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RESEARCH ARTICLE

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Synthesis and application of phenolic resin internally toughened by chain extension polymer of epoxidized soybean oil

Abstract A novel epoxidized soybean oil (ESO) internally toughened phenolic resin(ESO-IT-PR) with both good toughness and excellent thermal stability was prepared as the matrix resin of copper clad laminate (CCL). FTIR was adopted to investigate the molecular structure of modified phenolic resins and SEM was used to observe the micro morphology of their impacted intersections. The properties of CCLs prepared with these modified phenolic resins were studied to determine the optimal process and investigate the toughening mechanism. The main modifying mechanism is the etherification reaction between phenol hydroxyl and ESO catalyzed by triethanolamine and the chain extension polymerization between ESO and multi-amine gives the long-chain ESO epoxy grafting on the phenolic resin prepolymer. when the ESO content is 30% and the curing agent content is 7%, the ESO toughened phenolic resin possesses optimal performance. The flexible ESO epoxy shows significant toughening effect and it crosslinks with the phenolic resin to form an internally toughened network, which is the key factor for improving the solderleaching resistance of CCL prepared with this modified phenolic resin.

Keywords phenolic resins, toughness, epoxidized soybean oil, copper clad laminate, solderleaching resistance

1 Introduction

Phenolic resin is one of widely used thermosetting resins because of its low cost, high mechanical strength, excellent thermal ability, insulation, size ability, flame retardance and corrosion resistance, but its brittleness restricts the further application [1]. Tung oil toughened phenolic resin (TO/PR) possesses good toughness and heat resistance and has been adopted as the absolutely dominate matrix material for manufacturing paper copper clad laminate (P-CCL). However, the global total product of tung oil is only one thousand and fifty hundred tons, which can not meet the huge demand of economic development. The use of abundant and inexpensive resource as replacement material to prepare toughened phenolic resin for paper CCL is attracting great interest. Soybean oil is the most abundant vegetable oil and Kenni et al. have synthesized epoxidized soybean oil toughened phenolic resin for preparing laminate sheet [2–4]. But conventional epoxidized soybean oil modified phenolic resin (ESO/PR) requires rigorous reaction condition and its toughness is inferior to that of TO/PR. Therefore, the impact toughness and solderleaching resistance of paper clad copper laminates prepared with ESO/PR can not fully fulfill the requirement of following operation process.

Epoxidized soybean oil can not form long flexible chains by self-polymerization like tung oil and the short flexible chain segments have very limited toughening effect, which is the main reason that ESO/PR show relatively poor toughness [5]. All eopxide groups in ESO are internal epoxide groups of the main chain which show stronger steric hindrance effect for nucleophilic addition reaction. As a result, the reaction activity of ESO to phenolic resin is much lower than tung oil. The conversion ratio of epoxide groups in ESO is very low even after long reaction time at high reaction temperature and with strong basic catalysts [6]. Lower conversion yield of epoxide group results in that ESO don't act as part of the crosslinking network but as the suspending chain by etherification graft, even only blends with phenolic resin. This loose structure leads to low heat resistance of ESO/PR and the bad solderleaching resistance of P-CCL prepared with ESO/PR. The chain extension reaction of ESO

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and multi-amine can produce flexible ESO Epoxy with long chain structure and moderate branch degree, which has strong toughening effect [7].

This research adopts composite multi-amine as catalyst and chain extender to synthesize long chain ESO epoxy internally toughened phenolic resin with excellent toughness and heat resistance. The properties of P-CCL prepared with this modified phenolic resin can reach or be superior to R8700 enterprise standard of Hitachi Company. The mild reaction condition of this process makes it great application potential.

2 Experimental

2.1 Materials

Main material: Phenol (C.P., Jiantao Chemicals CO. LTD, China), formalin (C.P., 37% aqueous solution, Jiantao Chemicals CO. LTD, China), oxalic acid(A.R., Shanghai Hongguang Chemical Factory, China), triethanolamine (A.R., Tianjin Fuzhen Chemical CO. LTD, China), hexamethylenetetraamine (AR, Chengdu Chemical Reagent Institute), Epoxidized soybean oil and catalysts (one is a mixture of tertiary amine and the other is a mixture of multi-amine) were prepared in this laboratory. Bleached pulp paper was supplied by Jiantao Chemicals CO. LTD.

2.2 Synthesis method

Phenol, formalin solution (37 wt% formaldehyde) and right amount oxalic acid were added to a resin flask with a thermometer, reflex condenser and stirrer according to the synthesis formula ratio and then heated to 85°C. The temperature of the reactive system increased continually and eventually reached the boiling point because of thermopositive reaction. After 0.5 h of boiling reaction, the solution turned to turbid. When a suitable viscosity was reached, the condensation reaction was stopped and the mixture was dehydrated under vacuum to give a pale yellow transparent novolac PR prepolymer. When the temperature of the prepolymer was lowered to 80°C, some triethanolamine was added for neutralization. Then epoxidized soybean oil and tertiary amine mixture were added into prepolymer. The mixture was stirred at 120°C for about 1 h to give pale brown red ESO-IT-PR A. The reaction was further catalyzed by adding multi-amine at 120°C for 1 h, so that purplish red ESO-IT-PR B was obtained. Then the temperature of reactive mixture was lowered to 90°C and some toluene, whose weight is 10% of the total resin weight, was added. When the temperature of reactive mixture was lowered to 50°C, the hexamethylenetetramine solution of toluene and methanol were added into the reactive system with high stirring speed to obtain ESO-IT-PR solution.

According to the above mentioned method of synthesizing ESO-IT-PR, three catalysis methods (adopting mere teriary amine for preparing ESO etherified phenolic resin, using only multi-amine for preparing modified phenolic resin by blending with ESO chain extension polymer and using both of two catalysts to prepare phenolic resin modified by etherification and chain extension.) and six different amounts of ESO: 5, 10, 20, 30, 40, 50, 60 and 70 wt% (compared with the weight of phenol) with the same amount of PR were applied to make a series of ESO modified PR samples.

Eight pieces of bleached pulp paper were immerged into above ESO modified phenolic resin. After most of solvent was evaporated, they were dried at 170–175°C for three minutes to obtain the prepregs. The prepregs and copper foil with glue were pressed at 160°C and 6 MPa for 2.5 h and then at 40°C for thirty minutes in a hot-press instrument to give the copper clad laminate.

2.3 Analysis and test

The ESO-IT-PR specimens were purified by extraction with *n*-heptane to remove the unreacted epoxidized soybean oil. FTIR spectra were recorded with Perkin–Elmer IR2000 spectrometer. The notched izod impact strength and solderleaching resistance was measured following the specifications according to GB/T 5130-1997. The morphology of their impact fracture surfaces is observed with LEO 1530 VP Scan Electronic Microscope.

3 Results and discussion

3.1 Modification method of phenolic resin with ESO

According to literature, the reactions between phenolic hydroxyl and epoxide group under basic catalysis are all ring-opening addition reaction and the reaction activity between the resulting alcoholic hydroxy and epoxide group is fairly low. Therefore, under the effect of mixed tertiary amine catalyst and the phenolic hydroxyl, ESO can not form long flexible chain prepolymer by self-polymerization, but graft with phenolic resin prepolymer to give etherified phenolic resin [8]. But the reaction between ESO molecules and multi-amine can form chain extension polymer and crosslinking structure, whose main mechanism is that the reactive hydrogen atoms in primary amine of the mixed multi-amine react with epoxide group to produce secondary amine and subsequently give tertiary amine.

The reaction among multi-amine, residue epoxide group of etherified phenolic resin and free ESO can generate the flexible ESO epoxy grafted with the phenolic resin prepolymer. The reaction mechanism is showed in Fig. 1. After the curing process, the copolymer composed of phenolic resin prepolymer and ESO epoxy shows

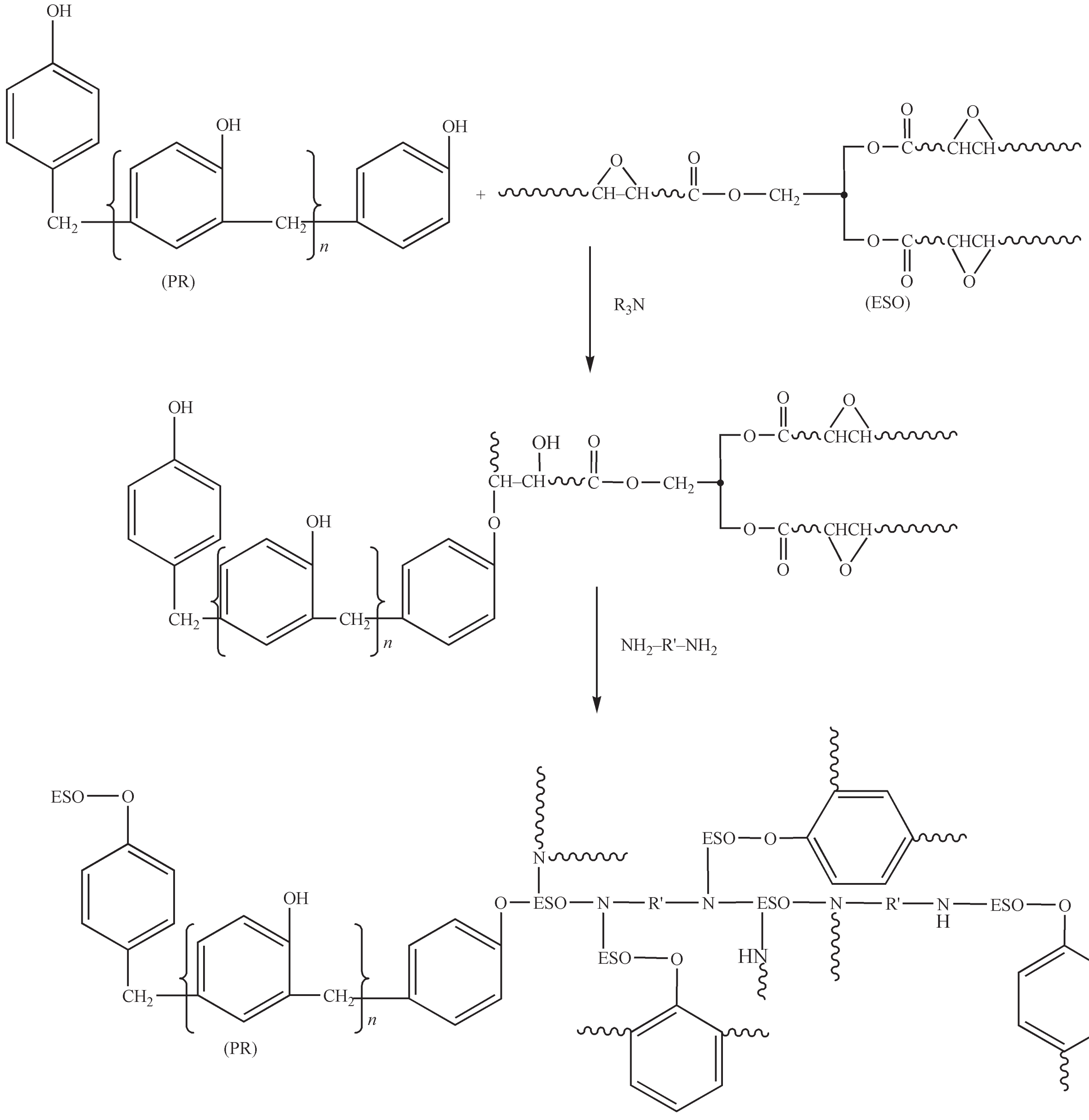


Fig. 1 Scheme of reaction mechanism of ESO-IT-PR

higher crosslinking density and thereby possesses excellent toughness and heat resistance.

Multi-amine, ESO and phenolic resin prepolymer all have high degree of functionality, so the chain extension reaction of ESO and crosslinking reaction are simultaneous. Crosslinking process is of great benefit to heat resistance, but excess crosslinking reaction will make the resin gel and cure in the resin reactor. Different multi-amine shows dissimilar reaction activity of chain extension and crosslinking reaction. In this synthesis process, composite multi-mine is adopted to make chain extension reaction dominate in the modification reaction. Meanwhile, acid catalyst and relatively high ratio of phenol to formaldehyde is used to prepare phenolic resin prepolymer with low molecular weight and linear structure in order to prevent modified phenolic resin from premature gel curing.

3.2 FTIR of modified phenolic resins

Figure 2 shows the FTIR spectra of the samples taken at three stages of ESO modifying reaction, one of them is linear PR prepolymer (curve 3), second one ESO-T-PR A (curve 2) and third ESO-T-PR B (curve 1). In curve 3, The stretching vibration of hydroxyl group in prepolymer shows a wide peak at 3342 cm^{-1} (hydrogen-bonded hydroxyl group) and a shoulder peak at 3528 cm^{-1} (free hydroxyl group). This indicates that there are great quantities of hydrogen-bonded hydroxyl group and free hydroxyl group in the prepolymer [9]. The peak at 819 cm^{-1} and 756 cm^{-1} respectively correspond to the characteristic absorption bands of phenol with 2,4 and 2,6 substitution. There is no strong peak in the range of 858–890 cm^{-1}, indicating that PR prepolymer has a linear structure. In curves 1 and 2, the

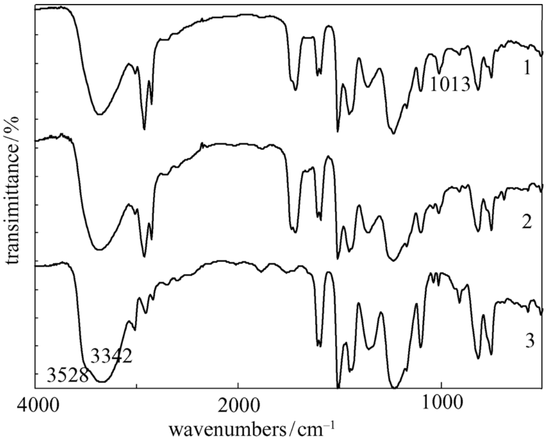


Fig. 2 IR spectra of linear PR prepolymer and modified phenolic resins
1) ESO-IT-PR B (modified phenolic resin by chain extension and etherification); 2) ESO-IT-PR A (etherified phenolic resin); 3) Linear PR prepolymer

peak at 1720 cm^{-1} and 2927 cm^{-1} are respectively due to the stretch-shrinking absorption bands of C=O and C–H, suggesting that the chemical reaction had happened between ESO and PR. In curve 1 strong increase is observed for the intensity in the 1013 cm^{-1} and 1257 cm^{-1} bands corresponding to the asymmetric stretch- shrink-vibrating peaks of phenol ether linkage(C–O–C). And with the progress of modification reaction, the characteristic absorption band of C–O–C enhances gradually, which means the phenol hydroxyl is etherified by ESO.

FTIR spectra of above three resins in the absorption region of 3000–3600 cm^{-1} are shown in Fig. 3. In the spectral curves of two products, the peaks of free hydroxyl vanish completely and the absorption band sites of hydrogen-bonded hydroxyls shift to the direction of higher frequency. This indicates that the hydrogen bonding in the modified products is hydroxyl-ether hydrogen bonding, whose strength is weaker than that of hydroxyl-hydroxyl [10]. The hydrogen bonding between phenolic resin prepolymer and its modified products makes different polymeric chain segment possess thermodynamic miscibility and further ensures the toughening effect, Storage Stability and even copolymerization structure of ESO modification.

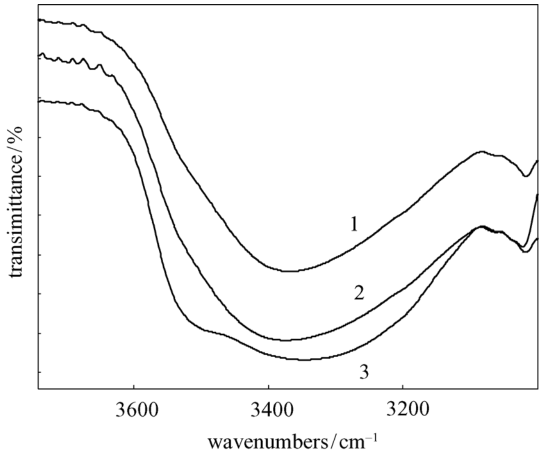


Fig. 3 IR spectra of hydroxyl in linear PR prepolymer and modified phenolic resins
1) ESO-IT-PR B (modified phenolic resin by chain extension and etherification);
2) ESO-IT-PR A (etherified phenolic resin); 3) Linear PR prepolymer

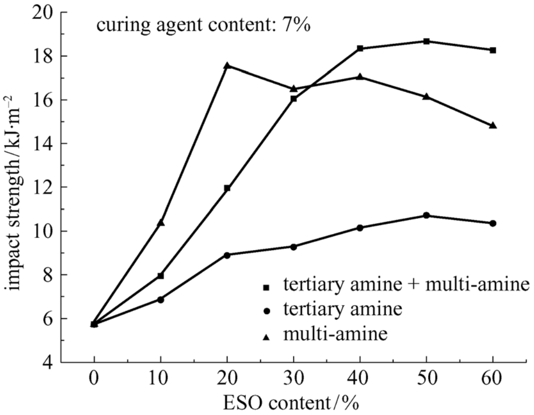


Fig. 4 Effect of ESO content on impact strength with different catalysts

3.3 Influence of catalysts and ESO content on modified phenolic resin

Influence of catalysis methods and ESO content on the impact strength and solderleaching resistance of corresponding P-CCL samples is shown in Fig. 4 and Fig. 5 respectively. The figures show that catalysis method has prominent influence on the properties of modified resins. Modified phenolic resin prepared by catalysis with tertiary amine shows inferior toughness, demonstrating that the toughening effect of mere etherifying reaction is limited, and little optimizing effect on toughness is observed while greatly increasing the ESO content. That shows chain extension reaction of ESO is difficult under this catalysis condition

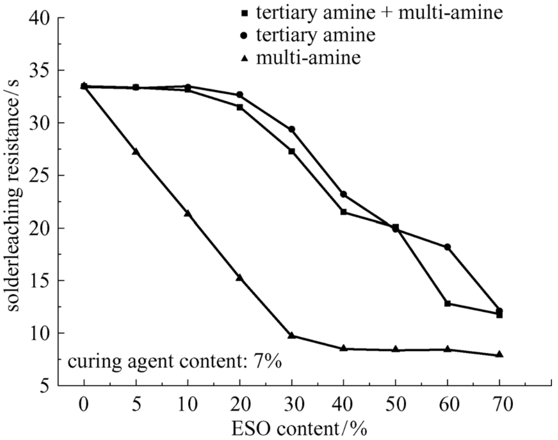


Fig. 5 Effect of ESO content on solderleaching resistance with different catalysts

and the external toughening from free ESO is insufficient. ESO modified phenolic resin with only multi-amine catalyst shows excellent toughening effect, demonstrating that multi-amine is effective chain extender for ESO and ESO chain extension polymer (ESO epoxy) possesses remarkable toughening effect. However, its solderleaching resistance decrease rapidly with the increasing of ESO content. The main reason can be attributed to that the chain extension polymer is actually a polymeric tertiary amine with steric hindrance, which results in its low etherification catalysis capability. Thereby, the degree of etherification graft reaction is very low and the blend of ESO epoxy and phenolic resin is its main modification mechanism. P-CCL prepared with the blend of ESO epoxy and phenolic resin can not meet the requirement of solderleaching resistance.

As shown in Fig. 4, Modified phenolic resin catalyzed by both tertiary amine and multi-amine shows excellent impact toughness and its impact toughness increases rapidly with increasing ESO content. When the ESO content is lower than 20%, since most ESO have be grafted to phenolic resin in the early stage of the modification reaction and no enough free ESO is provided for subsequent chain extension, the long chain polymer is rare and its toughness is inferior to that of the blend of ESO epoxy and phenolic resin. when the ESO content is more than 30%, its impact strength increases rapidly up to 16.05 kJ/m^2, which is more than that of unmodified phenolic resin (5.73 kJ/m^2) by 180%. Among the three catalysis methods, the laminate prepared by catalysis with both tertiary amine and multi-amine shows good solderleaching resistance, and the solderleaching resistance of laminate with this catalysis method is especially superior to the two other ones under the condition of high ESO content, both of which is attributed to its rigid crosslinking structure.

Figure 4 and Fig. 5 also show that impact strength of the samples increase rapidly with increasing ESO content. But when ESO content is more than 30%, toughening improvement is not obvious. For catalysis method with two catalysts, when ESO content is more than 30%, its solderleaching resistance begins to decrease accelerately. As far as cost is considered, the optimal ESO content is 30%.

3.4 Influence of curing agent content on solderleaching resistance

Influence of curing agent (hexamethylenetetraamine) content on the solderleaching resistance of ESO-IT-PR is shown in Fig. 6. The figure shows that the solderleaching resistance of ESO-IT-PR increases with hexamethylenetetraamine content up to 7%. When curing agent content is more than 7%, not only is increasing curing agent not good to solderleaching resistance, but also it results in lower water resistance and insulation. Take cost and mechanical properties into considered, optimal curing agent content is 7% of the total resin weight.

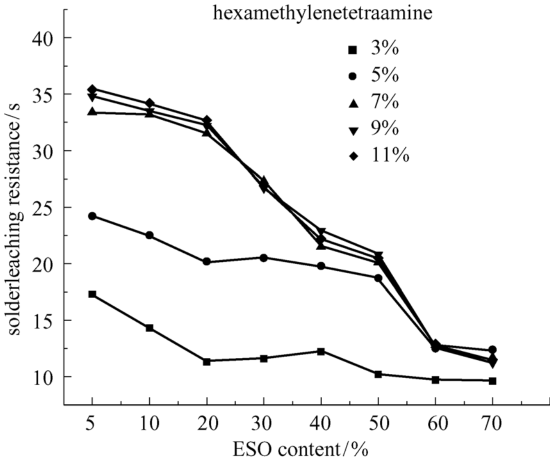


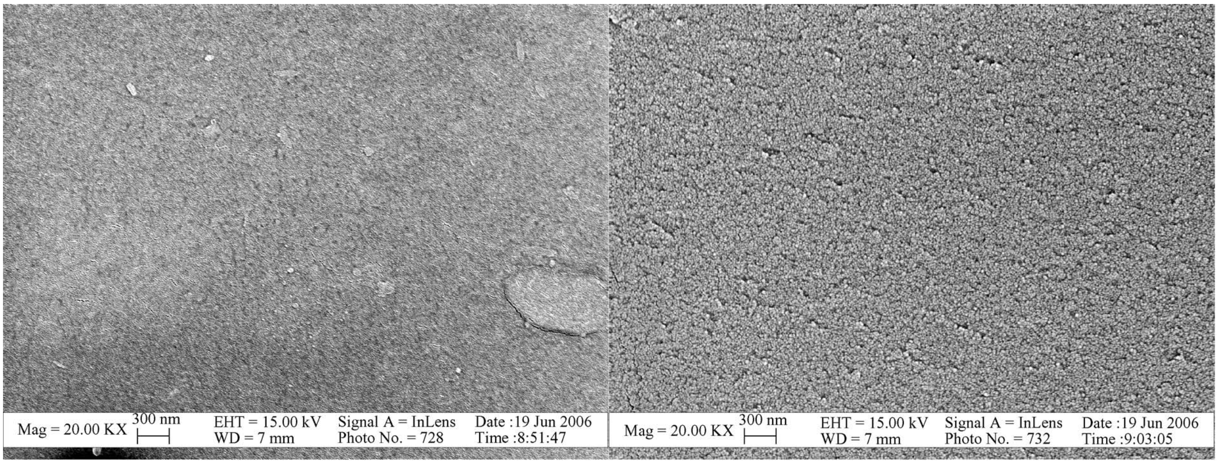
Fig. 6 Effect of curing agent and ESO content on solderleaching resistance

3.5 Morphology of modified phenolic resins

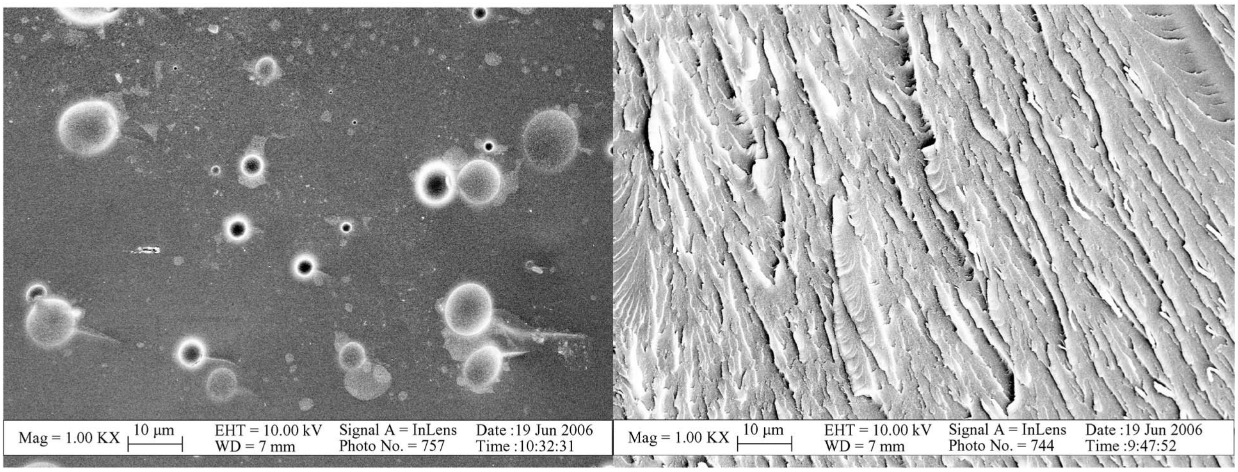
The SEM micrographs of normal PR and modified phenolic resins with different catalysts are shown in Figs. 7(a–d) respectively. The SEM image of the normal PR (Fig. 7a) is smooth brittle fracture surface. Etherified phenolic resin prepared with tertiary amine catalyst exhibits one phase with a small crack which means a very weak toughening effect, indicating that its toughness mechanism is crazing effect but not shear yield. The morphology of the fracture surface of modified phenolic resin prepared with multi-amine catalyst displays some cavities and phase-separated domains on the continuous phase. These cavities come from free ESO epoxy resin with longer molecular chain and less miscibility with phenolic resin. This phenomenon demonstrates that the blend of ESO chain extension polymer and phenolic resin is its main toughening mechanism [11]. Fig. 7(d) shows that there are many irregular ridges and deformation lines in continuous phase of ESO-IT-PR, indicating its toughness is superior to the two other modified phenolic resins. It can be concluded by comparing Fig. 7(c) and Fig. 7(d) that, for modified phenolic resin with both tertiary amine and multi-amine catalyst, long flexible chain with high toughening effect show high miscible with phenolic resin system because of the etherification reaction between ESO epoxy and phenolic resin. The grafting crosslinking structure make corresponding laminate good solderleaching resistance. The analysis about the morphology of the fracture surfaces of the samples is accord with the reaction mechanism mentioned in 3.1 [12].

3.6 Properties of P-CCL prepared with ESO-T-PR

Properties of P-CCL prepared with ESO-IT-PR whose ESO content and curing agent content is 30% and 7% respectively are listed in Table 1. The data show that the performance of P-CCL prepared with ESO-IT-PR is superior to R8700 enterprise standard of Hitachi Company.



(a) linear phenolic resin (b) catalysis with tertiary amine



(c) catalysis with multi-amine (d) catalysis with tertiary amine and multi-amine

Fig. 7 SEM photographs of the neat phenolic resin and ESO toughened phenolic resin with different catalysts

4 Conclusions

The FTIR figures indicate that the phenol hydroxyl is etherified by ESO and the hydrogen bonding between phenolic resin prepolymer and its modified products makes different polymeric chain segment possess thermodynamic miscibility. SEM figures show the main reason why ESO-IT-PR possesses excellent toughness and solderleaching resistance is that long flexible ESO epoxy with high toughening effect is produced by the reaction

Table 1 Main properties of copper clad laminate made of ESO modified phenolic resin

	Standard	ESO modified phenolic resin
solderleaching resistance 260°C/s	10	27
punch quality	4 - 4 - 4	5 - 5 - 4
moisture absorption/%	1.1	0.17
horizontal flexural strength/MPa	100	153.2
vertical flexural strength/MPa	100	159.1
peeling strength/MPa	1.0	19.6
insulation resistance/10^6 MΩ	0.1	5.75
insulation resistance D-2/100°C/MΩ	100	530
loss tangent	0.05	0.021
volume resistivity/10^4 MΩ m	1.0	5.1
surface resistance/10^5 MΩ	1.0	4.5
alkali resistance/5%NaOH, 40°C, 5 min	no change	no change
heat resistance/130°C, 1 h	no bubble and peeling	no bubble and peeling

between ESO and multi-amine, and etherification reaction can resolve the problem of the compatibility of ESO epoxy with the whole modified phenolic resin. ESO and hexamethylenetetraamine curing agent content show obvious influence on impact toughness and solderleaching resistance of the laminates. In this work, the synthesis process is catalysis with both tertiary amine and multi-amine, and the optimal ESO and curing agent content are 30% and 7% respectively. The reaction mechanism is that the etherification reaction between Phenol hydroxyl and ESO catalyzed by teritary amine and the chain extension polymerization between ESO and multi-amine gives the long-chain ESO epoxy grafting on the phenolic resin prepolymer.

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