A Comparative Study on the Properties of ABS/Clay Nanocomposites Prepared by Direct Melt Intercalation and In-situ Emulsion Polymerization Techniques

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Polybutadiene (PB) and acrylonitrile-butadiene-styrene (ABS) latexes were prepared by emulsifier-free emulsion polymerization. ABS/Montmorillonite (MMT) nanocomposites containing 5 wt% clay loadings were also synthesized by in-situ emulsifier-free emulsion polymerization method using a reactive in-situ clay modifier, and by direct melt intercalation technique using two different organoclays. The morphology and thermal stability of the nanocomposites were examined using X-ray diffraction (XRD), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The XRD and TEM results showed exfoliated-intercalated morphology with more uniform distribution of the clay layers for the nanocomposite prepared by in-situ emulsion polymerization, and intercalated morphologies with clay aggregates containing more clay layers for the nanocomposites prepared by direct melt intercalation technique. The basal spacing for the nanocomposite prepared by in-situ emulsion polymerization technique was calculated as 1.73 nm which was lower than 3.36 and 3.52 nm calculated for the melt intercalated nanocomposites using organoclays with one and two octadecyl chains in the organic modifier molecule, respectively. The TGA results showed an increase in the onset thermal degradation temperatures of the nanocomposites. The peak weight loss rate temperatures were obtained as 462.1, 470.4, 497.7 and 492.2ºC for neat ABS, in-situ emulsion polymerized and melt intercalated nanocomposites using organoclays with one and two octadecyl chains in the organic modifier molecule, respectively.

INTRODUCTION

Polymer/clay nanocomposites are a new class of materials with unique properties which cannot be obtained by the conventional composites. Nanostructural characteristics and interfacial bonding between the polymer and clay improve the mechanical [1], thermal [2], flame retardancy [3] and barrier [4] characteristics of the polymers. Nanocomposites may exist in two forms: intercalated, in which the polymeric chains are intercalated between the silicate layers with their regular alternation of galleries, or exfoliated in which the polymeric chains are intercalat-ed between the silicate layers with...
their regular alternation of galleries, or exfoliated in which the silicate layers are completely delaminated and uniform layer spacing is lost [5].

ABS is an important engineering thermoplastic because of its good processability and excellent physical and mechanical properties. However, one of the main drawbacks of ABS polymers is low thermal stability and poor flame retardancy which can be improved using nanoclay in the polymer matrix. Several methods have been reported for the preparation of ABS/clay nanocomposites, including in-situ emulsion polymerization [6-7], solvent/non-solvent [8] and direct melt intercalation methods [9-15]. Since ABS is commercially produced by emulsion polymerization in an aqueous media, due to the easy delamination of the Na-MMT in water it is possible to produce ABS/clay nanocomposites in a single step using unmodified hydrophilic Na-MMT clay. Jang et al. [6] reported preparation of the ABS/clay nanocomposites via in situ emulsion polymerization technique. A conventional emulsion polymerization recipe including rosin soap as emulsifier was used and an intercalated morphology which was not accompanied by delamination of the clay interlayer was obtained. Choi et al. [7] reported synthesis of the exfoliated ABS/clay nanocomposites through an emulsion polymerization recipe by initial polymerization of AN in the presence of clay and a reactive surfactant prior to the main graft copolymerization reaction. Although a very good dispersion of clay in the polymer matrix is reached in this method, homopolymerization of AN can potentially lead to the high yellowness of the final product which is not desirable. In addition, in this method increasing the viscosity of the reaction media, as a result of the higher clay and in-situ modifier contents especially at higher solid contents, limits the final solid content and consequently lowers the productivity. In the solvent/non-solvent method, as reported by Pourabas and Raeesi [8], an intercalated structure is obtained, however due to the use of very large amounts of the volatiles, from the practical point of view, the separation process is more expensive and less environmental friendly.

The direct melt intercalation is another method in which organoclays can simply be introduced into the polymer melt at the product finishing step. This method has been extensively studied by many researchers. Wang et al. [9] prepared ABS/MMT nanocomposites by direct melt intercalation using organically-modified clay with hexadecyl trimethyl ammonium bromide. In their further works, they studied the effect of clay particle size [10] and incorporation of the conventional flame retardants [11] on the thermal properties of the ABS/MMT nanocomposites prepared using the same organic clay modifier. They also studied the thermal properties of the polycarbonate/ABS/MMT polyblend nanocomposites prepared by melt intercalation technique [12]. Ma et al. [13] prepared ABS-graft-maleic anhydride/clay nanocomposites by the same method using octadecyl trimethyl ammonium bromide as clay modifier. Su et al. [14] used polybutadiene-modified clay and Zheng et al. [15] used methyl methacrylate oligomerically-modified clay for the preparation of ABS/MMT nanocomposites by direct melt intercalation method. Since the properties of the nanocomposites are affected by the very different nano-scale morphologies resulting from different methods of preparation, the first aspect of this work is the first attempt in which, the morphology and thermal stability of the polymer/clay nanocomposites particularly ABS nanocomposites, synthesized through in-situ emulsion polymerization and direct melt intercalation techniques as the main methods for the preparation of the nanocomposites are compared, in order to see whether the in-situ emulsion polymerized nanocomposite, in spite of its limitations has any remarkable advantages over the simple direct melt intercalated product. Furthermore, as seen in the literature, although different organically modified clays have been used for preparation of the ABS nanocomposites, the effect of molecular structure of the modifier on the morphology and thermal property of the ABS nanocomposites have not been studied. Therefore as the second aspect of this work, the effect of the number of the alkyl chains in the organic clay modifier molecule, on the morphology and thermal property of the melt-mixed nanocomposites, were studied using two different organoclays having one and two octadecyl chains attached to the ammonium group of the modifiers.

In our study, to eliminate the interaction between Na-MMT and anionic surfactant, polybutadiene and ABS nanocomposite latexes were synthesized by emulsifier-free emulsion polymerization technique.

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The similar condition was applied for the preparation of the neat ABS which was further used in fabrication of the melt intercalated nanocomposites. For obtaining a well dispersed morphology, a reactive clay modifier was used in the in-situ emulsion polymerized nanocomposite recipe. The neat ABS and ABS nanocomposites synthesized in this work were composed of 20 wt% PB rubber and a constant acrylonitrile/styrene weight ratio of 30/70.

**EXPERIMENTAL**

**Materials**

Commercial grade 1,3-butadiene (BD) was purified by condensing the vapour from a storage vessel into a 2-L steel recipient using a refrigerating system. Commercial grade styrene (ST) and acrylonitrile (AN) were purified by vacuum distillation. Other chemicals were used as received including potassium peroxydisulphate (KPS) as free radical initiator and 2-acrylamido-2-methyl-1-propanesulphonic acid (AMPS) as a reactive clay modifier, both from Aldrich, Germany, and potassium carbonate (KCB) as buffer from Merck, Germany. Na-MMT, Kunipia-F (KF) with a cation exchange capacity (CEC) of 119 meq./100 g and organoclays including Kunipia-T (KT) and Kunipia-D (KD) modified by trimethyl-octadecyl ammonium (TM) and dimethyldioctadecyl ammonium (DM) ions, respectively, were kindly supplied by Kunimine Co., Japan. The Na-MMT clay was dispersed in distilled deionized (DDI) water with the weight ratio of 22.5/1000 (clay/water) for 16 h at ambient temperature prior to the polymerization.

**Preparation of Polybutadiene by Emulsifier-free Emulsion Polymerization**

The emulsifier-free emulsion polymerization of BD was carried out in a 3.75 L stainless steel pressure reactor (Parr Instruments, USA), fitted with 8-bladed turbine impeller and two baffle plates located at 180° intervals. Aqueous solutions of the initiator and buffer containing 5 g of KPS and 2.55 g of KCB, with an appropriate amount of DDI water to reach 2000 g in the final reaction mixture, were charged into the reactor and the mixture was stirred at 320 rpm at ambient temperature under nitrogen atmosphere. The head space of the reactor was purged with gaseous BD and then evacuated. Finally 270 g of liquefied BD was charged into the reactor and the temperature was increased to 80°C. Polymerization was carried out at 80°C and 11 bar for about 4 h, then the pressure showed a continuous decrease as a result of the monomer conversion. After another 5 h, the reaction was stopped by cooling the reaction mixture and venting out the unreacted BD from the system. Polybutadiene (PB) latex with 10.6 wt% solid content and an average particle size of 121 nm measured by dynamic light scattering (SEM-633, SEMATech, France) was obtained.

**Preparation of ABS and ABS/Clay Nanocomposite by Emulsifier-free Emulsion Polymerization**

The graft emulsion polymerization was carried out in a 1-L glass reactor, equipped with a reflux condenser, a thermometer, a single baffle and a variable speed 6-bladed turbine impeller. The pre-specified amount of clay dispersion was charged into the reactor to obtain a nanocomposite (ABS-KF) with 5 wt% total clay content. An appropriate amount of PB latex containing 16 g of PB, 400 g of DDI water, 1.5 g of AMPS dissolved in 10 g of DDI water and 16 g of the monomer mixture (AN/ST:30/70) were added into the reactor and then temperature was increased to 70°C. The polymerization was initiated by addition of the aqueous solution of 0.5 g of KPS as initiator under nitrogen atmosphere. After 1 h, remaining 48 g of the monomer mixture with the same composition was continuously added using a syringe pump (Pilot A2, Fresenius vial, France) at a rate of 0.25 mL/min. After 5 h, temperature was increased to 80°C and was maintained for another 3 h.

In the case of neat ABS (ABS-neat) no clay and AMPS were added into the reaction system. Because of the presence of the initiator end-groups on the surface of the particles, the resulting latexes had a remarkable colloidal stability which underwent coagulation after applying a combined concentrated methanol/aluminium sulphate coagulating system. After isolation, products were several times re-dispersed in, and washed with water and methanol, respectively. Neat polymer and nanocomposite fine powders were obtained by drying the products at 50°C under vacuum for 48 h.
Preparation of ABS/Clay Nanocomposites by Direct Melt Intercalation

ABS-KT and ABS-KD nanocomposites were prepared by melt blending of the ABS-neat with KT and KD organoclays, respectively at 5 wt% clay loadings in a Haake internal mixer (HBI System 90, USA) for 15 min at 180°C and 100 rpm. The amount of organoclays which were used in the formulations was calculated according to the inorganic part of the modified clays based on the ash analysis which is shown in Figure 1.

Characterization

Wide-angle X-ray diffraction (WAXD) was used to study the clay interlayer spacing. The well known Bragg equation, \( n\lambda = 2d \sin\theta \) was applied for calculation of the d-spacing from the peak positions. The XRD analyses were performed on clay samples in the powdery form and on polymer samples in the shape of a disk with a thickness of 1 mm, which were pressed at 180°C and 25 MPa. The XRD patterns were generated using a X-ray diffractometer (X’Pert, Philips, Netherlands) at wavelength Cu K\( \alpha \) =1.54 Å operating at a voltage of 40 kV and a current of 40 mA at the rate of 2°/min and in the range of 1.5-10°. Morphology of the graft latex particles and nanostructure of the ultramicrotomed specimens of the nanocomposites were observed using a transmission electron microscope (TEM) (CM 200 FEG, Philips, Netherlands) with an operating voltage of 200 kV. The latexes were diluted with DDI water to a concentration of 0.04 wt% and to the 20 g of this solution 3 drops of a 2% aqueous OsO\(_4\) solution were added and allowed to stain the PB core in the graft polymer for 12 h. A drop of the stained latex was placed on a 400 mesh carbon-coated copper grid and dried. Nanocomposite samples for electron microscopy were sectioned from epoxy block with the embedded nanocomposites at room temperature using an ultramicrotome (Leica Ultracut UCT, Germany) with a diamond knife. Thermal stability of the samples was monitored using a Perkin Elmer thermogravimetric analyzer, (Pyris 1 TGA, USA) with a heating rate of 10°C/min in nitrogen atmosphere.

RESULTS AND DISCUSSION

TGA Analysis for the clays is shown in Figure 1. The first step weight loss at temperatures below 100°C is
due to the loss of unbound water. This value for KF is about 7 wt% and for KT and KD about 2.3 and 1.2 wt%, respectively. The second step weight loss for KF begins at about 500°C with gradually loss of 4.9 wt%, presumably due to bound water molecules [16]. The second step weight loss for organoclays begins at about 200°C due to degradation of the organic compounds with the values of about 27 and 41.8 wt% for KT and KD, respectively. The third step weight loss for organoclays begins at about 500°C similar to that of KF, due to bound water molecules with the values of 3.5 and 2.5 wt% for KT and KD, respectively.

Figure 2 shows the core-shell morphology of the ABS-neat and ABS-KF latex particles prepared by emulsifier-free emulsion polymerization. A relatively good distribution of the clay layers within a single latex particle for the ABS-KF nanocomposite is observed.

Figure 3 shows the XRD patterns of the neat ABS, pristine Na-MMT, organoclays, and corresponding ABS nanocomposites. The basal spacing of the clays and resulting nanocomposites corresponding to the peak positions shown in Figure 3, including each sample specification is summarized in Table 1. No peak is
observed for ABS-neat as expected. KF shows a diffraction peak at $2\theta=7.44^\circ$, corresponding to a d-spacing of 1.19 nm. For ABS-KF nanocomposite, the above mentioned original diffraction peak is completely disappeared and a broad peak with a very low intensity at about $2\theta=5.1^\circ$ corresponding to an average d-spacing of 1.73 nm is observed. The reason for such a low intensity is related to the partially exfoliation and disordered stacking of the clay layers in the nanocomposite and also the low number of the clay layers in the clay aggregates. Also the peak shifted to the lower angles as a result of the intercalation of the polymer chains into the clay galleries. Therefore, for this sample an exfoliated-intercalated structure is established which must be confirmed by TEM observations. The $d_{001}$ reflections for KT and KD organo-

![Figure 4. TEM Images of (a) ABS-KF, (b) ABS-KT, and (c) ABS-KD nanocomposites at low (left) and high (right) magnifications.](image-url)
Clays are observed at $2\theta = 4.18^\circ$ and $2.88^\circ$, corresponding to d-spacing of 2.11 and 3.06 nm, respectively. Calculation of the organic modifier loadings in both organoclays from TGA results (Figure 1) and comparing with those which are obtained using CEC, shows that both organoclays are almost in saturation state, therefore, since the organic ammonium compound used in the modification of KD is composed of two long chain alkyl groups instead of one in KT, the former exhibits a larger increase in d-spacing. Appearance of the $d_{001}$ reflection peaks at $2\theta = 2.63^\circ$ and $2.51^\circ$, corresponding to d-spacing of 3.36 and 3.52 nm for ABS-KT and ABS-KD nanocomposites, respectively, recommends intercalated morphologies for both samples.

To confirm the observed morphologies, bright field TEM analysis was performed on ultramicrotomed samples. Figure 4 shows the results for ABS-KF, ABS-KT and ABS-KD nanocomposites at two different magnifications. Due to the use of AMPS as a reactive clay modifier, and good dispersibility of the Na-MMT in water, ABS-KF shows a relatively uniform distribution of the clay layers in the polymer matrix. Both exfoliated and intercalated morphologies are observed. The TEM images of the ABS-KT and ABS-KD nanocomposites confirm the XRD results and show the intercalated morphologies with increased basal spacing with respect to that of ABS-KF. The number of layers in the clay aggregates of the ABS-KT and ABS-KD nanocomposites is however more than that of ABS-KF nanocomposite.

Figure 5 shows the TGA results for the neat ABS and ABS nanocomposites. As shown the onset thermal degradation temperatures for the nanocomposites moved toward higher temperatures representing the enhanced thermal stability of the nanocomposites. The peak weight loss rate temperatures, in which the maximum rate of degradation occurs, are 462.1, 470.4, 497.7 and 492.2°C for ABS-neat, ABS-KF, ABS-KT and ABS-KD nanocomposites, respectively. More improvements were found for the samples ABS-KT and ABS-KD which were prepared by direct melt intercalation technique. In other word, the intercalated morphology is more effective than exfoliated-intercalated morphology in thermal stability. Similar results on thermal stability of the ABS and PS nanocomposites were reported by Wang et al. [10] and Essawy et al. [17], respectively. Interestingly, ABS-KD in spite of its higher degree of intercalation and increased basal spacing shows a slightly lower thermal stability with respect to ABS-KT. The reason may be attributed to the mass of the polymer chains which intercalate into the basal spacing of the clays. The improvements in d-spacing for ABS-KT and ABS-KD nanocomposites with respect to the corresponding organoclays as shown in Table 1, are 1.25 and 0.46 nm, respectively. It means that a great proportion of the increase in the basal spacing for the sample ABS-KD is due to the presence of the larger mass of the ammonium compound organic modifier consisting of two long chain alkyl groups. Decreasing the amount of styrene-acrylonitrile chains intercalated into the clay layers leads to lower char formation and consequently decreased thermal stability.

### Table 1. Specification of the clays and corresponding nanocomposites.

<table>
<thead>
<tr>
<th>Clay $d_{001}$ (nm)</th>
<th>Nanocomposite $d_{001}$ (nm)</th>
<th>Increase in basal spacing (nm)</th>
<th>Nanocomposite composition PB / ST / AN / MMT / modifier</th>
</tr>
</thead>
<tbody>
<tr>
<td>KF</td>
<td>1.19</td>
<td>1.73</td>
<td>0.54</td>
</tr>
<tr>
<td>KT</td>
<td>2.11</td>
<td>3.36</td>
<td>1.25</td>
</tr>
<tr>
<td>KD</td>
<td>3.06</td>
<td>3.52</td>
<td>0.46</td>
</tr>
</tbody>
</table>

ABS-KT and ABS-KD nanocomposites, respectively.
CONCLUSION

ABS/Clay nanocomposites containing 20 wt% rubber contents and AN/ST weight ratio of 30/70 with 5 wt% clay loadings were synthesized through in-situ emulsifier-free emulsion polymerization and direct melt intercalation techniques. The morphology and thermal stability of the nanocomposites were examined using XRD, TEM and TGA analysis. Exfoliated-intercalated morphology with more uniform distribution of the clay layers and intercalated morphologies with clay aggregates containing more clay layers were established for the nanocomposites prepared by in-situ emulsion polymerization and direct melt intercalation methods, respectively. Nanocomposites prepared by direct melt intercalation showed higher thermal stabilities in comparison with the neat ABS and the one prepared by in-situ emulsion polymerization. Results also showed that the direct melt intercalation method using an organoclay having one long alkyl chain in the modifier, because of its capability in intercalation of the greater amounts of the polymer chains into the clay galleries, gives the better result in thermal stability.

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