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Study on polyblending epoxy resin adhesive with lignin I-curing temperature

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ABSTRACT

As a three-dimensional amorphous biopolymer composed of phenylpropanoid units linked together by ether and carbon–carbon bonds, lignin is considered to be one of the most promising future organic resources not only because it is renewable, but also because it is second only to cellulose in abundance among the naturally occurring polymers. Due to its phenolic ether structure, lignin can be used to blend with other polymers to improve the heat-resistance of the polymers. So, in this study, a type of epoxy resin adhesive polyblended with corn straw enzymatic hydrolyzed lignin was prepared, and the effect of curing temperature on the adhesive joint shear strength of the epoxy resin adhesives under room temperature and high temperature respectively was also studied. The curing degree for the curing reaction of the epoxy resin was examined by FTIR analysis. The apparent activation energy for modified epoxy resin was calculated by DSC analysis. The results showed that the epoxy resin adhesive blended with corn straw enzymatic hydrolyzed lignin exhibited excellent shear strength under room and high temperature. The curing temperature of epoxy resin showed a considerable influence on the performance for the epoxy resin adhesive. The mentioned epoxy resin adhesive can be used to adhere polymer composites in which high temperature shear strength was required.

1. Introduction

Epoxy resins are considered as one of the most important classes of thermosetting polymers and widely used in various fields of coating, high performance adhesives and other engineering applications [1]. Especially, in the field of adhesives, epoxy resin adhesives are recognized as one of the important adhesives, since they can bond various materials such as steels, copper, wood, iron, cement, plastic and composites [2]. In usual applications epoxy resins are rarely used without the incorporation of some other materials. Filling or polyblending are both used to enhance their performance by providing additional mechanical properties or modifying the physical characteristics of the blends. In the case of epoxy resin, a number of polymers and plasticizers have been used in epoxy resin polyblends including nylon [3], rubber [4–7], engineering thermoplastics [8], polyurethane [9–11] and phenolic resins [12]. In most cases, these polymers have functional groups capable of reacting with the epoxy.

As a three-dimensional amorphous biopolymer composed of phenylpropanoid units linked together by ether and carbon–carbon bonds, lignin is considered to be one of the most promising future organic resources not only because it is renewable, but also because it is second only to cellulose in abundance among the naturally occurring polymers. It is considered that the most important chemical functional groups in lignin molecules structure include the aromatic group, hydroxyl, methoxyl, carbonyl and carboxyl groups, etc. [13,14]. Its microstructure makes it an interesting raw material for a wide variety of applications. Due to its phenolic ether structure, lignin can be used to blend with other polymers to improve the heat-resistance of the polymers.

In the past, some researchers studied lignin based epoxy resins prepared from lignin [15–18]. The chemical modification in the course of the preparation of lignin based epoxy resins added to the cost of preparation, at the same time, complex chemical and macromolecular structure for lignin made the task of quality control very difficult. These may be some of the reasons for limited application in lignin based epoxy resin adhesives. In this study, a polyblending epoxy resin adhesive was prepared. The polyblending adhesive obtained at room temperature was a physical mixture between an epoxy resin polymer and the corn straw enzymatic hydrolyzed lignin. And the effect of curing temperature on the bonding strength under room temperature and high temperature respectively was studied.

2. Experimental

2.1. Materials

Corn straw enzymatic hydrolyzed lignin with bulk density of 0.6 g/cm^3 and carboxyl content of 2.12% was supplied by Songyuan LaiHe Chemicals Co., Ltd. of China, dried at 50 °C for 24 h in

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vacuum oven before blending. Bisphenol A epoxy resin trademarked with WRS618 with an epoxy value of 0.48–0.54 (eq/100 g) was supplied by Wuxi Resin Factory of Bluestar New Chemical Materials Co., Ltd. of China, The cure agent polyamide resin trademarked with TY-200 with the amine value of 200–230 (mgKOH/g) was supplied by Tianjin Yanhai Chemical Co., Ltd., of China. The substrate material used in the adhesive joints was aluminum alloy and carbon fiber/epoxy resin composite.

2.2. Preparation of adhesive and adhesion of substrate material

The epoxy resin adhesive was prepared according to undermentioned mass ratio of epoxy resin/polyamide = 100/70. The polyblending epoxy resin adhesive with lignin was prepared as follows: epoxy resin:polyamide:lignin (mass ratio) = 100:70:8.5 (lignin content of 5%).

The aluminum substrate surface was treated by immersing it in a sulfuric acid–sodium dichromate solution at 60 °C for 15 min after mechanical polish, the solution for treatment was prepared as follows (mass ratio): $Na_2Cr_2O_7$:H_2SO_4:H_2O = 1.5:20:15, washing it with distilled water to remove acidic traces and dry it at 60 °C–65 °C for 30 min. The surface of the carbon fiber/epoxy resin composite was mechanicaly polished and then wiped by ethanol before being adhered.

2.3. Tests and analysis

Single-lap shear joints aluminum substrates with the size of 101.6 mm × 25.4 mm × 1.62 mm were used for evaluating the adhesive shear strength by tension loading with an overlap length of 12.7 mm. The adhesives were applied across both sides of the overlap area and cured at room temperature and high temperature respectively. During the cure, the specimens were under a constant pressure of 0.05 MPa. After curing, these specimens were tested on 4465 Electromechanical Systems provided by Instron Corporation at the speed of 5 mm/min and the test temperature of 25 °C and 80 °C respectively according to ASTM D-1002. The FTIR spectra analysis of the adhesives was obtained in BRUKER vector 22 Fourier transform infrared spectroscopy using potassium bromide (KBr) disc. Differential scanning calorimetric (DSC) analyses were performed on a DSC 6220 provided by Seiko Instruments Inc. in a nitrogen atmosphere. Calibration was achieved using indium standard samples. Scans were run at heating rates of 5° C/min, 10 °C/min, 15 °C/min and 20 °C/min.

3. Results and discussion

3.1. Bonding properties

3.1.1. Curing at room temperature

In general, the most common and useful type of adhesion test is the shear test. Through shear strength test, the performance of the adhesive could be evaluated in the case of adhering the same material. It is well known that curing temperature affects the performance of adhesives seriously. To study the effect of curing temperature on the performence of the epoxy resin adhesive, the epoxy resin adhesive and the polyblending adhesive are cured at room temperature (23 °C) for 72 h; and the shear strength under room temperature and the temperature of 80 °C for epoxy resin adhesive and the adhesive polyblended with lignin cured at room temperature is shown in Table 1.

Table 1
Shear strength for two epoxy resin adhesives cured at room temperature.

	Shear strength (MPa, 23 °C)	Shear strength (MPa, 80 °C)
Epoxy resin adhesive	15.32	2.03
Polyblending epoxy adhesive	18.76	2.19

From Table 1, it can be concluded that the shear strength for the epoxy resin adhesive could be improved by the introduction of lignin. Just as we have known, the performance for the epoxy resin adhesive was determined by the curing degree of the epoxy resin, especially for the performance under high temperature. The data in Table 1 showed that the polyamide curing agent can cure epoxy resin at room temperature, but the degree of curing could not achieve a satisfied situation, as a result, the shear strength at the temperature of 80 °C presented a lower value. By polyblending the lignin, the shear strength for the epxoy resin adhesive under room temperature and the temperature of 80 °C both improved. It indicated that the enzymatic hydrolyzed lignin could promote the curing reaction of epoxy resin, and the curing degree was enhanced accordingly, which increased the shear strength both for room temperature and for the temperature of 80 °C. But unfortunately, the degree of improvement of the shear strength of the epoxy resin adhesive polyblended with lignin was still small, which showed that the degree of curing for the epoxy resin could not achieve the best level yet.

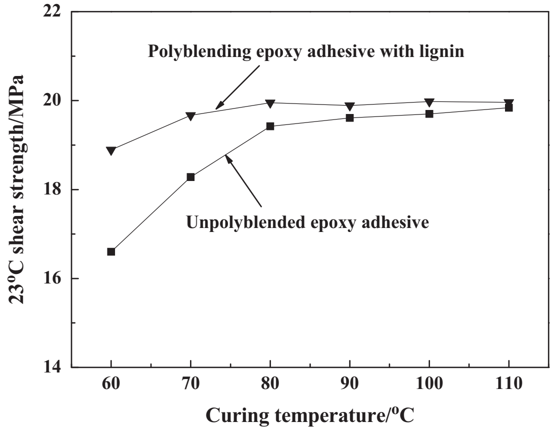

Fig. 1. Room temperature shear strength for two epoxy resin adhesives cured at various temperatures.

3.1.2. Curing at high temperature

To further study the effect of curing temperature on the performance of the epoxy resin adhesives, the curing reaction for the epoxy resin adhesives under high temperature was carried out. Figs. 1 and 2 show the shear strength for two epoxy resin adhesives under room temperature and the temperature of 80 °C which cured at various temperatures for 4 h.

From Figs. 1 and 2, it can be seen that the shear strength for two epoxy resin adhesives increased obviously with the increase in curing temperature. Polyblending epoxy resin adhesive with lignin shows a better performance compared with unpolyblended epoxy resin adhesive. The results for high temperature shear strength indicated that elevating curing temperature would be propitious to increasing the curing degree for the epoxy resin, which resulted in the improvement of the shear strength for epoxy resin adhesives. The lignin polyblended in epoxy resin adhesive would react with epoxy resin under a higher curing temperature due to its activated groups such as carboxyl and hydroxyl group, which increases the cross-linking density for the polyblends, as a result, the polyblended epoxy resin adhesive shows a better shear strength compared with unmodified ones.

From the figures, it also can be seen that the shear strength of the adhesive cured at a temperature of 110 °C improved slightly

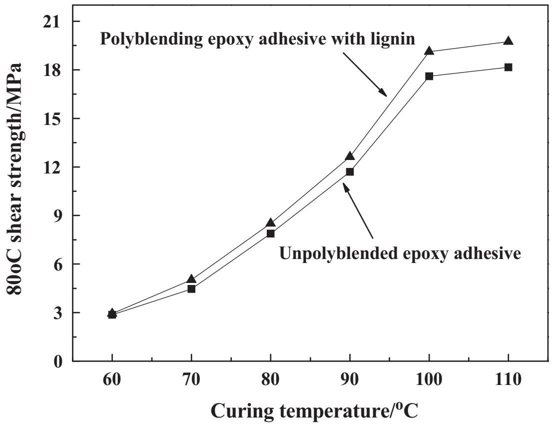

Fig. 2. 80 °C shear strength for two epoxy resin adhesives cured at various temperatures.

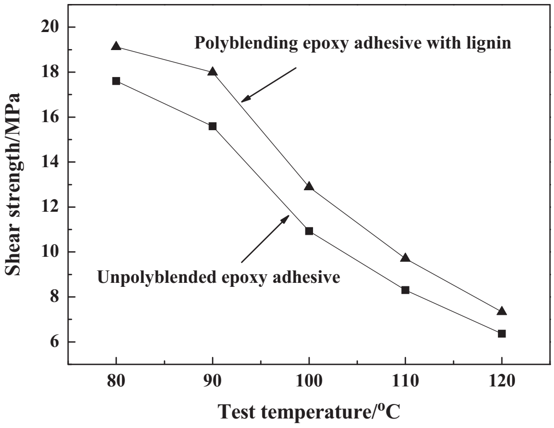

Fig. 3. Shear strength for two epoxy resin adhesives under various temperatures.

than that cured at a temperature of 100 °C. It can be concluded that the curing degree for the epoxy resin increased with the increase in the curing temperature, when curing temperature reaches 100 °C, the curing degree for epoxy resin tends to saturation, and the curing of epoxy resin tends to be complete. Thus, an optimized curing temperature of epoxy resin adhesive polyblended with lignin was chosen as 100 °C.

3.1.3. *Shear strength for adhesives under high temperature*

In order to study the heat resistance of epoxy resin adhesive, the shear strength of the bonding joint under various temperatures was also tested. The shear strength for two epoxy resin adhesives under various temperatures is shown in Fig. 3; therein, the epoxy resin adhesive was cured at a temperature of 100 °C for 4 h.

From Fig. 3 it can be seen that the shear strength of adhesives decreased with increasing test temperature. It is well known that the cured epoxy resin polymers would present concerned glass transition temperature (T_g) determined by curing agent and curing process. When the ambient temperature exceeds the T_g temperature of polymers, the polymers chain would stand in viscoelasticity state, which reduces the cohesion strength of the polymers, and the bonding shear strength would reduce accordingly. From the figure, it is also believed that the heat resistance for polyblending epoxy resin adhesive was better than that for unpolyblended epoxy adhesive. As mentioned above, there are lots of chemical functional groups in lignin's molecular structure including phenolic hydroxyl and carboxyl groups; the phenolic hydroxyl and carboxyl groups would react with epoxy resin in the course of the curing reaction, and the polyblends having more cross-linking density and higher T_g temperature would exhibit better heat resistance. This is the reason the polyblended epoxy resin adhesive shows better shear strength under high temperature. The results for high temperature shear strength affirmed ulteriorly that enzymatic hydrolyzed lignin could participate in the curing reaction of the epoxy resin, which improves the performance of the epoxy resin.

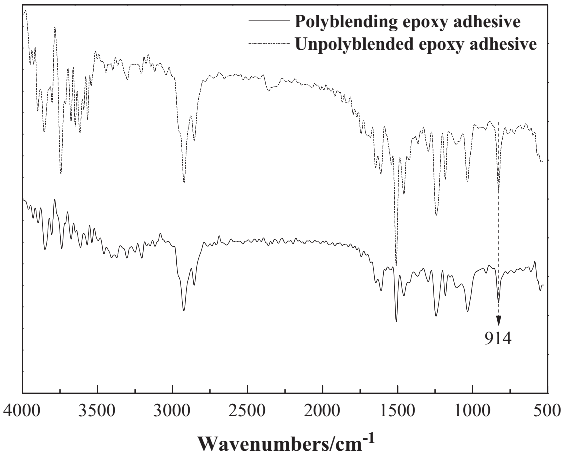

Fig. 4. FTIR spectra for two epoxy resin adhesives cured at room temperature.

3.2. *FTIR analysis.*

The FTIR spectra for the epoxy resin adhesive and the polyblended epoxy resin adhesive with lignin cured at room temperature for 72 h are shown in Fig. 4. FTIR spectrum analysis was employed to characterize the raw materials and analyze the changes in the epoxy resin structure during its curing reaction, mainly to observe the introduction of new functional groups or the disappearance of the existing ones.

It can be seen from Fig. 4 that, the absorption peak at wave number 914 cm^{-1} which is attributed to the stretching vibration absorption of epoxy group for unpolyblended epoxy resin adhesive showed a stronger peak intensity than that of polyblended epoxy resin adhesive. The result further indicated that the lignin could promote the curing of epoxy adhesive, which resulted in a better performance of the adhesive. This result is consistent with that obtained by the above bonding properties analysis of the adhesives cured at room temperature.

The FTIR spectra for the epoxy resin adhesive and the polyblended epoxy resin adhesive with lignin cured at the temperature of 100 °C for 4 h are shown in Fig. 5. From the figure, it can be indicated that there was no stretching vibration absorption of epoxy group at 914 cm^{-1} in the FTIR spectra for two epoxy resin adhesives, which showed that the adhesives were cured completely under the temperature of 100 °C for 4 h. This result is also consistent with that obtained by the above mechanical properties analysis for the adhesives cured at high temperature.

3.3. *Curing kinetic analysis*

The kinetic parameters of activation energy are important to understand the curing of the adhesive. Only if the exterior energy was more than the activation energy of reactive molecules, could the curing reaction of the adhesive be conducted and completed. DSC curves of polyblended epoxy resin adhesive with lignin and unpolyblended epoxy resin adhesive at different heating rates are shown in Figs. 6 and 7 respectively. From Figs. 6 and 7, it can be seen that the polyblending of lignin reduced the peak temperature value of

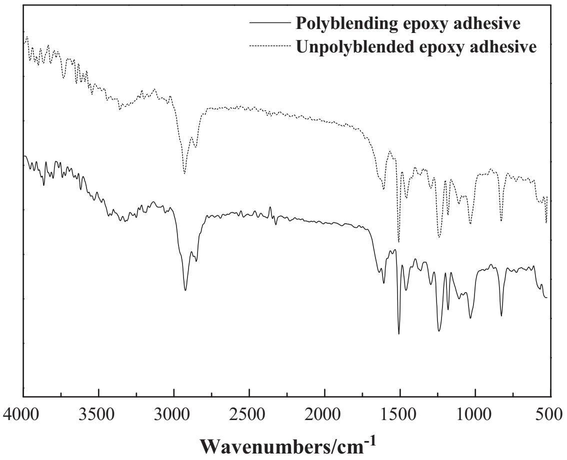

Fig. 5. FTIR spectra for two epoxy resin adhesives cured at the temperature of 100 °C.

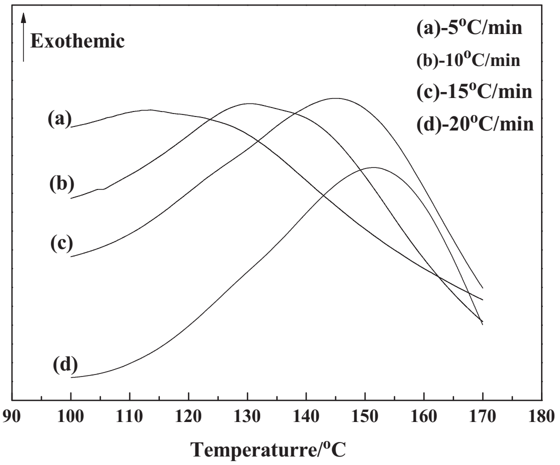

Fig. 6. DSC curves of polyblending epoxy resin adhesive with lignin at different heating rates.

exothermic peak for the curing reaction of epoxy resin, which indicated that the lignin could promote the curing of epoxy resin.

Curing kinetics of epoxy resin adhesives would be studied according to Kissinger equation (the data can be obtained from Figs. 6 and 7):

$$\frac{d[\mathrm{In}(\beta/T_P^2)]}{d(1/T_P)} = -\Delta E/R$$

where β is the constant heating rate (K/min), T_p is the top-peak temperature (K), R is the ideal gas constant (8.314 J/mol K), and ΔE is the apparent activation energy (kJ/mol). The curve of $\ln(\beta/T_P{}^2)$ versus $1/T_P$ for two epxoy resin adhesives for which the data can be obtained from Figs. 6 and 7, are shown in Figs. 8 and 9 respectively.

From Fig. 8, the apparent activation energy of polyblended epoxy resin adhesive with lignin can be calculated as 41.262 kJ/mol. From Fig. 9, the apparent activation energy of epoxy resin adhesive can be calculated as 60.929 kJ/mol. From the analysis for the apparent activation energy, it can be concluded that lignin could promote the curing of epoxy adhesive. The result is consistent with that obtained by the above analysis.

3.4. Bonding strength for carbon fiber/epoxy resin composite

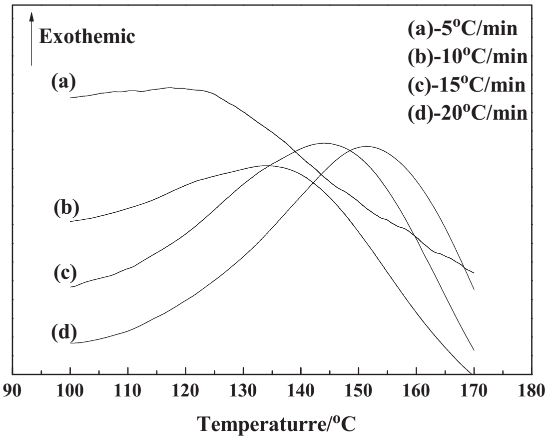

Fig. 7. DSC curves of unpolyblended epoxy resin adhesive at different heating rates.

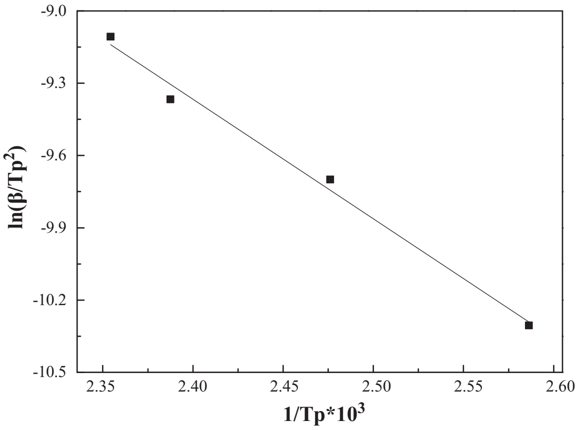

Fig. 8. Curve of $\ln(\beta/T_P{}^2)$ versus $1/T_P$ for polyblended epoxy resin adhesive with lignin.

Carbon fiber/epoxy resin composites have been widely used for structural applications due to their excellent mechanical properties, and the study on the adhesion of carbon fiber/epoxy resin composites also attracted lots of researchers accordingly. Among the bonding of carbon fiber/epoxy resin composites, the bonding strength under high temperature is one of the key properties which people are usually concerned with. So, in this study, the bonding strength of carbon fiber/epoxy resin composites bonded with the polyblended epoxy resin adhesive under high temperature was also tested, as shown in Fig. 10, wherein, the adhesive was cured at a temperature of 100 °C for 4 h.

From Fig. 10, it can be believed that though the shear strength of bonding joint using polyblended epoxy adhesive with lignin reduced with the increase in test temperature, the shear strength of bonding joint still kept a better bonding strength, exceeding 8.0 MPa at the temperature of 120 °C. And it is shown that the epoxy resin adhesive can be modified by polyblending corn straw enzymatic hydrolyzed lignin as the means of simplifying techniques and reducing cost, and the polyblended epoxy resin adhesive with lignin can be used for the adhesion of carbon fiber/epoxy resin composite with better high temperature bonding strength.

4. Conclusion

A type of modified epoxy resin adhesive can be prepared by polyblending corn straw enzymatic hydrolyzed lignin into epoxy resin. The curing temperature of epoxy resin showed a considerable influence on the performance for the epoxy resin adhesive. The curing reaction for epoxy resin adhesive cured by polyamide under room temperature could not achieve completion. And

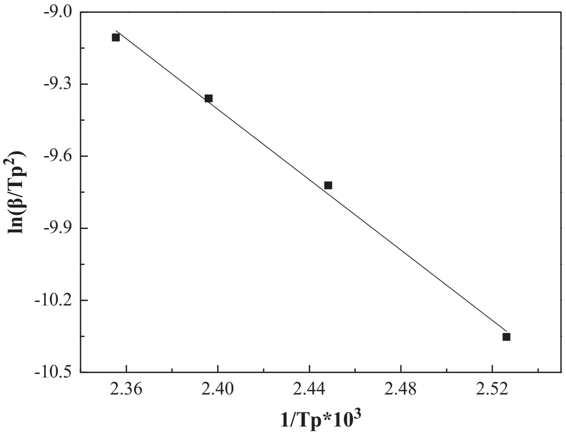

Fig. 9. Curve of $\ln(\beta/T_P{}^2)$ versus $1/T_P$ for epoxy resin adhesive.

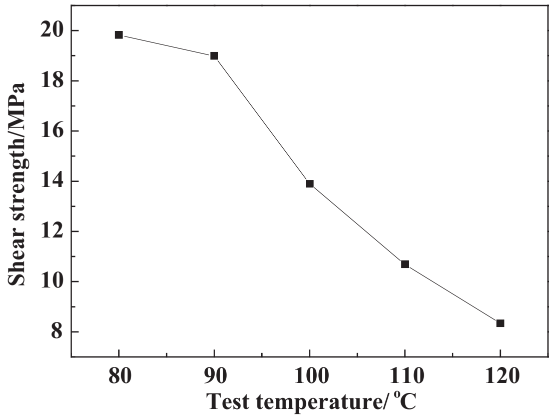

Fig. 10. Different temperature shear strength of adhesive bonding epoxy/carbon fiber composite.

elevating curing temperature would be propitious to the increase of the curing degree for the epoxy resin. The lignin can promote the curing of epoxy resin and react with epoxy resin to increase the curing degree of the curing reaction and crosslinking density for the cured adhesive, which made the polyblended epoxy resin adhesive showed a better bonding performance than that for unpolyblended epoxy resin adhesive. The mentioned polyblended epoxy resin adhesive can be used to adhere polymer composites such as carbon fiber/epoxy resin composites in which high temperature shear strength was required.

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References

[1] Sun ManLing, Wu JiaYi. Application Principle and Technology of Epoxy Resin. Beijing: China Machine Press; 2002.

[2] Petrie, Edward M. Epoxy Adhesive Formulations. New York: McGraw-Hill Book Company; 2005.

[3] Zhong Zhikai, Guo Qipeng. Miscibility and cure kinetics of nylon/epoxy resin reactive blends. Polymer 1998;39:3451–8.

[4] Minfeng Zeng, Xudong Sun, Huiquan Xiao, et al. Investigation of free volume and the interfacial, and toughening behavior for epoxy resin/rubber composites by positron annihilation. Radiation Physics and Chemistry 2008;77:245–51.

[5] Russell Bobby, Chartoff Richard. The influence of cure conditions on the morphology and phase distribution in a rubber-modified epoxy resin using scanning electron microscopy and atomic force microscopy. Polymer 2005;46:785–98.

[6] Balakrishnan S, Start PR, Raghavan D, et al. The influence of clay and elastomer concentration on the morphology and fracture energy of preformed acrylic rubber dispersed clay filled epoxy nanocomposites. Polymer 2005;46:11255–62.

[7] Khoee Sepideh, Hassani Narges. Adhesion strength improvement of epoxy resin reinforced with nanoelastomeric copolymer. Materials Science and Engineering A 2010;527:6562–7.

[8] Rico Maite, López Joaquín, Ramírez Carmen, et al. Phase diagram of different epoxy-amine precursors modified with a thermoplastic: effect of structure of epoxy-amine system on miscibility. Polymer 2005;50:569–77.

[9] MacKinnon Alexander J, Pethrick Richard A, Jenkins Stephen D, et al. Investigation of thermoplastic-modified thermosets: positron annihilation and related studies of an amine-cured epoxy resin. Polymer 1994;35:5319–26.

[10] Rosu Dan, Rosu Liliana, Mustata Fanica, et al. Polyurethane-epoxy based copolymers: influence of chemical structure over photoinduced birefringence. Reactive and Functional Polymers 2012;72:478–85.

[11] Yeganeh Hamid, Lakouraj Moslem Mansour, Jamshidi Sadegh. Synthesis and properties of biodegradable elastomeric epoxy modified polyurethanes based on poly(ε-caprolactone) and poly(ethylene glycol). European Polymer Journal 2005;41:2370–9.

[12] Chen Kun-Lung, Shen Yun-Hwei, Yeh Mou-Yung, et al. Complexes of imidazole with poly(ethylene glycol)s as the thermal latency catalysts for epoxy-phenolic resins. Journal of the Taiwan Institute of Chemical Engineers 2012;43:306–12.

[13] Wang Jiashu, Manley St John R, Feldman D. Synthetic polymer–lignin copolymers and blends. Progress in Polymer Science 1992;17:611–46.

[14] Feldman D, Banu D, Natansohn A, et al. Structure–properties relations of thermally cured epoxy-lignin polyblends. Journal of Applied Polymer Science 1991;42:1537–50.

[15] Sun Hongguang, Sun Gang, Lv Hong, et al. DSC study on the effect of cure reagents on the lignin base epoxy cure reaction. Journal of Applied Polymer Science 2007;105:2332–8.

[16] Ismail Tuan Noor Maznee Tuan, Hassan Hazimah Abu, Hirose Shigeo, et al. Synthesis and thermal properties of ester-type crosslinked epoxy resins derived from lignosulfonate and glycerol. Polymer International 2010;59:181–6.

[17] Shigeo Hirose, Tatsuko Hatakeyama, Hyoe Hatakeyama. Synthesis and thermal properties of epoxy resins from ester-carboxylic acid derivative of alcoholysis lignin. Macromolecular Symposia 2003;197:157–70.

[18] Nonaka Y, Tomida B, Hatano Y. Synthesis of lignin/epoxy resin in aqueous systems and their properties. Holzforschung 1997;51:183–7.