

STUDY ON THE CARDANOL-ALDEHYDE CONDENSATION POLYMER CONTAINING BORON-NITROGEN COORDINATE BOND*

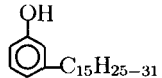
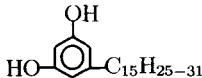
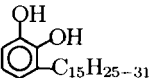
LIN Jinhua (林金火) and HU Binghuan (胡炳环)

(Institute of Polymer Science, Fujian Teachers University, Fuzhou, 350007, China)

Abstract Cardanol-aldehyde condensation polymer containing boron-nitrogen coordinate bond (CFBN) has been synthesized and characterized by IR, XPS, HPLC and DTA-TG. Its properties were also investigated. The results show that the coating film of CFBN has excellent physico-mechanical properties, good anticorrosive properties and stable at high temperature.

Keywords Cardanol; Cardanol-aldehyde condensation polymer; B-N coordinate bond

INTRODUCTION

Cashew nut shell liquid (CNSL), a brown thick liquid, contains about 90% cardanol () and about 10% cardol ()^[1], which are similar to urushiol () in structure. For many years, CNSL has been used in the preparation of coating and adhesive^[2,3]. The cashew-nut lacquer (CF) prepared by the reaction of CNSL with formaldehyde has been widely used in artistic decoration, building materials and furnitures for its durable, hard, bright and wear-resisting coating film. But it has limited use industrially because of its drawback such as being corroded by alkali. In order to improvement of its alkali resistance, the studies on the modification with epoxy resin and maleic anhydride have been carried out by a few investigators^[4,5], but even then these products are still corroded by strong alkalis. In our earlier publication^[6], urushiol polymer containing boron-nitrogen coordinate bond has demonstrated to have high anticorrosive properties. This paper deals with the synthesis, characterization and properties of cardanol-formaldehyde

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condensation polymer containing boron-nitrogen coordinate bond (CFBN), which has excellent physico-mechanical and anticorrosive properties and stable at high temperature.

EXPERIMENTAL

Materials

Cashew nut shell liquid was obtained from Shantou Native-product company. 36% formaldehyde, boric acid, 1,6-hexamethylene diamine and other chemicals used in this work were of reagent grade.

Preparation of CFBN

A round-bottomed flask fitted with an agitator, a condenser and thermometer was employed for the preparation.

Boron-contained cardanol-formaldehyde condensation polymer (CFB) was prepared by adding a weighed quantity of 36% formaldehyde and a small amount of 10% NaOH to 150g of CNSL and the mixture was heated to 70~75°C with continuous stirring for 1 hour, then a known amount of boric acid and 150g xylene was added and heated to 138~140°C with continuous stirring for 2~3 hours. The water in the system was removed as a binary azeotrope with the xylene used. On cooling, a brown thick xylene solution of CFB was obtained. To the stirring xylene solution of CFB was added dropwise a known amount of 50% absolute alcohol solution of 1,6-hexamethylene diamine. The reaction mixture was further stirred for about 30min at room temperature, the finally product CFBN was obtained.

Testing and measurements

For testing and measurement, CFBN and CFB were casted on clean glass and PE films, then dried under reduced pressure and at room temperature.

Infrared spectra of CFBN and CFB were recorded on a Perking-Elmer 577 Spectrophotometer in the region 4000~400cm⁻¹ by using PE film as the internal reference. X-ray photoelectron spectra were scanned on a Shimadzu 650B spectrometer. Liquid chromatography was performed on a Shimadzu LC-6A high performance thin liquid spectrograph with RID-6A differential detector, using Waters PS as standard, THF as eluent and PL-GEL as separating column. DTA-TG analysis was conducted using a Shimadzu DT-40 Thermal Analyzer under air at a flow rate of 40mL/min, 3~5mg of sample was used. The heating rate was programmed as 10°C/min. The

resulting curves were recorded using a Shimadzu C-R6A data processing unit. The physico-mechanical properties were tested according to the Chinese Testing Standard of Coatings (Bureau of State Standard).

RESULTS AND DISCUSSION

Effect of monomer ratio on the properties of CFBN

The reaction of cardanol-formaldehyde addition compound with boric acid can proceed quite smoothly and completely, and the product obtained has high thermal stability. However, it is hygroscopic and readily hydrolysed by atmospheric moisture. In order to improve its property, its reaction with diamine was examined. The experimental results show that the properties of product thus obtained depend highly on the molar ratio of cardanol, formaldehyde, boric acid and 1,6-hexamethylene diamine. The details of synthesis and properties are given in Table 1. It can be found from Table 1 that the product has good properties as the molar ratio of cardanol: aldehyde:boric acid: diamine being 1 : 2.2 : 0.5 : 0.25.

Table 1 Effect of monomer ratio on properties of films

c:f:b:h*	Hard drying time (h)	Hardness	Flexibility (mm)	<u>Resistance to</u>	
				Water	40% NaOH
1 : 3 : 1 : 0.5	4	3H	3	+	+
1 : 2.2 : 0.8 : 0.5	4	3H	3	+	+
1 : 2.2 : 0.5 : 0.25	4	3H	1	+	+
1 : 2.2 : 0.8	≤ 24	2H	1	—	/
1 : 2.2	≤ 24	2H	1	+	—
1 : 1.2 : 0.3 : 0.15	4	3H	2	+	—
1 : 0.8 : 0.6 : 0.3	> 24	HB	/	—	/

* c, f, b and h indicate cardanol, formaldehyde, boric acid and hexamethylene diamine, respectively.

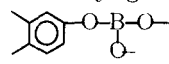
+ Indicating that the films were water-tolerant or alkali-resistant

— Indicating that the films were not water-tolerant or alkali-resistant

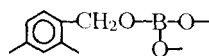
Structural characterization

Infrared spectra The infrared spectra of CF, CFB and CFBN are shown in Fig. 1. There is no strong absorption peak of hydroxy group (ν_{OH}) at $3500\sim 3300\text{cm}^{-1}$ in

the IR spectrum of CFB due to the reaction of boric acid with hydroxy groups in cardanol-aldehyde condensation polymer (CF). The appearance of two stretching vibration absorption bands of B—O bond attached to phenyl and alkyl groups at 1430cm^{-1} and $1380\sim 1340\text{cm}^{-1}$ suggests the presence of



and



structure in CFB.

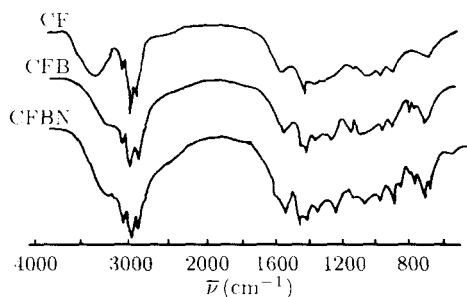


Fig. 1 IR spectra of CF, CFB and CFBN

Comparing with the IR spectrum of CFB, the IR spectrum of CFBN shows a downward shift of $7\sim 15\text{cm}^{-1}$ in B—O stretching vibration, indicating the formation of coordinate linkages between boron atom and the nitrogen atom of hexamethylene diamine and thereby weakening B—O bond order. Moreover, the IR spectrum of CFBN shows a new absorption band in the re-

gion $3200\sim 3080\text{cm}^{-1}$ due to the presence of $-\text{NH}_2$ group. A red shift in the N—H stretching frequency is also an indication for the participation of nitrogen atom of $-\text{NH}_2$ group in the B—N coordinate bond formation.

X-ray photoelectron spectroscopy X-ray photoelectron spectroscopic data of CFB, CFBN and 1,6-hexamethylene diamine are presented in Table 2. It is found

Table 2 XPS data of CFB, CFBN and Diamine

Sample	CFB	CFBN	Hexamethylene diamine
B _{1s}	192.9	191.8	
N _{1s}		399.8	398.8

that the B_{1s} binding energies of CFB and CFBN are at 192.9eV and 191.8eV, and the N_{1s} binding energies of CFBN and diamine are at 399.8eV and 398.8eV, respectively. The decrease of the binding energy of boron atom and the increase of the binding energy of nitrogen atom of CFBN are probably caused by the partial shifting of the electron in the nitrogen atom to the boron atom. Therefore, it is confirmed that B—N coordinate bond is present in CFBN.

DTA-TG analysis The thermolysis curves of CF and CFBN are presented in Fig. 2. The DTA curves show that the endothermic peaks of CF and CFBN appear at

394.2°C and 437.3°C, respectively and the TG curves show the highest rate of weight loss occurs at this same temperature. The decomposition temperature of CFBN is higher than that of CF. This result reveals that CFBN is more thermally stable than CF due to the existence of B—N coordinate bond in CFBN.

Liquid chromatography The chromatograms of CFB and CFBN are shown in Fig. 3. After the solvent (xylene) was removed, CFB could easily dissolve in THF while CFBN could not dissolve completely in THF. The HPLC performance results show that the average molecular weight and the breadth of molecular weight distribution of CFB are $\overline{M}_n = 6.15 \times 10^3$,

$\overline{M}_w = 3.36 \times 10^4$ and $\overline{M}_w/\overline{M}_n = 5.46$, and that of the dissolvable fraction of CFBN are $\overline{M}_n = 5.85 \times 10^3$, $\overline{M}_w = 2.79 \times 10^4$ and $\overline{M}_w/\overline{M}_n = 4.77$, respectively.

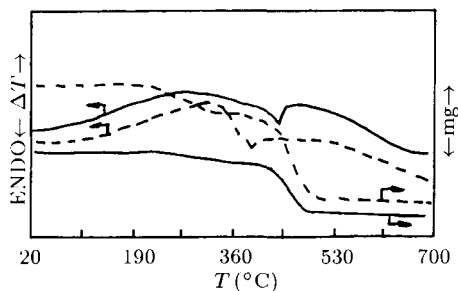


Fig. 2 DTA and TG curves
—:CFBN; ---: CF

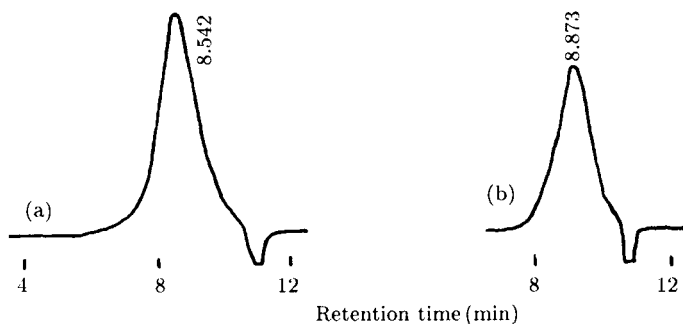


Fig. 3 HPLC chromatograms of CFB (a) and CFBN (b)

Properties of CFBN coating film

Physico-mechanical properties The CFBN film was casted from its solution on glass and metal plate, and its physico-mechanical properties were measured. The results are given in Table 3. It clearly shows that the physico-mechanical properties of CFBN are similar to those of cashew-nut lacquer^[7].

Anticorrosive properties The experimental results of anticorrosive properties of CFBN film coated on metal rod are listed in Table 4.

Thermal stability During the course of drying, the casting film of CFBN can un-

dergo further crosslinking and forms a three-dimensional network polymer through its unsaturated long-side chain in the presence of lead manganese cobalt drier. The dried film is stable to heat and can not be melted. The TG curves show that the limiting temperature of no weight loss for CFBN and CF appear at 244°C and 184°C, and their total weight loss at 700°C are 67.95% and 75.67%, respectively. The isothermal ageing result (see Table 5) also reveals that CFBN is higher thermal stability than CF.

Table 3 Physico-mechanical properties of CFBN film

Items	CFBN	Cashew-nut lacquer
Content (%)	55±5	55 ± 5
Viscosity (B-4 cup) (S)	90 ~ 150	90 ~ 150
Surface drying time (min)	< 30	< 30
Hard drying time (h)	4	< 20
Clearness (%)	≥ 100	≥ 100
Adhesion, grade	2	2
Flexibility (mm)	1	1
Impact (cm)	50	50

Table 4 The anticorrosive properties of CFBN film

<u>Chemical media</u> con. (%)		Testing Time (h)	CFBN	Cashew-nut lacquer
H ₂ SO ₄	70	2160	+	+
	30	2160	+	+
	10	2160	+	+
HCl	10	2160	+	+
	5	2160	+	+
NaOH	40	2160	+	-
	10	2160	+	-
NaCl	Saturated solution	2160	+	+
	5	2160	+	+
Alcohol	95	2160	+	+
Xylene	100	2160	+	+
THF	100	168	+	-

- + Indicating that the films do not appear blister, cracking spot or spoiled.
- Indicating that the films appear blister, cracking spot or spoiled.

From the TG curve of CFBN, the reaction order and average activation energy of thermal decomposition were estimated by using simple graphic method^[8]. The

result suggests that the thermal decomposition of CFBN follows first-order kinetics and its average activation energy E is 39.8Kcal/mol.

Table 5 Isothermal ageing of films in air

Film	Isothermal ageing Temp (°C)	Cumulative weight loss (%) after					
		5h	10h	15h	25h	30h	40h
CF	220	1.05	3.21	4.02	5.49	6.28	7.61
CFBN	220	0.08	1.75	2.61	3.11	4.58	4.76

CONCLUSION

Cardanol-aldehyde polymer containing boron-nitrogen coordinate bond synthesized from cashew nut shell liquid, formaldehyde, boric acid and hexamethylene diamine has excellent physico-mechanical properties, good resistant to strong acids, strong alkalis, salt solutions as well as several organic solvents, and stable at high temperature. Therefore, it has the promising prospect for the application as an anticorrosive coating.

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