

# BSL-Based Coatings for Bamboo Protection

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**ABSTRACT:** Bhilawanut shell liquid is a natural product, and because of its phenolic nature it undergoes reactions similar to those of phenol. Surface coatings based on BSL were prepared from formaldehyde, styrene, hexamine, and epichlorohydrin for the protection of bamboo surfaces. BSL-based coatings were applied on bamboo and the performance of these coatings was evaluated by accelerated and chemical resistance tests. It was observed that these coatings can be used for the protection of bamboo from corrosive environments. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 487–493, 1998

**Key words:** bhilawanut shell liquid; surface coatings; bamboo protection; chemical resistance

## INTRODUCTION

Bhilawanut shell liquid (BSL) is an indigenous extract from the shells of nuts of *Semecarpus ana-cardium* (Linn) and form an important raw material for surface coatings<sup>1</sup> which is phenolic in nature. A variety of surface coatings based on BSL have been developed.<sup>2,3</sup> Moisture-resistant and nonflammable sealing and adhesive compositions have also been developed from bhilawa oil.<sup>4–6</sup> The available information on the chemistry of BSL shows that it is a rich source of bhilawanol ( $C_{21}H_{32}O_2$ ). The structure of bhilawanol is shown in Figure 1. In view of the structure as shown in the figure, BSL exhibits the unique properties of orthodihydric phenols which can be utilized profitably in the coating industry.<sup>7</sup> Coatings based on cashew nut shell liquid (CNSL) and industrial waste fly ash have already been developed for the protection of bamboo surfaces from a corrosive environment, but these coatings have poor mechanical film properties.<sup>8,9</sup> This article relates to the preparation of BSL-based coatings and assessment of their characteristics, particularly for the protection of bamboo surfaces.

## EXPERIMENTAL

### Materials

BSL was extracted from the shells of the bhilawanut by a solvent extraction method using hexane. The extracted BSL was analyzed and found to have specific gravity 0.817, nonvolatile matter 68%, iodine value 250, pH 8.74, and moisture content 1.633%, which was used for making surface coatings. All the other materials, namely formalin, styrene, hexamine, and epichlorohydrin, used for making various products were of laboratory reagent grade.

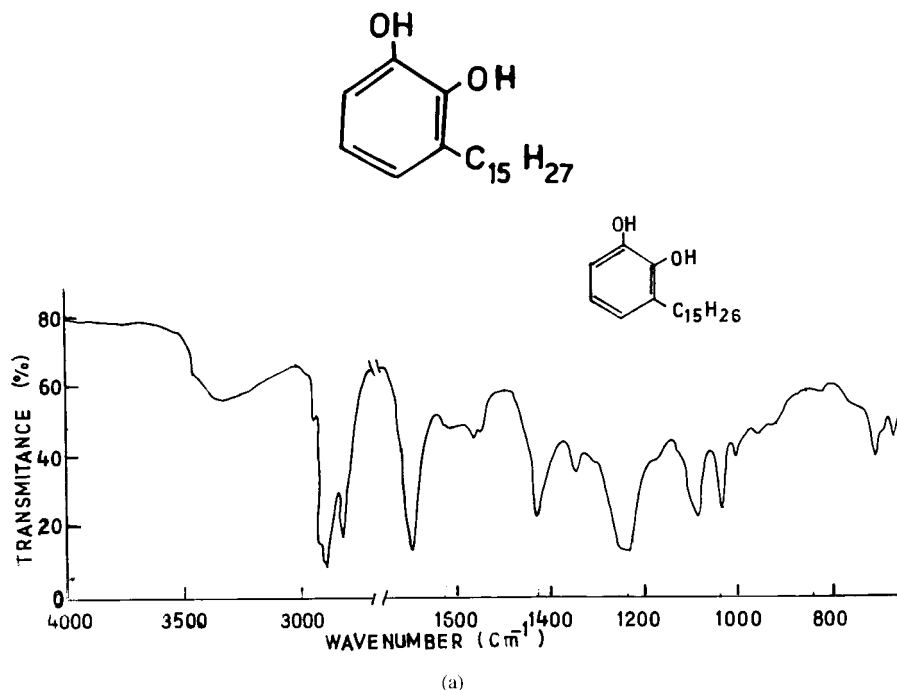
### Preparation of BSL-Phenol-Formaldehyde Resin

The resin formation reaction was carried out in a round-bottom flask; phenol and formalin were taken together, caustic soda was dissolved in 10 mL of water and added to the reactants, and reacted under reflux at a temperature of 85°C for 1 h. BSL, phenol, formalin (37%), and sodium hydroxide were used as 0.13, 0.64, 0.86, and 0.13 moles, respectively. The curing agent  $CuCl_2$  was added as 5% on resin.

### Preparation of BSL-Styrene Resin

BSL, placed in a three-neck flask fitted with a stirrer, a thermometer, and a Y-adaptor, was

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**Figure 1** Structure of bhilawanut shell liquid (BSL). (a) IR spectrum of BSL.

heated to temperatures from 100 to 150°C. About one-fourth of the total required quantity of the initiator (methyl ethyl ketone peroxide) used was added to the system. Styrene containing half the total required quantity of the initiator was then added dropwise through the Y-adapter. After the monomer addition was over, the rest of the initiator was added and heating was continued until the desired conversion of the styrene monomer to polymer was obtained as evidenced by the reduced rate of reflux of the material. The following recipe was used. The recipe used (in mol) were BSL (0.32), styrene (0.67), methyl ethyl ketone peroxide (initiator) (0.06), and curing agent (mixture of Co, Pb, Mn naphthanates as 0.3, 0.03, and 0.003% respectively).

#### Preparation of BSL-Epoxy Resin

The preparation was carried out in a half-liter reaction flask equipped with a stirrer, a thermom-

eter, and a condenser. After adding the reactants (BSL and epichlorohydrin), the catalyst (NaOH) was added portionwise in two installments. At the end, the unreacted epichlorohydrin was removed by vacuum distillation. The resin formed was dissolved in toluene and filtered to separate the salt. The resin was recovered by distilling toluene under vacuum. The recipe used (in mol) were BSL (0.1), epichlorohydrin (0.38), 50% sodium hydroxide (0.37), and curing agent (5% on resin).

#### Characterization of Coatings

The properties of resin coatings were determined as per standard specification and tabulated in Table I. The nonvolatile matter is the determination of the total solids available for film formation and for the estimation of volatile organic compounds. The nonvolatile content was determined according to ASTM D1259-85. The viscosity of all

**Table I** Physical Properties of Resin Coatings

Coating	Clarity	Nonvolatile Matter (%)	Viscosity Centipoise (30°C)	pH	Drying Time	Specific Gravity	% Yield of the Resin
BSL	Blur	88%	518	8.74	30 min	0.817	—
BSL-Phenol	Clear				50 min		
Formaldehyde		86%	328	8.85		1.12	92
BSL-Styrene	Clear	68%	35	8.33	3 h	0.87	90
BSL-Epoxy	Clear	72%	30	8.85	28 h	1.032	87

the resin systems was determined at 30°C after the reaction was over except for the BSL-styrene resin, which was obtained in a semisolid state and dissolved in xylene to make a 50% solution. The pH of the coatings were measured according to ASTM D-4613. The coatings were also characterized by employing IR spectroscopy.

### Preparation of Coated Specimens

The bamboo specimens were prepared according to IS:8242 and cleaned with a brush. The surface was roughened with emery paper. A selected coating was applied by brush. The coated specimens were completely air dried and allowed to dry. Similarly, mild steel panels (10.0 cm × 15.0 cm) were degreased using trichloroethylene, pickled in dilute hydrochloric acid, washed, and dried. The dried panels were coated with prepared resins after adding dryers as mentioned above by brush.

These coated panels were subsequently subjected to the following tests.

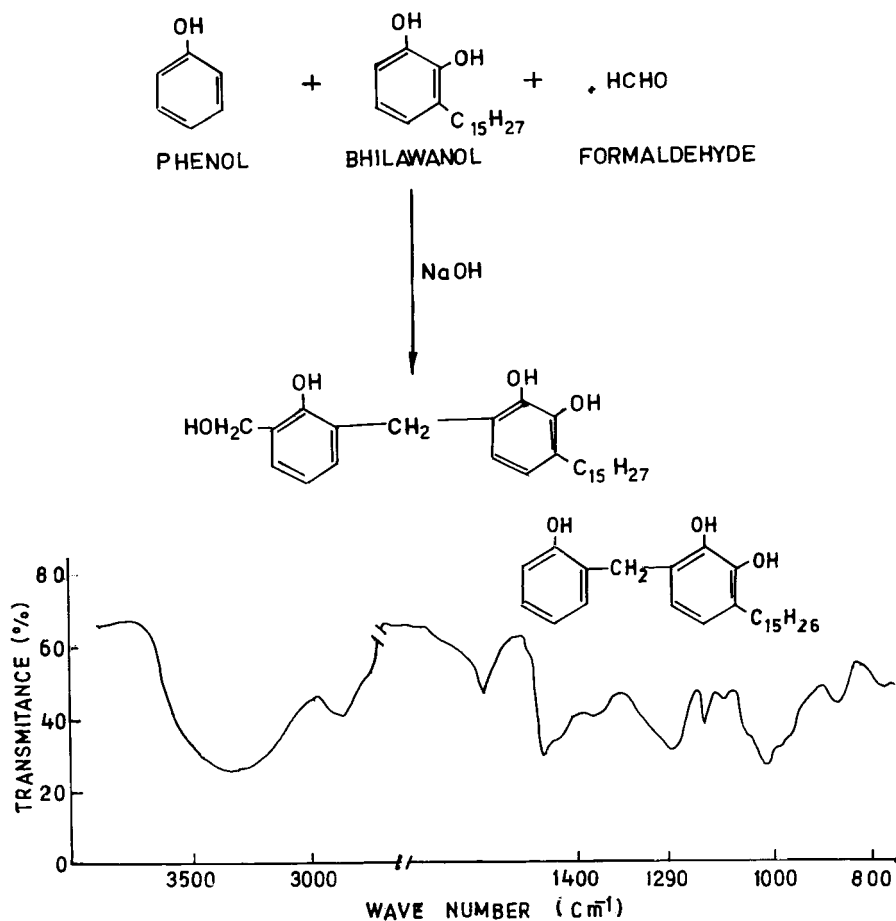
### Evaluation of Film Properties of the Coating Compositions

The mechanical and chemical properties of BSL-based coatings developed were determined and the results are shown in Tables II and III. The scratch hardness of the coatings were measured with a scratch hardness tester (AIM-601), which meets the requirements of IS:101. The impact testing was done by the falling weight method according to ASTM DEF 1053.

## RESULTS AND DISCUSSION

### IR Analysis of BSL

The IR analysis of BSL [Fig. 1(a)] shows a sharp band at 3000  $\text{cm}^{-1}$  attributed to aliphatic C—H



(a)

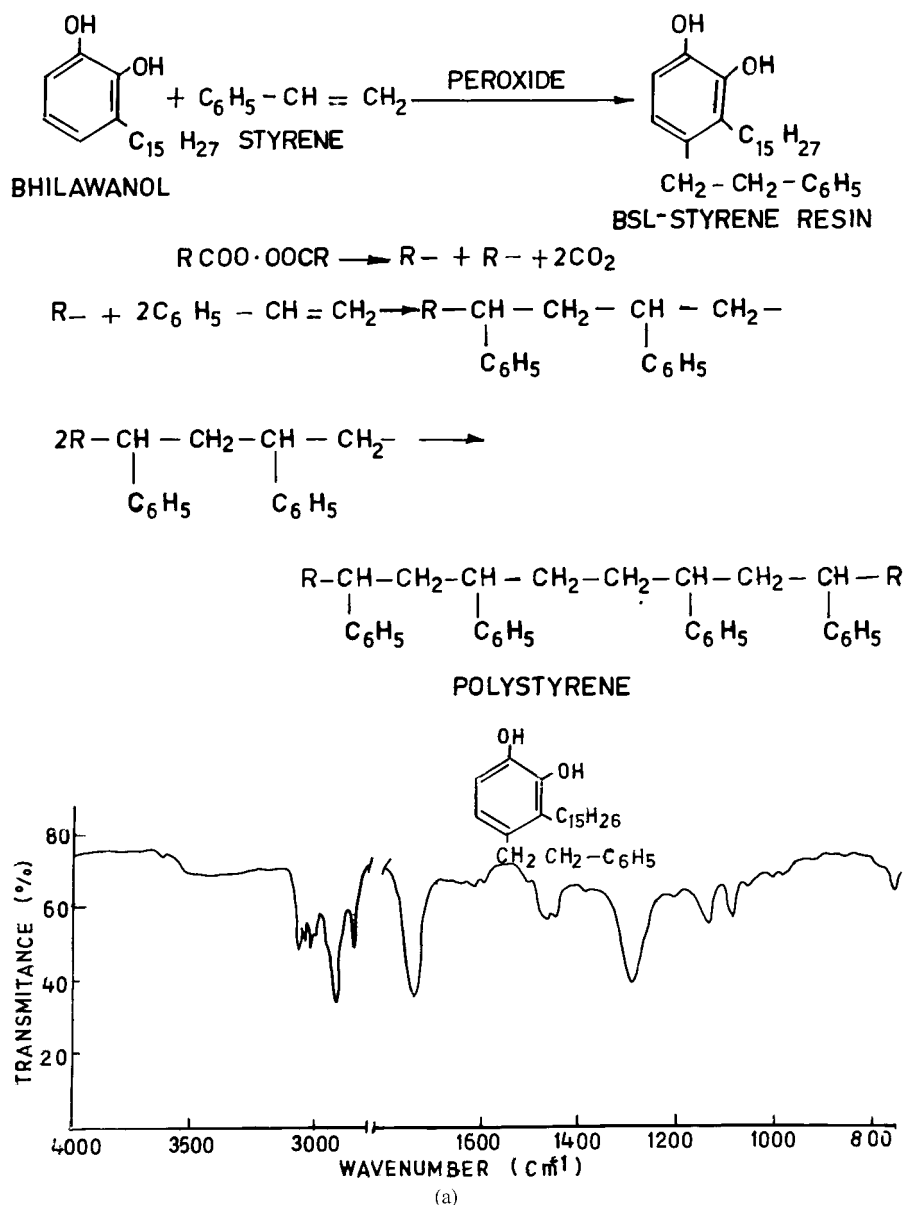
**Figure 2** BSL-phenol-formaldehyde resin. Reaction mechanism. (a) IR spectrum of BSI-phenol-formaldehyde resin.

stretching vibration. A band at  $1600\text{ cm}^{-1}$  is due to an aromatic ring. A band at  $1450\text{ cm}^{-1}$  is attributable to  $-\text{CH}$  vibration. A band at  $1370\text{ cm}^{-1}$  is due to  $-\text{CH}$  wagging vibration. A band at  $1260\text{ cm}^{-1}$  is attributed to symmetric stretching of  $\text{C}-\text{O}$  bonds. A band at  $1050\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$  is due to alcohols. A band near  $730\text{ cm}^{-1}$  is due to the five adjacent hydrogens at monosubstituted benzene. A peak at  $700\text{ cm}^{-1}$  is due to mono-meta and symmetrical trisubstitution have a ring bending vibration.

### IR Analysis of BSL-Phenol-Formaldehyde Resin

The reaction among BSL, phenol, and formaldehyde may be explained as shown in Figure 2.

The formation of resin was supported by IR analysis. The IR spectrum of BSL-phenol-formaldehyde resin [Fig. 2(a)] shows bands at  $3000\text{--}3500\text{ cm}^{-1}$  attributed to the OH group of the phenol. Normal bands at  $1600$  are due to  $\text{X}=\text{Y}$  double bond stretching vibration. A peak at  $1470\text{ cm}^{-1}$  is due the aliphatic- $\text{CH}_3$  group. A band at  $1450\text{ cm}^{-1}$  is attributed to  $-\text{CH}_2$  asymmetrical deformation. Bands at  $1200\text{ cm}^{-1}$  are due to the presence of alcohols. A band at  $1010\text{ cm}^{-1}$  is attributable to the presence of primary alcohols. A band at  $880\text{ cm}^{-1}$  is due to symmetrical trisubstitution have a ring bending vibration.



**Figure 3** BSL-styrene resin. Reaction mechanism. (a) IR spectrum of BSL-styrene resin.

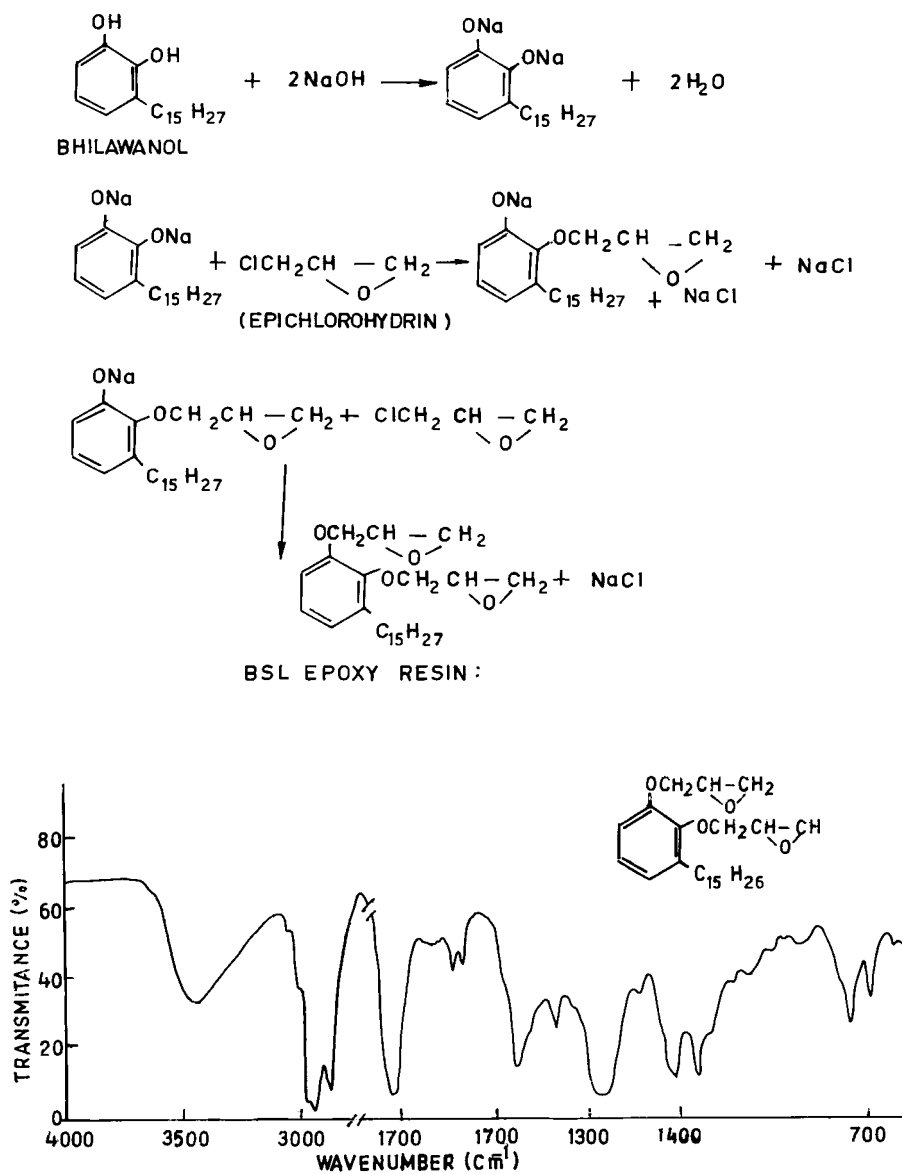
### IR Analysis of the BSL Styrene Resin System

The reaction of BSL with styrene may be shown as in Figure 3. The resin formation is supported by IR analysis of the product. Formation of the short chain polystyrene along with the BSL-styrene resin is inevitable. IR spectrum of BSL styrene resin [Fig. 3(a)] shows a band at  $3000\text{ cm}^{-1}$  attributed to alkene C—H stretch. A band at  $1730\text{ cm}^{-1}$  is attributable to a carbonyl group of aldehydes. A small peak at  $1600\text{ cm}^{-1}$  is due to olefins. A peak at  $1450\text{ cm}^{-1}$  is attributed to —CH asymmetrical deformation of hydrocarbon. A band at

$1280\text{ cm}^{-1}$  is due to alcohol absorption. A band at  $1110\text{ cm}^{-1}$  is attributable to C—O bonds of alcohols. A band at  $1060\text{ cm}^{-1}$  is due to the presence of primary alcohols. A band at  $920\text{ cm}^{-1}$  is attributable to vinyl compounds. A peak at  $700\text{ cm}^{-1}$  is due to aromatic trisubstitution having ring bending vibration.

### IR Analysis of BSL-Epoxy Resin

The reaction between BSL and epichlorohydrin may take place as shown in Figure 4. The IR spec-



(a)

Figure 4 BSL-epoxy resin. Reaction mechanism. (a) IR spectrum of BSL-epoxy resin.

trum of BSL-epoxy resin [Fig. 4(a)] shows bands at  $1300\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$  are due to the presence of aromatic ether group which are the characteristic absorption bands of epoxy resins. A band at  $720\text{ cm}^{-1}$  is due to a carbonyl group of aldehydes. A band at  $1580\text{ cm}^{-1}$  is attributed to asymmetric stretching of the X—Y—X bond in the aromatic ring. A band at  $1450\text{ cm}^{-1}$  is attributed to aromatic groups.

### Properties of Coating Compositions

Table I shows the characteristics of coating based on BSL. All the coating compositions are clear and the nonvolatile matter was 86% in case of BSL-phenol-formaldehyde resin and 68% for BSL-styrene resin, and it was 72% for BSL-based epoxy resin. The highest viscosity was shown by BSL-phenol-formaldehyde resin and the lowest viscosity was shown by BSL-styrene. The pH of BSL-phenol-formaldehyde coating was 8.85, BSL-styrene was 8.83, and the pH of BSL-based epoxy was found to be 8.80. The BSL-phenol-formaldehyde resin had the lowest drying time and the BSL-based epoxy resin had the longest drying time of 28 h.

### Mechanical Film Properties

Table II shows the mechanical properties of coating compositions based on BSL. These coatings were subjected to direct and indirect impact testing using 1 kg weight from 70 cm. BSL-epoxy passed both direct and indirect testing as no cracking or detachment of the film was observed. BSL-phenolic resin passed indirect impact and failed in direct impact testing. BSL-styrene passed both direct and indirect testing. A maximum scratch hardness value of 2.3 kg was shown

by BSL-epoxy coating, and a minimum hardness value of 1 kg was shown by BSL coating; BSL-phenolic showed a value of 1.5 kg. The film thickness of BSL-epoxy coating was 18 microns, BSL-phenolic coating was 30 microns, and styrene coating was 22 microns.

### Film Condition after 24 Hours

The BSL-phenol-formaldehyde coating and BSL-styrene coating were nontacky after 24 h, whereas the BSL-epoxy coating was slightly tacky after 24 h.

### Chemical Resistance

Water and chemical resistance of coatings based on BSL is shown in Table III. The chemical resistance properties of resins were found to be generally good. In acidic medium the resins showed poor resistance which is due to the reaction of phenolic resins with acid. In a mildly acidic medium like ammonium sulfate the resin coatings seems to be unaffected. With the corrosive chemicals medium, such as calcium chloride, calcium hydroxide, sodium bicarbonate, and sodium hydroxide solutions, the BSL-phenol formaldehyde and BSL-epoxy coatings have better resistance than the BSL-styrene resin. All these coatings showed poor resistance toward a 5% solution of urea.

### CONCLUSIONS

The coatings were prepared using BSL and the coatings and the coated bamboo were evaluated in immersion and accelerated tests. The results showed that the performance of the coating was

**Table II Mechanical Film Properties of Coating Compositions from BSL**

Type of Coating	Impact Test 1 kg from 70 cm		Scratch Hardness (kg)	Film Condition after 24 h	Coating Thickness ( $\mu$ )
	Direct	Indirect			
BSL	F <sup>a</sup>	P <sup>b</sup>	1.0	NT <sup>c</sup>	16
BSL-Phenol-Formaldehyde	F	P	1.5	NT	30
BSL-Styrene	P	P	1.2	NT	22
BSL-Epoxy	P	P	2.3	ST <sup>d</sup>	18

<sup>a</sup> F, fail.

<sup>b</sup> P, pass.

<sup>c</sup> NT, nontacky.

<sup>d</sup> ST, slightly tacky.

**Table III Chemical Resistance Tests of the Coated Bamboo Specimens**

Spec. No.	Properties	BSL-Phenol-Formaldehyde	BSL-Epoxy	BSL-Styrene
1	% Increase in weight due to water absorption	4.5	6.8	5.7
2	In distilled water	No deterioration of the film	No effect	No effect
3	In 2% sodium bicarbonate	No visible change	No visible change	Partial removal of coating
4	In 5% sodium hydroxide	No change	No effect	Partial removal of coating
5	In 3% sodium chloride	No visible changes	Slightly blushed	Slightly blushed
6	In 3M calcium chloride	No removal of coating	No effect change	No visible change
7	In 2% sulfuric acid	No visible change	Disintegration of coating	Slightly blushed
8	In 5% urea	Slight blistering	Slightly blushed	Disintegration of coating
9	In 5% ammonium sulfate	No visible change	No effect	No visible change
10	In 5% calcium hydroxide	No change	No effect	Slight blistering

generally good in all the tests. Hence the coating based on BSL can be used for the protection of bamboo from corrosive environments, especially the BSL-phenol-formaldehyde coating, which showed better chemical resistance than the other two coatings, which may be used successfully in protecting bamboo and bamboo products from corrosive environments. BSL-epoxy coating showed better mechanical film properties which can be used as protective coating where good mechanical film properties are required.

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