Preparation and properties of epoxy-modified tung oil waterborne insulation varnish

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ABSTRACT: This work aimed to develop a novel epoxy-modified tung oil waterborne insulation varnish with blocked hexamethylene diisocyanate as a curing agent. The Diels–Alder reaction between tung oil and maleic anhydride, and the ring-opening esterification reaction of epoxy resin were confirmed. The conversion rate of epoxy was explored as a function of reaction time and temperature. The effects of epoxy resin content on the thermal stability, water absorption and insulation properties (insulation strength, volume resistivity, and surface resistivity) of films were investigated, and the resistances of films to salted water were evaluated. The increase in epoxy resin contents could improve the thermal stability and insulation properties of films, and decreased the water adsorption of films, but when the epoxy resin content reached 30% and above, the water solubility of resin became poor. After being immersed in 3.5 wt % NaCl solution, the electrical insulation strength of films were lower than that in dry state, and decreased as the immersed time prolonged. In particular, the electrical insulation strength loss of films increased significantly for epoxy resin content at 15% and below. Furthermore, the increase of epoxy resin content could improve the hardness and adhesion of films, but the flexibility of films became worse. On the basis of experimental, the epoxy resin content at 25% was appropriate to prepare waterborne epoxy-modified tung oil resin. The resulting varnish may have potential as an immersing insulation varnish for the spindle of electric motor. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42755.

INTRODUCTION

The release of volatile organic compounds from coating is an environmental issue at present.[1–4] To alleviate the problem, waterborne varnish has been recognized due to its environmental friendliness and low toxicity.[5–8] Owing to its high adhesion, outstanding corrosion resistance and good insulation, epoxy resin has been widely used as an important industrial raw material in metal corrosion protection,[9,10] waterproof,[11,12] adhesive,[13,14] insulation,[15,16] and other industrial fields.[17,18] Much valuable work has been done on the investigation of waterborne epoxy resin[19,20] or waterborne polymer composites based on epoxy resin.[1,8,21,22] Seed oils have been traditionally used as resins or components in organic coatings,[23,24] due to their appealing advantages such as easy availability, environmental friendliness, inherent biodegradability,[25] low cost, and easy modification.[26–28]

Tung oil, a kind of seed oils extracted from the seeds of tung tree, is a promising resultant material in China,[29] which shows the advantages of faster drying, better water resistance and higher hardness.[30] The major constituent of tung oil is a glyceride composed of alpha-elaeostearic acid (cis-9, trans-11, trans-13-octadecatrienoic acid),[31] which can easily undergo Diels-Alder reaction with a dienophile.[30,32–34] The highly unsaturated and conjugated triene system of tung oil makes it easily to be chemically modified. In the past research, Diels-Alder reaction had been successfully applied to synthesize acrylate tung oil resin,[35] tung oil–rosin adduct,[36] tung oil based alkyd,[33] and diacrylate-tung oil copolymers.[34] However, no report was found on tung oil modified by epoxy resin to obtain excellent performance of waterborne insulation vanish at present to the best of our knowledge.

In our previous work,[37] acrylate-modified tung oil waterborne insulation varnish has been reported. As an important series work toward waterborne insulation varnish based tung oil, the purpose of this study was to develop a novel epoxy-modified tung oil waterborne insulation varnish *via* Diels-Alder addition reaction between tung oil and maleic anhydride (MA), and the ring-opening esterification reaction of epoxy resin. The synthetic route
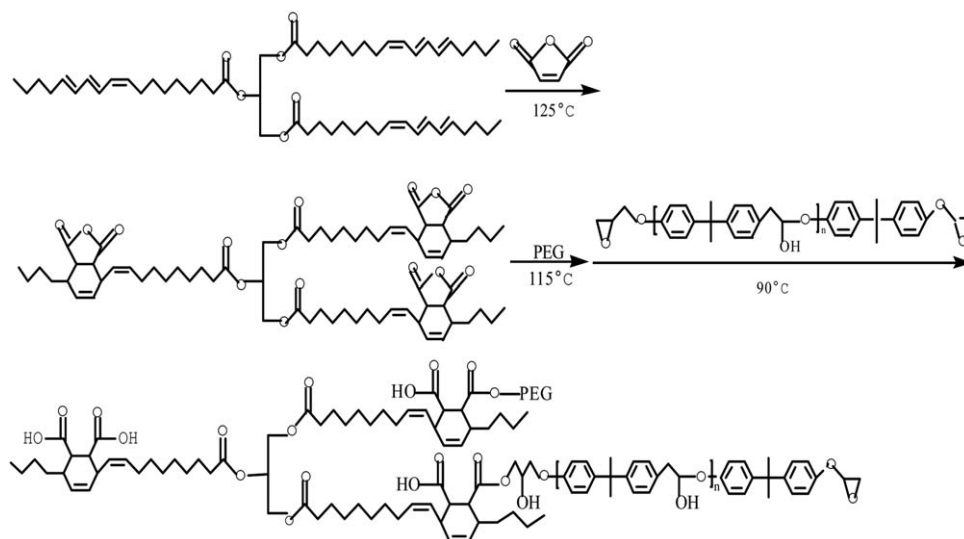
Scheme 1. Synthetic route and reaction mechanism of epoxy-modified tung oil resin.

and reaction mechanism of epoxy-modified tung oil resin was displayed in Scheme 1. Attention was focused on the conversion rate of epoxy as a function of reaction time and temperature, the effects of epoxy resin content on the thermal stability, water absorption and insulation properties (insulation strength, volume resistivity and surface resistivity) of films, and the resistances of films to salted water.

EXPERIMENTAL

Materials
The epoxy resin was commercial diglycidyl ether of bisphenol-A epoxy (E-51) purchased from Wuxi Resin Factory of Bluestar new Chemical Materials (Wuxi, China), with an epoxy value of 0.51 mol/100 g. Tung oil was a commercial product purchased from Jiangsu Donghu Bio-energy Plant Plantation (China), with a yellow color and a specific gravity of 0.935–0.940 at 25°C. Poly (ethylene glycol)−1000 (PEG-1000, $M_v = 1000$) was purchased from Aladdin Industrial (Shanghai, China). MA, triethanolamine, N,N-dimethyl ethanolamine, hexamethylene diisocyanate (HDI), and methylethylketoxime (MEKO) were purchased from Shanghai Lingfeng Chemical Reagent (Shanghai, China). The epoxy resin and tung oil were of technical grade, and all the other chemical reagents used were of analytical grade.

Synthesis
Synthesis of Waterborne Epoxy-Modified Tung Oil Resin. The synthesis of tung oil anhydride was performed in a 250 mL three-neck round bottom flask equipped with mechanical stirrer, nitrogen inlet, reflux condenser in an oil bath. According to our previous work,[37] 30 g tung oil and 7.5 g MA were added into the flask. After the mixture was heated up to 120–130°C and reacted for 1.5 h, the yellowish transparent tung oil anhydride adduct was under vacuum for 10 min to remove the residual monomer.

As the above adduct was cooled down to 115°C, 10 g n-butanol, and 20 g PEG-1000 were added and the reaction was kept for 2 h. At the same time, required amount of epoxy resin (10, 15, 20, 25, and 30%, based on the weight of tung oil) were dissolved in the equal amount of medium composed of ethylene

glycol butyl ether and n-butanol with the volume ratio of 2 : 3 at 65°C. The predissolved epoxy resin was added dropwise into the flask when the temperature was cooled to 90°C, and then the calculated triethanolamine (1%, based on the weight of epoxy resin) was added into the system to catalyze the reaction for 2.5 h. When the system was cooled to room temperature, 10 g isopropanol, and 10 g propylene glycol monomethyl ether were added. Meanwhile, the pH value of the system was adjusted to ∼8.0–8.5 by N,N-dimethyl ethanolamine. Finally, the curing agent blocked HDI prepared was added into the system and stirred for 0.5 h to give a pale yellow transparent waterborne epoxy-modified tung oil resin. According to our previous work,[37] required HDI was blocked by MEKO at 80°C for 4 h to obtain blocked HDI beforehand (the molar ratio of HDI/MEKO was employed at 1 : 2 during blocking reaction, and the required HDI was based on the molar ratio of the NCO/OH at 1 : 1.1, herein, the molar of ─OH was adopted to be equal to the molar of MA and the molar of E-51).

Curing of Waterborne Epoxy-Modified Tung Oil Resin. A square copper sheet (4.0 × 7.5 × 0.1 mm³) polished with 800-grit emery paper was used as a substrate. The as-prepared epoxy-modified tung oil resin was diluted by equal amount of deionized water, and then coated on the copper sheet by immersing method. Finally, the films were cured in the oven at 125°C for 3 h.

MEASUREMENT AND CHARACTERIZATION

Determination of Epoxy Value and Conversion Rate of Epoxy
The epoxy value of epoxy-modified tung oil resin was determined according to hydrochloric acid-acetone method (GB 1677-81) based on titration of unreacted HCl (remaining after acid hydrolysis of epoxy group in the HCl/dioxane mixture) with ethanol NaOH solution using phenolphthalein as indicator. The epoxy value of resin was calculated as follows:

$$E = \frac{(V_1 - V_2) \times C}{10m} \qquad (1)$$

where E is epoxy value (mol/100 g), V_1 and V_2 refer to the consumption volume (mL) of NaOH solution for blank and sample,

respectively, C is the concentration of NaOH solution (mol/L), and m is the weight of the resin. The conversion rate of epoxy was calculated as follows:

$$E_c = \frac{0.51 - E}{0.51} \times 100\% \qquad (2)$$

where E_c is the conversion rate of epoxy.

Structure and Thermodynamic Analysis

The structures of epoxy resin, tung oil, and the cured film were characterized by Fourier transform-infrared spectroscopy (FTIR), which was taken on a Nicolet 6700 spectrometer (Thermo Nicolet, USA) with KBr pellets. Thermal stability was assessed using a TGA 209 thermogravimetric analyzer (Netzsch, Germany). Tests were done under nitrogen at a scan rate of 10°C/min over a temperature range of 25–700°C. The glass transition temperature (T_g) was studied by differential scanning calorimetry (DSC) using a Mettler Toledo (Im Langacher, Switzerland) DSC-851e instrument. Approximate 5–10 mg weighed samples were sealed in 40 μL aluminum crucible and heated from 40 to 190°C at the rate of 10°C/min under a nitrogen flow of 20 mL/min.

Water Absorption

The water absorption of dried films was evaluated in a bath with deionized water at room temperature for 24 h. The water absorption of film was calculated as follows:

$$W = \frac{m_2 - m_1}{m_1 - m_0} \times 100\% \qquad (3)$$

where W is the water absorption of film, m_0 is the weight of copper sheet, m_1 is the weight of dried sample, and m_2 is the weight of sample with absorbed water.

Insulation Properties

The electrical insulation strength was carried out by using Quadtech (Marlborough, MA) Guardian 20 kV HiPot tester.[37] The electrical insulation strength (E) was calculated according to the following equation:

$$E = \frac{V}{d} \qquad (4)$$

where the V is breakdown voltage and the d is the thickness of the film.

The volume and surface electrical resistivities were determined by the two probe method at room temperature using a high resistivity meter model ZC-36 (Shanghai Sixth Meter, China). The volume resistivity (ρ_v) was calculated according to the following equation:

$$\rho_v = R_v \frac{A}{d} \qquad (5)$$

where R_v is volume resistance (Ω), A is the area of sample's contact electrode (cm^2), and d is the thickness of film (cm). The surface resistivity (ρ_s) was calculated according to the following equation:

$$\rho_s = R_x \frac{P}{g} \qquad (6)$$

where R_x is surface resistance (Ω), P is effective perimeter of guarded electrode (cm), g is the distance between electrodes (cm).

Salted Water Resistance

Salted water resistance test was performed in 3.5 wt % NaCl solution at 25°C, and the electrical insulation strength of each specimen was measured. To evaluate the corrosion resistance, the surface of the specimen after being immersed in NaCl solution for 7 days was observed with scanning electron microscopy (SEM; SU8020, Hitachi, Japan).

Mechanical Performance

The mechanical performances of films, such as adhesion (GB/T 9286-1998, a cross-hatch adhesion testing), pencil hardness (GB/T 6739-1996), and flexibility (GB/T 1731-93) were measured, respectively.

RESULTS AND DISCUSSION

Conversion Rate of Epoxy

Figure 1(A) shows the change of the conversion rate of epoxy for epoxy-modified tung oil resin as a function of reaction temperature and time. It can be seen from Figure 1(A), the conversion rate of epoxy was dependent on reaction time and temperature. With the rising of temperature, the probability of collisions among molecules increased, which favored the ring-opening esterification reaction for epoxy. In addition, a slowdown trend in the increase of conversion rate was presented in each curve; especially, the increase was very slightly after 2.5 h. As the reaction proceeded, the viscosity of reaction system increased, which inhibited the ring-opening esterification reaction for epoxy, correspondingly, the conversion rate of epoxy decreased. However, gel reaction would occur at high temperature. According to our experimental results, a temperature at 90°C was more appropriate to prepare waterborne epoxy-modified tung oil resin.

Structure of Films by FTIR Analysis

Figure 1(B) showed the FTIR spectra of epoxy resin, tung oil, and epoxy-modified tung oil film, respectively. In the spectrum of epoxy resin, absorbance at 913 cm^{-1} was assigned to epoxy group, absorbances at 1612, 1509, and 1461 cm^{-1} were attributed to the characteristic absorption of C=C skeleton vibration for the aromatic ring.[38] In the spectrum of tung oil, absorbances of stretching vibration of —CH$_3$ and —CH$_2$ were presented at 2917 and 2850 cm^{-1}, while the strong absorbance at 1739 cm^{-1} was ascribed to the stretching vibration of C=O in ester group. Additionally, the three absorbances at 3018, 989, and 964 cm^{-1} were associated with the tung oil's conjugated double bonds.[39] As compared to spectrum of tung oil, the characteristic three absorbances of tung oil conjugated double bonds were not found in the spectrum of epoxy-modified tung oil film, indicating that the conjugated triene on tung oil molecules had reacted with the unsaturated double bonds on MA through a Diels–Alder reaction to form tung oil anhydride adduct. Furthermore, absorbance at 1112 cm^{-1} associated with the stretching vibration of C—O—C was enhanced and the characteristic epoxy ring vibration absorbance at 913 cm^{-1} disappeared. This information implied the desired chemical reaction was achieved by opening epoxy ring to allow epoxy resin to react onto the end of tung oil anhydride molecule chain (Scheme 1).

Thermal Stability Analysis

As the insulated system of electric appliance usually produce heat during working process, the thermal stability of film is an
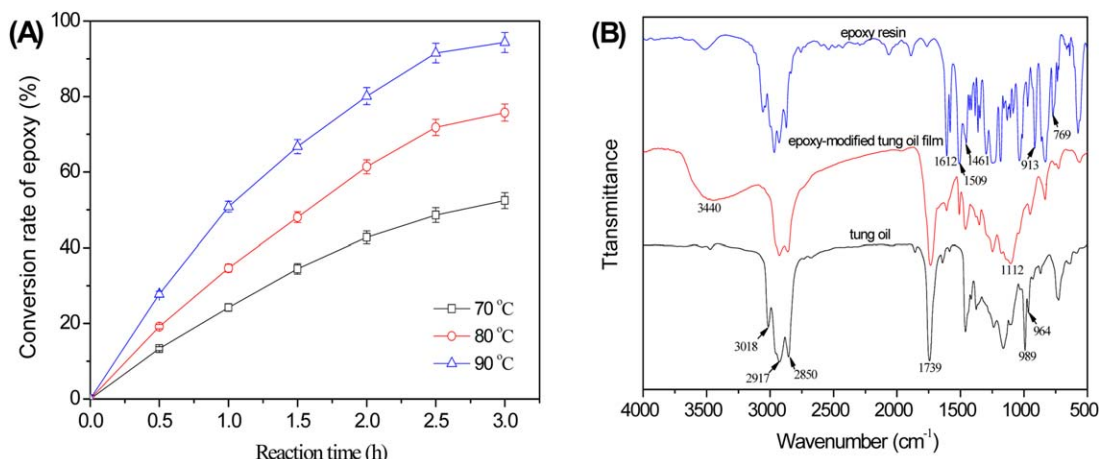
Figure 1. (A) Conversion rate of epoxy for epoxy-modified tung oil resin as a function of reaction temperature and time; (B) FTIR spectra of samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

important factor to be considered toward insulation varnish. Figure 2(A) illustrated the TGA curves of the films with different epoxy resin contents, correspondingly, the DTG (derivative thermogravimetry) curves were depicted in Figure 2(B). As shown in Figure 2(A), three-stage degradation was presented in each curve. The loss in stage I was corresponding to the evaporation of the high boiling solvent remaining in the film, and trace dehydration condensation of residue hydroxyl and carboxyl groups. A serious weight loss caused by the cleavages of C—O and C—C linkages was presented in stage II. The last stage (stage III) was associated with the degradation of the char residue. According to Figure 2(A,B), the residual amount and maximum decomposition rate temperatures (T_{max}) of films were depicted in the insets of Figure 2(A,B), respectively. It was noteworthy that the parameters (T_{max} and residual amount) associated with thermal stability of films showed an increase in values (T_{max}: 397→409°C and residual amount: 8.3→15.2%, respectively) as the epoxy resin contents increased from 10 to 30 wt %. This information indicated that the incorporation of epoxy resin improved the thermal stability of film owing to the increasing number of aromatic ring derived from epoxy resin.

For further investigating the influence of epoxy resin content on thermal stability, DSC measurements were carried out to study the glass transition temperature (T_g) of the films. As could be seen in Figure 3, only one T_g appeared in each DSC curve, and T_g moved to high temperature (76.7→95.3°C) as the epoxy resin content increased from 10 to 30 wt % (Figure 3: inset). The presence of only one T_g indicated the whole system was very uniform,[6] and further verified that the desired chemical reaction was achieved (Scheme 1) as a supplement to FTIR analysis. Furthermore, the increase in T_g with increasing epoxy resin content demonstrated that the incorporation of epoxy resin showed a positive effect on the T_g of the polymeric matrix and promoted the thermal stability. As it was mentioned before, the number of aromatic ring on the main chain of the molecule increased with increasing epoxy resin content. These rings could improve the rigidity of the molecular chain and limited the movement of polymer segments, resulting in an increase in the values of T_g.

Water Absorption of Films

The water absorption of film plays an important influence on the insulation properties of the insulation varnish. In this work,
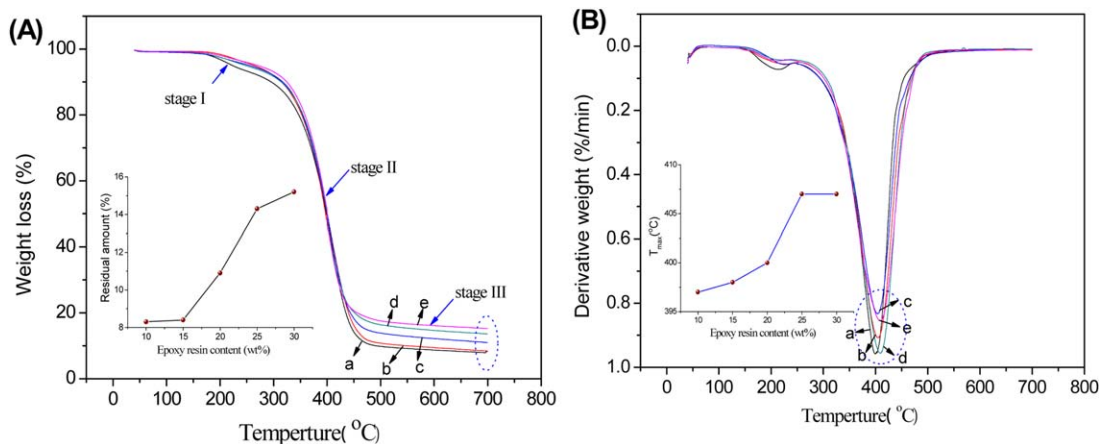

Figure 2. (A) TGA curves of films, inset: residual amount versus epoxy resin contents; (B) DTG curves of films, inset: T_{max} versus epoxy resin contents. Letters (a–e) were associated with the films with epoxy resin content at 10, 15, 20, 25, and 30 wt %, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
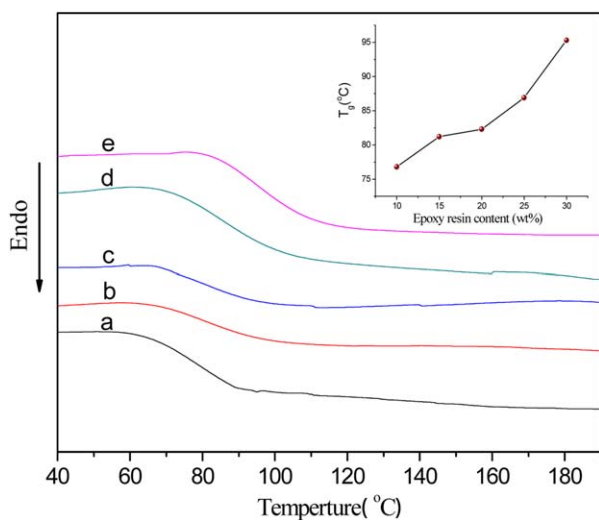
Figure 3. DSC curves of samples with epoxy resin contents at: (a) 10, (b) 15, (c) 20, (d) 25, and (e) 30 wt %, inset: T_g versus epoxy resin contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the water absorption of films was performed in a bath with deionized water at room temperature for 24 h and the results were illustrated in Figure 4. As shown in Figure 4, water absorption of the films decreased from 3.6 to 1.0% as epoxy resin content was raised from 10 to 30 wt %. At given dosage of MA and PEG monomers, more epoxy resin would react with more carboxyl groups by the ring-opening esterification reaction. As a result, the water absorption of the films was decreased attributing to the reducing of carboxyl groups with increasing epoxy resin content. It is well known that the lower water absorption of the film would have a positive effect on the insulation properties of the film.

Insulation Properties of Films
Electrical insulation strengths of the films in dry and wet states were illustrated in Figure 5. Similar uptrend was observed in electrical insulation strength of the films with increasing epoxy
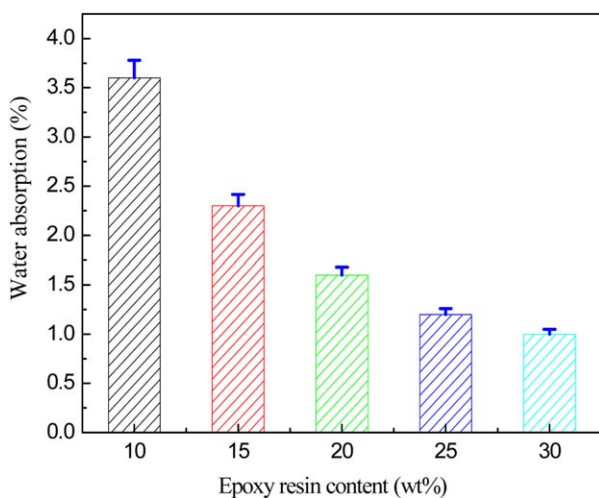

Figure 4. Water absorption of films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
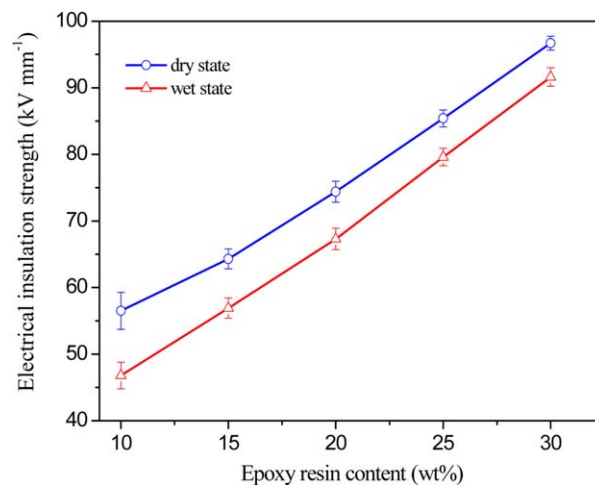

Figure 5. Electrical insulation strength of films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resin content in both dry and wet states. Owing to the significant insulation performance, the more epoxy resin occupied in polymer composite matrix, the higher electrical insulation strength of films exhibited. Additionally, an increase in epoxy resin content would cause the decrease in quantity of carboxyl groups in polymeric matrix as epoxy resin could react with carboxyl groups by the ring-opening esterification reaction, correspondingly, the conductivity of the films reduced and the insulation performance of the films were improved.[40] Furthermore, the electrical insulation strength in wet state showed lower than that in dry state at each given epoxy resin content, owing to the absorbed water as mentioned before.

The common logarithm of volume resistivity and surface resistivity for the films with varying epoxy resin contents in dry and wet states were depicted in Figure 6. As could be seen from Figure 6(A), the films showed an increase in the volume resistivity with increasing epoxy resin content in both dry and wet states, and the values of the volume resistivity of the films in dry state at each given epoxy resin content was higher than that in wet state. Notably, the changes in the values of the volume resistivity of the films in dry and wet state diminished as epoxy resin content increased. Similar relationships were observed in surface resistivity of the film [Figure 6(B)]. This information could be well explained by the amount of epoxy resin incorporated into the polymeric matrix. With increasing epoxy resin content, the carboxyl groups in polymeric matrix decreased. As a result, the water absorption of the films decreased; meanwhile, the volume resistivity and surface resistivity of the films were improved significantly.

Salted Water Resistance of Films
To evaluate the influence of salted water on electrical insulation strength as a function of epoxy resin content, the films were immersed in 3.5 wt % NaCl solution at room temperature, and the results were shown in Figure 7(A). According to Figure 7(A), the electrical insulation strength loss of each film as function of time was illustrated in Figure 7(B). Similar uptrend in electrical insulation strength was presented for the films with increasing epoxy resin content in dry state and after being
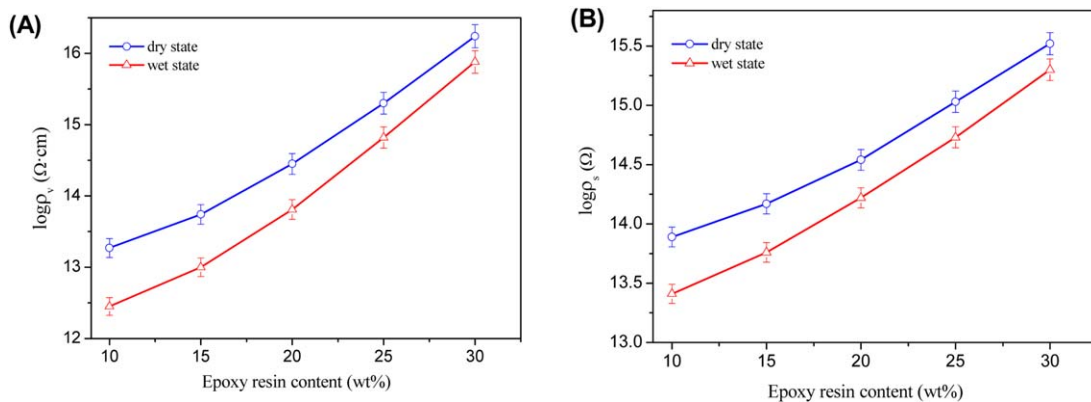
Figure 6. Common logarithm of volume resistivity (A) and surface resistivity (B) of films versus epoxy resin contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
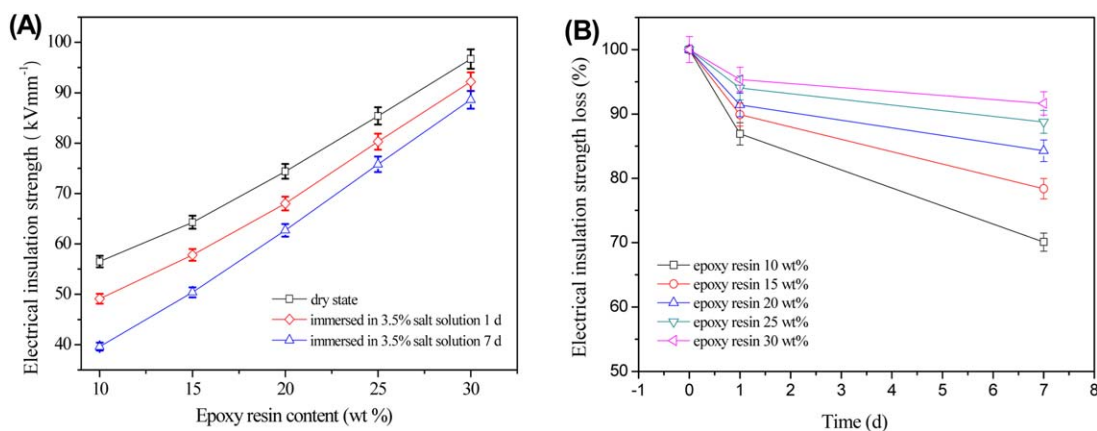

Figure 7. Electrical insulation strength (A) and electrical insulation strength loss (B) of films (Immersed in 3.5% NaCl solution at 25°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
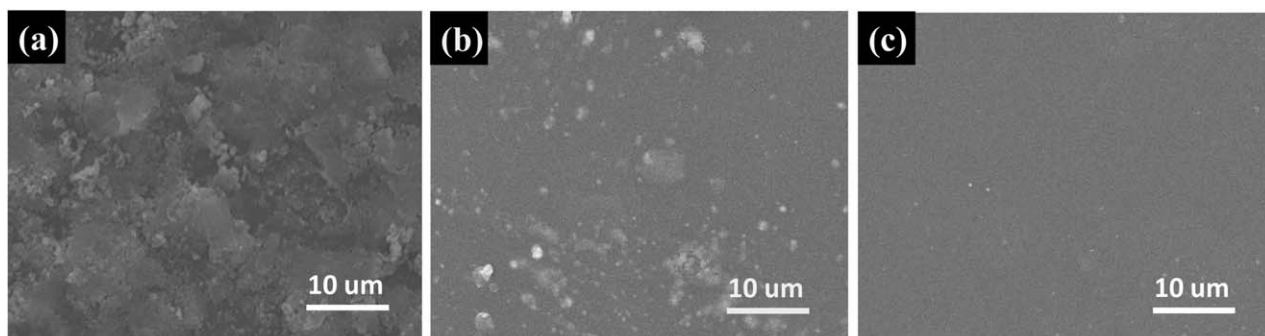

Figure 8. SEM photographs of film surface with epoxy resin content at: (a) 10, (b) 15, and (c) 25 wt % (immersed in NaCl solution at 25°C for 7 d).

Table I. Effect of Epoxy Resin Content on Film Mechanical Properties

| Epoxy resin content (%) | Vanish | | Film | | | |
	Water solubility	Appearance	Thickness (μm)	Pencil hardness (H)	Flexibility (mm)	Adhesion (grade)
10	Better	Transparent	44.1	3	3	3
15	Good	Transparent	44.9	3	3	2
20	Good	Transparent	45.6	4	3	1
25	Good	Transparent	46.4	4	2	0
30	Poor	Turbid	47.2	4	2	0

immersed in NaCl solution, meanwhile, the electrical insulation strength of films after being immersed in NaCl solution was lower than that in dry state at each given epoxy resin content, and decreased as the immersed time prolonged [Figure 7(A)]. At epoxy resin content below 20 wt %, a significant increase in electrical insulation strength loss of film was found after being immersed in NaCl solution [Figure 7(B)], and the representative film surfaces after being immersed in NaCl solution for 7 d were observed by SEM (Figure 8). As could be seen from Figure 8, the blisters on surface of the films were disappearing gradually with the increase of epoxy resin content. No obvious blisters were observed when epoxy resin content was at 25% and above. With increasing epoxy resin content, the hydrophilicity of the films decreased and the diffusion of Na^+ or Cl^- into the polymeric matrix was inhibited, therefore, the electrical insulation strength loss of the films reduced.

Water Solubility of Vanish and Mechanical Properties of Films

Epoxy resin exhibits strong adhesion, good corrosion resistance, and high hardness, while tung oil has good flexibility. To obtain a suitable film with good comprehensive performance, the effects of epoxy resin contents on water solubility and film mechanical properties (thickness, hardness, flexibility, and adhesion) were evaluated and the results were summarized in Table I. As shown in Table I, the hardness and adhesion of films were enhanced with increasing the epoxy resin content, whereas, the flexibility of films and water solubility of resin became poor. In the epoxy-modified tung oil molecule, epoxy resin contributed to the rigidity, while tung oil contributed to the flexibility. Moreover, the increase in epoxy resin content decreased the hydrophilicity of the resin, especially, the prepared vanish was turbid when epoxy resin content reached 30%. Thereby, the content of epoxy resin at 25% was selected as an appropriate content to prepare waterborne epoxy-modified tung oil resin.

CONCLUSIONS

In this study, a novel epoxy-modified tung oil waterborne insulation varnish has been developed and the varnish could be solidified at 125°C with blocked HDI as curing agent. The conversion rate of epoxy resin was dependent on reaction time and temperature. The increase in epoxy resin contents could not only improve the thermal stability and insulation properties of films, but decreased the water adsorption of films also. After being immersed in NaCl solution, the films showed a significantly increase in electrical insulation strength loss of films with epoxy resin content below 20 wt %. Additionally, as the epoxy resin content increased, the hardness and adhesion of films increased, but the water solubility of resin and flexibility of films became poor. The results showed that, the electrical insulation strength of the films was not less than 85.4 kV mm^{-1} when epoxy resin content was at 25 wt % and above. This waterborne epoxy-modified tung oil resin may have potential as an immersing insulation varnish for the spindle of electric motor.

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