Toughness Improvement of Epoxy Composites Using a Kind of Environment-Friendly Bio-Based Polyester Polyol

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Abstract
Epoxy resin (EP) is a thermosetting resin with prominent performances and wide applications. However, the inherent brittleness limits its development in the engineering materials area. A liquid bio-based polyester polyol (LLP) with flexible long chains was synthesized in this study by melt polycondensation of corn straw lignin. After being compounded with EP (LLP/EP), the mechanical property, micromorphology and thermal behavior of the composite were evaluated. The experimental result indicated that the fracture brittleness of EP composite was decreased by importing the LLP. The bending and impact strength were up to 113.67 MPa and 51.29 kJ/m² for 10%-LLP/EP, which were 5.25% and 27% higher than those of unmodified EP. The results of this work build new avenues for the efficient utilization of lignin and the development of low-cost, high-performance and well environmentally adaptable EP composite by renewable resources.

Keywords Lignin · Polyester polyol · Epoxy resin · Toughening · Composite
**Introduction**

Epoxy resin (EP) has been widely used in coatings, adhesives, and electronics because of its good adhesive strength, superior insulation, and excellent chemical corrosion resistance. However, the fragility of the cured product is strong, which greatly limits the application in engineering materials [1–3]. Therefore, the toughening modification of EP has become the hotspot of the current research.

Due to the superiorities of high reactivity and being renewable, lignin is considered to have enormous potential in material modification and thus has attracted particular attention [4, 5]. However, lignin as a powder modifier can easily agglomerate in the matrix resin resulting in poor interfacial adhesion. To solve the above problems, an overwhelming number of studies have focused on the chemical modification of lignin to toughen epoxy resin.

Wang et al. [6] provided a two-step approach to synthesizing epoxide demethylated lignin modified the epoxy resin to acquire excellent tensile strength and elongation at break consequently. The aromatic structure and polar groups of lignin also improve the thermal stability of composites. Similar findings had been reported by Liu et al. [7], who synthesized carboxylic acid-functionalized alkali lignin (AL–COOH) and integrated it with anhydride-cured epoxy networks. Without sacrificing its tensile modulus and strength, they found the epoxy matrix could be significantly toughened when the system contained 1 wt% AL–COOH. However, the elongation at the break of the composites decreased with the increase of AL–COOH content. They considered that the rigid AL–COOH could not adapt to the same strain as the epoxy matrix during the tensile process.

This study designed and synthesized a novel liquid bio-based polyester polyol (LLP) with flexible long chains by corn straw lignin using a very simple one-step method. Different from the previous ways, such as adding rubber particles [8, 9], thermoplastic elastomers [10, 11], interpenetrating networks (IPNs) [12], flexible curing agents [13], LLP derived from biomass resources is low-cost, simple to prepare and easier compatible with resin. Consequently, this toughening strategy gave EP composites a bright future in the development of casting or potting materials.

**Materials and Methods**

**Materials**

Corn straw lignin with an average particle size of 11 μm, a purity of 94.8%, and a phenolic hydroxyl content of 12.9% was provided by Longli Biotechnology Co., Ltd. (Shandong, China). The lignin was kept in a vacuum oven at 60 °C for three days to remove the moisture before using it. Epoxy resin (E-54) was bought from Nantong Xingchen Synthetic Materials Co., Ltd. (Jiangsu, China). A low-molecular-weight polyamine curing agent (TY-200) was purchased from Yanhai Chemical Co., Ltd. (Tianjin, China), and its amine value was 230 ~ 260 mgKOH/g. Ethylene glycol, neopentyl glycol, and sebacic acid were supplied by Sinopharm-Group Chemical Reagent Co., Ltd. (China). Antimony trioxide (Sb₂O₃) was purchased from Zhanyun Chemical Co., Ltd (Shanghai, China).

**Synthesis of LLP**

Lignin, as a polyl, was successively added into a four-port flask with ethylene glycol, neopentyl glycol and sebacic acid. Wherein, the weight ratio of lignin to ethylene glycol was 1: 1. The molar ratio of ethylene glycol, neopentyl glycol and sebacic acid added was 1: 3: 4. All the raw materials were heated to completely melt by an electric heating sleeve. The specific process was carried out as follows. At pre-polycondensation, the system was heated to 140 °C for 1 h. Then, segmented polymerization occurred from 150 to 250 °C for 5 h. In the post-polycondensation stage, the temperature of the system was reduced to 100 °C, and the reaction continued for 2 h in the presence of the Sb₂O₃ catalyst to increase the reaction rate [14, 15]. The whole polymerization needed to be carried out under reduced pressure (vacuum gradually increased to 0.08 Mpa) and nitrogen protection in order to avoid the material being subjected to long periods of high-temperature oxidation and get rid of by-products in time. The screening and optimization of the synthetic process of LLP are shown in the Supplementary Material.

**Preparation of LLP/EP Composites**

The E-54, TY-200, and the dehydrated LLP were blended (E-54: TY-200 = 1: 1 wt%) and stirred evenly with a glass rod, and rotated in a vacuum defoamer for 5 min to remove bubbles. The viscous mixture was slowly cast into the polytetrafluoroethylene (PTFE) mold and then placed in an oven, cured under a curing condition of 50 °C/3 h + 120 °C/2 h, as shown in Scheme 1. As the addition of LLP increased from 0 to 5%, 10%, 15% and 20%, the epoxy resin composites toughened by LLP were named 0%-LLP/EP, 5%-LLP/EP, 10%-LLP/EP, 15%-LLP/EP, and 20%-LLP/EP, respectively.

**Characterizations**

**Viscosity Test of LLP**

The rotational viscometer (NDJ-5 s) was used to determine the viscosity and flow behavior of LLP. According to its approximate viscosity, the appropriate rotor size and speed were chosen and tested in parallel three times.
Measurement of acid value and hydroxyl value of LLP

The acid value of lignin-based polyester polyols was obtained according to the HG/T 2708–95. The calculation Eq. (1) is as follows:

\[ X_1 = \frac{(V - V_0)c \times 56.11}{m} \]  

The hydroxyl value of lignin-based polyester polyol was measured according to the HG/T 2709–95. The calculation Eq. (2) is as follows:

\[ X_2 = \frac{(V - V_0)c \times 56.11}{m} + X_1 \]

\( X_1 \)— the acid value (mg KOH/g); \( X_2 \)— the hydroxyl value (mg KOH/g); \( V \)— the consumption of KOH standard titration solution when titrating sample (ml); \( V_0 \)— the consumption of KOH standard titration solution in blank test (ml); \( c \)— the concentration of KOH standard titration solution (mol/L); \( m \)— the weight of the sample (g).

Fourier infrared spectroscopic analysis (FTIR)

The chemical analysis of corn straw lignin and liquid lignin polyester polyol (LLP) was appraised by FTIR spectrometer (TENSOR II FT-IR, BRUKER) coupled with an attenuated total reflectance (ATR) mode. Each sample was acquired in the 4000–400 cm\(^{-1}\) spectral range with a scanning resolution of 4 cm\(^{-1}\).

Mechanical Property Test

The bending test was gone through a universal microcomputer-controlled testing machine (CMT-5504) at 25 °C equipped with a 5 kN of a load cell. The impact strength of unnotched specimens was performed by a pendulum impact testing machine (XJC-25Z) according to GB/T1043.1–2008. Both experimental figures were gotten from an average value of 6 specimens.

Dynamic Thermomechanical Analysis (DMA)

Dynamic thermomechanical analysis (DMA) which is used to assess the storage modulus (\(E'\)) and the tan \(\delta\) value was performed on a NETZSCH DMA 242E analyzer from –30 to 160 °C under the condition of a three-point bending mode. It was determined upon heating each sample at a heating rate of 5 °C/min at the frequency of 1 Hz.

Thermal Gravimetric Analysis (TGA)

The thermal stability of the cured epoxy resin with different LLP was investigated through a thermogravimetric analyzer (Q Series-TGA Q50). Each sample (about 8 mg) was placed...
in a standard Al$_2$O$_3$ crucible and heated from 25 to 600 °C at a heating rate of 10 °C/min under an N$_2$ flow of 20 mL/min. All the thermal degradation parameters were calculated in the analysis software.

**Scanning Electron Microscope (SEM)**

The morphology of cured epoxy resin was observed via SEM (Apreo, Thermo Scientific). Cross-sections of the samples were made by cryo-fracture using liquid nitrogen and put into an airtight dryer. Prior to imaging, each sample was coated with Pt and tested at an accelerating voltage of 5 kV.

**Results and Discussion**

**Characterization of LLP**

Compared with the original lignin, the hydroxyl characteristic peak at 3450 cm$^{-1}$ and the conjugated carbonyl peak at 1650 cm$^{-1}$ disappeared, while the ester characteristic peak of LLP appeared at 1732 cm$^{-1}$. It can be seen from Fig. 1 that lignin participates in the polycondensation reaction as an alcohol compound.

Various parameters of the LLP are listed in Table 1. The low viscosity LLP prepared in this experiment will not cause the viscosity of the system to increase sharply. It is convenient for the subsequent experimental manipulation. Both acid value and hydroxyl value are in a suitable range, which will make a good interaction between LLP and matrix resin.

**Mechanical Properties of EP Composites**

The bending strength of the cured EP with different amounts of LLP is shown in Fig. 2a. The maximum value of ca.114 Mpa was obtained when the LLP amounted to 10%. Compared with pristine EP, it increased by ca.5.25%. With the persistent addition of LLP, the bending property of composites decreased slightly after reaching the peak but still maintained close to the original level. This result shows when LLP accounts for a low proportion in the epoxy resin system (the mass fraction is less than 15%), the flexible segment in its structure does not reduce the yield deformation ability of cured epoxy resin. Regarding the improvement of bending strength, it is believed that the alcohol hydroxyl groups contained in the LLP participate in the curing reaction of epoxy resin, which promotes the deepening of crosslinking degree. On the other hand, hydroxyl groups that do not involve in the reaction may also form intermolecular or intramolecular hydrogen bonds. They can absorb more energy during deformation, thus further improving their bending resistance. The impact strength of the epoxy resin is an important index to determine its toughness. As can be seen from Fig. 2b, in contrast to the unmodified epoxy resin (40.34 kJ/m$^2$), the impact strength of the cured epoxy resin modified by LLP could be significantly improved. The maximum impact strength reached 51.29 kJ/m$^2$ which got an increase of about 27%. It means that the addition of an appropriate amount of liquid polyester polyol can play an important role in toughening the matrix resin. Since the LLP can be well dissolved in the epoxy resin, the flexible chains in its structure increase the free volume in the three-dimensional network. When the resin was impacted by an external force, the movement of the molecular chain was easier [16].

**Micromorphology**

Figure 2c showed the fractural cross-sectional SEM images of 0%-LLP/EP, 10%-LLP/EP and 20%-LLP/EP, respectively. When the amount of LLP was no more than 10%, its impact cross-section merely showed sparse wrinkles. It could also be seen from the figure of 10%-LLP/EP that a large number of crazing areas and sidestep-like gullies occurred inside the EP. The toughening mechanism of LLP can be fully explained according to the theory of craze and shear ribbon proposed by Bucknall et al. [17]. In our system, LLP acted as the core of stress concentration to induce plenty of crazes and shear ribbons. Besides, the flexible long chain of LLP

| Sample | Viscosity at 25 °C (mPa·s) | Hydroxyl Value (mg/g) | Acid Value (mg/g) |
|-------|--------------------------|----------------------|------------------|
| LLP   | 22.7~23.4                | 142~145              | 0.25~0.4         |

![Fig. 1 FTIR spectra of Lignin and LLP](image-url)

Table 1 General properties of LLP

![Table 1 General properties of LLP](table-url)
could control the development of crazes and stop them from changing into destructive cracks. The stress field at the tip of the striation induced the generation of a shear band, and the shear ribbon also prevented the further development of the striation. The generation and spread of crazes or shear ribbons are needed to consume a large amount of energy, thus significantly improving the impact strength of materials. As the LLP continued to add, the microphase separation structure or even over-plasticizing phenomenon appeared in the composite materials [18]. At this point, the impact strength of the composites tended to decrease, which was consistent with the above mechanical analysis.

**Thermal Analysis of EP Composites**

Figure 3a and b showed the curves of storage modulus and loss factor with temperature obtained by DMA analysis to characterize the viscoelasticity and glass transition
temperature ($T_g$) range of LLP/EP composites. In Fig. 3a, the storage modulus of LLP/EP composites was higher than that of pure epoxy resin. The increase in storage modulus predicts better elasticity of the material after modification with its greater ability to store elastic deformation energy. The ability of the epoxy composites to revert to original deformation was also stronger when the stress was removed. All the curves in Fig. 3b were unimodal, indicating that LLP had good compatibility with matrix resin. With the increase of LLP addition, the maximum value of tan δ moved to the low-temperature region in a small range [19]. As shown in Fig. 3c and d, a significant thermal decomposition hysteresis was observed by the TGA test. It indicated that the thermal stability of EP composites toughened by LLP was well maintained. This was all attributed to the special chemical structure of lignin [20]. Based on the above analysis, the comprehensive analysis showed that the EP composites exhibited optimal performance in all aspects when the amount of LLP was up to 10%.

**Conclusions**

In this work, we corroborated the approach of epoxy resin composites with advantageous toughness by using liquid lignin-based polyester polyol (LLP) with flexible long chains as the toughening agent. SEM images confirmed that the fracture cross-section of 10%-LLP/EP composite was rough, then craze and shear ribbon was obvious. The mechanical test results suggested that the impact strength of the epoxy resin composite with 10wt% LLP was 27% higher than the untoughened epoxy resin. Also,
its bending strength was increased by about 5 MPa. The results of DMA showed that the storage modulus of the epoxy composites increased after adding LLP. The 10% LLP/EP had the highest dynamic elastic modulus and the best toughening effect. Furthermore, both DMA and TGA results indicated that the glass transition temperature, as well as the thermal properties of LLP/EP composites, did not decrease significantly when the addition of LLP was 10wt%. This paper provides a novel idea for the utilization of corn straw lignin, in which the epoxy resin composite presented outstanding performances at a lower cost.

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Author Contribution XS: applies oneself to the investigation. LX: applies oneself to the conceptualization and writing-review & editing.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Zhang YT, Pang H, Wei DD et al (2019) Preparation and characterization of chemical grouting derived from lignin epoxy resin. Eur Polym J. https://doi.org/10.1016/j.eurpolymj.2019.05.003
2. Zhan ZS, Zhang YL, Zhang Y (2019) Improving the flame retardancy and electrical conductivity of epoxy resin composites by multifunctional phosphorus-containing polyaniline. Mater Lett. https://doi.org/10.1016/j.matlet.2019.127092
3. Zhang JH, Chen SY, Qin B et al (2019) Preparation of hyperbranched polymeric ionic liquids for epoxy resin with simultaneous improvement of strength and toughness. Polymer. https://doi.org/10.1016/j.polymer.2019.01.003
4. Ralph J, Lapierre C, Boerjan W (2019) Lignin structure and its engineering. Cur Opin Biotechnol. https://doi.org/10.1016/j.copbio.2019.02.019
5. Chong TY, Law MC, Chan YS (2021) The potentials of corn waste lignocellulosic fibre as an improved reinforced bioplastic composites. J Polym Environ. https://doi.org/10.1007/s10924-020-01888-4
6. Wang F, Kua J, Pan HS et al (2018) Study on the demethylation of enzymatic hydrolysis lignin and the properties of lignin-epoxy resin blends. Wood Sci Technol. https://doi.org/10.1007/s00226-018-1024-z
7. Liu WS, Zhou R, Goh HL et al (2014) From waste to functional additive: toughening epoxy resin with lignin. ACS Appl Mater Inter. https://doi.org/10.1021/ami500642n
8. Tsang WL, Taylor AC (2019) Fracture and toughening mechanisms of silica- and core-shell rubber-toughened epoxy at ambient and low temperature. J Mater Sci. https://doi.org/10.1007/s10853-019-03893-y
9. Filippo MD, Alessì S, Palmese G et al (2020) Electrospun rubber/thermoplastic hybrid nanofibers for localized toughening effects in epoxy resins. J Appl Polym Sci. https://doi.org/10.1002/app.48501
10. Feng LB, He X, Zhang YP et al (2021) Triple roles of thermoplastic polyurethane in toughening, accelerating and enhancing self-healing performance of thermo-reversible epoxy resins. J Polym Environ. https://doi.org/10.1007/s10924-020-01923-4
11. Feghali E, van de Pas Daniel J, Parrott AJ et al (2020) Biobased epoxy thermoset polymers from depolymerized native hardwood lignin. ACS Macro Lett. https://doi.org/10.1021/acsmacrolett.0c00424
12. Lee SE, Jeong E, Lee MY et al (2016) Improvement of the mechanical and thermal properties of polyethersulfone-modified epoxy composites. J Ind Eng Chem. https://doi.org/10.1016/j.jiec.2015.09.022
13. Hu K, Bao LX, Chen XF et al (2018) Synthesis of castor oil-derived decanediamide as a novel flexible asphalt-modified epoxy resin curing agent. Adv Polym Tech. https://doi.org/10.1002/adv.21760
14. Sun N, Lai YY, Xu YS et al (2020) Preparations and properties of polyurethane adhesives modified by corn straw lignin. BioRes. https://doi.org/10.15376/biores.15.2.3970-3983
15. Sun N, Di MW, Liu Y (2021) Lignin-containing polyurethane elastomers with enhanced mechanical properties via hydrogen bond interactions. Int J Biol Macromol. https://doi.org/10.1016/j.ijbiomac.2021.06.038
16. Zavareh S, Samandari G (2014) Polyethylene glycol as an epoxy modifier with extremely high toughening effect: formation of nanoblend morphology. Polym Eng Sci. https://doi.org/10.1002/pen.23733
17. Bucknall CB, Smith RR (1965) Stress-whitening in high-impact polystyrenes. Polymer. https://doi.org/10.1016/0032-3861(65)90028-5
18. Liang X, Li XI, Tang Y et al (2021) Hyperbranched epoxy resin-grafted graphene oxide for efficient and all-purpose epoxy resin modification. J Colloid Interface Sci. https://doi.org/10.1016/j.jcis.2021.12.068
19. Yin XY, Xie ZP, Liu Q et al (2021) Synergistic toughening of epoxy resin by CTBN and CM-β-CD. J Appl Polym Sci. https://doi.org/10.1002/app.51248
20. Li JM, Zhang ZY, Zhang Y et al (2021) Synergistic effect of lignin and ethylene glycol crosslinked epoxy resin on enhancing thermal, mechanical and shape memory performance. Int J Biol Macromol. https://doi.org/10.1016/j.ijbiomac.2021.10.035

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