Flame Retardant Nanocomposites of Polystyrene-Modified Sepiolite Clay

Shaﬁ Ur Rehman 1, Sana Javaid 2-3, Muhammad Shahid 1*, Tariq Yasin 4 and Badar Rashid 5

1 School of Chemical and Materials Engineering (SCME), National University of Sciences and Technology (NUST), Islamabad 44000, Pakistan.
2 School of Natural Sciences (SNS), National University of Science and Technology (NUST), Islamabad 44000, Pakistan.
3 Department of Chemistry, University of Wah, Quid Avenue, Wah Cantt, Rawalpindi 47040, Pakistan.
4 Department of Chemistry, PIEAS, Islamabad 45650, Pakistan.
5 Dean of Research and Development (R & D), National University of Technology NUTECH, Islamabad 44000, Pakistan.

Abstract. Flame retardancy is the property that is highly demanded when it comes to deal with plastics in different industries. In this research general purpose polystyrene (GPPS) and modified sepiolite clay are melt blended together to fabricate flame retardant nanocomposites. Structural analysis were performed with the help of Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) techniques. Morphological analysis of the fabricated nanocomposites were carried out using scanning electron microscope (SEM). As a result of better clay dispersion in polymer matrix and intermolecular interactions, mechanical properties are also improved. The standard procedure (ASTM D4986-20) was followed for observing the flame retardancy of the fabricated nanocomposites. Tangible decrease is noted up to 48% in burning rate of the optimum sample which reflects improvement in flame retardancy.

1. Introduction

Polymers and plastics are the choice of many researchers when it comes to light weight, excellent machinability, dimension stability, optics, and superior mechanical properties [1-4]. Almost 70% of the manufacturing industries around the globe are currently producing products of polymers and plastics [5, 6]. However, plastics associated products have the handicap of lower fire retardancy, which need to be addressed. In the recent past, this issue is contended by many researchers i.e. mixing carbon nano tubes (CNTs), trichloroethyl phosphate (TCEP), phosphorus, boron powder, magnesium hydroxide and carbon microspheres in variety of polymers [7-9].

Sepiolite clay is the most feasible and convenient choice when it comes to lower price, easy availability, ecofriendly, fibrous structured and continuous octahedron of [SiO4] and [MgO6] making it a better and suitable filler for polymer matrix [10-12]. Addition of sepiolite clay can certainly increase the flame retardancy of the plastics. However, its
modification can be beneficial in terms of better dispersion within the matrix. Figure 1, shows the octahedron of sepiolite clay, comprises of oxygen, silicon, magnesium and hydrogen [13].

2. Experimental

In this work, sepiolite clay is modified by using vinyl tri-ethoxy silane (VTES). The composites are fabricated as per composition given in table 1. The operational parameters of twin screw extruder are adjusted for optimum dispersion of filler in matrix. First, the mixing was carried out at low spin of the twin screw extruder, where the rollers were adjusted at 10 rpm and temperature maintained at 60 °C. This results in better digestion of the poured ingredients. After the digestion is completed, the rpm increased to 60 and temperature raised upto 210 °C for 120 sec. During this period the cross-linking agent, Di-methacrylate (DMC) is added drop wise. The same process is repeated for all the fabricated samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crosslinker (g)</th>
<th>Irganox 1010 (g)</th>
<th>Stearic Acid (g)</th>
<th>Polymer (polystyrene) (g)</th>
<th>Filler (sepiolite) (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>10</td>
<td>0.0</td>
</tr>
<tr>
<td>S1</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>9.9</td>
<td>0.1</td>
</tr>
<tr>
<td>S2</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>9.8</td>
<td>0.2</td>
</tr>
<tr>
<td>S4</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>9.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

3. Result and Discussion

3.1 FTIR Analysis

The FTIR spectra of the modified sepiolite (m-SP) and neat sepiolite clay are reflected in figure 2 and spectra of the nanocomposites is shown in figure 3. The associated
characteristic peaks of sepiolite clay are present at 690, 1010 and 1210 cm$^{-1}$ respectively. The spectra of modified sepiolite clay shows the stretching vibrations in the region 3500 to 3650 cm$^{-1}$ and bending vibrations at 1670 cm$^{-1}$ of the functional group (O–H), which corroborate the surface modification of the sepiolite clay [14]. The absorption peaks of (Si–O) are observed at 965, 1022 and 1212 cm$^{-1}$ and the bending vibration for (Si–O–Mg) is vivid at 550 cm$^{-1}$ in figure 3. These linkages provide us information about the successful octahedral-tetrahedral linkage among the sepiolite clay and polymer matrix [15].

![Figure 2. FTIR spectra of modified and neat Sepiolite](image)

![Figure 3. FTIR spectra of samples (S0), (S1), (S2) and (S4)](image)
3.2 XRD Analysis

The X-ray diffraction results obtained from respective samples are reflected in figure 4. The pristine sample S0, demonstrates amorphous nature of PS with a broad peak at 20.1°. The % crystallinity keep on increasing as a result of filler addition upto 47% in S4 sample. This reflects the good interfacial interactions among the filler and matrix.

![Figure 4. XRD patterns of the composite samples S0, S1, S2 and S4](image)

3.3 SEM Scans

The surface of the fabricated samples and their morphologies are investigated using scanning electron microscope. The results shown in figure 5, depicts better dispersion of sepiolite clay in polystyrene matrix. Although sepolite clay is famous for its entanglements and agglomerations within the polymer, however modification process of the clay can surely yield better results.
3.2 XRD Analysis

The X-ray diffraction results obtained from respective samples are reflected in figure 4. The pristine sample S0, demonstrates amorphous nature of PS with a broad peak at 20.1°. The % crystallinity keep on increasing as a result of filler addition upto 47% in S4 sample. This reflects the good interfacial interactions among the filler and matrix.

Figure 4. XRD patterns of the composite samples S0, S1, S2 and S4

3.3 SEM Scans

The surface of the fabricated samples and their morphologies are investigated using scanning electron microscope. The results shown in figure 5, depicts better dispersion of sepiolite clay in polystyrene matrix. Although sepolite clay is famous for its entanglements and agglomerations within the polymer, however modification process of the clay can surely yield better results.

Figure 5. SEM analysis of the composites samples S0 in (a), S1 in (b), S2 in (c) and S4 in (d)

3.4 Flame Retardant Analysis

ASTM D4986-20 is used to assess the composite samples' flame retardancy. The different visuals of the test are shown in figure 5. It is worth mentioning that the burning rate of the samples keep on decreasing as a result of filler addition to it as shown in table 2. The optimum sample S4 shows a remarkable decrease of 48% in burning rate, depicts an increase in flame retardancy. The tabulated data obtained as a result of ASTM D4986-20 is given below.

Table 2. Flame retardant test data

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Loading of (m-SP)</th>
<th>Measured Rate of Burning in (cm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S0)</td>
<td>0%</td>
<td>50</td>
</tr>
<tr>
<td>(S1)</td>
<td>1%</td>
<td>36</td>
</tr>
<tr>
<td>(S2)</td>
<td>2%</td>
<td>31</td>
</tr>
<tr>
<td>(S4)</td>
<td>4%</td>
<td>24</td>
</tr>
</tbody>
</table>
3.5 Mechanical Properties

Mechanical properties in terms of tensile strength (TS) and young modulus (E) are shown in figure 6a and 6b respectively. It is quite vivid in figure (6a) that the tensile strength increases steadily upon sepiolite addition from 38.7 to 46.3 MPa. Similarly in figure (6b) the values of young modulus (E) increased from 3.01 to 3.92 GPa. These increment emulates the better dispersion and linkage formation among the filler and matrix.

Figure 6. Flame retardancy analysis of the composites samples at different stages

4. Conclusion

As a result of this research, we were able to fabricate the flame retardant plastic composites. The filler used in this work is sepiolite clay which is inexpensive, easily available and ecofriendly. Apart in decreasing the burning rate upto 48%, thermal stability and tailored mechanical properties are also achieved.

5. Acknowledgement

The first phase of this research was carried out at School of Chemical and Materials Engineering (SCME) National University of Science and Technology (NUST, H-12 Campus), Pakistan, while the second phase completed at Department of Chemical
Engineering & Materials Science, Michigan State University (MSU), East Lansing, MI 48824, USA.

**Author contribution**

Shafi Ur Rehman performed the experiments, data analysis, wrote the original manuscript. Dr. Muhammad Shahid supervised, Sana Javaid reviewed and validated the results. Tariq Yasin facilitated in extruding and fabrication of composites, Badar Rashid provided the precursors and testing facilities for experiments.

**Conflict of interest**

All authors in the research have no conflict of interest.

6. **References:**