Synthesis and Characterization of Poly (Vinyl Acetate)/MMT Nanocomposite Flame Retardant

Mamata Sahu¹, Ramakanta Samal², Trinath Biswal³, Prafulla K Sahoo*¹

¹Department of Chemistry, Utkal University, Vani Vihar, Bhubaneswar 751004, India
²Department of Chemistry, Rajendra College, Bolangir 767002, India
³Department of Chemistry, VSS University of Technology, Burla 768018, India
psahoochemuu@gmail.com

Abstract

Current environmental benign and flame retardant poly (vinyl acetate) (PVAc)/montmorillonite (MMT) clay nanocomposites were prepared by emulsifier free emulsion technique in microwave (MW) oven. MMT clay was incorporated as additional filler in PVAc/MMT nanocomposites to improve the homogeneity of the ‘physical’ barrier, since clay produces silicon-oxy-carbide (Si–O–C) char on heating. The fine dispersion of the MMT and the interactions between PVAc and clay created significant improvement of the flame retardancy which has been evaluated using cone calorimeter. The presence of clay in PVAc/MMT nanocomposites was characterized with infrared (IR), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The fire retardancy of PVAc/MMT nanocomposites caused by the formation of Si–O–C char was characterized by scanning electron microscopy (SEM). The biodegradation property was tested by activated sludge water via water absorbency and was further confirmed from SEM for its better commercialization and ecofriendly nature.

Keywords

Emulsifier Free Emulsion; Microwave; Nanocomposites; Flame Retardant; Biodegradation

Introduction

Polymer-clay nanocomposites have become one of the most popular nanocomposites, since Nylon-6/MMT nanocomposites were invented by Toyota research group in 1993 [Kojima et al 1993]. Various polymers [Aminabhavi et al 1987 and 1989] clays, processes and characterizations associated with the polymer-clay nanocomposites have been reported in the last few decades. Most of the results suggested that only a few weight percentage of clay can effectively improve strength, thermal stability and gas barrier properties.

In our previous papers, we prepared PBA/SS [Sahoo, Prafulla K, Mohapatra Rumki 2003], PAN/SS [Sahoo, Prafulla K, Samal, Ramakanta, Swain, Sarat K and Rana, Pradip K. 2008] nanocomposites, and PMMA Samal, Ramakanta and Sahoo Prafulla K 2006 D nanoparticles by emulsifier free emulsion polymerization method, a clean and prevailing method for manufacture of polymeric lattices. It is also easier to dissipate heat than other polymerization methods. Recently, we have successfully adopted the emulsifier free emulsion polymerization to fabricate the PMMA/MMT nanocomposites, simply by intercalating the PMMA into MMT with an initiator potassium monopersulfate (KMPS). However the PMMA/MMT nanocomposite latex particles are too rigid to form a film by casting, so their applications are limited in packaging, adhesive and coating industries. And for better application in these fields PVAc and its nanocomposites have long been used. PVAc and its copolymers have advantage over these templates due to the maintenance of the superstructures of the monomers during the polymerization Warson H and Finch CA 2001.

The study of polymer/clay nanocomposites with superior thermal, mechanical and barrier properties as compared to virgin polymer Bhat, Santoshkumar D and Aminabhavi, Tejraj M 2006 D has become more attractive by recent demonstrations Kumar, Annamalai P, Depan, Dilip, Tomer, Namrata S and Singh Raj P 2009 and Zhang, Xingui and Loo, Leslie S. 2009 D of their flame retardant properties, namely a significant decrease in the peak heat release rate (PHRR), a change in the char structure, and a decrease in the rate of mass loss during combustion in a cone calorimeter Sahoo, Prafulla K and Samal, Ramakanta 2007, Porter D, Metcalfe E, Thomas MJK 2000D and Gilman, Jeffrey W.1999D. Polymer-clay nanocomposi-
tes are believed to be a new promising approach in fire retardancy due to their great potential in forced flaming conditions, for instance, the reduction of the flame spread and fire propagation. The Si–O–C char were first formed on polymer-clay nanocomposites which improved their thermal and fire retardant properties due to their great potential in forced flaming conditions, for instance, the reduction of the flame spread and fire propagation. The most dominant mechanism in their improved fire retardancy is the accumulation of clay layers at the combusting surface of the condensed phase serving as a barrier to O₂ supply and the pyrolysis gases.

Previously, PVAc/MMT nanocomposites have been prepared by bulk radical Liu, Pinggui, Gong, Kecheng, Xiao, Peng and Xiao, Min2000., melt blending Gelfer et al 2005, soap-free emulsion Chien, An-T and Lin, King-F 2007 polymerization methods by using additives/fillers like graphite oxide Liu, Pinggui, Gong, Kecheng, Xiao, Peng and Xiao, Min. 2000, southern clay Duquesne, S, Jama, C, Bras, ML, Delobel, R, Recourt P and Gloaguen, JM2003, multi-walled nanotube Duquesne, S, Jama, C, Bras, ML, Delobel, R, Recourt P and Gloaguen, JM 2004, bentonite clay Preston, Christopher ML, Amarasinghe, Gandara, Hopewell, Jefferson L, Shanks, Robert A and Mathys Zenka.2004, etc and also their various properties were studied. But to the best of our knowledge no research group in the available literature has employed the flame retardant properties and the role of clay in PVAc/MMT nanocomposites.

Further, studies on green polymeric materials, which avoid the use of any toxic or noxious components in their manufacture and could be naturally biodegradable, are in demand as they reduce the hazardous effect of plastics and other polymeric compounds on environment.

**Experimental Materials**

Vinyl acetate (VAc), was distilled under reduced pressure before being used to remove the inhibitor. The initiator, potassium monopersulfate (KMPS) (Acros), was directly used and all other reagents were from E. Merck, India (AR grade) and were used after purification by standard techniques. MMT clay with cation exchange capacity (CEC) of 90-mequiv/100 g was from Himedia India Ltd.

**Synthesis of PVAc/MMT Nanocomposite**

The microwave reactor was reconstructed from a Whirlpool T120 microwave oven. The electromagnetic energy was produced by a magnetron at 2.45 GHz; the power could be adjusted between 0 and 700 W continuously. The temperature of the reaction system was monitored with an IR temperature pickup. With an internal cooling flask, the temperature could be adjusted precisely and independently of the microwave power in microwave-assisted polymerization by taking known amount of distilled VAc in 4/5th part deionised water via stirring with *in situ* developed CuSO₄ (0.1M)/EDTA (0.1M) complex. At the same time, desired amount of MMT was dispersed in rest 1/5th part of water at same condition for 1 min with constant stirring. The MMT suspension was added to the reaction vessel containing VAc and stirred with constant velocity at 400 to 600 rpm in N₂ atmospheric pressure, and then the flask was heated with 700 W microwave irradiation. After a temperature of 60°C was attained in 1 min, the microwave power was reduced to 40 W to maintain the temperature. Then requisite amount of initiator KMPS solution was carefully injected to the reaction mixture. The polymerization was accomplished in 2 h. Then the polymerization was terminated by the addition of 0.1 M ferrous ammonium sulfate solution keeping the reaction vessel in ice cold water. The precipitate polymers were filtered and purified by washing with distilled water and toluene. Then it was dried at 40°C in vacuum oven till a constant mass was formed.

**Characterization**

The IR spectra of PVAc (degree of polymerization, ~3600), and PVAc /MMT nanocomposite, in the form of KBr pellets were recorded with Perkin-Elmer model Paragon-500 FTIR spectrometer. The interaction of PVAc into the silicate layer was confirmed by using a XRD monitoring diffraction on Philips PW-1847 X-ray crystallographic unit equipped with a Guinier focusing camera CuKα radiation. Nanoscale structure and surface morphology of PVAc/MMT were investigated by means of TEM (H-7100 Hitachi Co), operated at an accelerating voltage of 100 Kv and SEM JEOL Ltd, Japan model 5200 SEM, coating it with gold at different magnifications.

Thermal properties were measured by using a Shimadzu DTA-500 system. It was carried out in air from room temperature to 600°C at a heating rate of 10°C/min.

The fire performance of the PVAc/MMT
nanocomposites were evaluated in a horizontal orientation using a Cone Calorimeter Zanetti, M, Kashiwagi, T, Falqui, L and Camino G. 2002 in accordance with the procedure Lewin et al 2003 outlined in AS/NZS 3837:1998, which was based on ISO 5660-1:1993, with dimensions 100 x 100 x 4 mm$^3$ at a heat flux of 35 kWm$^{-2}$. All the specimens were tested in triplicate using a retaining frame with data collection intervals of 5s. The combustion parameters determined include time to ignition (TTI), rate of heat release (HRR), total heat released (THR), effective heat of combustion, mass loss rate (MLR), carbon monoxide and carbon dioxide yield.

In TTI, time required for the entire surface of the sample is to burn with a sustained luminous flame, whereas in peak heat release rate (PHRR), it expresses the maximum intensity of a fire Weil, Edward D, Patel, Navin G, Said, MM, Hirschler, Macrelo M, and Shakir, S 1992 indicating the rate and extent of fire spread. Fire Performance Index, FPI (m$^2$/s/kW)—defined as the ratio of TTI to PHRR that is parameter related with the time to flashover (or the time available for escape) in a full-scale fire situation Hirschler, MM and Shakir, S. 1992.

Parameters related with the smoke evolution were also obtained, such as total smoke released (TSR) calculated by integrating the smoke released rate (SRR), average of CO (Av.CO) emission, CO/CO$_2$ weight ratio and smoke density, measured by the decrease in transmitted light intensity of a helium neon laser beam photometer, and expressed in terms of average smoke extinction area (Av.SEA). Smoke Parameter, SP (MW/kg) is defined as the product of Av.SEA and PHRR. This parameter is indicative of the amount of smoke generated in a fire situation Scudamore, MJ, Briggs, PJ and Prager FH 1991.

Tensile bars of PVAc/MMT were obtained on a Van Dorn 55 HPS 2.8 F mini injection molding machine under the following processing conditions: a melt temperature of 150°C, a mold temperature of 25°C, an injection speed of 40 mm/s, an injection pressure of 10 MPa, a holding time of 2 s, with a total cycle time of 30 s. Tensile measurements on injection molded samples of nanocomposites were performed according to ASTM D-638-00 using an Instron test machine Model 5567. Tests were carried out at a crosshead speed of 50 mm/min and a 1 kN load cell without the use of an extensometer. All tests were performed at room temperature and the results were the average of five measurements. The highest value of standard deviation was 15%.

The activated sludge water was collected from tank areas receiving toilet and domestic wastewater. In most areas of our country, the waste materials after use are dumped usually near the sludge and the sludge water contains many microorganisms (bacteria, fungi, yeast, etc.) responsible for the biodegradation of waste materials. The sludge was collected Federle et al 2002 in a polypropylene container, which was filled completely and then fully closed. Then, the wastewater was brought to the lab immediately. After settling for about 1h, the total solid concentration was increased to 5000 mg/L. The activated sludge water and a polymer sample (0.2g) were incubated together in a sterilized vessel at room temperature (28± 2°C). Duplicate samples were removed at time intervals for biodegradation study via weight loss. Vessels containing polymer samples without sludge water were treated as controls Liu, Ying-L, Hsu, Chih-Y and Hsu Keh-Y. 2005.

**Results and Discussion**

From the series of experiments, it was found that the PVAc was exfoliated into gallery structure of silicate by the catalytic action of Cu(II)/EDTA complex with help of the initiator KMPS in MW oven. The complex initiating system helps to stabilize the emulsion latex to a high conversion level in the absence of emulsifier. The initiation is a surface catalysis with adequate energy transfer from the complex to the initiator KMPS, resulting in a complex initiation mechanism deviating from a simple path of decomposition.

**Infrared Spectra (FTIR)**

![FTIR](image)

**FIGURE 1. FTIR OF (A) PVAc AND (B) PVAc/MMT (5% w/v) (S) NANOCOMPOSITE.**

A representative FT-IR spectrum of a sample is illustrated in Fig. 1. The peak at 1739 cm$^{-1}$ >C=O, and characteristic peaks at 1239, 1020 cm$^{-1}$ C–O, and 1375
cm⁻¹ CH₃ corresponding to PVAc are clearly seen. In Fig. 1(b), the Si-O-Si bond stretching showed peak at 850–1050 cm⁻¹ which was absent in Fig. 1(a), indicating the presence of silicate in the PVAc/MMT nanocomposite matrix.

**X-ray Diffraction (XRD)**

The systematic arrangement of the silicate layers of the intercalated/exfoliated nanocomposites has been elucidated by XRD in calculating interlayer spacing with the help of Bragg’s equation. Due to the intercalation of PVAc into galleries of silicate of MMT via emulsion polymerization, the d-spacing of PVAc/MMT nanocomposites increased with shifting of 2θ to lower values. The XRD pattern of PVAc/MMT nanocomposites as shown in Fig. 2 (c) indicated the complete disappearance of clay peak which concluded the better dispersion and exfoliation of silicate layers over PVAc matrix at lower concentration i.e. ≤ 5% w/v of MMT. If the concentration of MMT is increased in PVAc matrix, then exfoliated structure is changed to intercalated structure as shown in Figure 2 (b), which has been explained in our previous paper Sahoo, Prafulla K and Samal, Ramakanta 2007 and further evidence from corresponding TEM Figure 3 (a) and (b).

**Transmission Electron Microscopy (TEM)**

TEM studies are necessary to verify the extent of exfoliation/intercalation achieved as shown in Figure 3 (a) and (b) for 5 wt % and 10 wt % samples. In Figure 3 (a) and (b), it is shown that the MMT layers are well dispersed in the PVAc matrix. Although the MMT layers still retain their orientation to some degree, the MMT are highly delaminated into some thin lamellas by PVAc with a dimension of about 1~2 nm in thickness when MMT content is ≥ 5 %, the layered structure of the MMT is generally intercalated in the polymer matrix (Fig. 3(a)). But at lower concentration of MMT i.e. ≤ 5%, the silicate layer fully destroy their orientation, which have good agreement with their XRD. On the basis of the evidence from XRD and TEM, the PVAc/MMT nanocomposites with a highly exfoliated or intercalated structure have been successfully prepared via an in situ intercalation process in the neutral aqueous media.

**TG Analysis**

The thermal properties of the nanocomposite materials have been evaluated by TGA as shown in Figure 4. The difference between decomposition temperature (T_d) of the nanocomposite and that of the free polymer became more pronounced as the silicate content was increased. In contrast to PVAc, the onset of decomposition for PVAc/MMT nanocomposites is shifted towards a higher temperature with inclusion of MMT, indicating an enhancement of the thermal stability upon intercalation. The PVAc/MMT nanocomposite exhibited higher thermal stability due
to the higher decomposition onset temperature than that of PVAc, which can be attributed to the nanoscale silicate layers preventing out-diffusion of the volatile decomposition product Chalais, Stephane, Laszlo, Pierre and Mathy and Arthur1986. On the other hand, since the inorganic part (silicate) of the nanocomposite film almost did not lose its weight during the heating period, the shift of weight loss to higher temperature region might be simply due to that the nanocomposite films possessed relatively small amount (about 4 wt %) of organic polymer that contributed to the weight loss.

**Cone Calorimeter**

Flame retardant mechanism of PLSN by physical barrier methods is due to the formation of Si–O–C (carbonaceous-silicate) char, which acts as insulating barrier for flow of heat and mass. Out of various methods TTI is one which defines the time that a material can withstand the heat flux radiated by a fire before it experiences sustained flaming combustion. It was found from Table 1 and Figure 5, that the TTI of the PVAc/MMT nanocomposites were lower than virgin PVAc i.e., ignition times for nanocomposites were lower than virgin polymer due to the first decomposition of MMT clay at lower temperature present in nanocomposites correlated with previous report Sahoo, Prafulla K and Samal, Ramakanta 2007, Ray, Suprakash S, Okamoto, Kazuaki and Okamoto Masam 2003.

PHRR is one of the most important parameters associated with the flammability and combustion of materials. The samples which have low value of PHRR are better fire retardants than those of high HRR value. The HRR value PVAc/MMT nanocomposites was observably decreased even in the presence of a small amount of silicate. It was found from Table 1 and Figure 5, that the PHRR value of virgin polymer was more than any PVAc/MMT nanocomposites. Due to the formation of Si–O–C ceramic char residue (Fig. 4 (f, g)) by MMT present in PVAc/MMT, nanocomposites (PLSN) act as an insulating protective barrier by reducing the heat and mass transfer between the flame and sample, which has been explained by Gilman, Jeffrey W, Kashiwagi, T. 2000 and also explained in Figure 5. Further, with increasing % of MMT content in the polymer nanocomposites, the HRR values decreased as shown in Figure 5 (b-d) curves. The reduction of PHRR (A) values was proportional to the fraction of clay present in the nanocomposite at low concentrations Gilman, Jeffrey W1999 1999 but the rate of decrease of PHRR value was approximately independent of % of MMT clay at higher concentration was explained in our previous paper PMMA/MMT nanocomposite Sahoo, Prafulla K and Samal, Ramakanta 2007, also given by Gilman, Jeffrey W, Kashiwagi, T, Giannelis, EP, Manias, E, Lomakin, S, Lichtenhan, JD and Jones P. 1998. Total heat released (THR) is a factor which means the total amount of heat evolved during combustion. In the figure the area occupied by the curve is known as THR. From Fig. 5 and Table 1, it is found that the THR values of PVAc/MMT nanocomposites are lower than that of virgin PVAc and decrease is independent of MMT content at higher concentration i.e. ≥ 10% that means are occupied by the curve is same.

**Table 1** Cone Calorimeter Data of PVAc/MMT Nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>TTI (s)</th>
<th>PHRR kWm⁻²</th>
<th>THR MJm⁻²</th>
<th>MLR g/s x10⁻³</th>
<th>Av.CO (kg/kg)</th>
<th>PSEA (m²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAc+0% w/v MMT</td>
<td>63</td>
<td>887±20</td>
<td>68±5</td>
<td>56±5</td>
<td>3.8</td>
<td>228</td>
</tr>
<tr>
<td>PVAc+5% w/v MMT</td>
<td>48</td>
<td>614±19</td>
<td>64±5</td>
<td>43±5</td>
<td>3.0</td>
<td>363</td>
</tr>
<tr>
<td>PVAc+10% w/v MMT</td>
<td>46</td>
<td>482±19</td>
<td>63±5</td>
<td>41±5</td>
<td>2.9</td>
<td>406</td>
</tr>
<tr>
<td>PVAc+15% w/v MMT</td>
<td>44</td>
<td>412±19</td>
<td>63±5</td>
<td>40±5</td>
<td>2.8</td>
<td>489</td>
</tr>
</tbody>
</table>

The mass loss rate (MLR) is a measure of the extent of thermal decomposition and subsequent volatilization of a combustible material in fire. The relationship between the MLR and HRR is linear i.e., it is another factor which describes the fire retardant properties or the heat release capacity depends on the maximum mass loss rate or the heat of combustion of the decomposition products at that temperature. From Table 1, it is found that the MLR value of PVAc/MMT nanocomposites has decreased, with the addition of
MMT in the virgin polymer and this decrease with increasing % of MMT. The value was correlated with the rate of mass loss from a polymer-silicate hybrid when exposed to heat, which was significantly reduced compared with the pure polymer. Le, BM, Camino, G, Bourbigot, S and Delobel, R 1998.

Additionally, several other parameters were measured simultaneously during the cone calorimetry experiments. Those included measurement of the effective heat of combustion, specific extinction area (SEA) (smoke emission) and carbon monoxide and carbon dioxide emissions. Carbon monoxide is recognized as one of the most toxic gaseous products in fires and is a reaction product of the incomplete combustion of volatiles at the fire/composite boundary. It can also be a by-product of the decomposition of certain polymers. From Table 1, it was observed that the decrease of average CO (AvCO) in case of nanocomposite is due to the lower PHRR is explained by Mouritz, AP, Mathys, Z and Gibson, AG 2006. The decrease in the peak smoke emission is due to the presence of the organoclay which causes the decreases of PHRR, suggesting that the char layer that was formed prevented the degradation.

**Mechanical Properties**

The mechanical properties, including Young’s modulus, toughness, yield stress and strain of all the nanocomposites prepared in this study, together with the corresponding values of the virgin polymer are shown in Figure 6 (a). All the nanocomposites exhibit post yield elongation. The Young’s modulus and tensile strength are plotted in Figure 6 (b) as a function of clay content. Both the Young’s modulus and tensile strength steadily increased with clay content. It is noteworthy that tensile modulus increases by 30% and tensile strength by 16% with the addition of 5 wt% clay to PVAc, which is consistent with Kojima, Y, Usuki, A, Kawasaki, M, Okada, A, Fukushima, Y, Kurauchi, T and Kamigaito, O. 1993. The role of clay as a reinforcing agent in PVAc matrix is clearly manifested. The property implying that interfacial bonding between layered silicates and PVAc is stronger. However, a comprehensive understanding of the interfacial interaction between PVAc and MMT is lacking. It has been believed that the higher parity between the surface polarities of PVAc and MMT leads to platelet exfoliation of clay among the polymer matrix, resulting in more efficient reinforcement effect. The toughness of nanocomposites decreased tremendously with increasing silicate content which is in accordance with our previous work PBA/SS Sahoo, Prafulla K, Samal, Ramakanta, Swain, Sarat K and Rana, Pradip K 2008 and also the results obtained earlier Swain Sarat K and Isayev AI 2007.

**Biodegradation**

Biodegradation by activated sludge is less in case of PVAc than that of PVAc/MMT nanocomposites. The biodegradation is increased with increasing percentage of MMT (Table 2). From this observation, it was confirmed that the growth of microorganisms are more in case of nanocomposite due to the presence of hydrophilic MMT content. The percentage weight loss
of nanocomposites is more than the hydrophobic PVAc. The water absorbency is less in case of PVAc, which results in its reducing the biodegradation. The SEM Figure 7 of PVAc/MMT shows more networking surface and regular but, after biodegradation, the surface seems to be rough and unclear, which confirm the microorganisms mediated degradation of the PVAc/MMT nanocomposite.

TABLE 2 BIODEGRADATION OF PVAC/MMT NANOCOMPOSITES BY ACTIVATED SLUDGE WATER

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>% of Weight Loss Days</th>
<th>Water Absorbency Q (g H2O/g Sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>S0</td>
<td>2.11</td>
<td>7.22</td>
</tr>
<tr>
<td>S5</td>
<td>14.81</td>
<td>29.87</td>
</tr>
<tr>
<td>S10</td>
<td>8.58</td>
<td>18.24</td>
</tr>
<tr>
<td>S15</td>
<td>10.64</td>
<td>21.64</td>
</tr>
</tbody>
</table>

**FIGURE 7. SEM OF PVAc/MMT NANOCOMPOSITE (A) BEFORE AND (B) AFTER BIODEGRADATION 30 DAYS.**

**Conclusion**

PVAc/MMT nanocomposites were prepared by novel, cost effective, non-conventional emulsifier free emulsion technique in MW oven. XRD results showed a disorder layer structure due to intercalation/exfoliation of polymer into the layered silicate is further conformed by TEM analysis. These composites are further characterized by TGA and exhibited improved properties of thermal stability with good fire retardant properties. The developed novel flame retardant PVAc/MMT nanocomposites exhibits significant properties thereby inducing hydrophilic character to hydrophobic matrix and most importantly, shows good biodegradability. To conclude, as the synthesized nanocomposites are ecofriendly environmental benign green synthesis by MW, they may open the door for future prospects as commercial flame retardants.

**REFERENCES**


Gilman, Jeffrey W, Kashiwagi, T. Polymer-Clay Nanocomposites; Pinnavaia TJ, Beall GW. Eds.; John