

Curing Mechanism of Condensed Polynuclear Aromatic Resin and Thermal Stability of Cured Resin

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Abstract: In order to improve the thermal stability of condensed polynuclear aromatic (COPNA) resin synthesized from vacuum residue, 1,4-benzenedimethanol was added to cure COPNA resin. The curing mechanism was investigated by proton nuclear magnetic resonance spectrometry, solid carbon-13 nuclear magnetic resonance spectrometry and Fourier transform infrared spectroscopy. Microstructures of the uncured and the cured COPNA resins were studied by scanning electron microscopy and X-ray diffractometry. The thermal stability of COPNA resins before and after curing was tested by thermogravimetric analysis. The element composition of the cured COPNA resin heated at different temperatures was analyzed by an element analyzer. The results showed that the uncured COPNA resin reacted with the cross-linking agent during the curing process, and the curing mechanism was confirmed to be of the electrophilic substitution nature. Compared with the uncured COPNA resin, the cured COPNA resin had a smooth surface, well-ordered and streamlined sheet structure with more crystalline solids, better molecular arrangement and orientation. The weight loss process of the uncured and cured COPNA resins was divided into three stages. Carbon residue of the cured COPNA resin was 41.65% at 600 °C, which was much higher than 25.02% of the uncured COPNA resin, which indicated that the cured COPNA resin had higher thermal stability.

Key words: condensed polynuclear aromatic resin, synthesis, vacuum residue, curing, thermal stability

1 Introduction

The condensed polynuclear aromatic (COPNA) resins have attracted considerable attention for their potential application as novel heat-resistant materials thanks to their good lubricity, mechanical properties and mouldability. The COPNA resins with a three-dimensional network structure were initially prepared by Otani S. in the 1980s^[1]. In the earlier studies, pure polycyclic aromatics, including phenanthrene, naphthalene, anthracene, and pyrene, were used as monomers^[2-4], resulting in a high cost of COPNA resins. Recently, some cheap materials with high aromatic content, such as coal tar pitch, petroleum pitch, ethylene tar, FCC slurry oil, and vacuum residue have been successfully used to prepare the COPNA resins^[15-9].

Most of the relevant research works have been focused on the reaction mechanism and the properties of the uncured resins synthesized from different raw materials. There were few reports focusing on the curing mechanism and thermal behavior of the cured resins^[10], especially for the resins synthesized from complicated materials. The

heat resistance of the cured resins synthesized from rich aromatic materials was not significantly higher than the uncured resins according to our preliminary studies^[8-9].

In this work, we attempt to improve the heat resistance of the cured COPNA resins by adding the curing agent into the uncured COPNA resin produced from vacuum residue. The curing mechanism, microstructure and thermal stability of the COPNA resins before and after curing were investigated.

2 Experimental

2.1 Raw materials

The COPNA resin was synthesized in the laboratory according to the procedures described in the literature^[9]. The reagent 1,4-benzenedimethanol (A.R.) used as the curing agent was purchased from the Sinopharm Chemical Re-

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agent Company, China. Chloroform (A.R.) was obtained from the Xilong Chemical Co., Ltd., China.

2.2 Preparation of cured COPNA resin

Firstly, the COPNA resin was dissolved in chloroform, and then 1,4-benzenedimethanol was added into the solution according to a certain ratio. The cured COPNA resin was obtained after the solvent was evaporated and the residue was heated at 200 °C for 2 h in a nitrogen flow of 50 mL/min.

2.3 Characterization

The uncured and the cured COPNA resin samples were characterized by the proton nuclear magnetic resonance spectrometry ($^1\text{H-NMR}$), the solid carbon-13 nuclear magnetic resonance spectrometry ($^{13}\text{C-NMR}$) and the Fourier transform infrared spectroscopy (FT-IR). The surface texture and the heat resistance of the resins were investigated by the scanning electron microscopy (SEM) and the thermogravimetric analysis (TGA). The state of hydrogen atoms in the resins was characterized by a Bruker AV500 $^1\text{H-NMR}$ spectrometer, using TMS as the internal standard and CDCl_3 as the solvent. The sweep length was 10 000 Hz, and the resonance frequency was 500 MHz. The solid carbon-13 NMR (CP TOSS $^{13}\text{C-NMR}$) spectra were collected using a Bruker Avance II 400 spectrometer operating at 100 MHz for ^{13}C . The rotor spin speed was 5 000 Hz. For all samples, the optimum relaxation delay (D1) and the contact time were 4 s and 30 ms, respectively. The FT-IR spectra of the uncured and the cured COPNA resins were recorded on a Shimadzu 8400S FT-IR spectrometer in the transmittance mode. The scan frequency of each spectrum was 15 s^{-1} . The scanning electron microscopy (SEM) was carried out using a Philips XL30 environmental scanning electron microscope. The accelerated voltage was 20 kV, and the samples were coated with aurum in vacuum. Thermal properties of the resins were studied by a Shimadzu DTG-60 thermogravimetric analyzer at a heating rate of $10\text{ }^\circ\text{C/min}$ under a nitrogen flow of 50 mL/min. The X-ray diffraction (XRD) analyses were carried out with a Rigaku Miniflex instrument operating at a tube voltage of 40 kV and a tube current of 40 mA. The $\text{CuK}\alpha$ ($\lambda=1.5405\text{ \AA}$) radiation was selected as the monochromatic energy radiation. Elemental analysis was performed on a Vario EL organic element

analyzer. The element contents of C, H and O in the cured COPNA resins that were heated at different temperatures were analyzed.

3 Results and Discussion

3.1 $^1\text{H-NMR}$ analysis

The $^1\text{H-NMR}$ spectra can reveal the distribution of protons in different chemical environments. Figure 1 displays the $^1\text{H-NMR}$ spectra of the uncured and the cured COPNA resins. Table 1 shows the contents of the different hydrogen atoms observed by $^1\text{H-NMR}$ spectra based on the peak areas, where H_A , H_{A1} , H_{A2} and H_{A3} refer to the aromatic hydrogen and the hydrogen attached to the simple cyclic aromatics, the double-cyclic aromatics and the three-cyclic aromatics, respectively. $\text{H}_{\alpha 1}$ and $\text{H}_{\alpha 2}$ denote the hydrogen in groups of $\alpha\text{-CH}_3$, $\alpha\text{-CH}_2$ and $\alpha\text{-CH}$ that are connected with one aromatic ring and two aromatic rings, respectively. Similarly, H_β and H_γ refer to the hydrogen in $\beta\text{-CH}_2$, $\beta\text{-CH}$, and $\gamma\text{-CH}_3$ that is connected with the aromatic ring^[11-13]. These differences in hydrogen atom content can be used to analyze the changes of hydrogen atoms during the curing process, which is beneficial to the explanation of the mechanism for curing of the COPNA resins.

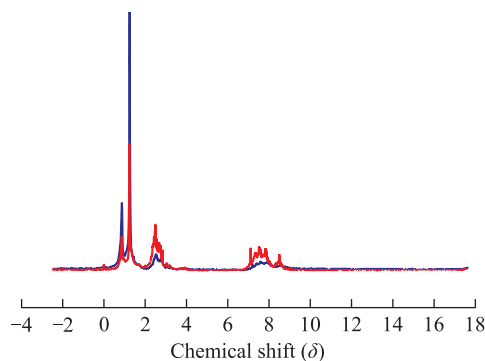


Figure 1 $^1\text{H-NMR}$ spectra of uncured and cured COPNA resins

Table 1 shows that the H_{A1} content of the cured COPNA resins is slightly higher than that of the uncured COPNA resin. This might be caused by 1,4-benzenedimethanol, which had a number of aromatic hydrogen atoms attached to simple cyclic aromatic ring. In addition, it was noteworthy that, after curing, the contents of H_A , H_{A2} , H_{A3} and $\text{H}_{\alpha 1}$ reduced from 43.02%, 16.82%, 10.01% and 28.01% to 34.70%, 10.87%, 4.92% and 18.41%, respectively. At the same time, the content of $\text{H}_{\alpha 2}$ increased from 8.00% of

Table 1 Contents of different H bands in uncured and cured COPNA resins

Item	Content, %						
	H _A	H _{A1}	H _{A2}	H _{A3}	H _{a1}	H _{a2}	H _γ
Uncured COPNA resin	43.02	9.55	16.82	10.01	28.01	8.00	4.73
Cured COPNA resin	34.70	10.81	10.87	4.92	18.41	21.84	17.21

the uncured COPNA resin to 21.84% of the cured resin. The above results indicated that during the curing process some methylene groups attached to one aromatic ring reacted with another aromatic hydrocarbons, and meanwhile, some hydrogen atoms attached to the aromatic ring were replaced.

3.2 Solid-state ¹³C-NMR analysis

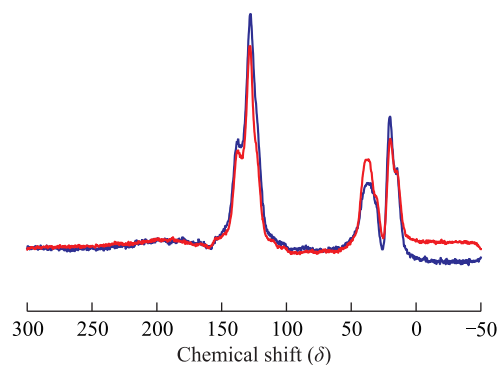
According to the literature^[11, 13-17], aliphatic carbon atoms (C_S) and aromatic carbon atoms (C_A) can be detected by the ¹³C-NMR spectrometry. Moreover, aliphatic carbon atoms can be divided into C_{S1}, C_{S2} and C_{S3}, and aromatic carbon atoms can be divided into C_{AH}, C_{ARN} and C_{AO}. The classification and results of carbon distribution of carbon types are given in Table 2.

Table 2 Assignment for ¹³C-NMR chemical shifts

Symbol	Assignment	δ
C _{S1}	CH ₃ -α, CH ₃ -β and CH ₃ -γ attached to aromatic ring	0—22
C _{S2}	CH ₂ -α, CH ₃ -β attached to aromatic ring in ethyl, propyl or naphthenic groups	22—32
C _{S3}	CH ₂ -α attached to aromatic ring	32—55
C _{AH}	Aromatic carbon atoms bound to hydrogen	100—130
C _{ARN}	Aromatic carbon atoms substituted by chain or hydroaromatic ring	130—150
C _{AO}	Aromatic carbon atoms substituted by -OH or -OR	150—170

Figure 2 presents the solid-state ¹³C-NMR spectra of the uncured and the cured COPNA resins. Solid-state ¹³C-NMR peak areas are a semi-quantitative measure of the relative contributions of different functional groups to the organic carbon that is present in a sample. Although the carbon peak areas cannot be used to accurately estimate the contents of each kind of carbon functional groups, but the ratio of carbon peak areas can reflect the relative change of various carbon atoms in the COPNA resin before and after curing. The area ratio of the peaks at chemi-

cal shift (δ) of 100—130 to that of 130—150 ($S_{100-130}/S_{130-150}$) reflects the relative amount of C_{AH} to C_{ARN}. Similarly, the area ratio of the peaks at δ of 32—55 to δ of 0-32 (S_{32-55}/S_{0-32}) reflects the relative amount of C_{S3} to C_{S1} and C_{S2}, respectively. Specifically, the $S_{100-130}/S_{130-150}$ ratio of the uncured and the cured COPNA resins was found to be 1.376 2 and 1.233 7, respectively, whereas the S_{32-55}/S_{0-32} ratio of the uncured and the cured COPNA resin was 0.621 8 and 0.752 3, respectively. These changes indicated that the electrophilic substitution reaction of aromatic hydrocarbon occurred during the curing process, resulting in not only the replacement of aromatic hydrogen, but also the decrease of C_{AH}, and the increase of C_{ARN} and CH₂-α attached to aromatic ring. The results were in agreement with the ¹H-NMR analysis.

**Figure 2** ¹³C-NMR spectra of uncured and cured COPNA resins

3.3 FT-IR analysis

The FT-IR spectra of the uncured and the cured COPNA resins are shown in Figure 3. The peak near the wave-number of 3 045 cm⁻¹ was ascribed to stretching vibrations of aromatic C-H bonds. The peak near 1 460 cm⁻¹ was attributed to the bending stretching of CH₃ and CH₂ groups. The peak near 1 380 cm⁻¹ was related to the asymmetrical deformation vibration of CH₃ groups. These

peaks between 900 cm^{-1} and 600 cm^{-1} were caused by the out-of-plane vibration of aromatic C-H bonds. The peak near $1\,600\text{ cm}^{-1}$ corresponded to aromatic C=C bond^[18-19]. Many researchers^[20-21] have reported a linear relationship between the absorbance ratio of bands in the range from $1\,460\text{ cm}^{-1}$ to $1\,380\text{ cm}^{-1}$ (A_{1460}/A_{1380}) and the molar ratio of methylene to methyl groups ($n(\text{CH}_2)/n(\text{CH}_3)$) in molecules. Therefore, the trend for change of methylene group relative to methyl group during the curing process can be found by comparing the A_{1460}/A_{1380} values of the uncured and the cured COPNA resins. The A_{1460}/A_{1380} value increased from 1.277 1 of the uncured COPNA resin to 1.337 7 of the cured COPNA resin, which indicated that the $n(\text{CH}_2)/n(\text{CH}_3)$ value increased during the curing process of the resins. We believe that the addition of curing agent, which contains a number of methylene groups, contributes to the changes. The area ratio of the peaks at $670\text{--}900\text{ cm}^{-1}$ and $1\,600\text{ cm}^{-1}$ ($S_{670-900}/S_{1600}$) can be used to characterize the substitution degree of hydrogen atoms attached to aromatic rings. The lower the $S_{670-900}/S_{1600}$ value is, the more the hydrogen atoms that are attached to aromatic rings are substituted. The $S_{670-900}/S_{1600}$ values reduced from 3.339 2 of the uncured COPNA resin to 2.019 5 of the cured resin, which indicated that some aromatic hydrogen atoms were substituted and the degree of cross-linking increased during the curing process. This analysis was consistent with the ^1H -NMR and ^{13}C -NMR analyses.

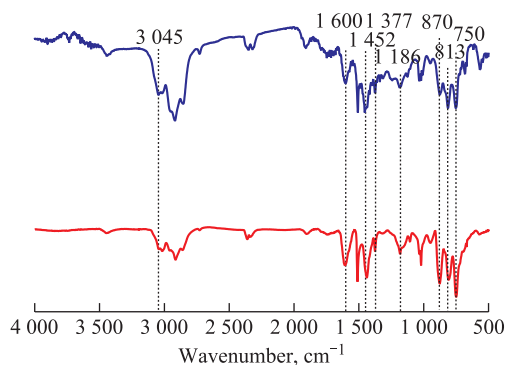


Figure 3 FT-IR spectra of uncured and cured COPNA resins

3.4 Curing mechanism of COPNA resin

Based on the results of ^1H -NMR, ^{13}C -NMR and FT-IR spectrometric analyses, it can be concluded that the elec-

trophilic substitution reaction occurs between the uncured COPNA resin and the curing agent. Firstly, the alcoholic hydroxyl groups of 1,4-benzenedimethanol react on protons under the acidic condition to give benzyl carbonium ions, and then the electrophilic substitution reaction occurs via subsequent attack of the benzyl carbonium ions on aromatic rings of COPNA resin. Thus, macromolecular compound with a three-dimensional network structure is formed. The curing mechanism and the molecular structure model of the resins are shown in Figure 4.

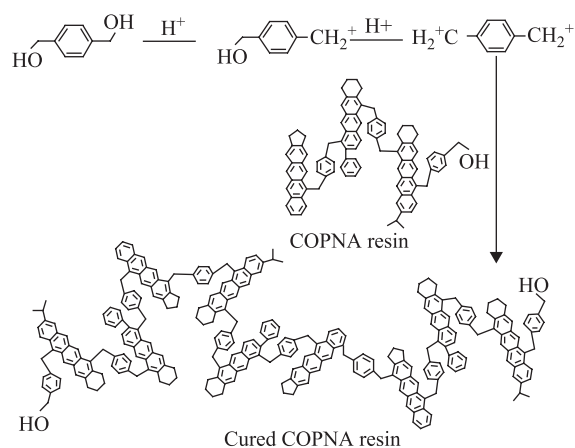


Figure 4 The curing mechanism of COPNA resins

3.5 SEM analysis

Figure 5 presents the SEM images of the uncured and the cured COPNA resins. The photographs of smaller magnification exhibited that the uncured and the cured COPNA resins were both of irregular blocky shape. A larger magnification revealed that the uncured COPNA resin with a rough surface and cross-section had no apparent orientation texture, thereby indicating that the uncured COPNA resin was isotropic. However, the cured COPNA resin displayed a well-ordered streamlined sheet structure. This might be due to the occurrence of the cross-linking reaction between the condensed aromatic sheet and 1,4-benzenedimethanol during the curing process, which could lead to a better molecular arrangement and orientation of the cured COPNA resin.

3.6 XRD analysis

The XRD patterns of the uncured and the cured COPNA resins are shown in Figure 6. It can be seen from Figure 6 that both the uncured and the cured COPNA resins rep-

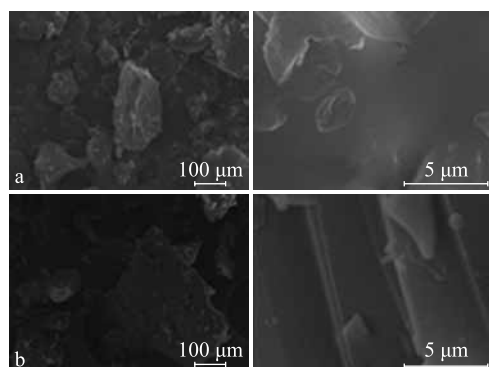


Figure 5 SEM images of uncured (a) and cured (b) COPNA resins

resented a broad band between 10° and 30° , indicating that the resins were amorphous in structure generally. The XRD parameters of the resins are given in Table 3. The two weak peaks of uncured COPNA resin at 21.48° and 23.72° were assigned to the γ -band, which is thought to be the packing distance of saturated structures (aliphatic chains or condensed saturated rings)^[23], while the cured COPNA resin exhibited eight weak peaks. The five former peaks were classified to be the γ -peak, and two other peaks centered at 25.36° and 43.68° were considered to be (002) and (100) diffraction of the graphite^[24]. All these data indicated that more crystalline solid appeared while the condensation degree of COPNA resin was increased, and a graphite-like carbon material was generated during the curing process. It can be concluded that the cured COPNA resin has a better molecular arrangement and orientation than the uncured resin just as mentioned in Section 3.5.

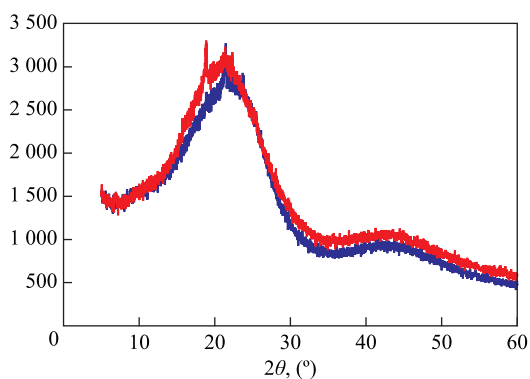


Figure 6 XRD patterns of uncured and cured COPNA resins

Table 3 XRD parameters of uncured and cured COPNA resins

Sample	$2\theta_{002}$, ($^\circ$)	d_{002} , nm
Uncured COPNA resin	21.48	0.414 3
	23.72	0.375 0
Cured COPNA resin	16.34	0.542 4
	17.52	0.506 3
	18.81	0.471 7
	21.41	0.415 1
	22.36	0.397 6
	25.36	0.351 2
	29.43	0.303 5
	43.68	0.207 2

3.7 Thermal behavior analysis

The TG-DTG curves of the uncured and the cured COPNA resins are shown in Figures 7 and 8. The TG-DTG curves illustrated that the weight loss of the uncured and the cured COPNA resins could be divided into three stages. Based on the first weight loss stage in TG-DTG curves, we can confirm that the temperature acting on

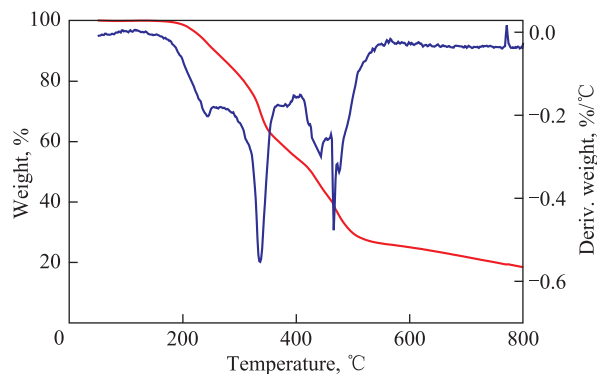


Figure 7 TG-DTG curves of uncured COPNA resin

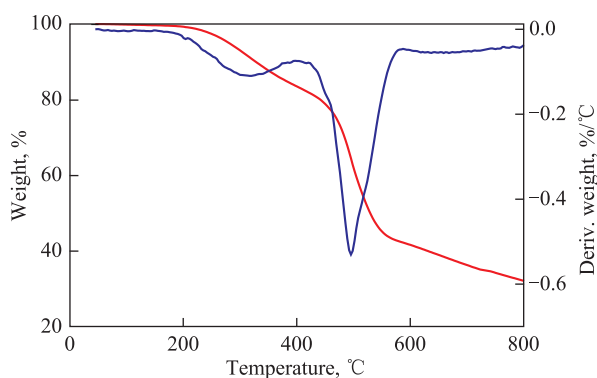


Figure 8 TG-DTG curves of cured COPNA resin

the uncured and the cured COPNA resins ranged from 230 °C to 350 °C and from 280 °C to 460 °C, respectively, in which the weight loss was mainly ascribed to the evaporation of water and uncrosslinked low molecular weight compounds. In the second weight loss stage, the temperature acting on the uncured and the cured COPNA resins ranged from 350 °C to 520 °C and 460 °C to 580 °C, respectively, in which the weight loss was mainly caused by the removal of light molecules generated from the multiple and complex reactions (cracking, polymerization, condensation, etc.). In the third stage, the resins were already transformed into a semi-coke solid state. In this interval, small molecules, such as H₂ and CH₄, were evolved from the cyclization and aromatization reactions^[24-27].

The DTG curve of the uncured COPNA resin showed that there were four maximum weight loss rate ($T_{\max}$) peaks appearing at 244 °C, 336 °C, 443 °C and 465 °C, respectively. However, in the case of DTG analysis of the cured COPNA resin, only two $T_{\max}$ peaks appeared at 317 °C and 495 °C. This shows that thermal decomposition mechanisms of the uncured and the cured COPNA resins are slightly different.

Table 4 shows the thermogravimetric parameters of the uncured and the cured COPNA resins. It can be observed that all the temperatures relating to the initial weight loss (T_i), the maximum weight loss rate ($T_{\max}$) and the final weight loss (T_f) of the cured COPNA resin were much higher than those of the uncured COPNA resin. T_i is one of the main criteria for heat stability of resins. The higher the value of T_i , the higher the thermal stability is. The weight loss rate of the cured COPNA resin was only 17.41% at 400 °C, which was remarkably lower as compared to that of the uncured resin (45.28%). Although

Table 4 Thermogravimetric parameters of uncured and cured COPNA resins

Sample	Temperature, °C				-ΔW, %
	T_i	T_f	ΔT	$T_{\max}$	
COPNA resin	229	540	311	244, 336, 443, 465	25.02
Cured COPNA resin	280	584	304	317, 495	41.65

Notes: T_i , temperature of initial weight loss; T_f , temperature of final weight loss; $\Delta T = T_f - T_i$; $T_{\max}$, temperature of maximum weight loss rate; -ΔW, carbon residue at 600 °C.

a lot of light molecules generated from the cracking, polymerization and condensation reactions were removed, the carbon residue of the cured COPNA resin still remained at 41.65% at 600 °C, which was much higher than that of the uncured COPNA resin (25.02%). The results mentioned above revealed that the cured COPNA resin exhibited a higher favorable thermal stability than the uncured resin. A possible explanation could be that the process of curing increased the crosslinking degree of COPNA resin. The aromatic molecules were connected by the curing agent to form the 3-D structured molecules, which could lead to a better thermal stability.

Table 5 shows the results of the elemental analysis of the cured COPNA resin heated at different temperatures. It can be observed that the contents of O and H elements in the cured COPNA resin heated at 400 °C were lower than that in the case of 200 °C, which was attributed to the removal of uncrosslinked low molecular weight compounds as mentioned above. The content of H element in the cured COPNA resin heated at 600 °C was much lower than that in the case of 400 °C, which was caused by the polymerization and condensation reactions. In addition, the C/H ratio of the cured COPNA resin increased with an increasing heating temperature, which indicated that the condensation degree of the cured COPNA resin was improved gradually. The elemental analysis was consistent with the previous conclusion of TG-DTG analysis.

Table 5 Elemental compositions of cured COPNA resin heated at different temperatures

Temperature, °C	Elements content, %				C/H
	C	H	O	Others	
200	89.7	6.4	1.5	2.4	1.17
400	91.8	6.1	0.7	1.4	1.25
600	93.3	3.5	0.7	2.5	2.22

4 Conclusions

The cured COPNA resin with high thermal stability has been successfully synthesized by heating a mixture of the uncured resin with a curing agent. The curing reaction mechanism is confirmed to be electrophilic substitution reactions. Due to the cross-linking reaction between the condensed aromatic sheet and the curing agent, the cured

COPNA resin with a well-ordered streamlined structure and a smooth surface showed that it had a more crystalline solid and a better molecular arrangement and orientation than the uncured resin. Thermogravimetric analyses indicated that the weight loss of the uncured and the cured COPNA resins both could be divided into three stages. The temperatures of T_i , T_f and T_{max} of the cured COPNA resin were found to be higher than those of the uncured resin. The carbon residue of the cured COPNA resin was as high as 41.65% at 600 °C. The results show that the cured COPNA resin has preferable thermal stability and exhibits enormous potential in the application of heat resistant materials.

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The Shenhua Ten-Million-Ton-Class MTO and Derivatives Project Has Been Approved by The State Development and Reform Commission

According to the news released on March 24, 2015 by the Shaanxi People's Government Website, the Shenhua recycle-economy project for comprehensive utilization of coal at Yulin had been approved on March 16, 2015 by the State Development and Reform Commission (as evidenced by the SDRC document [Energy 2015] No. 508.)

This project, which is a major demonstration project for deep processing of coal envisaged in the state plan, is located in the northern region of the Clear Water Coal Chemical Industry Park at the Yushen Industrial District of Yulin city. The investment in this project totals 121.6 billion RMB, and the construction items cover mainly a coal mine with a production capacity of 13 Mt/a, a 700-MW cogen project, and other 23 chemical units including such processes as coal gasification, methanol synthesis,

methanol-based olefins production (MTO), and olefin derivatives production. The product slate of this project is aimed at specialty chemicals, which cover four product lines, viz.: ethylene oxide, propylene oxide, acrylic acid and butanol/octanol products to manufacture more than one hundred brands derived from ten kinds of alcohols, acids, esters, amines and ethers.

This project will embody the world's advanced techniques. The process technologies adopted by the 23 process units to be constructed are in the world's front rank. The process units for manufacture of propylene oxide, ethanolamine/ ethylidene amine, polyether polyol and mixed glycol ether are major commercial units that are for the first time licensed to China to greatly raise the technical level for the production of olefins-based downstream fine chemicals to a higher rung.