Preparation and Thermal Properties of Phenolic Resin-Silica Nanocomposites via Solvothermal Method

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ARTICLE INFO

Article history:
Received 3 August 2015
Accepted 28 October 2015
Available online 31 October 2015

Keywords:
Phenolic resin, silica content, nanocomposites, preparation, thermal properties

ABSTRACT

Phenolic resin-silica nanocomposites samples in pellet shape have been successfully prepared by intercalation of polymer solution through the hot pressing method. The phenolic resin is modified with organic elastomers of silica nanoparticles, which is about 20 nanometer in diameter. The change of density and porosity was studied based on the addition of silica content in the phenolic resin composites. The densities of composites increased with the addition of the silica content from 10 wt.% to 40 wt.%. On the other hand, the porosity percentage was decreased with increasing of silica contents. The curing behaviors of phenolic resin and phenolic resin-silica nanocomposites samples were observed with Differential Scanning Calorimeter (DSC) under nitrogen atmosphere. A typical nanocomposites samples weight was around 3.00-5.00mg heating rate 10°C/min from 30°C to 200°C. Consequently, the physical properties of the phenolic resin-silica nanocomposites were improved with the addition of 10 wt.% to 30 wt.% silica contents, as compared to that of the pure phenolic resin.

INTRODUCTION

In recent years, polymer/layered silicate (PLS) nanocomposites have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in materials properties when compared with virgin polymer or conventional micro- and macro-composites. These improvements include high modulus, increased strength and heat resistance, decreased gas permeability and flammability and increased biodegradability of biodegradable polymers. On the other hand, there has been considerable interest in theory and simulations addressing the preparation and properties of these materials and they are also considered to be unique model systems to study the structure and dynamics of polymers in confined environments (Suprakas Sinha Ray and Masami Okamoto, 2003).

Although the intercalation chemistry of polymers when mixed with appropriately modified layered silicate and synthetic layered silicates has long been known, the field of PLS nanocomposites has gained momentum recently. Two major findings have stimulated the revival of interest in these materials: first, the report from the Toyota research group of a Nylon-6(N6)/Montmorillonite (MMT) nanocomposite, for which very small amounts of layered silicate loadings resulted in pronounced improvements of thermal and mechanical properties; and second, the observation by Vaia at it is possible to melt-mix polymers with layered silicates, without the use of organic solvents. Today, efforts are being conducted globally; using almost all types of polymer matrix(Suprakas Sinha Ray and Masami Okamoto, 2003). This review highlights the major developments in this area during the last decade. The different techniques used to prepare PLS nanocomposites, their physicochemical characterization and the improved materials properties that those materials can display; their processing and probable application of PLS nanocomposites (Suprakas Sinha Ray and Masami Okamoto, 2003).

The resulting interaction between the modifiers preoccupied in organosilicates and phenolic resin and on the morphology and curing behavior, (Min Ho Choi, 2000) tried to synthesize of the phenolic resin-layered silicate nanocomposites. They obtained the modification of layered silicate the resulting interaction between organic modifier and phenolic resin played an important role in determining the stable nanostructure and final morphology of phenolic resin-layered silicate nanocomposites (Min Ho Choi, 2000).

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To overcome the resol type phenolic resin this has never been used in the polymer/layered silicate nanocomposites field because of difficulty in making linear resol type phenolic oligomers (Ho Yun Byun, 2001), tried to synthesize the phenolic resin-layered silicate nanocomposites. They have synthesized of the phenolic resin-layered silicate nanocomposites using various layered silicates by melt intercalation. To investigate the thermal decompositions of phenolic resin/intercalated kaolinite/asbestos cloth nanocomposites, (Ahmad Reza Bahramian, et al., 2007) using thermal analysis techniques and the kinetics parameters were determined to clarify the thermal degradation mechanism.

Based on the above discussion, there is no doubt that layered silicate (inorganic polymer) has a very high potential to improve phenolic resin applications. Hence, this research is aimed to investigate the structure of phenolic resin modification by addition of layered silicate

**Experimental:**

In this work, the solution method is employed for nanocomposites samples preparation. Solid phenolic resin and silica content were mixed mechanically then stirred in a beaker at room temperature for 1 hour to form homogeneous solutions, followed by curing at 200°C for 10 minutes on a hot press. The mixing weight ratios of phenolic resin composites and silica solution selected in the study are 100:0, 90:10, 80:20, 70:30, 60:40 and 50:50. Nanocomposites sample were presented as PxSy, where P is phenolic resin composites, S is silica solution, x and y is the weight ratios of each component respectively. For examples, P80S20 is the mixture of 80 wt. % phenolic resin composites (P) and 20 wt. % of the silica solution. The final nanocomposites samples were in pellet shape with the diameter of 30 mm. The curing behaviors of phenolic resin and phenolic resin-silica nanocomposites samples were observed with Differential Scanning Calorimeter (DSC) under nitrogen atmosphere. A typical nanocomposites samples weight was around 3.00-5.00 mg heating rate 10°C/min from 30°C to 200°C.

**RESULT AND DISCUSSION**

The density values for each nanocomposites sample are shown in Table 1. The table shows the weight values of the nanocomposites samples in air and in distilled water conditions.

![Fig. 1: Density values of the phenolic resin composite addition with the silica content (weight percentage).](image)

From Table 1, the density values of phenolic resin composites addition with silica content (P100S0, P90S10, P80S20, P70S30 and P60S40) nanocomposites samples are 82.1 kg/m³, 41.2 kg/m³, 81.0 kg/m³, 116.5 kg/m³ and 204.4 kg/m³ respectively. Figure 1 shows the density values dependence of silicate content (weight percentage).

The density of phenolic resin–silica nanocomposites is higher than that of pure phenolic resin. The density values of phenolic resin is increase slightly with the addition of silica content from 10 wt.% - 40 wt.%. Since the density of silica content is higher than that of pure phenolic resin composites. The nanocomposites samples which have higher density value, shows that the nanocomposites is heavier samples than the nanocomposites samples which have lower the density value. These result agrees with the one reported by Ma et al., (2005).

The porosity percentage values for each nanocomposites sample are shown in Table 2. The values of porosity for the phenolic resin–silica nanocomposites samples (P100S0, P90S10, P80S20, P70S30 and P60S40) are 1.2%, 2.4%, 1.3%
0.9% and 0.5% respectively.

**Table 2:** Porosity values of the nanocomposites samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Porosity (100%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P100S0</td>
<td>1.2</td>
</tr>
<tr>
<td>P90S10</td>
<td>2.4</td>
</tr>
<tr>
<td>P80S20</td>
<td>1.3</td>
</tr>
<tr>
<td>P70S30</td>
<td>0.9</td>
</tr>
<tr>
<td>P60S40</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Fig. 2:** Porosity value of the phenolic resin addition with the silica content (weight percentage).

Figure 2 illustrates the porosity percentage versus silica content (weight percentage) of the nanocomposites sample. The porosity decreases with the mixing ratio of silica content 10 wt.% - 40 wt.%.

The change in porosity of the phenolic resin nanocomposites should correlate with the change in density of the phenolic resin nanocomposites. The relationship between the porosity and density is shown in Figure 3.

**Fig. 3:** Density of the phenolic resin addition with silica content (weight percentage) with porosity.

Higher porosity gives lower density value for the phenolic resin-silica nanocomposites (from 10 wt.% to 40 wt.%). Comparing the results in Figure 5.1 for phenolic resin nanocomposites, as the silica solution content increases, the density increase, however the porosity percentage decreases. This is in agreement with (Ma et al., 2005).

The thermal properties of phenolic resin-silica nanocomposites samples have been calculated is presented which in Table 3. The glass transition temperature, Tg of the nanocomposites were determined after one the inflection point of the glass transition region on the Differential Scanning Calorimeter (DSC) thermograph that was obtained by heating at a rate of 10°C/min from 30°C to 200°C under nitrogen circulation. The enthalpy of the nanocomposites was obtained at peak area on the DSC thermograph.

**Table 3:** Thermal properties of the nanocomposites sample

<table>
<thead>
<tr>
<th>Properties</th>
<th>Weight (mg)</th>
<th>Transition Temperature (°C)</th>
<th>Enthalpy (J/g)</th>
<th>T first peak (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P100S0</td>
<td>3.410</td>
<td>143.44</td>
<td>150.1749</td>
<td>67.05</td>
</tr>
<tr>
<td>P90S10</td>
<td>2.637</td>
<td>157.46</td>
<td>2.3089</td>
<td>159.11</td>
</tr>
<tr>
<td>P80S20</td>
<td>2.231</td>
<td>156.96</td>
<td>132.8417</td>
<td>57.55</td>
</tr>
<tr>
<td>P70S30</td>
<td>4.209</td>
<td>155.07</td>
<td>280.3927</td>
<td>59.19</td>
</tr>
<tr>
<td>P60S40</td>
<td>3.932</td>
<td>153.91</td>
<td>99.6301</td>
<td>73.81</td>
</tr>
</tbody>
</table>

The values of the Transition Temperature for the phenolic resin composites addition with silica
content weight percentage were shown in Figure 4.

**Fig. 4:** Transition Temperature of the phenolic resin composites addition with silica content (weight percentage).

The addition of silica content decreases the curing reactivity of the phenolic resin nanocomposites which can be also demonstrated by the decrease in the glass transition temperature. For the pure phenolic resin, the glass transition temperature is 143.44 °C. For the 10wt. % of silica content on the phenolic resin nanocomposites, the glass transition temperature is 157.46 °C which is 14.02 °C higher than pure phenolic resin. This width of transition increases with addition of silica content. The value of Tg obtained for 20wt. % of silica content is 156.96 °C, for 30wt. % of silica content is 155.07 °C and for 40wt. % of silica content is 153.91 °C. Incorporation of silica content weight percentage into phenolic resin system has significant effect on the Tg value. Glass transition temperature, Tg decrease with increase of silica content in the amount of phenolic resin. The enthalpy of curing reaction of the phenolic resin was altered from 2J/g - 280 J/g when the addition with 10wt. % - 40wt. % of the silica content. This is due to the fact that the reaction is incomplete when the silica content is dissolved in phenolic resin and far apart to bond each other. The enthalpies of the nanocomposites are presented in Figure 5.

**Fig. 5:** Enthalpy values of the phenolic resin composites addition with silica content (weight percentage).

The enthalpies of the curing reaction as a function of porosity are depicted in Figure 6.

**Fig. 6:** Enthalpy of curing reaction of phenolic resin addition with silica content with porosity.

From figure 6, as the porosity is reduced from 2.5% to 1%, the magnitude of the enthalpy is increases from 2.3J/g to 280J/g. This indicates that more bonding is occurring per unit mass of the solution as the porosity decreases. However, the porosity is further reduced that the magnitude of the enthalpy drops due the fact that most of the solution did not penetrate the pores.

**Conclusion:**

In this research, synthesized phenolic resin-silica nanocomposites using different weight ratios of phenolic resin and layered silicate prepared via intercalation have been successfully prepared. The characterizations of phenolic resin-silica nanocomposites samples found in the present study.
can be summarized as follows:
1. The addition of silica content on the phenolic resin composites play an important role in determining the pore/porosity on the surface structure and final morphology of the phenolic resin-silica nanocomposites.
2. The brittleness of the phenolic resin composite was reduced with the addition of 30 wt.% and 40 wt.% silica content on nanocomposites. The brittleness of nanocomposites can be reduced if porosity percentage on the nanocomposites is low and the Young’s modulus and energy to break is high.

REFERENCES


