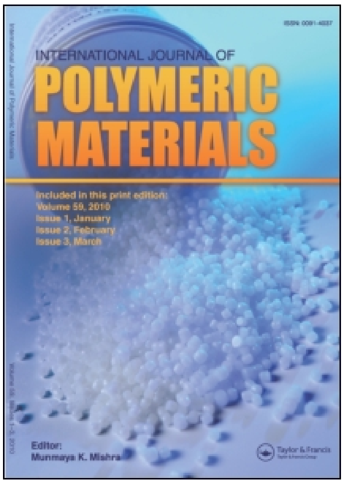

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Synthesis and Thermal Properties of Boron-Nitrogen Containing Phenol Formaldehyde Resin/MMT Nanocomposites

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The nanocomposites of boron-nitrogen containing phenol formaldehyde resin (BNPFR) and organic-montmorillonite (O-MMT) (BNPFR/MMT) were synthesized from phenol, formaldehyde, boric acid, ammonia water and montmorillonite. The thermal properties of nanocomposites were characterized. The results show that the remaining weight fraction of BNPFR is 68.82% at 750°C, but the hybrid nanocomposite (BNPFR/MMT) is 75.51%. At 900°C, the remaining weight fraction of 7% O-MMT containing nanocomposites is 72.89%, which is 11.46% higher than BNPFR. The mechanical loss peak temperature T_p of BNPFR/MMT nanocomposites is 194.6°C, which is higher 7.3°C than that of BNPFR.

Keywords boric acid, montmorillonite, nanocomposites, phenol formaldehyde resin, thermal analysis

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INTRODUCTION

Phenolic formaldehyde resins (PFR) are used principally in reinforced thermosetting materials and adhesives. To improve the flame retardant and thermo-oxidative resistance of PFR, the addition of boron has been reported [1–4]. The effectiveness of borate as the flame-retardant in various materials has been explained by the formation of nonpenetrable glass coating in these materials upon their thermal degradation. The glass coatings exclude oxygen and prevent further propagation combustion. Some reports have been appeared on the synthesis, curing and thermodegradation process of boron-containing phenol-formaldehyde resin (BPFR) [3–6]. But the general BPFR are extremely sensitive to moisture. To improve the hydrolytic resistance of BPFR, the resins of containing B-N have been synthesized [2,7]. The nature and mechanism of the exfoliation process of the surface-modified layered-silicate nanoparticles in the crosslinking epoxy network have been investigated. Lan demonstrated that the exfoliation of the clay is not only dependent on the reactivity of the resin system but also on the rate of intercalation of the resin [8]. The clay nanocomposites of epoxy resin, novolac resin and thermal plastic resin (such as Nylon-6, PET, fiber and PSt, et al.) had been prepared [8–10]. But the descriptions of synthesis and thermal properties for nanocomposites of boron-nitrogen containing phenol formaldehyde resin/montmorillonite (BNPFR/MMT) have been lacking until now. We have synthesized the boron-nitrogen containing phenol formaldehyde resin [7]. In this work, the BNPFR/MMT nanocomposites were prepared, and the structure and thermal properties were investigated by X-ray diffraction (XRD), torsional braid analysis (TBA) and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

Phenol, boric acid, formaldehyde solution (37 wt%), oxalic acid, 25% ammonia water, toluene, *n*-butyl alcohol and paraformaldehyde were all analytical pure grade, and were supplied by Tianjin Chemical Reagent Co. (China). Na^+-montmorillonite with the cation exchange capacity (CEC) value of about 100 mmol/100 g was purchased from Qingshan Chemistry Agent Factory in Lin'an (China). $CH_3(CH_2)_{15}(CH_3)_3NBr$, the surfactant of clay, was purchased from the Institute of Xinhua Active Material in Changzhou (China).

Preparation of Organically Modified Montmorillonite

20 g of Na^+-montmorillonite were dispersed into 500 mL distilled water at 80°C. 9 g $CH_3(CH_2)_{15}(CH_3)_3NBr$ were dispersed in 100 ml distilled water, then

poured in the hot water solution of Na^+-MMT and stirred vigorously for 1 h at 80°C. A white precipitation was formed, and separated by centrifugation, then washed several times with distilled water until no bromide was detected in the filtrate by one drop of 0.1 mol/L $AgNO_3$ solution. The resulting O-MMT was dried in a convection oven at 80°C. The dried O-MMT was ground with a freezer/mill. The sieved O-MMT powder less than 36 µm was characterized and applied.

Synthesis of BNPFR/MMT Nanocomposites

52.88 g phenol, 16.50 g formaldehyde solution, 6.25 g ammonia water and 3.70 g O-MMT were put into a four-necked round-bottom flask, equipped with a stirrer, a thermometer and a condenser. First, the mixture was treated with ultrasonic at room temperature for 2 h, then stirred and heated to 70°C. The reaction was maintained at this temperature for 90 min, then the water that was in the formaldehyde solution and formed during the reaction in vacuum was removed. In the second step, 11.25 g boric acid, 0.32 g oxalic acid, 6.25 mL toluene and 14.81 g *n*-butyl alcohol were added to this system, and refluxed for 2 h to remove the formed water. In the third step, 19.38 g paraformaldehyde were added, the temperature was heated to 110°C and held for 2 h, and then the residual solvent in vacuum was removed. Finally the yellow solid resin of BNPFR/MMT nanocomposite was obtained.

Changing the dosage of O-MMT, the nanocomposites with different O-MMT content were obtained.

Characterization of O-MMT and Nanocomposites

XRD analysis: X-ray diffraction patterns were recorded by monitoring the diffraction angle 2θ from 1.5–10° on the X-ray diffractometer (Rigaku-D/max-rB, Germany). The X-ray diffractometer was equipped with a Cu*K*a ($\lambda = 0.1542$ nm) radiation source operated at 40 kV and 100 mA. The scanning speed and the step size used were 2°/min and 0.02°, respectively.

A Pyris-6 thermobalancer (Perkin-Elmer Co., USA) was used to determine the weight loss behavior of BNPFR and nanocomposites during degradation. The resins was cured at 180°C for 2 h. About 8 mg of sample powder was introduced into the thermobalance, then heated to 900°C at 20°C/min under a nitrogen flow of 40 mL/min.

A cleaned glass fiber braid was first dipped in resin-acetone solution for about 30 min, and then taken out. When the solvent in the braid was completely evaporated in vacuum, the braid was placed in a heated oven with a constant temperature of 180°C. After curing at this temperature for 2 h, the braid was taken out and cooled to room temperature, and the dynamic mechanical properties of nanocomposites were investigated with a torsional braid analyzer (TBA, GDP-4, Jilin Universal Instrument Co., China) with a heating rate of 2°C/min. The maximal mechanical loss temperature (T_p) was determined.

RESULTS AND DISCUSSION

X-ray Diffraction Analysis

The X-ray diffraction patterns for BNPFR/MMT nanocomposites containing different O-MMT content cured under the temperature of 180°C are shown in Figure 1. As reported [11], when polymer chains are inserted into the galleries of mintmorillonite, the lattice spacing is enlarged. These XRD patterns reveal the change of O-MMT basal spacing that occurs in the BNPFR curing process. For the BNPFR/MMT nanocomposites, it is noteworthy that the (001) diffraction peak, corresponding to the basal spacing of montmorillonite d_{001}, shifted to a lower angle comparable to that of O-MMT, and the peak intensity increased with increasing O-MMT content.

As shown in Figure 1, the X-ray diffraction peak occurs at (2θ) decrease from 5.23° to 4.02° for O-MMT, according to $2d\sin\theta = n\lambda$, the distance between the layer of clay increased from 1.69 nm of MMT to 2.19 nm. We also find that the peak of diffraction (001) for the 7% O-MMT/BNPFR nanocomposite disappeared in the XRD patterns. It is because the minimum diffraction angle (2θ) detected by X-ray diffractometer is 1.5°. According to the Bragg formulation $2d\sin\theta = n\lambda$, the distance between layers is calculated as 5.88 nm. So the disappearance of the diffraction peak can show that the distance between layers of clay nanocomposites is 5.88 nm, at least. As Pinnavaia pointed out [8], the

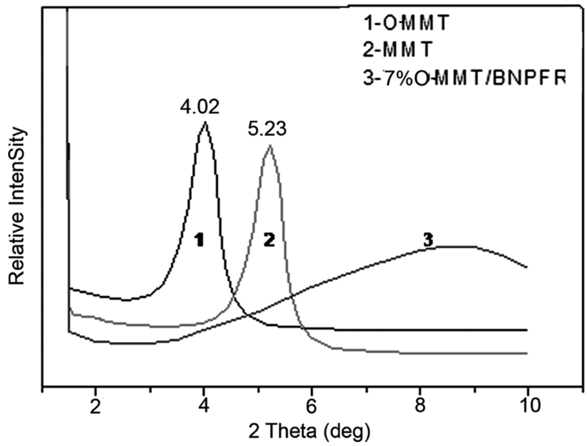

Figure 1: X-ray diffraction of the clay, o-MMT and BNPFR/MMT nanocomposites.

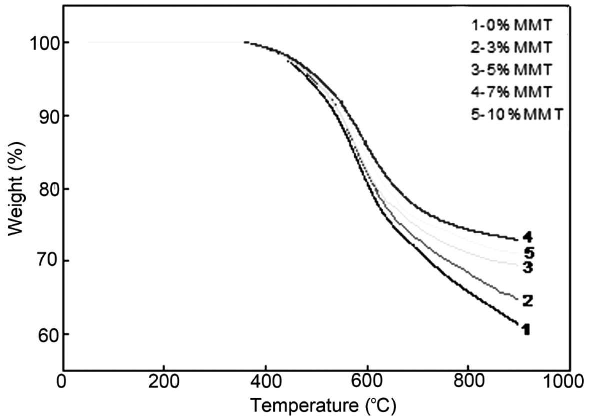

Figure 2: TG curves of PFR, BNPFR and BNPFR/MMT nanocomposites.

lattice spacing of the intercalated nanocomposite increases, but Bragg diffractions still exist in the diffractogram, which shifted to a lower angle. If the lattice spacing continues to increase, exfoliated nanocomposite is formed, leading to the disappearance of the Bragg diffraction. XRD results show that exfoliated MMT had been formed.

TG Analysis of BNPFR/MMT

Figure 2 shows the thermal weight loss curves of different resins at 20°C/min heating rate. The weight loss data are shown in Table 1. It can be seen from Figure 2 and Table 1, the weight loss of general phenol formaldehyde resin (PFR) before 350°C is about 5%, but the BNPFR and BNPFR/MMT had no weight loss at this temperature. It can be seen also that with the increasing O-MMT content, TG curves shift to high temperature, but the curves are down when the O-MMT content is over 7%. The weight loss of BNPFR and BNPFR/MMT can be divided into three stages. The first stage from 350–410°C is the loss of water, ammonia and formaldehyde, which produced from the curing and decomposing of some groups, the weight loss

Table 1: TG datas of PFR, BNPFR and BNPFR/MMT nanocomposites.

Temperature/°C	PFR/%	0 wt% MMT/%	3 wt% MMT/%	5 wt% MMT/%	7 wt% MMT/%	10 wt% MMT/%
400	92.88	99.14	99.25	99.30	99.34	99.32
500	80.49	93.62	94.38	94.57	95.15	94.95
600	41.04	80.61	81.95	82.34	85.78	84.25
700	6.16	71.44	72.97	74.69	77.37	75.84
800	0	65.89	68.38	71.25	74.31	72.78
900	0	61.43	64.87	69.45	72.89	70.98

of less than 7%. The second stage is 410–620°C, which is the principal stage and the weight loss may be caused by the breakage of some ether linkages, methylene bridges and other weak linkages [3,6]. The third stage is the breakage of B-N, B-O linkage and the carbonation of benzene ring.

As seen from Table 1, the general phenol formaldehyde resin had decomposed completely at 750°C, but the residual amount of BNPFR is 65.89% at 800°C, and it is 61.43% at 900°C. The residual amount of BNPFR/MMT (7 wt% O-MMT) is 74.31% at 800°C, and is 72.89% at 900°C; it is higher at 11.46% than BNPFR. The results indicate that the BNPFR/MMT nanocomposite has better thermal stability than BNPFR and it is best when the O-MMT content is 7%. The thermal stability of nanocomposites can be attributed to the fact that the stronger interaction between BNPFR molecules and MMT confine the activity of the macromolecule chains, and MMT layers can suppress the emanation of the small molecule effectively when a degradation reaction originated, resulting in the decrease of the degradation velocity of the composites [11]. Therefore, the heat stability of nanocomposite is increased.

Kinetics of Thermal Degradation

The TGA data are analyzed on the basis of the Madusdanan-Krishnan-Ninan method [12,13] to the main stage, which can be expressed by the following equation:

$$\ln\frac{G(a)}{T^{1.92}} = \ln\frac{AE_a}{\Phi R} + 3.77 - 1.92\ln E_a - \frac{E_a}{RT} \tag{1}$$

where A is the pre-exponential factor in the Arrhenius equation, E_a is the apparent activation energy, R is the universal gas constant, Φ is the heating rate, T is absolute temperature, and $G(a)$ is the integral form of the conversion dependence function. The correct form of $G(a)$ depends on the proper mechanism of degradation reaction. Different expression of $G(a)$ for some solid-state reaction mechanisms can be described as follows: in first order $(n = 1)$, $G(a)$ is $-\ln(1-a)$; in second order $(n = 2)$, $G(a)$ is $1/(1-a)$; in third order $(n = 3)$, $G(a)$ is $1/(1-\mathrm{a})^2$.

In dynamic TGA experiments, the weight change of the sample is regarded as a function of temperature and conversion α can be expressed as:

$$\alpha = \frac{W_0 - W_T}{W_0 - W_\propto} \tag{2}$$

where W_0 is the initial weight, W_T is the residual weight at temperature T, and W_∞ is the final weight. Therefore, using the TGA curves and Eq. (1), the conversions are calculated for the main degradation stage. The plots of $\ln G(\alpha)/T^{1.92}$ vs. $1/T$ for different mechanism functions, the apparent

Table 2: The kinetic parameters of thermal degradation of 7%MMT/BNPFR at 20°C/min heating rate.

7%MMT/BNPFR	Reaction order	Correlation coefficient	ΔE_a (kJ/mol)	ln$A$ (S^{-1})	Standard deviation
Second stage	1	0.9990	76.30	3.50	0.0110
	2	0.904	9.379	1.28	0.0434
	3	0.959	31.49	3.56	0.0904
Third stage	1	0.9942	35.84	0.44	0.0260
	2	0.888	61.77	7.24	0.271
	3	0.908	139.6	18.96	0.547

activation energy ΔE_a (kJ/mol) and pre-exponential factor ln$A$ can be calculated; these data are collected in Table 2.

As can be seen in Table 2, in the second stage, the linear correlation coefficient obtained by the first order mechanism is 0.9990, the ΔE_a is 76.30 kJ/mol, and the standard deviation is 0.0110, which is better than those using the second and third mechanism. In the third stage, the linear correlation coefficient obtained by the first order mechanism is 0.9940, the ΔE_a is 35.84 kJ/mol, and the standard deviation is 0.0260, which is also better than that of using the second and third mechanism. So the main thermal degradation reaction of BNPFR/MMT nanocomposites follows first order kinetics.

TBA Analysis

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 resins [14]. DSC is usually used to determine the T_g of polymer, but it is not a best method for thermosetting polymers, especially at a higher conversion, because the shift of the DSC curve will be very little and unconspicuous at that time. TBA is usually used to determine the T_g of thermosetting polymers. There is a one-to-one relationship between the T_g and the degree of cure. T_g is particularly useful at high conversion and after vitrification because of the nonlinearity of T_g vs. conversion reaction [15,16]. There is a one-to-one relationship between T_g and the maximal mechanical loss temperature (T_p). After the specimens were cured for 2 h at 180°C, the TBA data of BNPFR and BNPFR/MMT (7% O-MMT) are shown Figure 3. As seen from Figure 3, they all have mechanical loss peaks T_p, the peak temperature T_p of BNPFR/MMT nanocomposites is 194.6°C, which is higher 7.3°C than that of BNPFR. T_gs of BNPFR/MMT nanocomposites for different O-MMT content which result from TBA measurements are shown in Table 3. As seen from Table 3, they have different glass transition behaviors for the samples which have different O-MMT content. T_g has a maximal value when the O-MMT

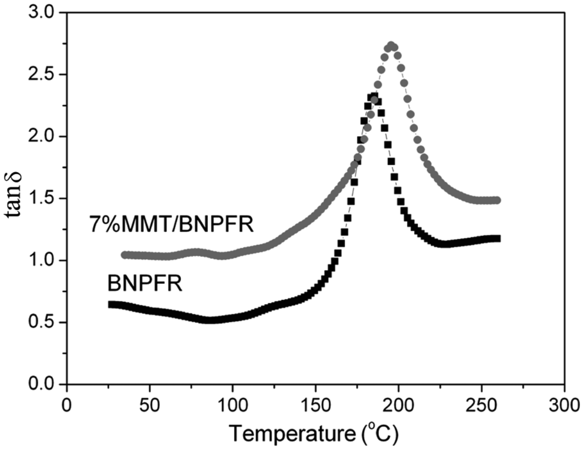

Figure 3: TBA curves of BNPFR and BNPFR/MMT nanocomposites.

Table 3: Glass transformation temperature of nanocomposites.

	0%MMT	3%MMT	5%MMT	7%MMT	10%MMT
T_g/°C	187.3	188.2	192.1	194.6	192.4

content is 7%. This result is coincident with the thermal stability of BNPFR/MMT nanocomposites. It is also shown that the BNPFR/MMT nanocomposites have higher rigidity than that of commercial polymeric materials at higher temperatures.

CONCLUSIONS

The nanocomposites of boron-nitrogen containing phenol formaldehyde resin/organic-montmorillonite (BNPFR/MMT) could be synthesized from phenol, formaldehyde, ammonia water and montmorillonite by a one-step intercalation polymerization method. The hybrid nanocomposites (BNPFR/MMT) have a higher thermal stability, and the initial thermal degradation temperature is about 100°C higher than that of common phenol resin. As the temperature reached 900°C, the remaining weight fraction of 7% O-MMT containing BNPFR nanocomposites had still 72.89% residue weight, which is 11.46% higher than that of BNPFR, and the maximal mechanical loss temperature (T_p) is 194.6°C and 7.3°C higher than BNPFR.

REFERENCES

[1] Hirohata, T., and Misaki, T. *J. Soci. Mater. Sci. Japan* **36**, 401 (1987).

[2] Hoofel, H. B., Kiessling, H. J., Lampert, F., and Schonrogge, B. *German Publicity Pat.* 2436359 (1975).

[3] Gao, J., Xia, L., and Liu, Y. *Polym. Degrad. Stab.* **83**, 71 (2004).

[4] Mohamed, O. A., Adriane, L., and Temisha, M. *Polymer* **44**, 7353 (2003).

[5] America Patash Chem. Corp. *Br. Pat.* 957611 (1964).

[6] Liu, Y., Gao, J., and Zhang, R. *Polym. Degrad. Stab.* **77**, 495 (2002).

[7] Gao, J., Su, X., and Xia, L. *Inter. J. Polym. Mater.* **54**, 949 (2005).

[8] Lan, T., Kaviratna, P. D., and Pinnavaia, T. J. *Chem. Mater.* **7**, 2144 (1995).

[9] Sanchez-Olivares, G., Sanchez-Solis, A., and Manero, O. *Inter. J. Polym. Mater.* **57**, 245 (2008).

[10] Gao, J., and Zhao, M. *Inter. J. Polym. Mater.* **57**, 101 (2208).

[11] Kornmann, X., Lindberg, H., and Berglund, L. A. *Polymer* **42**, 1303 (2001).

[12] Liu, Z. H. (1991). *Introduction to Thermal Analysis*, Chem. Indu. Pub. Co., Beijing, pp. 99.

[13] Madhusudanan, P. M., Krishnan, K., and Ninan, K. N. *Thermoch. Acta* **97**, 189 (1986).

[14] Simon, S. L., and Gillham, J. K. *J. Appl. Polym. Sci.* **47**, 461 (1993).

[15] Gillham, J. K. *Polym. Int.* **44**, 262 (1997).

[16] Venditti, R. A., and Gillham, J. K. *J. Appl. Polym. Sci.* **64**, 3 (1997).