: SEM micrograph of the flexural fracture surface of recycled polypropylene (R) and the composite samples showing filler/matrix interactions.

In RFALA0, 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 improvement in interfacial bonding was evident especially in case of RFALA1 and RFALA2. SEM micrographs of RFALA1 and RFALA2 at higher magnification are shown in Figure 3.6b.
To further evaluate the influence of LA coupling agent on structural reorganization of the polymer molecules, XRD and DSC analysis were carried out.

3.2.6 X-ray diffraction analysis (XRD)

The crystalline morphology of the matrix was considerably influenced by the presence of LA moieties at the interface which was investigated by XRD analysis. The X-ray diffractograms of R, FA, and FALA5 are shown in Figure 3.7a and of the composites (RFALA0, RFALA1, RFALA2, RFALA3 and RFALA5) are shown in Figure 3.7b.

**Figure 3.6b:** SEM micrograph of the flexural fracture surface of RFALA1 and RFALA2 at higher magnification

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In Figure 3.7a, R showed a diffraction pattern similar to a standard polypropylene with sharp peaks and an amorphous halo underneath. The Bragg reflections were observed at $2\theta = 14.1^\circ$, $16.8^\circ$, $18.5^\circ$, $21^\circ$ and $22^\circ$ respectively which were similar to that of polypropylene and these positions corresponded to the indexed planes of $\alpha$ monoclinic planes of (110), (040), (130), (111), and (131) respectively [Nath et al., 2009, Tortorella et al., 2008]. The characteristic peaks of fly ash, both in surface coated and uncoated forms, were observed at $2\theta = 26.6^\circ$. 

Figure 3.7a: XRD analysis of recycled polypropylene (R), FA and FAL A5
Figure 3.7b: XRD analysis of the composite samples

In the composites (Figure 3.7b), a reduction in peak intensity and sharpness was evident 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 ash 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 [Satpathy et al., 2011]. The composites showed the characteristic peaks of the monoclinic (110), (040), and (111) planes respectively. In the composites, only 50% R was present; so decrease in both the non crystalline and crystalline portions occurred which resulted in reduction of the peak intensities, as evident in Figure 3.7b.

The calculated %crystallinity and crystallite size values are given in Table 3.2.
Table 3.2: % Crystallinity and crystallite size of recycled polypropylene (R) and the composite samples obtained from the XRD analysis

<table>
<thead>
<tr>
<th>Samples</th>
<th>% Crystallinity [% C] and crystallite size (nm) [CS]</th>
<th>Peak Positions (20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>% C 80 95 65 65 68</td>
<td>14 17 18 21 22</td>
</tr>
<tr>
<td></td>
<td>CS 52 47 52 47 37</td>
<td></td>
</tr>
<tr>
<td>RFALA0</td>
<td>% C 80 81 - 84 -</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CS 21 21 - 11 -</td>
<td></td>
</tr>
<tr>
<td>RFALA1</td>
<td>% C 88 88 64 72 69</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CS 86 64 156 129 52</td>
<td></td>
</tr>
<tr>
<td>RFALA2</td>
<td>% C 89 88 61 72 73</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CS 86 72 64 85 43</td>
<td></td>
</tr>
<tr>
<td>RFALA3</td>
<td>% C 84 84 59 63 58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CS 86 65 86 125 43</td>
<td></td>
</tr>
<tr>
<td>RFALA5</td>
<td>% C 83 82 73 72 61</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CS 85 73 64 129 43</td>
<td></td>
</tr>
</tbody>
</table>

Among all the LA treated composites, the highest % crystallinity and crystallite size was observed in RFALA2 (110 plane, at 2θ =14°) followed by RFALA1. A significant increase was observed in crystallite size of all the LA treated FA/R composites compared to that of RFALA0 reconfirming the changes in the crystalline orientation in presence of LA.
3.2.7 Differential scanning calorimetry (DSC)

The melt crystallization temperature \( (T_c) \), crystallization enthalpy \( (\Delta H_c) \) obtained from the cooling cycle and the melting point \( (T_m) \), melting enthalpy \( (\Delta H_m) \) values obtained from the second heating cycle are given in Table 3.3. The DSC curves of the composites (second heating cycle) are given in Figure 3.8.

Table 3.3: \( T_c \), \( T_m \) and the enthalpies \( (\Delta H) \) of recycled polypropylene (R) and the composite samples during DSC cooling and second heating cycle

<table>
<thead>
<tr>
<th>Composite Samples</th>
<th>DSC Cooling Cycle</th>
<th>DSC 2(^{nd}) Heating Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( T_c ) (^{\circ}\text{C})</td>
<td>( \Delta H(J/g) )</td>
</tr>
<tr>
<td>R</td>
<td>123</td>
<td>87</td>
</tr>
<tr>
<td>RFALA0</td>
<td>113</td>
<td>55</td>
</tr>
<tr>
<td>RFALA1</td>
<td>114</td>
<td>39</td>
</tr>
<tr>
<td>RFALA2</td>
<td>114</td>
<td>41</td>
</tr>
<tr>
<td>RFALA3</td>
<td>113</td>
<td>36</td>
</tr>
<tr>
<td>RFALA5</td>
<td>113</td>
<td>35</td>
</tr>
</tbody>
</table>
Figure 3.8: DSC curves (second heating cycle) of recycled polypropylene (R) and the composite samples

From the cooling cycle it was observed that the melt crystallization peak during the cooling cycle (T_c) appeared in all the composites between 113°C-114°C, whereas the T_c for unreinforced R appeared at 123°C. This significant lowering in melt crystallization temperature could be due to the presence of 50 wt% of FA. The melt crystallization enthalpies observed in the cooling cycle of the surface treated
composites were lower than that observed in RFALA0. However, among the composites RFALA2 showed slightly higher exothermic $\Delta H_e$ value (30J/g) during melt crystallization compared to other treated composites.

In the second heating cycle, R showed slightly higher single melting peak with higher enthalpy value than the composites. In RFALA0, a single sharp peak ($T_m$) was observed at 157°C along with a distinct $T_g$ at -16°C and a small but distinct endothermic peak at 126°C. A distinct glass transition temperature ($T_g$) was observed in both R and RFALA0 where no coupling agent was present (Figure 3.8), whereas in all LA coated FA/R composites no sharp glass transition was observed which might be due to effect of LA coupling agents at the interface which restricted the chain mobility of the amorphous region of the composites. Presence of multiple peaks in RFALA0 and bimodal melting peaks in the LA coated FA/R composites could be related to the occurrence of several crystallographic forms of polypropylene which were earlier reported. [Somnuk et al., 2009].

The bimodal peaks also resulted in lower endothermic enthalpy values with RFALA2 (41 J/g) being the highest among the composites. The high exothermic and endothermic values of RFALA2 among the composites corroborated with the XRD results where RFALA2 had the highest % crystallinity value (89%) at $\theta$=14°. Thus, significant structural re-orientation in the R matrix was evident in presence of LA coupling agent in the composites.

It can be concluded from various tests that enhancement in mechanical properties especially in case of RFALA2 was resultant of two phenomenon: i) improved interfacial interaction, specially in presence of 2 weight% lauric acid and ii) crystalline reorientation of R matrix in presence of LA coated FA particles.
3.2.8 Thermogravimetric analysis (TGA)

Thermal stability of the composites was studied through TGA analysis (Figure 3.9).

Figure 3.9 TGA plot of the recycled polypropylene (R) and the composite samples

The change of weight with respect to temperature (Figure 3.9) revealed that the onset of degradation started at around 280°C in R and it encountered 100% weight loss. FA is noncombustible. On its incorporation the onset of degradation temperature increased and the amount of weight loss decreased in all the composites. The composites showed a continuous drop in weight between 250°C to 450°C. In RFALA0, RFALA1, RFALA2, RFALA3 and RFALA5, the onset of degradation appeared at 300°C, 350°C, 320°C, 240°C and 230°C respectively. Higher onset of degradation in RFALA1 followed by RFALA2 indicates stronger interface and higher crystalline packing of the polymer molecules which enhanced the thermal stability.
Thus, incorporation of FA did enhance the thermal stability of the composites. The presence of the LA at 1 and 2 wt% resulted in better thermal stability. RFALA2 showed the greatest enhancement in mechanical properties among the composites and also increase in its crystalline content was observed. Thus better interfacial bonding and structural reorientation resulted in better thermal stability of the composites. However, RFALA3 and RFALA5 did not show any improvement in their thermal properties. This result also corroborated well with our earlier observations of mechanical and thermal properties.

From the TGA results it could be concluded that incorporation of LA coated FA in recycled polypropylene matrix in the optimum concentration of 1 and 2 wt% resulted in improved thermal properties of the composites.

3.3 Conclusions

Lauric acid was used as a coupling agent between recycled polypropylene and fly ash particles for the first time where filler and matrix were present in 1:1 weight ratio. The concentration of the coupling agent was varied from 1 to 5 weight% with respect to the fly ash weight. Efficient surface coating of FA did take place with LA as evident from TEM and FTIR studies. This surface coating resulted in an enhanced compatibility with the polymer chains resulting in an increase in flexural modulus in RFALA2 with respect to the uncoated FA/R composite. Impact strength and DMA analysis also supported this observation. XRD analysis revealed crystalline reorientation along with increase in % crystallinity in RFALA2. This structural reorientation was further confirmed by the DSC results. 1 and 2 wt % LA coated FA/R composites showed enhanced thermal stability with respect to RFALA0. Lauric acid was thus found to be an effective coupling agent for FA/R composites.