

Improvements of heat resistance and adhesive property of condensed poly-nuclear aromatic resin via epoxy resin modification

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Abstract: A bisphenol epoxy resin was used as modifier to increase the heat resistance of condensed poly-nuclear aromatic (COPNA) resin. The basic properties of COPNA resin and modified resin were characterized by Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (¹H-NMR), vapor pressure osmometry (VPO) and elemental analysis (EA). Average structural parameters of resins were calculated by the improved Brown-Ladner method, and heat resistance of resins was tested by thermogravimetric analysis (TGA). The chemical structure, mechanical properties and heat resistivity of the resin/graphite composites prepared with different resins were compared. The results show that the adhesive property and heat resistance of COPNA resin can be remarkably improved by addition of 5 wt.% epoxy resin. The reason is that the reactions between epoxy groups of epoxy resin and hydroxyl groups of COPNA resin improve the heat resistance and adhesive property of COPNA resin. Electric motor brushes with good mechanical properties and low electrical resistivity were successfully prepared by using the modified resin as binder.

Key words: COPNA resin, modification, epoxy resin, heat resistance, mechanical property

1 Introduction

COPNA resin, firstly reported in 1986 (Otani, 1986), has attracted considerable attention as a novel thermosetting material (Lin et al, 2010a; 2010b; Tanemura et al, 2011; 2012; Wu et al, 2012a; 2012b; 2013). It can be used as binder with good lubricity, mechanical properties and mouldability. In the early stages, the raw materials for preparation of COPNA resin were confined to pure aromatic substances (Nakajima et al, 1995; Nawa, 1996). Recently, petroleum- and coal-derived fractions have been employed to prepare COPNA resin with the aim of reducing costs (Guo et al, 2002; Li et al, 2008; Shi et al, 2012; Wu et al, 2012a; 2012b; 2013).

In our previous work, COPNA resin with good adhesive property was successfully synthesized via the reaction between thermally treated oil and 1, 4-benzenedimethanol (Wu et al, 2013). However, the thermal decomposition temperature of the COPNA resin cured at 200 °C was still below 250 °C, far low of that needed for industrial applications. To obtain resin with better heat resistance, epoxy resin was added

to the COPNA resin as a modifier, which was supposed to react with hydroxyl groups in COPNA resin. The resultant modified resin as well as COPNA resin was characterized by elemental analysis (EA), infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (¹H-NMR), vapor pressure osmometry (VPO) and thermogravimetric analysis (TGA). Finally, the modified COPNA resins as binder were mixed with graphite to prepare electric motor brushes, and their mechanical properties and electrical resistivity were studied.

2 Experimental

2.1 Raw materials

Toluene was obtained from Tianjin Chemical Reagent Company, China. Quinoline was bought from Tingxin Chemical Reagent Company, China. Bisphenol epoxy resin (E44) was purchased from Wuxi Resin Company, China. Chloroform was bought from Concord Technology Company, China. COPNA resin was synthesized from thermally treated oil and 1,4-benzenedimethanol as cross-linking agent at 150 °C in our lab (Wu et al, 2013). All reagents used in this work were of analytical grade.

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2.2 Preparation of modified resin

Epoxy resin was heated to 110 °C and kept in a vacuum oven for 20 min to remove water. COPNA resin (50.0 g) was put in a reaction kettle equipped with a thermometer and mechanical stirrer and heated to 150 °C in a nitrogen flow of 40 mL/min, and then the above epoxy resin was rapidly added into the kettle just after the COPNA resin had completely melted and the mixture was stirred for 10 min. Finally, the modified COPNA resin was obtained.

2.3 Curing process of resins

COPNA resin (10.0 g) and modified COPNA resin (10.0 g) were separately put in crucibles. The crucibles were heated to 200 °C at a heating rate of 0.25 °C/min under a nitrogen flow of 50 mL/min, and then kept for 2 h. Finally, the infusible and insoluble cured resins were obtained.

2.4 Preparation of resin/graphite composite

COPNA resin or modified resin (10.0 g) was dissolved in chloroform, and then graphite (30.0, 23.3, 18.6, or 15.0 g) was added into the solution. The mixture was stirred and heated to 80 °C, until all the chloroform had evaporated. Then the resin/graphite composite was molded at 30 MPa and 120 °C. After that, the molded sample was heated to 300 °C at a heating rate of 0.25 °C/min under a nitrogen flow of 50 mL/min, and then kept for 2 h.

2.5 Characterization

The modified resin and the COPNA resin were characterized by FT-IR, ¹H-NMR, EA, VPO, TGA, etc.

In thermogravimetric analysis (TGA), 10 mg sample was placed in a platinum crucible of a DTG-60 thermogravimetric analyzer (Shimadzu, Japan), and heated from room temperature to 800 °C at a heating rate of 10 °C/min under a nitrogen flow of 50 mL/min.

FT-IR spectra were recorded on a 8400S FT-IR spectrometer (Shimadzu, Japan) in transmittance mode. The scan frequency of each spectrum was 15 s⁻¹ with a resolution of 0.85 cm⁻¹.

An AV500 ¹H-NMR spectroscopy analyzer (Bruker, German) was used to characterize the state of hydrogen in the modified resin and the COPNA resin, with chloroform as solvent, trimethylphenylsilane as an internal standard, a sweep length of 10,000 Hz, and a resonance frequency of 500 MHz.

Elemental analysis (EA) was performed with an Element Vario EL organic element analyzer (Elementar, German). The structural parameters of the modified resin were calculated by the improved Brown-Ladner method (Boucher et al, 1990).

The VPO molecular weight of the resins was determined at 40 °C with a K-7000 vapor pressure osmometer (Knauer, German), with chloroform as solvent, and dibenzoyl as a standard.

The contents of ash, toluene insolubles (TI) and quinoline insolubles (QI) were determined according to the international standards ISO 6245-1982, ISO 6376-1996, and ISO 6791-1981, respectively. The softening point of resins was determined according to ASTM D36-66.

Mechanical properties of resin/graphite composites were also studied. The flexural and compressive strengths of the composites were examined with a WDW-G universal material testing machine (Tenson, China), hardness was examined with a HS-19GDV scleroscope (Yuke, China), and electrical resistivity was determined according to JB/T8133-2-1999.

3 Results and discussion

3.1 Basic properties of resins

Epoxy resin has epoxy groups (as shown in Fig. 1), which are active and can be cross-linked to COPNA resin. The cured COPNA resin is insoluble and infusible, but its heat resistance does not meet the requirement of industrial applications, and needs to be improved. Fig. 1 shows the influence of epoxy resin content on the residual carbon yield of modified resin after it was kept in air at 500 °C for 2 h. It can be seen that the residual carbon yield increased at first and then decreased with increasing epoxy resin. The maximum of residual carbon yield was at 5 wt% of epoxy resin. In the following discussion, the content of epoxy resin is all 5 wt%.

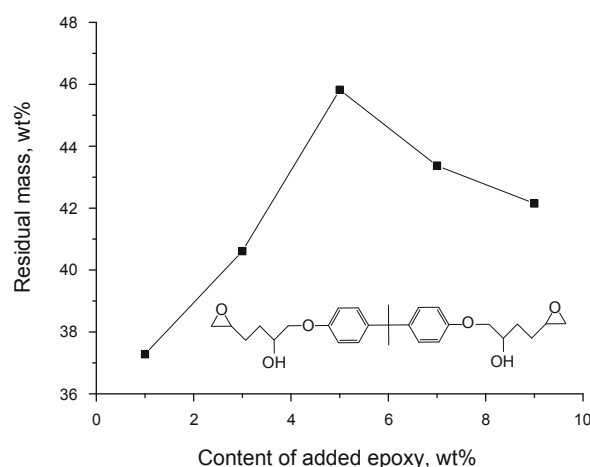


Fig. 1 Influence of epoxy resin content on the residual carbon yield of modified resin

Table 1 shows the basic properties of COPNA resin and modified COPNA resin with 5 wt% epoxy resin. It can be seen that after modification with 5 wt% of epoxy resin, the average molecular weight of COPNA resin increased from 1,412 to 1,962, the residual carbon yield increased from 32.6 wt% to 45.8 wt%, and the TI and QI values all increased. The value of TI-QI, the key parameter determining binding property, increased significantly from 12.4 wt% of COPNA resin to 20.3 wt% of modified COPNA resin. The above results indicated that the modified resin with high residual carbon yield and high TI-QI value is a more promising binder than the initial COPNA resin. From the EA data in Table 1, it is easily seen that the content of O is increased from 1.5 to 2.1 wt% after addition of epoxy resin.

3.2 FT-IR analysis

The FT-IR spectra of COPNA resin and modified resin are shown in Fig. 2. Peaks at 3,420-3,550 cm⁻¹ were attributed to N-H and O-H stretching vibration. The larger peaks at 3,420-

Table 1 Properties of COPNA resin and modified COPNA resin

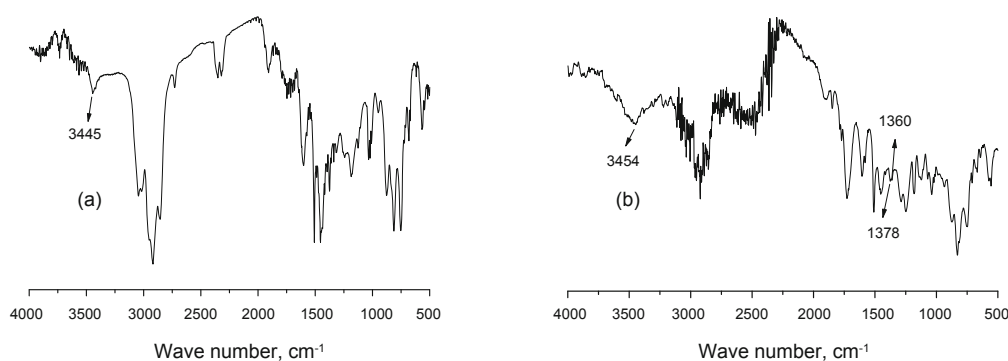
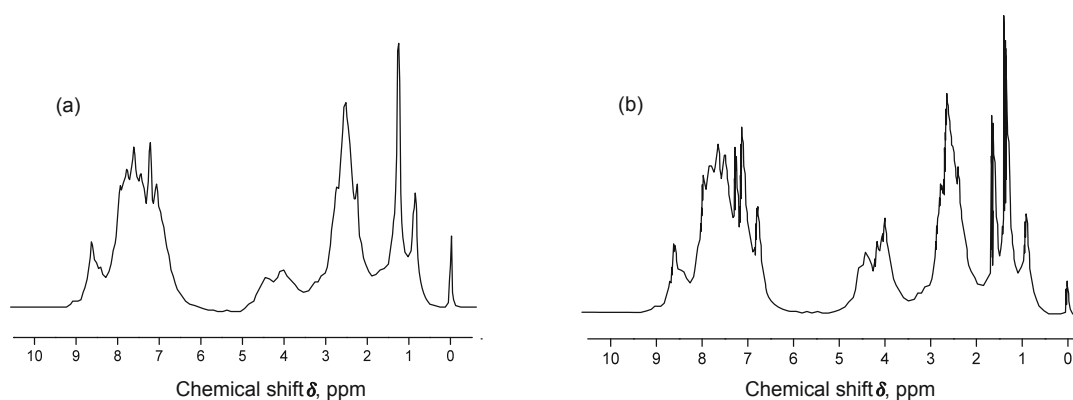
Properties	COPNA resin	Modified COPNA resin
M	1412	1962
CR, wt. %	32.6	45.8
QI, wt. %	5.6	6.4
TI, wt. %	17.9	26.7
(TI-QI), wt. %	12.4	20.3
Softening point, °C	110	112
C, wt. %	89.1	88.9
H, wt. %	6.1	7.0
N, wt. %	0.4	0.3
O, wt. %	1.5	2.1
C/H	1.22	1.06

Notes: M, average molecular weight; CR, residual carbon ratio; QI, quinoline insoluble; TI, toluene insoluble

$3,550\text{ cm}^{-1}$ of modified resin compared with those of COPNA resin suggested more hydroxyl groups. The peaks at $1,378$ and $1,360\text{ cm}^{-1}$ in Fig. 2 (b) were assigned to symmetrical dimethyl of epoxy resin. The peak of epoxy group at 910 cm^{-1} did not appear in both Fig. 2 (a) and (b), indicating that epoxy resin had reacted with COPNA resin and produced ether alcohol during the modification process.

3.3 $^1\text{H-NMR}$ analysis

Fig. 3 gives the $^1\text{H-NMR}$ spectra of COPNA resin and modified resin. It was noteworthy that there were more peaks at $\delta 1.0\text{-}2.0$ in Fig. 3(b), indicating more hydrogen atoms of methyl groups in the modified resin. Peaks of modified resin at $\delta 3.5\text{-}5.0$ (Fig. 3(b)) were larger than those of COPNA resin (Fig. 3(a)), suggesting that more hydroxyl groups existed in modified resin. The large peaks at $\delta 6.0\text{-}9.0$ in Fig. 3(b) were attributed to the absorption resonance of hydrogen in aromatic rings. Peaks at $\delta 6.6\text{-}7.2$, $\delta 7.2\text{-}7.8$ and $\delta 7.8\text{-}8.3$ were assigned to hydrogen attached to simple, double and three

**Fig. 2** FT-IR spectra of COPNA resin (a) and modified resin (b)**Fig. 3** $^1\text{H-NMR}$ spectra of COPNA resin (a) and modified resin (b)

ring aromatics, respectively (Ahmaruzzaman et al, 2008; Molina V et al, 2010; Biswas et al, 2013). The peaks at $\delta 6.6\text{-}7.2$ were enhanced greatly in the modified resin due to more hydrogen atoms being attached to simple cyclic aromatics.

3.4 Modification mechanism of COPNA resin using epoxy resin

The average structural parameters of the COPNA and

modified COPNA resins, including the average total carbon number (C_T), the average total hydrogen number (H_T), the ratio of aromatic carbon number to total carbon number (f_A), average condensation degree of aromatic rings (H_{AU}/C_A , atomic hydrogen to carbon ratio of the hypothetical unsubstituted aromatic molecule), hydrogen replacement rate surrounding aromatic rings (Σ) and average total rings (R_T), can be obtained by the improved Brown-Ladner method

based on the results of FTIR, $^1\text{H-NMR}$, EA and average molecular weight analysis. The average structural parameters of the resins are shown in Table 2, in which the S, O and N levels are negligible. The modification mechanism and averaged molecular structure of modified resin are shown in Fig. 4.

Table 2 Average molecular structural parameters of COPNA and modified resin

Samples	C_T	H_T	f_A	H_{AU}/C_A	Σ	R_T
COPNA resin	104.8	86.1	0.77	0.68	0.25	19.3
Modified resin	145.2	137.3	0.74	0.79	0.27	23.0

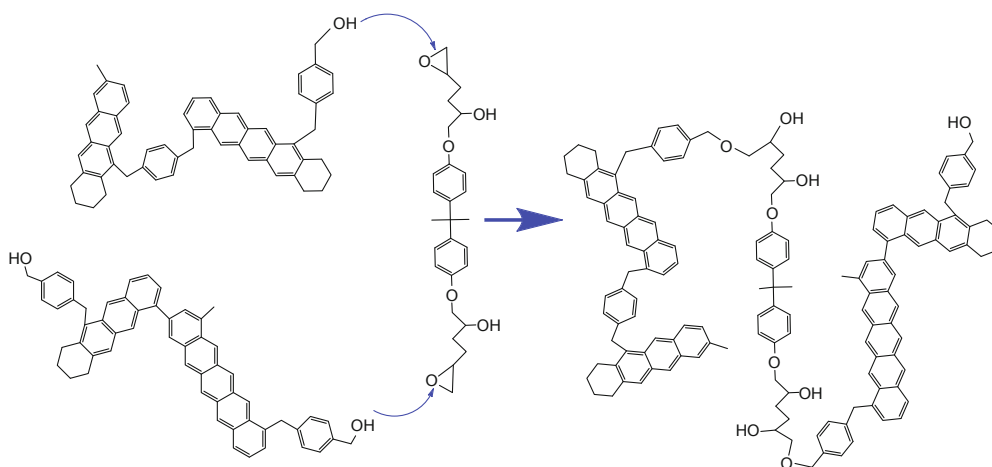


Fig. 4 Modification mechanism and averaged molecular structure of modified resin

3.5 Heat resistance

Fig. 5 shows the thermal decomposition behavior of cured COPNA resin and modified resin in nitrogen atmosphere. It can be clearly seen that the thermal decomposition temperature of cured COPNA resin was around 236 °C, while that of cured modified resin was as high as 384 °C. When the temperature was higher than 236 °C, the light fraction of COPNA resin escaped and resulted in the significant weight loss. After modification, some light fraction of COPNA resin was connected with epoxy resin and polymerized into large molecules, resulting in the slow changing of the TG curve (Fig. 5(b)) as shown in Fig. 5. At 500 °C, the residual weight of modified resin was still 47.1 wt%, much higher than 30.7 wt% of COPNA resin, indicating the cured modified resin has better heat resistance than cured COPNA resin. In other words, addition of a small amount of epoxy resin (5 wt%) can effectively increase the heat resistance of cured COPNA resin. The high initial decomposition temperature and high TI-QI value indicated that modified resin was a good candidate for heat resistant binder.

3.6 Mechanical properties of resin/graphite composite

The mechanical properties and resistivity of cured composites are shown in Fig. 6. Fig. 6(a) and (b) showed that

As shown in Table 2, R_T value increased from 19.3 of COPNA resin to 23.0 of modified resin, and H_{AU}/C_A also increased remarkably, indicating the increase of polymerization degree after modification. Because the epoxy resin has more saturated carbon atoms, the value of f_A decreased from 0.77 to 0.74. COPNA resin molecules were polymerized into large molecules through the reaction between hydroxyl groups and epoxy groups. When the hydroxyl groups in COPNA resin were completely reacted, the polymerization reactions between COPNA resin and epoxy resin ended. Excessive epoxy resin escaped at high temperature, resulting in the decrease of residual carbon yield of modified resin as shown in Fig. 1.

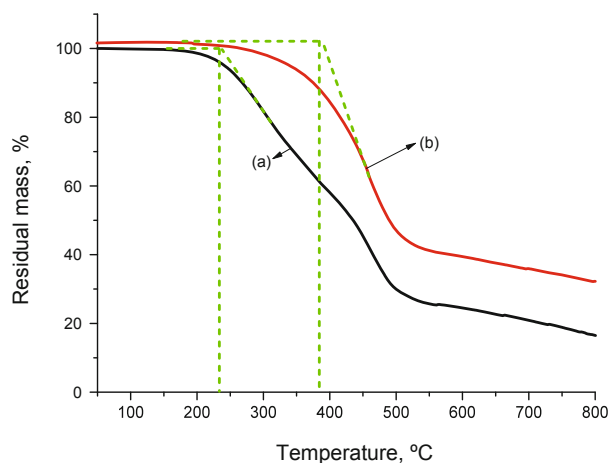


Fig. 5 TG curves of cured COPNA resin (a) and modified resin (b)

with increasing resin content from 25 wt% to 35 wt%, the flexural and compressive strengths of both the composites increased, and the modified resin based composite possessed higher flexural and compressive strengths than COPNA resin based composite. When the resin content was higher than 35 wt%, the flexural and compressive strengths of COPNA resin based composite decreased while those of modified resin based composite still increased. It is noted that the COPNA resin and modified resin can act as binder and contribute to

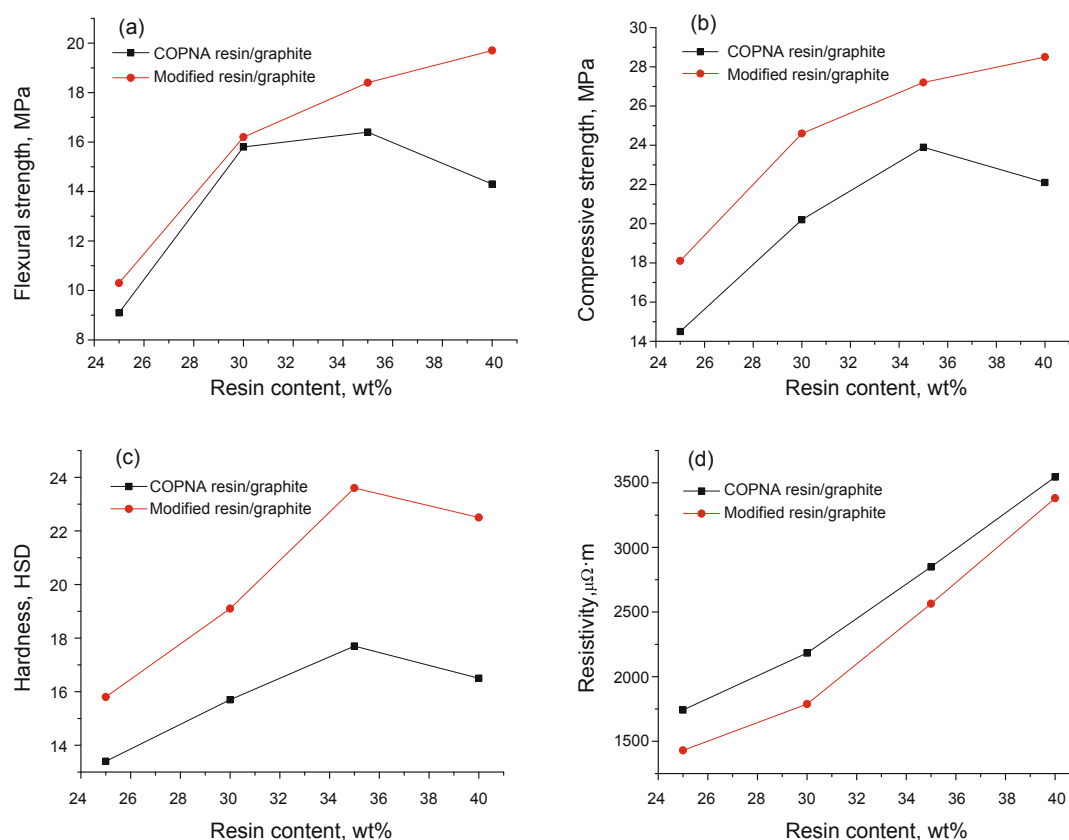


Fig. 6 Properties of cured composites: (a) flexural strength, (b) compression strength, (c) hardness, and (d) resistivity

the molding of the resin/graphite composite. However, when the COPNA resin was overabundant (higher than 35 wt.%), the escape of low molecular weight elements in COPNA resin lowered the strength of the resin/graphite composite. The modified resin with 5 wt% epoxy resin had better heat resistance in than COPNA resin (Fig. 5), resulting in higher flexural and compressive strengths of modified resin based composite than that of COPNA resin based composite at high resin content. The hardness of COPNA resin based and modified resin based composites in Fig. 6(c) increased with increasing resin content, and achieved maximum at 35 wt% of resin content. The modified resin based composite was much harder than the COPNA resin based composite. Low resistivity is usually needed for resin as binder. Because the electrical resistivity of COPNA resin and modified resin was much higher than that of graphite, the resistivity of COPNA and modified resin based composites increased rapidly with increasing resin content (Fig. 6(d)), and the resistivity of the modified resin based composite was lower than that of the COPNA resin based composite, so it is suitable to be used as a binder.

4 Conclusions

A bisphenol epoxy resin was successfully used as a modifier to increase the performance of COPNA resin. The adhesive properties and heat resistance of COPNA resin were remarkably improved by addition of 5 wt% epoxy resin. This is very instructive for the application of COPNA resin

as a binder at high temperature. The reaction between epoxy groups in added epoxy resin and hydroxyl groups in COPNA resin increases the heat resistance and adhesive properties of COPNA resin. Electric motor brushes made from modified resin/graphite composites exhibit good mechanical properties and low electrical resistivity, indicating potential future applications of the modified resin.

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