Preparation and characterization of boron-nitrogen coordination phenol resin/SiO$_2$ nanocomposites

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Abstract. The boron-nitrogen-containing phenol-formaldehyde resin (BNPFR)/SiO$_2$ nanocomposites (BNPFR/SiO$_2$) were synthesized in-situ, and structure of BNPFR/SiO$_2$ nanocomposites was characterized by FTIR, XRD and TEM. The loss modulus peak temperature $T_p$ of BNPFR/SiO$_2$ nanocomposites cured with different nano-SiO$_2$ content are determined by torsional braid analysis (TBA). The thermal degradation kinetics was investigated by thermogravimetric analysis (TGA). The results show that nano-SiO$_2$ particulate with about 50 nm diameter has a more uniformly distribution in the samples. The loss modulus peak temperature $T_p$ of BNPFR/SiO$_2$ nanocomposite is 214 °C when nano-SiO$_2$ content is 6 wt%. The start thermal degradation temperature $T_{10}$ is higher about 30 °C than pure BNPFR. The residual rate (%) of nanocomposites at 800 °C is above 40 % when nano-SiO$_2$ content is 9 %. The thermal degradation process is multistage decomposition and following first order.

Keywords: boron-nitrogen-coordination; phenol-formaldehyde resin; nanocomposites; nano-SiO$_2$; thermal analysis

1. Introduction

Phenolic-formaldehyde resin (PFR) is an excellent thermosetting resin, which has the good mechanical properties and heat resistance. They are widely used to prepare fiberglass-reinforced laminate, molding compounds, thermal insulation materials, coating, and adhesive, especially in the high-technology fields, such as spaceflight, rocketry, and so on (De et al. 2007). However, the phenolic hydroxyl, ether bond and methylene in the structure of phenolic resin are easily oxidized. These shortcomings will decrease the heat resistance, oxidation resistance and mechanical properties of materials. In order to improve its performance, the phenolic resins called boron-containing phenol-formaldehyde resin (BPFR) were obtained by introducing inorganic element boron into the resolve and novolac phenolic resin (Abdalla et al. 2003, Martin et al. 2006, Liu et al. 2002, Gao et al. 2004 and 2010). The effectiveness of the borate as the flame-retardants in various materials has been explained by their formation of non-penetrable glass coating in these materials when they are heated. The glass coatings exclude oxygen and prevent further propagation combustion. However, the general BPFR is extremely sensitive to moisture or water, because of the unsaturating property of boron atom. These shortcomings will restrict the range of
applications and storage condition of BPFR. In order to improve the hydrolytic stability and physical properties of BPFR, many researchers have done some works, such as modified by B-N or, B-O coordination, layered-silicate nanoparticles, nanoparticles, etc (Gao et al. 2004 and 2010, Wang et al. 2008, Hoofel et al. 1975). But the coordination structure of boron atom in foregoing reported resins has not fully formed in the synthesized process, so they have yet not very good water resistance.

Organic/inorganic hybrid nanocomposites prepared in situ created inorganic phase method have become a fascinating new field of research in materials science (Siramanont et al. 2009, Yuvaraj et al. 2010). Nanostructure hybrid organic-inorganic composites typically exhibit superior mechanical properties than the parent materials. Many polymers, including polyimide, epoxy resin, polystyrene, poly (dimethyl siloxane) et al, have been used to produce hybrid nanocomposites (Rund, et al. 2012, Nayak et al. 2012, Kusmono et al. 2010). Chiang C. and Byun H.Y. et al had reported that the common phenol-formaldehyde resins were modified by nanosilica formed from hydrolytic condensation of tetraethoxysilane or organic-montmorillonite (Chiang et al. 20004, Byun et al. 2001).

We have reported the synthesis of organic-inorganic hybrid boron-containing phenol-formaldehyde resin/SiO$_2$ nanocomposites, but it is not contained boron-nitrogen coordination structure (Gao et al. 2008). Wang D. C. et al had reported the preparation and thermal stability of general boron-containing phenolic resin/clay nanocomposites (Wang et al. 2008). But these resins have yet not good water resistance. To the best of our knowledge, there is no precedent report on the synthesis of boron-nitrogen coordination containing phenol-formaldehyde resin (BNFR)/ SiO$_2$ nanocomposites from Phenol, boric acid, aminoethyl alcohol and paraformaldehyde, and in situ created nano-SiO$_2$. In this work, the boron-nitrogen coordination containing phenol-formaldehyde resin/SiO$_2$ nanocomposite (BNFR/SiO$_2$) was synthesized. The structure and the distributions of silicon element were characterized by Fourier-transform infrared spectroscopy (FTIR), energy dispersive X-ray spectrometry (EDS) and transmission electron microscope (TEM), respectively. The loss modulus peak temperature $T_p$ was determined by torsional braid analysis (TBA). The kinetics of thermal degradation and thermal stability were determined by thermogravimetry analysis (TGA).

2. Experimental details

2.1 Materials

Phenol, boric acid, aminoethyl alcohol, paraformaldehyde, sodium hydroxide, ethanol, 37% aqueous formalin and acetone were all analytically pure grade, which were supplied by Tianjin Chemical Co. China; Tetramethoxysilane (TMOS) was supplied by Jintan Chemical Co. of Zhejiang, China.

2.2 Synthesis of BNFR/SiO$_2$ nanocomposites

The aminoethylbiphenli borate was synthesized according to the method from literature (Zhai et al. 2008). 0.2 mol Phenol, 0.1 mol boric acid and 30 mL toluene were put into a four-necked round bottom flask, equipped with a stirrer, a thermometer and an oil-water segregator. The mixture was heated to 120 °C and held at this temperature for 30 min, then was gradually heated to 180°C and
Preparation and characterization of boron-nitrogen coordination

maintained at this temperature for 3 h until theoretic quality water was removed out from reaction system and the biphenol borate was obtained. Then the system temperature was reduced to 60°C and added 0.1 mol aminoethyl alcohol to it, and reaction continuous for another 4 h. The water formed in the reaction and un-reactants were removed in vacuum. The product was wished with water and extracted with ethyl ether, then dried with anhydrous MgSO₄. The aminoethylbiphenyl borate (AEBPB) was obtained after removed ethyl ether in vacuum, which structure as Scheme 1.

First, 1 mol AEBPB, 2.6 mol paraformaldehyde, 1 g oxalic acid and 30 mol toluene were put into a four-necked round bottom flask, equipped as forenamed. The mixture was heated to 120°C and held at this temperature for 2 h. The toluene and water formed in the reaction were removed in vacuum. In the second step, 80 mL ethanol was added into this system with 7.15 g TMOS (3 wt% SiO₂) dropping at 80°C, and continued reaction for another 3 h. Finally, the BNPFR/SiO₂ nanocomposites as a semi-transparent yellow solid was obtained after the water and ethanol were removed in vacuum.

By changing the dosage of TMOS, the BNPFR/SiO₂ nanocomposites with different SiO₂ content were obtained.

The general boron-containing phenol-formaldehyde resin (BPFR) was synthesized according to the method from literature (Liu et al. 2002), the mole ratio of phenol : formaldehyde : H₃BO₃ is 3 : 3.9 : 1.

2.3 Equipment and Characterization Procedures

FTIR spectrometer (FTS-40, Bro-Rad, USA) was used to investigate the structure of BNPFR/SiO₂ nanocomposite. The resin was dissolved in acetone and then coated as a thin film on a potassium bromide plate. When the solvent in the film was completely evaporated in vacuum, the potassium bromide plate was scanned from 400 cm⁻¹ to 4000 cm⁻¹ by the FTIR spectrometer.

The distribution of silica was characterized by means of energy dispersive X-ray spectrometry (EDS). Resin was heated and pressed to 1.0 mm thickness plate, and then was determined by EDS (Thermo Noran Co. USA), the accelerate voltage was 25 kV and resolution was 128×128.

A transmission electron microscope (TEM, JEM-100CX, JEOL, Japan) was used to determine the size and distribution of nanosilica. The sample was prepared by frozen sectioning method. The testing voltage was 100 KV and resolution was 0.14 nm.

The thermal stability of the samples was characterized by using a thermogravimetric analyzer (TGA, Pyris-6, Perkin-Elmer, US) operating under a nitrogen atmosphere. About 10 mg BNPFR/SiO₂ power cured at 180°C for 2h was introduced into the thermobalance, and then heated from 25°C to 800°C at 20°C/min heating rate and in nitrogen flow 20 mL/min.

A cleaned glass fiber braid was first dipped in resin-acetone solution for about 30 min, and then the acetone was completely evaporated in vacuum. The specimens were cured at 185°C in an oven for 2 h. Then, they were removed and cooled to room temperature, and the dynamic mechanical properties of BNPFR/SiO₂ nanocomposites were investigated with a torsional braid analyzer (TBA, GDP-4, Jilin University, China) at the heating rate of 2°C min⁻¹. The maximal mechanical loss peak temperature (Tₚ) could be obtained. Because it has one-to-one relationship between Tₚ and mechanical loss peak temperature TP, these Tₚ temperatures were obtained by adopting the above method.

The hydrolytic stability of resins was determined by a half-life of acid-base titration method (Shen et al. 1999). The 0.1 mol/L NaOH solution in which the NaOH mol amount equivalent to half the mol amount of boron in resin was added into mixed solution of 50 mL water and 5 mL...
glycerol (containing 4 drop phenolphthalein) with agitated, and recording the time of changed color.

3. Results and discussion

3.1 Structure of BNPFR/SiO$_2$ nanocomposite

Fig. 1 is the FTIR spectra of BNPFR and BPFR. According to data from literature (Shen et al. 1999, Shen 1982, Gao 1990), the principal absorption bands of BPFR are: the hydroxyl group –OH at 3300-3500 cm$^{-1}$, the benzene ring at 1600 cm$^{-1}$ and 750 cm$^{-1}$, the phenol borate B-O at 1350 cm$^{-1}$, the methylene group -CH$_2$- at 1450 cm$^{-1}$ and 2920 cm$^{-1}$, benzyl hydroxyl group at 1250 cm$^{-1}$, ether linkage C-O at 1100 cm$^{-1}$, C-N at 1580 cm$^{-1}$, -OH and –NH at 3300-3500 cm$^{-1}$. Comparison the FTIR spectra of BNPFR and BPFR in Fig. 1, it is seen that the absorption band of B-O bond at 1350–1380 cm$^{-1}$ in BNFR has disappeared, which shows that the coordination structure of B-N had formed in BNPFR. The result is coincident with that the result of IR absorption band of borate will disappear in B-O coordination structure (Tu et al. 1981, Hoofel et al. 1975, Gao et al. 1990). Another, it can also see that the absorption band of hydroxyl group –OH at 3300-3500 cm$^{-1}$ in the BNPFR has disappeared, which shows that the aminoethylbiphenli borate has formed.

Schem. 1 molecular structure of aminoethylbiphenli borate

![Schem. 1 molecular structure of aminoethylbiphenli borate](image)

Fig. 1 FTIR spectra of BNPFR and BPFR
Fig. 2 The silicon element distributions of 3 and 9 wt% BNCFR/SiO$_2$

Fig. 3 TEM images of 9%SiO$_2$/BNCFR nanocomposites

3.2 EDS and TEM analysis

Fig. 2 shows the silicon element distribution in the 3, 9 wt% BNPF/BNCFR/SiO$_2$ nanocomposites, respectively. In the Fig. 2, the white point is SiO$_2$ particulate which was formed from TMOS. Comparison the silicon element distribution in Fig. 2, it can find out that the silicon element has a more uniformly distributed, only a small amount of conglomeration, and the density of SiO$_2$ particulate increase with the increasing additive amount of TMOS.

Dispersion and size of nano-SiO$_2$ is observed with TEM and shown in Fig. 3. As seen from Fig. 3, the size of nano SiO$_2$ is about 40-60 nm in diameter and more uniformly dispersed in the BNPF matrix. The results of EDS and TEM analysis show that in-situ formed nano-SiO$_2$ from TMOS had more homogeneous distributed in the BNPF and organic-inorganic hybrid nanocomposite had been obtained.

3.3 Torsional braid analysis

Because the glass transition temperature ($T_g$) can be used effectively to monitor the molecular motion and curing reaction, and has a relationship between the $T_g$ and the degree of cure. $T_g$ has
been used directly as a parameter of heat-resistance for polymer and as a parameter for conversion in the analysis of reaction kinetic models for thermosetting polymers (Gillham 1997). TBA method can be used to determine the \( T_g \) of the thermosetting system, and it is particularly useful at high conversion and after vitrification because of the non-linearity of \( T_g \) versus conversion (Venditti et al. 1997). DSC is usually used to determine the \( T_g \) of polymer, but it is not a best method for thermosetting polymers, especially at higher conversion, because the shift of DSC curve will be very small and inconspicuous at that time. TBA is usually used to determine the maximal mechanical loss temperature (\( T_p \)) of thermosetting polymers (Gillham 1997, Brandalise et al. 2009, Doyle et al. 2003), which has a one-to-one relationship between \( T_g \) and \( T_p \). The higher \( T_p \), the higher \( T_g \) is, which depends on the curing conditions, such as amount of cross-linked agent, cure temperature and time.

Fig. 4 is the TBA curves of BNPFR/SiO\(_2\) nanocomposites curing 120 min at 180°C. As seen from Fig. 4, the loss modulus curve has one bigger and relatively narrow peak at 200°C for 3 wt% SiO\(_2\) BNPFR/SiO\(_2\) nanocomposite, the 6 wt% SiO\(_2\) BNPFR/SiO\(_2\) nanocomposite has a relatively broad peak at 214°C, which is 14°C higher than that of 3 wt% SiO\(_2\) BNPFR/SiO\(_2\) nanocomposite under the same curing condition. The reasons are probably between the surfaces of nano-SiO\(_2\) with BNPFR molecular exist physical absorption and chemical cross-linking with formation of C-O-Si bond during curing process, which effectively hinder the motion of polymer molecule chains. However, the loss modulus peak temperature \( T_p \) for 9 wt% SiO\(_2\) BNPFR/SiO\(_2\) nanocomposite and 12 wt% SiO\(_2\) BNPFR/SiO\(_2\) nanocomposite are not only higher than that of 6 wt% SiO\(_2\) BNPFR/SiO\(_2\) nanocomposite, contrary, their \( T_p \) are lower than it. Table 1 is the \( T_p \) of BNPFR/SiO\(_2\) nanocomposites which has different SiO\(_2\) content. The reasons are probably relative with congregation of nano-SiO\(_2\) when it has a higher content. The result shows that BNPFR and BNPFR/SiO\(_2\) nanocomposite have a highest \( T_p \) at 214°C.

![Fig. 4 TBA curves of BNPFR/SiO\(_2\) nanocomposites](image)

<table>
<thead>
<tr>
<th>SiO(_2) Content</th>
<th>( T_p )/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 %SiO(_2)</td>
<td>200</td>
</tr>
<tr>
<td>6 %SiO(_2)</td>
<td>214</td>
</tr>
<tr>
<td>9 %SiO(_2)</td>
<td>199</td>
</tr>
<tr>
<td>12 %SiO(_2)</td>
<td>191</td>
</tr>
</tbody>
</table>
3.4 Thermal stability and degradation Kinetics

In order to investigate the thermal stability of BNPFR and BNPFR/SiO$_2$ nanocomposites, the resin powders cured 120 min at 180°C were used to determine the thermal weight loss behavior. Fig. 5 shows the TG curves of BNPFR and BNPFR/SiO$_2$ nanocomposites with different content of nano-SiO$_2$.

As seen from Fig. 5, the thermal degradation process of BNPFR can be primarily divided into two stages. For pure BNPFR, the first degradation stage is from 275 to 350°C, the second degradation stage is from 376 to 800°C. For BNPFR/SiO$_2$ nanocomposites, the thermal degradation process can be primarily divided into three stages. The first degradation stage is from 306 to 466°C, which is higher 25-30°C than BNPFR; the second degradation stage is from 467 to 606°C; the third stage is 607 to 800°C. Table 2 shows the residual weight (%) of resins at different temperature. As seen from Fig. 5 and Tab. 2, the nanocomposite has a higher starting degradation temperature and a higher residual weight than pure BNPFR before 700°C. The reason is probably that in-situ formed nano-SiO$_2$ can adsorb a mass of polar groups in BNPFR, and form strong interaction with molecular chains of BNPFR, which include physical absorption and chemical cross-linking with formation of C-O-Si bond. So the thermal stability of BNPFR was improved by the in-situ formed nano-SiO$_2$. Particular, it has a higher residual weight and increase with increasing SiO$_2$ content.

To determine the kinetic parameters of thermal decomposition from the thermo-gravimetric data, the first step is to evaluate the conversion of reaction. The weight change of sample is regarded as a function of temperature and the conversion $\alpha$ can be expressed as follows

$$\alpha = \frac{W_0 - W_T}{W_0 - W_\infty}$$

where $W_0$ is the sample weight in $i$ stage, $W_T$ is the residual weight of the sample at temperature $T$.

![Fig. 5 TG curves of BNPFR/SiO$_2$ with different nano-SiO$_2$](image)
Table 2 The residual rate of SiO$_2$/BNPFR nanocomposites at different temperature

<table>
<thead>
<tr>
<th>SiO$_2$/BNCFR</th>
<th>0 %SiO$_2$</th>
<th>3 %SiO$_2$</th>
<th>6 %SiO$_2$</th>
<th>9 %SiO$_2$</th>
<th>12 %SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 °C</td>
<td>91.69</td>
<td>96.03</td>
<td>95.07</td>
<td>95.57</td>
<td>96.33</td>
</tr>
<tr>
<td>400 °C</td>
<td>62.98</td>
<td>72.75</td>
<td>76.64</td>
<td>73.17</td>
<td>74.73</td>
</tr>
<tr>
<td>600 °C</td>
<td>46.46</td>
<td>56.55</td>
<td>58.13</td>
<td>59.39</td>
<td>62.61</td>
</tr>
<tr>
<td>deducting SiO$_2$</td>
<td>55.5</td>
<td>63.65</td>
<td>65.84</td>
<td>67.39</td>
<td>70.61</td>
</tr>
<tr>
<td>700 °C</td>
<td>40.91</td>
<td>46.17</td>
<td>48.34</td>
<td>49.76</td>
<td>57.39</td>
</tr>
<tr>
<td>deducting SiO$_2$</td>
<td>44.51</td>
<td>50.76</td>
<td>53.04</td>
<td>54.49</td>
<td>61.58</td>
</tr>
<tr>
<td>800 °C</td>
<td>31.99</td>
<td>29.16</td>
<td>30.50</td>
<td>40.32</td>
<td>48.76</td>
</tr>
<tr>
<td>deducting SiO$_2$</td>
<td>25.97</td>
<td>24.36</td>
<td>24.72</td>
<td>31.22</td>
<td>36.37</td>
</tr>
</tbody>
</table>

\[
\frac{d\alpha}{dt} = k(T) f(\alpha) \tag{2}
\]

\[
k(T) = A \exp\left(-\frac{E_a}{RT}\right) \tag{3}
\]

\[W_w\] is the final weight at that stage. Therefore, According TGA curves and Eq. (1), the conversions are calculated for different degradation stages.

In solid-state reaction system, the kinetics of thermal degradation is described as follows

\[
\text{Where } \frac{d\alpha}{dt} \text{ is the degradation rate, Eq. (3) is the Arrhenius equation, } A \text{ is the pre-exponential factor in the Arrhenius equation, } E_a \text{ is the apparent activation energy, } R \text{ is the universal gas constant, } T \text{ is the absolute temperature. In TGA experiments, heating rate } \beta = \frac{dT}{dt} \text{ is a constant, so heating rate is regarded as a function of temperature, which depends on the time. So the reaction rate can be expressed as}
\]

\[
\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \cdot \frac{dT}{dt} = \beta \frac{d\alpha}{dT} \tag{4}
\]

\[
\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha) \tag{5}
\]

By applying the temperature integral term to Eq. (5), we can obtain Eq. (6) as follow

\[
G(\alpha) = \int^\alpha_0 \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int^\alpha_0 \exp\left(-\frac{E_a}{RT}\right)dT \tag{6}
\]

where \(G(\alpha)\) is the integral form of the conversion dependence function, the correct form of \(G(\alpha)\) depends on the proper reaction mechanism. Differential expression of \(G(\alpha)\) for some
solid-state reaction mechanism can be described as following: in first order \((n = 1)\), \(G(\alpha) = -\ln(1-\alpha)\); in second order \((n = 2)\), \(G(\alpha) = 1/(1-\alpha)\); in third order \((n = 3)\), \(G(\alpha) = 1/(1-\alpha)^2\) (Maron et al. 1974).

In this work, because of the degradation of BNPFR/SiO\(_2\) nanocomposite is a mult-stage process, the TGA data were analyzed base on the Madhusudanan-Krishnan-Ninan method (MKN method) (Madhusudanan et al. 1986), which can be expressed by the following equation

\[
\ln \left( \frac{G(\alpha)}{T^{1.92}} \right) = \ln \left( \frac{AE_a}{\beta R} \right) + 3.77 - 1.92 \ln E_a - \frac{E_a}{RT}
\]

(7)

where \(A\), \(R\), \(E_a\), \(\beta\) and \(T\) had same meanings with the forenamed equations. According to the principle that the probable mechanism has higher linear correlation coefficient value \((r)\) and lower standard deviation value \((a)\), the probable mechanism functions are deduced from the calculated results and shows in Table 3. As seen from Table 3, the two degradation stages are all following first order kinetic mechanism. The activation energy \(E_a\) can be obtained from plots of \(\ln \left[ (G(\alpha)/T^{1.92}) \right] \) vs. \(1/T\) and are listed in Table 3.

### 3.5 Hydrolytic stability

The hydrolytic stability of resins was determined by a half-life of acid-base titration method (Shen et al. 1999) and show in Table 4. As seen from Table 4, the BNPFR has a better hydrolytic stability, when the boron content is all 0.00175 mol, the color change time of BPFR is only 1 min, though BNPFR is 36 min, which is 36 times longer than BPFR, for 0.0525 mol amount, the BPFR is 21 min, though BNPFR is 145 min, which is 7 times longer than BPFR. The hydrolysis time is associated with dosage of glycerol added in BNPFR, the more glycerol added, the shorter hydrolysis time. Though, these data have shown that the BNPFR has a better hydrolytic stability than BPFR. This is because the boron atom exhibit three valence, in the BNPFR has a coordination structure of \(B \leftrightarrow N\), in here, the shell electronic configuration of the boron atom has a noble gas or octet configuration, so the BNPFR has a better hydrolytic stability than general boron-containing phenol-formaldehyde resin.
4. Conclusions

The boron-nitrogen-containing phenol-formaldehyde resin (BNPFR) can be synthesized from Phenol, boric acid, aminoethyl alcohol and paraformaldehyde. The BNPFR/SiO$_2$ nanocomposite can be prepared in-situ by ethanolysis of Tetramethoxysilane in BNPFR solution. The nano-SiO$_2$ with about 50nm diameter has more homogeneous distribution in the samples. The loss modulus peak temperature $T_p$ of BNPFR/SiO$_2$ nanocomposite is 214°C when nano-SiO$_2$ content is 6wt%. The start thermal degradation temperature $T_{di}$ is higher about 30°C than pure BNPFR. The residual rate (%) of the nanocomposites at 800°C is above 40% when nano-SiO$_2$ content is 9%.

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