

CHARACTERIZATION AND PROPERTIES OF URUSHIOL POLYMER CONTAINING BORON-NITROGEN COORDINATE BOND*

LIN Jinhua (林金火) and CHEN Wending (陈文定)

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

ABSTRACT

Urushiol polymer containing B—N bond (PUBN) was synthesized with urushiol-boron polymer and diethylene triamine. Its structure was characterized by XPS, IR, UV, HPLC, DTA-TG and elemental analysis. The physico-mechanical and anticorrosive properties of the polymer were also investigated. The results show that the coating of PUBN can be hardened in 2 h at room temperature and its film has excellent physico-mechanical properties and good anticorrosive properties.

INTRODUCTION

Chinese lacquer, as an excellent natural coating, has been studied and utilized for thousands years. However, it has been still an important work to improve the lacquer because of its inherent drawbacks such as high viscosity, low drying rate, drying only at definite temperature and humidity, giving sensitivity to human skin and being corroded by alkali^[1]. In order to improve its properties, a lot of works has been done for modification by using formaldehyde, styrene, epoxy derivatives and dry oils^[2], but these products can not meet a full need of industrial purposes. An improved lacquer possessing both the same properties as Chinese lacquer and high drying rate at room temperature is desired in industrial art and lacquer ware. On the basis of our previous work for urushiol metal chelate polymer^[3,4], we have obtained an urushiol polymer containing B—N coordinate bond (PUBN) which has excellent physico-mechanical properties and chemical properties and can be hardened in 2—3 h at room temperature by the reaction of urushiol-boron polymer (PUB) with diethylene triamine. In the present paper, its structure and properties are characterized and reported.

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EXPERIMENTAL

1. Materials

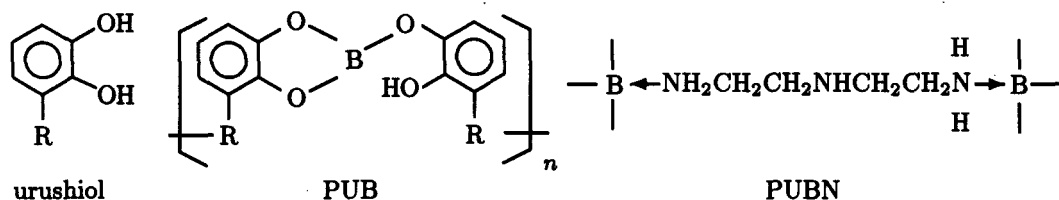
Urushiol was extracted by ethanol from Chinese lacquer, and then the solvent was removed under reduced pressure. Tri-*n*-butyl borate was prepared by the method given in literature [5], its boiling point is 103–105°C/11.57 kpa. Diethylene triamine and other chemicals used in this work were reagent grade.

2. Preparation of PUB and PUBN

PUB was prepared by adding 0.15 mole of tributyl borate to 0.3 mole of urushiol and the mixture was heated to 140–145°C with continuous stirring for 3 h and then dried in vacuum.

PUBN (in xylene-ethanolic solution) was prepared by adding a weighed quantity of 10% ethanolic solution of diethylene triamine to a 50% xylene solution of PUB dropwise with continuous stirring for about 10 min at room temperature. PUBN was precipitated out while ethanol was used as the solvent of PUB. The obtained precipitate was washed with ethanol and dried under reduced pressure.

The structural formulas of Urushiol, PUB and PUBN may be schematically represented as follows:



where R is $\text{—C}_{15}\text{H}_{25\text{—}31}$ containing 0–3 double bonds.

3. Testing and measurements

C, H, B and N contents were obtained using a Carlo-Erba 1106 elemental Analyzer. Infra-red spectrum of PUBN powder was recorded as KBr pellet, and urushiol and PUB were measured in chloroform solution with a Perkin-Elmer 577 spectrophotometer in the region 4000–400 cm^{-1} . X-ray photoelectron spectra were recorded on a Shimadzu 650 B spectrometer. Ultra-violet spectra of urushiol and PUB were recorded on a Shimadzu UV-2201 spectrophotometer using absolute ethanol as solvent. DTA-TG curves were obtained using a Shimadzu DT-40 Analyzer under nitrogen at a flow rate of 40 ml/min. The sample weight used was 3–5 mg. The heating rate was programmed as 10°C/min. Liquid chromatography was performed on a Shimadzu LC-6A HPLC with RID-6A differential detector using PS (Waters) as standard. The physico-mechanical and chemical properties were tested according to the Chinese Testing Standard of coatings (Bureau of State Standard).

RESULTS AND DISCUSSION

1. Structural characterization of PUB and PUBN

(1) Ultra-violet spectrum The Ultra-violet spectral data listed in Table 1 can be assigned as follows: the absorption frequencies at 272 and 282 nm is ascribed to the benzene $\pi - \pi^*$ transition, and 225 nm to the unsaturated side chain ($-\text{R}$) $\pi - \pi^*$ transition in urushiol. In comparison with urushiol, the peaks of benzene $\pi - \pi^*$ transition are shifted to 265, 268 and 273 nm, and the peak of $-\text{R} \pi - \pi^*$ transition disappears in PUB. From these data, it can be suggested that a new B—O bond is formed and the unsaturated side chain is polymerized.

(2) Liquid chromatography The chromatograms of urushiol and PUB are shown in Fig.1. According to the retention time and mol. wt. of urushiol, we can predict that PUB is a polydisperse polymer, whose average MW of the major composition (about 60%) is 1.25×10^3 .

(3) Infra-red spectra The infra-red spectra of urushiol and PUB are shown in Fig. 2. A comparison of their IR spectra indicates that the absorption peak of PUB at $35000\text{--}3300\text{ cm}^{-1}$ is weakened. This phenomenon can be attributed to the reaction of hydroxy groups of urushiol with boron compound. The 986 cm^{-1} , 948 cm^{-1} ($\nu\text{--C=C--C=C--}$) and 3008 cm^{-1} ($\nu\text{=C--H}$) peaks disappear completely and thus indicate the polymerization of conjugated double bonds in the side chain. In Fig. 2(b), a new strong band appears in the region $1480\text{--}1420\text{ cm}^{-1}$ which indicates the presence of B—O bond with aryl ring^[6]. A comparative study of Fig. 2(b) and (c) indicates that the IR spectrum of PUBN has a strong broad band in the region $3500\text{--}3200\text{ cm}^{-1}$ indicating the presence of $-\text{OH}$, $-\text{NH}_2$ and $-\text{NH}$ groups, a peak at 1350 cm^{-1} due to B—N bond, and a shift of $1480\text{--}1420\text{ cm}^{-1}$ to $1450\text{--}1420\text{ cm}^{-1}$ ($\nu_{\text{B--O}}$) due to a decrease in the B—O bond order on coordination of nitrogen to boron^[7].

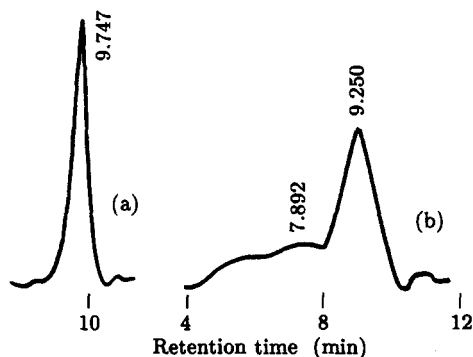


Fig. 1 HPLC chromatograms of (a) urushiol and (b) PUB

Table 1 Ultra-violet absorption peaks of PUB and urushiol

Sample	λ_{max} (nm)			
Urushiol	272	282	225	
PUB	265	268	273	/

(4) X-ray photoelectron spectra The results of electron binding energy measurement of PUB and PUBN are presented in Fig. 3. It is found that the B_{1s} binding energies of PUB and PUBN are at 193.7 eV and 192.6 eV, respectively. The decrease of the binding energy of boron atom of PUBN is probably caused by the partial shifting of electron in the nitrogen atom to the boron atom. Thus, it is confirmed that PUBN is an urushiol polymer containing B—N coordinate bond.

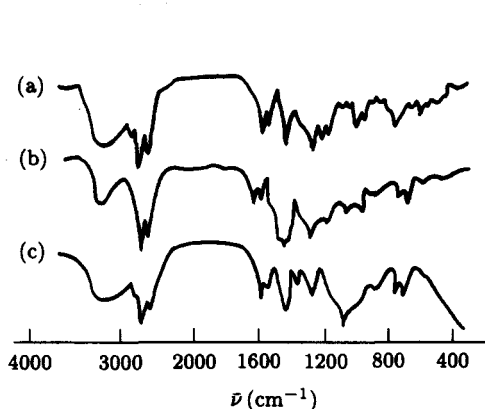


Fig. 2 IR spectra of (a) urushiol, (b) PUB and (c) PUBN

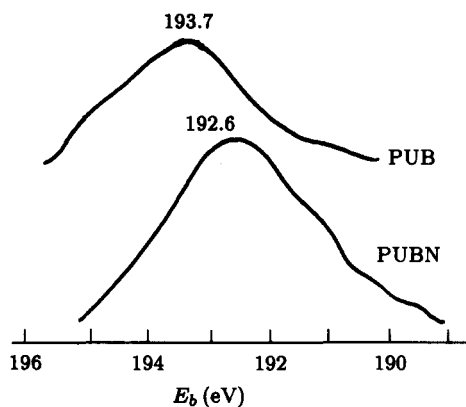


Fig. 3 B_{1s} electron binding energy of PUB and PUBN from XPS

(5) Elemental analysis The result of elemental analysis of PUB and PUBN is tabulated in Table 2. The percentages of C, H and B in PUB are in agreement with the calculated values of proposed structural formula. It is difficult to calculate theoretically out the elemental percentage of PUBN, but it can be found from the experimental data that the mole ratio of the repeat unit of PUB to diethylene triamine is about 1:0.47. Thus, we may assume that all the boron atoms in PUB have taken part in the coordination reaction.

Table 2 Elemental analysis of PUB and PUBN

Sample	Found/calc. (%)			
	C	H	B	N
PUB	78.82/78.75	8.92/9.53	1.78/1.72	/
PUBN	77.53	9.86	1.62	3.05

(6) DTA and TG analysis The thermogram of PUB and PUBN is exhibited in Fig. 4. The DTA curves show that the largest endothermic peaks of PUB and PUBN appear at 430.3 and 458.4°C, respectively, and the TG curves show that the highest rate of weight loss appears at the same temperature. The decomposition temperature of PUBN is higher than that of PUB. This result reveals that PUBN

is more thermally stable than PUB because the former contains B—N coordinate bond.

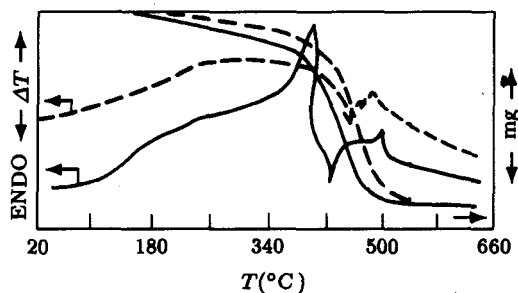


Fig. 4 DTA and TG curves of PUB — and PUBN - - -

2. Properties of PUBN coating film

(1) Physico-mechanical properties The PUBN solution was coated on glass and metal plate, and the drying speed and physico-mechanical properties were measured by the method of the National Coating Standard. The results are given in Table 3. It clearly shows that all the properties are improved with the increase amount of diethylene triamine. As the used amount of diethylene triamine is 4.5%, the properties are similar to those of urushiol formaldehyde varnish, but the drying speed is faster.

Table 3 Physico-mechanical properties of PUBN film

Properties	Weight fraction of diethylene triamine (%)						
	0	1.0	2.0	3.0	4.5	5.5	UF*
Surface dry (h)	72	4	0.5	0.5	< 0.5	< 0.5	0.5
Hard dry (h)	168	34	8	5	2	2	34
Brightness (%)	98	102	104	111	112	103	130
Adhesion (grade)	2	2	1	1	1	1	1
Flexibility (mm)	1	1	1	1	1	1	1
Pencil hardness	6B	6B	5B	3B	H	H	2H
Impact (cm)	10	10	15	15	35	35	50

*UF is urushiol-formaldehyde varnish^[3]

Anticorrosive properties: In order to investigate the chemical properties of PUBN film containing 4.5% diethylene triamine, the anticorrosive test of films coated on metal rod was carried out. The testing results are listed in Table 4. It is found that PUBN is more stable than PUB in all chemical media, and similar to urushiol formaldehyde varnish. The reason for its higher stability is the presence of B—N coordinate bond.

Table 4 The anticorrosive properties of PUBN film

Chemical media	Testing time (h)	PUB	PUBN	UF
H ₂ O	168	—	+	+
10%HCl	168	+	+	+
10% NaOH	168	—	+	+
10% NaCl	720	—	+	+
Alcohol	360	—	+	+
Xylene	168	—	+	+
THF	168	—	+	—

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

— denoting that the films appear blister, cracking spot or spoiled.

To sum up the discussion above, it can be concluded that PUB is the polymerized diurushiol borate through unsaturated side chain in urushiol, and PUBN is formed from the coordination of PUB and diethylene triamine in which the boron atoms are bonded to the nitrogen atoms. The coating film of PUBN can dry quickly, and its properties are similar to that of the urushiol formaldehyde varnish, therefore, it has a promising prospect for the application as a quick-drying paint in industrial art and lacquer ware, etc.

Keywords:

Urushiol-boron polymer; Diethylene triamine; B—N coordinate bond

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