

THE SYNTHESIS OF URUSHIOL TITANIUM CHELATE POLYMERS AND THEIR STRUCTURAL CHARACTERISTICS*

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ABSTRACT

The synthetic method and structural characteristics of urushiol-titanium chelates (UT) and urushiol-titanium chelate polymer for anticorrosive coatings have been studied.

Two kinds of coating films made from UT polymer show excellent physico-mechanical properties and possess good chemical resistance to strong acids and alkalis, many kinds of salt solutions and organic solvents, stable at high temperature.

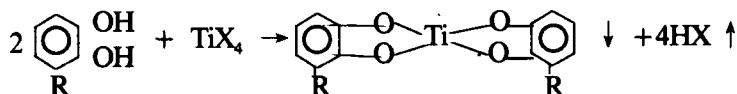
INTRODUCTION

Chinese lacquer (urushi) is a natural product of lacquer tree. It has enjoyed the reputation of being a "paint king" for its excellent chemical properties in forming durable, hard, bright, anticorrosive and abrasive film. It is widely used in artistic decoration, building materials, textiles equipments and furnitures. But it has limited use in industrial purposes because of its drawbacks such as high viscosity, low drying rate, drying only in definite temperature and humidity, giving sensitivity to human skin and being corroded by alkali^[1].

For the improvement of its properties, a lot of work have been made for modification by using formaldehyde, ethylene, epoxy derivatives and dry oils, but none of these products can maintain the good urushi properties of Chinese lacquer. For this purpose, the authors have tried to use metallic compound for preparing urushiol chelates, which have not been recorded in literature. In our previous papers^[2, 3], aluminium chelates giving a good resistance to heat and antimony chelates possessing flame retarding property have been reported. This paper deals with both of synthetic methods and structural properties of titanium chelates. The results show that urushiol titanium chelates possess excellent anticorrosive properties.

EXPERIMENTAL

1. Reaction sequence



here $\text{R} = \text{C}_{15} \text{H}_{25-31}$

2. The synthesis of urushiol titanium chelates^[4]

In a 500 ml beaker filled with 100g of 50% urushiol-xylene solution, 10g of 10% TiCl_4 -xylene solution is added drop by drop with stirring. The temperature of the system

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raises automatically with the evolution of HCl gas. The mixture is heated under $130 \sim 140^\circ\text{C}$ for 1 h. The product obtained is proved to be urushiol-titanium chelates (UT) with a yield of 97%.

3. Preparation of urushiol-titanium chelate, anticorrosive coating material

UT is insoluble and infusible, so it cannot be treated with spraying. We have introduced an organo-titanium compound as an additive for the reaction of urushiol to form derivative which is soluble in organic solvent and a new type anticorrosive lacquer can be prepared as follows:

In a 500 ml beaker, add a stoichiometric amount of 50% urushiol xylene solution and organo-titanate solution, the reaction mixture is heated to 100°C for 30 min., then cross-linking agents is added and heated at $130 \sim 140^\circ\text{C}$ for 60 min. and cooled to 100°C , finally additive are added and the reaction mass is filtered to remove the residues. The filtrate has shown to be urushiol-titanium chelate anticorrosive lacquer (UTJ-1). By adding filler and xylene to the UTJ-1, the mixture is stirred and ground uniformly, the formed product is UTJ-2.

4. Testings

The determination of titanium content by the analysis of IR and MS spectra of UT and UTJ-1 samples, GPC, EMP and SEM testing of UTJ-1 and anticorrosive testing of UT, UTJ-1 and UTJ-2 against several chemicals have been made^[4,5].

RESULTS AND DISCUSSION

1. It is seen from Fig. 1 that the strong and broad peak is weakened at (b). This can be interpreted as that by the reaction of TiCl_4 , o-dihydroxy radical at urushiol are weakened or disappeared, as shown by the diagram in the 3008 cm^{-1} and 3060 cm^{-1} peak; which means that unsaturated side chain occurred in some oxidation polymerizations, with the disappearance of double bond. In Fig 1(a), it forms a single peak at $1592\text{--}1620$. That means the benzene skeleton changes under vibration, i.e. the formation of dimers or polymers occurred.

The 992 cm^{-1} , 982 cm^{-1} , 945 cm^{-1} and 772 cm^{-1} peaks in (b) also disappeared and a new 965 cm^{-1} peak appeared, indicating the oxidation and polymerization of unsaturated side chain, which was a result of the disappearance of conjugated double bond, so the unsaturated side chain transformed from cis to trans position. In Fig. 1(b) it appeared other new peaks at 465 cm^{-1} and 625 cm^{-1} which proved the presence of $\text{Ti}-\text{O}-\text{Ti}$ titanium-oxygen bond. As the reaction occurred at anhydrous condition, the hydroxyl group of urushiol $\text{C}_6\text{H}_4(\text{OH})_2$ formed $\text{Ti}-\text{O}-\text{Ti}$ bond, and the result was the appearance of

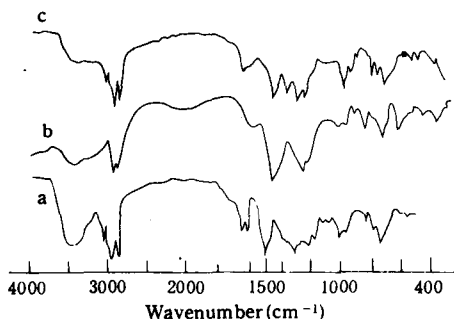
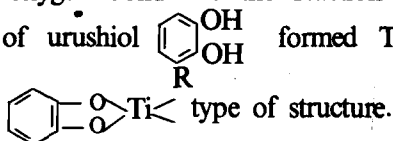
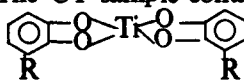
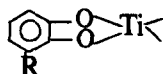
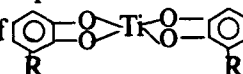


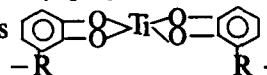
Fig 1 IR Spectra of the samples
a) urushiol, b) UT, c) UTJ-1.

The UT sample contains 11.84% Ti (TiO_2), coinciding with the stoichiometric content of Ti in  (11.83% TiO_2). From the MS test shown in Fig. 2a, the compound with mol. wt. of 676 amounted to 672–684, coinciding to that of the urushiol-titanium chelate.

2. From Fig. 1 (c), in comparison with 1(a), it showed that the strong peak at $3500\text{--}3200\text{ cm}^{-1}$ was weakened, which was due to the ortho hydroxyl group reacted with titanium compound. The new peaks appearing at 517 cm^{-1} and 522 cm^{-1} showed the presence of $\text{Ti}-\text{O}-\text{Ti}$ bond, that was the presence of  in UTJ-1, its

molecular structure possibly showed  unit.

The complexity of UTJ-1 mass spectrograph (2b) showed a lot of peaks of ions, which are similar to urushiol^[9], but UT is still more complex. It showed that UTJ-1 molecule underwent decomposition in forming several fragments with two new ionic peaks at 657 and 684 peaks. This also proved the presence of molecule with mol. wt. at 684 or larger. As 684 is the molecular weight of , this chelate contains R with

0–3 unsaturated double bonds. They polymerized to form polymers showing by the ionic bombardment of urushiol chelates  some breakages of side chain might occur, and with the loss of 1–2 radical of $-\text{CH}_3$ or $-\text{C}_2\text{H}_5$, the mass should be decreased to 657.

3. The GPC spectrograph is shown in Fig. 3 (Apparatus LC-6A high resolution liquid spectrograph; with RID-6A differential detector). The standard used is Waters PS standard (The standard curve is shown in Fig. 4).

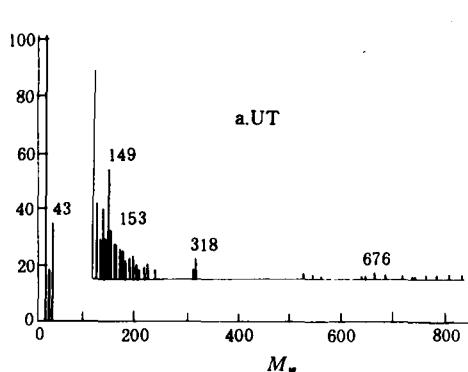


Fig 2a

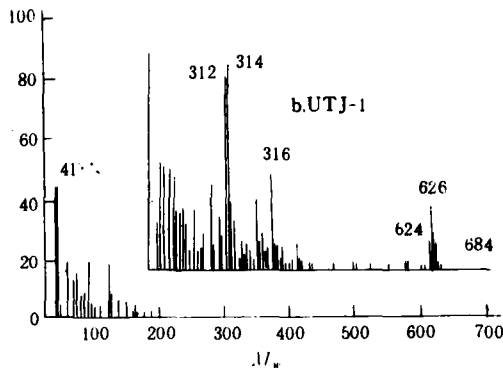


Fig 2b

Fig 2 Mass spectra of samples

a) UT; b) UTJ-1

Test condition: ionogenic temp., 180°C ; volatile temp., 235°C ; electronic energy of source of electron bombardment, 70 eV; accelerating voltage, 3kV.

Table 1 $M.W.$ and its distribution of UTJ-1

V_e (ml)	9.625	8.233	6.60	5.933
$M.W.$	316	4.1×10^3	1.12×10^5	5.1×10^5
Percentage (%)	3	90	4	3

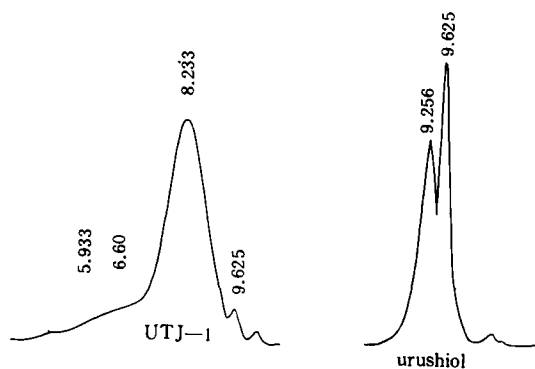
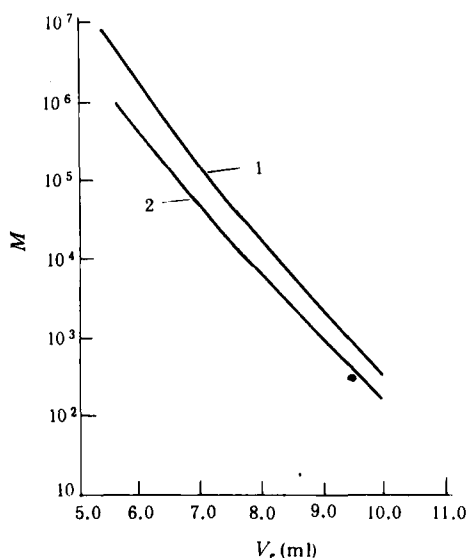


Fig 3 GPC of the samples of UTJ-1 and urushiol

Fig 4 M_w and V_e of PS and UTJ-1

The known values are $K_s = 1.17 \times 10^{-2}$, $\alpha_s = 0.725$. The monomer used for comparison is urushiol, and monomers of urushiol amount to more than ten types, but their molecular weight is only affected in very small range, and the average MW is 316. According to the literature, there are some dimers present in natural polymer, the structural unit of the mixture amount to more than ten categories^[7], and their average molecular weight approaches to 630. From Fig. 3 the peak value of urushiol is 9.625 and the dimer is 9.250. As shown by the standard curve (Fig 4), the peak value of PS, is from $[\eta] = KM^{\alpha}$, $[\eta]_s \cdot M_s = [\eta]_x \cdot M_x$, the constant of urushiol type of polymers $K_x = 1.705 \times 10^{-2}$, $\alpha_x = 0.8802$, can be calculated from constants of K_x and α_x . The general approximate equation can be obtained:

$$\lg M_x = \frac{1 + \alpha_s}{1 + \alpha_x} \cdot \lg M_s + \frac{1}{1 + \alpha_x} \cdot \lg \frac{K_s}{K_x}$$

From this equation we can calculate out the peak value with mol. wt. of UTJ-1 to be $4.1 \times 10^3 - 5.1 \times 10^5$ as shown in Table 1. Therefore UTJ-1 is a polymer. In Fig. 2 (b) a new ion peak appeared, which coincided with 672–684 mol. wt. of urushiol-titanium chelate of $\text{C}_6\text{H}_4(\text{O})_2\text{Ti}(\text{O})_2\text{C}_6\text{H}_4$, this might be the fragment of UTJ-1 polymer. Therefore it is proved that UTJ-1 is a polymer containing the structural unit of urushiol-titanium chelate.

UTJ-1 is different from UT, which is insoluble and infusible but UTJ-1 is soluble in some organic solvents. Because UTJ-1 solution consists of low polymers of urushiol and a part of titanium atom centres around chelate as intermediate, in which titanium atom is controlled in the reaction with only partial hydroxyl radicals of urushiol molecule. This intermediate has not formed chelate perfectly and is still soluble in organic solvents. The UTJ-1 solution possesses high viscosity for coating, which can be dried to form hard film. The distribution of Ti atom in the film is very uniform, which can be traced from the EMP map (Fig 5). The Ti atom is generally located at 7 to 9, distributed at the contour position.

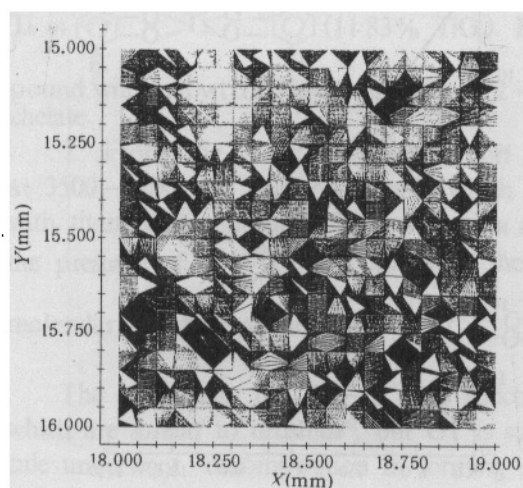


Fig 5a EMP Map--1

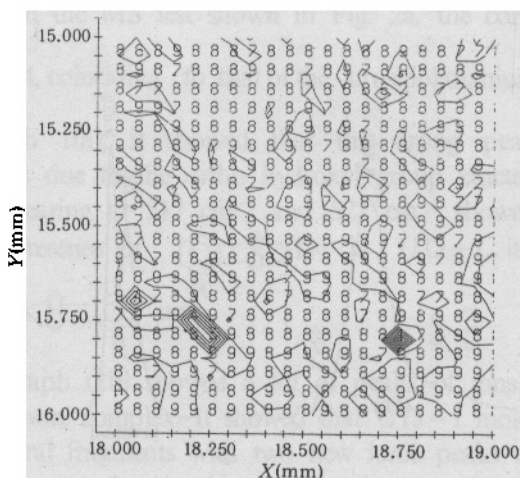


Fig 5b EMP Map--2

Fig 5 The distribution of titanium atom in the UTJ-1 film

Table 2 The anticorrosive tests of films at room temperature*

Corrosive mediums		UTJ-1		UTJ-2		Urushi	
Item	conc (%)	Time Results (y)		Time Results (y)		Time Results (y)	
NaOH	10	6	+	6	+	3d	-
	30	6	+	6	+	3d	-
	sat	6	+	6	+	3d	-
Na ₂ CO ₃	10	6	+	6	+	90d	+
	10	6	+	6	+	2	+
	30	6	+	6	+	—	—
H ₂ SO ₄	80	6	+	6	+	—	—
	85	500d	+	500d	+	20d	-
	98	40d	+	40d	+	4d	-
HCl	10	6	+	6	+	2	+
	30	6	+	6	+	2	+
	20	6	+	6	+	2	+
HNO ₃	40	7d	+	7d	+	2d	-
HF	40	6	+	6	+	2	+
HBr	20	6	+	6	+	—	—
Citric acid	nat	6	+	6	+	2	+
Sea water	indust.	6	+	6	+	6	+
Kerosene	indust.	7	+	7	+	6	+
Gasoline	indust.	6	+	6	+	6	+
Transformer oil	cp	6	+	6	+	6	+
Xylene	95	6	+	6	+	6	+
Alcohol							

* The thickness of UTJ-1 film=0.10 mm; UTJ-2 film=0.12 mm; urushi film=0.11 mm.

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

-Indicating that the films appear blister, cracking, spot or spoiled.

Fig 6 is the 1000 scan electron microscopic tracing of UTJ-1 film, showing that under this magnification it still has a uniform surface without particles, so it possesses good adhesive property and better mechanical strength.

4. The data^[9] of UT shows that the material is resistant to strong acids, strong alkalis, salt solutions as well as in several organic solvents; and it possesses good chemical stability when stayed on long duration in these solvents. It is also stable at elevated temperature such as in fusing NaOH at 320 ~ 340 °C for 2 hrs.

The tests are made according to the National Coating Standard, and the data are shown in Table 2 and 3 showing the UTJ-1 and UTJ-2 possesses anticorrosive properties better than that of urushiol so they have the promising prospect for the purpose of application as anticorrosive material in chemicals, petroleum, ship building, marine or hydraulic plant, etc.

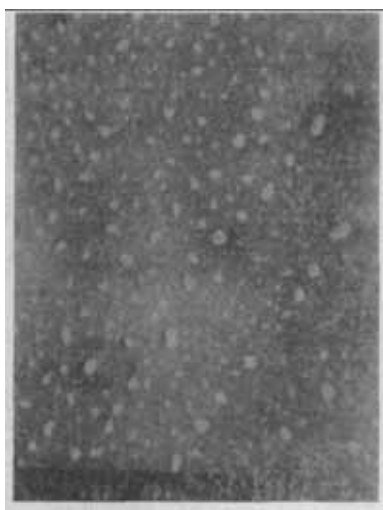


Fig.6 SEM photograph of UTJ-1 film

Table 3 The anticorrosive tests of films under elevated temperature*

Corrosive mediums			UTJ-1		UTJ-2		Urushi	
Item	conc (%)	temp (°C)	Time	results (h)	Time	results (h)	Time	results (h)
NaOH	cp	330+10	2	+	5	+	0.1	-
	50	80+1	2200	+	15300	+	4	-
Na ₂ CO ₃	10	80+1	10000	+	10000	+	1150	-
H ₂ SO ₄	10	80+1	15000	+	15300	+	10000	+
	70	80+1	15000	+	15300	+	8000	+
HCl	10	80+1	15000	+	8000	+	8000	+
	30	80+1	15000	+	8000	+	8000	+
H ₃ PO ₄	85	80+1	15000	+	15300	+	—	—
NH ₄ Cl	satd	80+1	15000	+	15300	+	10000	+
Sea water	nat	80+1	15000	+	15300	+	10000	+
Kerosene	indust	140+2	38	+	38	+	—	—
Alcohol	95	78	118	+	112	+	0.5	-
		45+1	—	—	—	—	4	-
		80	12	+	12	+	—	—
Benzene	cp	45+1	—	—	—	—	4	-
		80	12	+	12	+	—	—

* The thickness of UTJ-1 film=0.10 mm; UTJ-2 film=0.45; urushi film=0.11 mm.

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

- Indicating that the films appear blister, cracking, spot or spoiled.

Keywords:

Chinese lacquer; Urushiol-titanium chelate polymer; Anti-corrosive coating; Heat-stability

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