Modification of Urushiol Derivatives by Liquid Crystal Epoxy Resin

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Received 2 December 2014; Revised 26 January 2015; Accepted 26 January 2015

Academic Editor: Rong Lu

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Urushiolderivatives have vast potentials for using as coating materials. However, the cured coatings are quite brittle, limiting their applications. In this study, urushiol-furfural (UFUR) was chosen as an example of urushiol derivatives and a liquid crystal (LC) epoxy resin, tetramethylbiphenyl diglycidyl ether (TMBPDE), was for the first time utilized to modify UFUR. Fourier transform infrared spectroscopy and solid-state $^{13}$C nuclear magnetic resonance showed the reactions between TMBPDE and UFUR after the UFUR/TMBPDE composite resin was cured. Differential scanning calorimetry analysis showed that the $T_g$ significantly increased after the addition of TMBPDE. Thermogravimetry analysis indicated that the cured UFUR/TMBPDE composite resin exhibited increasing thermodecomposition temperature as the TMBPDE concentration increased, indicating its great potential for high temperature applications. Moreover, the presence of TMBPDE enhanced the toughness of UFUR as observed by impact test and reflected in the morphologies observed from SEM images of fracture surfaces. It would also be novel and effective to modify urushiol derivatives by the LC polymer.

1. Introduction

Oriental lacquer, known as the king of paints, has been used as coating materials for several thousand years in China [1]. It is a unique invention of uninterrupted civilization with 7000 years and becomes one of the most important sources of the chemistry in China [2]. Oriental lacquer is cut from phloem of the lacquer tree, an important economic tree of China [3]. The dried lacquer coatings possess a beautiful surface and high durability. Therefore, it has been used as decorative coatings to make life more beautiful and has become the symbol of wealth and status in ancient China [2, 4]. Lacquer has been also widely used in chemical, textile, industry, ship-building, mechanical, and electrical products [5]. However, the limited production causes the high price of natural lacquer, which limits its application [6]. Lacquer paint dries by enzymatic oxidation of laccase and autoxidation of urushiol unsaturated side chains [7]. The curing progress is really slow and is strongly affected by the environmental conditions such as humidity and temperature [8]. Moreover, lacquer has poor flexibility, adhesion, alkali resistance, and ultraviolet degradation resistance. Therefore, modification of original lacquer is essential to expand its application fields [9]. Takahisa et al. [10] developed hybrid lacquers composed of natural lacquer and amine-functionalized organic silane compounds that showed good drying property at low relative humidity. Kanehashi et al. [11] reported hybrid microwave-adsorption materials prepared from natural lacquer, epoxy, and organic silane compounds. The results suggested that the chemical reactions among natural lacquer, epoxy, and organic silane improved the hybrid properties such as drying, hardness, and molding.

In general, urushiol, which was the main component of lacquer, was extracted from lacquer and chemically modified to obtain the urushiol derivatives. The urushiol derivatives exhibited superior properties and were used in various fields. In 1960, urushiol formaldehyde resin was synthesized by condensation reaction of urushiol and formaldehyde, which was a significant progress for lacquer modification in China [12]. Zhang and He [13] used inorganic boron to modify the urushiol formaldehyde polymer. Compared with urushiol formaldehyde resin, urushiol organic boron product has a higher antioxidant capacity, heat resistance, and transient high temperature performance. In addition,
Liu [14] synthesized urushiol-furfural resin (UFUR) which could be formulated to a varnish with excellent abrasion-resistance. However, the varnish was very brittle. Therefore, they modified the UFUR by epoxy E-12. The modified varnish showed excellent mechanical properties, especially the abrasion-resistance, corrosion protection, and alkali resistance. UFUR could be cured by heating and it own some superior properties. Therefore, it is quite necessary to find new ways to modify UFUR.

Liquid crystal (LC) epoxy resins have been investigated because of their unique properties, for example, low shrinkage upon curing, good thermal stability, and excellent thermomechanical properties [15]. They combine the advantages of both LCs and epoxy resins. Compared to ordinary epoxy resins, crosslinked LC epoxy resins have higher fracture toughness [16]. Traditional epoxy resins can be improved by introducing LC domains into the amorphous matrix [17]. Unlike other toughening methods such as incorporating rubber particles, the presence of LC domains will not lead to a decrease in the glass transition temperature ($T_g$) or moduli of the material. These desirable properties make LC epoxy resins good candidates for a wide range of potential applications, such as optical switches, electronic packaging, and matrices for high performance composites [15]. Many efforts were directed towards the increase of toughness by introduction of LC epoxy resins in epoxy resins [18–21]. For example, Punchaipetch et al. [18, 19] copolymerized diglycidylether of bisphenol F networks and cured it with an anhydride curing agent as the matrix resins. DGE-DHBP enhances the toughness of the blended epoxy samples without decreasing the modulus of samples. However, to the best of our knowledge there are few researches on modification of UFUR with LC polymers.

In the current study, UFUR was chosen as an example of urushiol derivatives and an effective modification method was proposed. A LC epoxy resin, tetramethylbiphenyl diglycidyl ether (TMBPDE), was utilized to modify UFUR for high performance composites [15]. Many efforts were directed towards the increase of toughness by introduction of LC epoxy resins in epoxy resins [18–21]. For example, Punchaipetch et al. [18, 19] copolymerized diglycidylether of 4,4-dihydroxybiphenol (DGE-DHBP) with diglycidyl ether of bisphenol F networks and cured it with an anhydride curing agent as the matrix resins. DGE-DHBP enhances the toughness of the blended epoxy samples without decreasing the modulus of samples. However, to the best of our knowledge there are few researches on modification of UFUR with LC polymers.

In the current study, UFUR was chosen as an example of urushiol derivatives and an effective modification method was proposed. A LC epoxy resin, tetramethylbiphenyl diglycidyl ether (TMBPDE), was utilized to modify UFUR for the first time. The LC property of TMBPDE was investigated by polarized optical microscope (POM) from Leica (model DM 4500P equipped with a Linkam LTS-350 hot stage and TMS-94 temperature controller). A small amount of TMBPDE was placed on a microscope slide and then covered with a piece of cover glass. The formation and development of the LC phase were examined under polarized light. The sample was heated and cooled repeatedly from room temperature to 140 °C at a rate of 10 °C/min to investigate the change of birefringence.

The structure analyses of UFUR/TMBPDE composite resin on curing were conducted via FTIR spectra and solid-state nuclear magnetic resonance (NMR) spectra. FTIR spectra was recorded in a spectrum 100 FTIR spectrometer (FTS3000, BIORAD, USA) in the range from 4000 cm$^{-1}$ to 400 cm$^{-1}$. A potassium bromide pellet was used to support the IR sample. The sample was spread thinly on the potassium bromide pellet with a spatula, and the potassium bromide pellet was used as a blank. The solid-state 13C NMR spectra were recorded on a JNM-ECA400 (JEOL Co. Ltd., 100 MHz) using zirconium sample tubes with the CP/MAS method.

The effects of TMBPDE on the $T_g$ and thermal stability of the composite resin were investigated by differential scanning calorimetry (DSC). The effects of TMBPDE on the $T_g$ and thermal stability of the composite resin were investigated by differential scanning calorimetry (DSC).
calorimetry (DSC) and thermogravimetry (TG) analysis with a simultaneous thermal analysis (DSC/DTA-TG, NETZSCH, STA 409 PC Luxx, Germany) under the nitrogen atmosphere at a heating rate of 10 °C/min from 30 °C to 500 °C.

Impact strength was measured by an impact testing machine according to the GB/T1843-2008 standard. The samples were tested by the cantilever beam impact testing machine (Chengde Precision Tester XC-22, China). The sample was placed into the sample well and the pendulum bob fell through a vertical height on the surface. The morphologies of the fracture surfaces after impact tests were coated with gold and observed using SEM (Philips XL30, Dutch).

3. Results and Discussion

3.1. The UFUR/TMBPDE Composite Resin. It was generally believed that the ordered structure that was formed during cured process improved the toughness of the modified resins. If the composite resin was cured during the LC temperature range, more ordered mesogenic domains would be formed. Therefore, it is necessary to determine the LC temperature range. To investigate mesomorphic phase transition of TMBPDE, DSC and POM studies were carried out. The DSC thermogram of TMBPDE is shown in Figure 2. Only one endothermic peak was observed at about 107 °C in the heating scan, which was the melting of TMBPDE. However, the clearing point of LC was not found. The thermal behavior of some liquid crystal monomer is not well understood. For example, Liu et al. [22] found two phase transition peaks in the heating scan of DSC. Li and coworkers [15] were not able to detect any LC phase of 4,4'-diglycidyloxybiphenyl (BP) upon heating or observed a LC phase by POM. However, upon reacting with sulfanilamide, a smectic LC phase started forming after 20 min of the curing reaction. The TMBPDE had similar structure as BP. We were also not able to detect any LC phase of TMBPDE upon heating by DSC.

As we know, POM is a powerful tool for characterization of liquid phases. In order to clarify the mesophases of TMBPDE under POM, the samples were prepared by sandwiching a tiny power between two glass plates. Figure 3 shows the POM images of TMBPDE taken at different temperatures (200x magnification). TMBPDE started to melt at 107 °C, which is in good agreement with the DSC data. At the same time, LC birefringence was formed, which presents highly birefringent and nematic liquid crystal behavior. The texture color changed with increasing temperature. When the temperature was higher than 117 °C, the POM image turned to be completely dark due to the disappearance of the LC phase.

In order to examine the reaction between UFUR and TMBPDE in the composite resin during the curing process, the FTIR spectra of UFUR and UFUR with 15% TMBPDE before and after being cured were carried out. The results are shown in Figure 4. After the addition of TMBPDE, the peak at 910 cm⁻¹ due to the absorption of the epoxy group appeared. After the UFUR/TMBPDE composite resin was cured, the peak at 910 cm⁻¹ disappeared and the peak at 3400 cm⁻¹ due to the hydroxyl groups decreased, suggesting that polymerization between the epoxy group and the hydroxyl groups had occurred. A decrease in the hydroxyl group peak also promoted the oxidation of UFUR.

The solid-state ¹³C NMR spectra of TMBPDE, UFUR, and cured TMBPDE/UFUR composite resin are shown in Figure 5. The peak at ca. 17 ppm belonging to carbon of methyl on the urushiol aromatic ring of TMBPDE was detected in the spectrum of TMBPDE/UFUR composite resin. For TMBPDE, the oxygen atom substituted carbons on the epoxy group were detected at ca. 45 ppm and 52 ppm (Figure 5(a)). After the TMBPDE/UFUR composite resin was cured, the peaks of these carbons disappeared (Figure 5(c)), indicating that polymerization between TMBPDE and UFUR had occurred during curing.

In conclusion, although the LC phase of TMBPDE could not be detected by DSC, it could be observed by POM. The LC temperature range was from 107 °C to 117 °C. During curing, UFUR/TMBPDE composite resin was cured at 110 °C for 2 h and then 160 °C for 2 h. At 110 °C, TMBPDE presented a LC phase and it had enough time for the mesogenic segments to form LC domains during the curing process [15]. Figure 6 shows POM images of UFUR/TMBPDE composite resin taken at different temperatures (100x). The LC phase starts to appear above 100 °C. As the temperature increased, the LC phase did not disappear. After being further cured at 160 °C for 2 h, the LC domains would be “locked” in the network of the composite resin.

3.2. Thermal Properties. The cured thermosets are in glass state at room temperature. When the temperature was above its T_g, the uncured molecules could move in the micro-Brownian motion, which decreased the rigidity and strength. Therefore, the T_g is an important index to measure the heat resistance and available range of thermosetting resins. Therefore, it is necessary to study the effect of TMBPDE on the T_g of the composite resin. The relationship between the T_g and the TMBPDE content of the composite sample was evaluated by DSC. As shown in Figure 7, T_g of UFUR was about 187.2 °C. For UFUR/TMBPDE composite resins,
Figure 3: POM images of TMBPDE at different temperatures (200x): (a) 100°C; (b) 107°C; (c) 110°C; (d) 118°C.

Figure 4: FTIR spectra of samples ((a) UFUR; (b) TMBPDE-15 (uncured); (c) TMBPDE-15 (cured)).

Figure 5: $^{13}$C CP/MAS NMR spectra of samples ((a) TMBPDE; (b) UFUR; (c) TMBPDE-15 (cured)).

when TMBPDE content was less than 15%, $T_g$ of the composite resin increased as the TMBPDE content increased. When 15% TMBPDE was added, the $T_g$ of the composite resin increased from 187.2°C to 232°C. However, when the TMBPDE content reached 30%, the $T_g$ of the composite resin decreased to 224.1°C. Huang et al. [23] found that the novel liquid crystalline polymers, polydiethylene glycol bis(4-hydroxybenzoate) terephthaloyl and block copolymer, could enhance the $T_g$ of the o-cresol formaldehyde epoxy resin remarkably due to the rigid segments in the liquid crystalline polymers. Therefore, in this study, it is also proposed that the rigid segments in TMBPDE are the main reason why TMBPDE can improve $T_g$ of the composite resins. However, when the TMBPDE content was improved to 30%, $T_g$ was
Figure 6: POM images of UFUR/TMBPDE composite resin at different temperatures (100x): (a) 90°C; (b) 100°C; (c) 110°C; (d) 160°C.

Table 1: Thermodata obtained from DSC ($T_g$) and TG ($T_d$).

| Remarks    | $T_g$ (°C) | $T_d$ (°C) |
|------------|------------|------------|
| TMBPDE-0   | 187        | 330        |
| TMBPDE-5   | 195        | 335        |
| TMBPDE-15  | 232        | 345        |
| TMBPDE-30  | 224        | 352        |

lower than the former but much higher than that of UFUR. We found similar phenomenon to Huang et al. [23], who found that $T_g$ of the blends first increased and then decreased as the content of the liquid crystalline polymers is increasing. It was proposed that the molecular weight of TMBPDE was small. Therefore, when 30 wt% of TMBPDE was added, the structure density of the curing network would decrease, leading to the slight decrease of $T_g$ of TMBPDE-30. However, this problem will need to be further gone into.

Effects of TMBPDE on thermal stability of the composite resins were also investigated. Figure 8 shows the TGA curves for UFUR/TMBPDE composite resins with different TMBPDE contents. The thermal degradation temperature ($T_d$) was defined as the temperature when the samples lost 5% of their initial weight, and the results were summarized in Table 1. It can be seen that the $T_d$s of all UFUR/TMBPDE composite resins were higher than that of pure UFUR, indicating that the addition of TMBPDE enhanced thermal stability of UFUR. For the composite resins, the $T_d$s increased with the TMBPDE contents. When the content of TMBPDE was 15%, the $T_d$ of the composite resin increased to 352°C. The high value of the decomposition temperature can be ascribed to the presence of the biphenyl as rigid block. Therefore, TMBPDE strongly enhances the thermal stability of the UFUR/TMBPDE composite resin.

3.3. Impact Strength. Figure 9 shows the comparison of impact strength as a function of the TMBPDE contents. There was an increase in the impact strength of the composite resin on addition of the TMBPDE. When 30% TMBPDE was added, the UFUR/TMBPDE composite resin showed a four-fold increase in impact strength compared to pure UFUR. Punchaipetch [19] also has reported that the incorporation of a relatively small amount of the LC epoxy (diglycidyl ether of 4,4’-dihydroxybiphenol) could significantly enhance the toughness and $T_g$ of the blended epoxy samples.

The impact surfaces were investigated by SEM, as shown in Figure 10. The cured UFUR exhibited a brittle type of fracture behavior. For the cured composite resin with 5% TMBPDE, the fracture surface was very sharp with no plastic deformation. The crack grew in one direction because of the minimum resistance. When the addition of TMBPDE was increased to 15%, the rigid segments which were crosslinked in the UFUR matrix could absorb some impact energy,
resulting in improvement of the toughness. Therefore, the fracture surface exhibited ductile fracture with a river pattern where the multiple lines begin as a single line at the initiation point. For the composite resin with 30% TMBPDE, the furrow pattern at the starter crack region is found to be much bigger and coarser than that with 15% TMBPDE. Therefore, the toughness of TMBPDE-30 was higher than TMBPDE-15 by SEM.

The LC possesses a unique hierarchical microstructure in which, in the absence of external fields, they tend to form a macroscopically disordered polydomain, where each LC domain is defined as a region of uniform orientation [24]. For the LC thermoset, it exhibits exceptionally high fracture toughness. At low stress, crazes first take place within the isotropic amorphous domains and grow along the stress direction. Finally the crazes are hampered by the LC domains, which improved the impact strength of the LC thermoset [25]. For the UFUR/TMBPDE composite resin in our study, during curing, the LC phase of TMBPDE was “frozen” into the network, forming anisotropic LC domains surrounded by a macroscopically disordered polydomain. Therefore, the microdeformation and fracture mechanism of the LC thermoset could be extended to the case of the UFUR/TMBPDE networks and explain the reason for the impact strength improvement of the composite resin.

4. Conclusions

TMBPDE was utilized to modify the urushiol derivative, UFUR. The results showed that the $T_g$ significantly increased after the addition of TMBPDE. The UFUR/TMBPDE composite resin with 15% TMBPDE had a higher $T_g$ by 45°C compared with the pure UFUR. TGA analysis showed that the cured UFUR/TMBPDE composite resin exhibited increasing thermodecomposition temperature as the TMBPDE concentration increased, indicating its great potential for high temperature applications. Moreover, the presence of TMBPDE enhanced the toughness of UFUR as observed by impact test and reflected in the morphologies observed from SEM images of fracture surfaces. In conclusion, TMBPDE significantly enhanced the toughness of UFUR without sacrificing high $T_g$ and thermodecomposition temperature. It is supposed that the improvements of the properties are the effects of the mesogenic domains distributed in the network. These results also suggest that it would be a novel and effective way to modify other urushiold derivatives by a LC polymer.
Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This work was supported by Natural Science and Technology Ministry of China (ID: 2011BAD33B03) and the Key Technologies R&D Program of Tianjin, China (ID: 14ZXCXGX00680).

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