



Performance of UV curable lignin based epoxy acrylate coatings

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ABSTRACT

In this work, lignin based epoxy acrylate (LBEA) oligomer with various percentage of lignin was in situ synthesized with epoxy and acrylic acid. The first step was the etherification between lignin and epoxy to produce lignin based epoxy (LBE), and the second step was the esterification between LBE and acrylic acid to synthesize LBEA. Epoxy value and acid value were measured to determine the reaction conditions of the two steps, respectively. The structure of prepared LBEA was confirmed by Fourier infrared spectroscopy (FTIR) characterization. LBEA coatings were prepared through ultraviolet radiation curing method. The gel content, chemical resistance, mechanical properties and thermal properties of coatings were investigated. It was found that the mechanical properties and chemical resistance were much improved than those of epoxy acrylate (EA) resin with the addition of lignin. Thus, lignin was proved to be a new promising biomaterial which could be applied in biobased EA coatings.

1. Introduction

Ultraviolet radiation (UV) curing is recognized as the most effective method to transform liquid oligomer into a three-dimensional cross-linking solid polymeric material and no evaporative volatile solvents applied or produced as compared to the conventional materials [1–3]. UV-curing coating has been popular for decades because of its lower energy consumption, less environmental pollution, lower process costs, excellent film quality, fast reaction rates, solvent-free and high efficiency in production. Due to the foreseeable exhaustion of fossil feedstock and the increasing environmental concerns, the exploitation of biorenewable resources in UV-curable coatings provides a “green + green” solution to the current coating industry [4–8].

Epoxy acrylate (EA) resin is a kind of resin for UV curing coatings because of its excellent performance, such as outstanding adhesion, flexibility, hardness and chemical resistance [9]. Epoxy acrylate is produced by introducing vinyl ester groups and carbon–carbon double bonds into the epoxy resin [4], and can be cured with radical photoinitiators. The application of EA resins is limited in the light of its disadvantages, such as poor light aging resistance. Currently, in order to improve the performance and widen the application of EA resins, a variety of monomers and oligomers have already been explored to modify EA resins. The active epoxide or hydroxyl groups of EA can be used as active sites to react with other functional monomers [5].

With the increasing attention to environmental issue, people have begun to pay more attention to the application of natural polymers. Lignin is the second most sufficient natural macromolecule next to cellulose [10,11]. There are plenty of aromatic units in the lignin structure. It is also a kind of macromolecular compounds with high reactivity because of its ample functional groups [12]. Due to its advantages, such as abundant sources, low cost, biodegradability and renewability, lignin has received extensive attention [13]. Diane Schorr [14], José C. del Río [15] and other researchers have analyzed and characterized the structure of lignin in detail. However, the highly complex amorphous three-dimensional structure of lignin in which abundant aromatic rings link together through C–O–C and C–C bonds has not been completely elucidated although the primary structure has been well depicted [16–19]. So far, only small amount of lignin and its derivatives has been applied [20–22].

Chao [23] applied alkali lignin to prepare waterborne UV-curable polyurethane. They took the advantage of the phenol group on lignin to replace the polyol. The results showed that proper dosage of the lignin could change the micro-phase separation structure, and could improve the mechanical properties of the product. Tuan [24] used anhydrides to modify sodium lignosulfonate and applied the modified lignin to react with glycerol diglycidyl ether and ethylene glycol diglycidyl ether to synthesize bio-based epoxy resins. Lignin has also been applied to prepare lignin based composite materials [25].

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So far, there have been seldom studies to insert lignin into EA to prepare biobased UV-curable coatings, whose chemical resistance and mechanical properties could be much improved. In this paper, unpurified commercial organosolv lignin was in-situ synthesized with epoxy to get lignin based epoxy, and then react further with acrylic acid to produce lignin based epoxy acrylate (LBEA) oligomer, which was UV-cured into membrane coatings thereafter. The prepared biobased coatings were characterized in detail, and were proved to be promising in coating industry.

2. Experimental

2.1. Materials

The industrial grade organosolv lignin was received from Jinan Yanghai chemical. Its purity was 88% according to the acid-alkali purification method [26]. The industrial grade Epon827 epoxy resin was from the Shell Oil Company. Hydroquinone was from Aladdin Reagent (Shanghai) (99.0%). Dimethylformamide (DMF) and Acrylate (AA) were from Tianjin Guangfu Chemical with the purity of 99.5% and 99.0%, respectively. Pyridine was received from Tianjin Damao Chemical Reagent (99.5%). The industrial grade Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO) and Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (819) was from Nanjing Wali chemical, the industrial grade Isobornyl acrylate (IBOA) and Tripropylene Glycol Diacrylate (TPGDA) was from Nanjing Jiazhong chemical.

2.2. Synthesis of LBEA

The synthesis of LBEA was performed through two steps. In the first step, LBE was prepared by etherification reaction between lignin and epoxy with different percentages (0, 5, 10, 15, 20 and 25%, w/w) of lignin in the presence of DMF at the temperature of 80 °C ~ 100 °C. The reaction was carried out in 3-necked flask reaction kettle equipped with mechanical stirrer and water condenser for 1 ~ 4 h to obtain the LBE. The reaction process of the first step is shown in Table 1. The reaction route is shown in Scheme 1.

In the second step, LBEA was prepared by esterification reaction between LBE and acrylate with the presence of 0.2% hydroquinone and 0.2% pyridine at 80 °C. The required amount of acrylate was dropped in during a period of 30 min with stirring. The reaction was carried out for 0.5 ~ 1.5 h to obtain the LBEA, and the reaction time is shown in Table 1. The reaction route is shown in Scheme 2.

2.3. Curing of LBEA

The obtained LBEA were blended with photo initiator 819 (2.5 wt%), TPO (7.5 wt%), defoaming agent (5 wt%), flattening agent (5 wt%), diluent IBOA (15 wt%), TPGDA (15 wt%) at ambient temperature, and the mixture was stirred for several minutes to ensure a complete homogeneous mixing.

Table 1
Reaction conditions to prepare LBE and LBEA with different lignin content.

Sample	LBE		LBEA
	Reaction time at 80 °C (min)	Reaction time at 100 °C (min)	Reaction time at 80 °C (min)
EA	—	—	355
LBEA-5	120	125	90
LBEA-10	100	75	70
LBEA-15	100	70	55
LBEA-20	100	—	40
LBEA-25	60	—	35

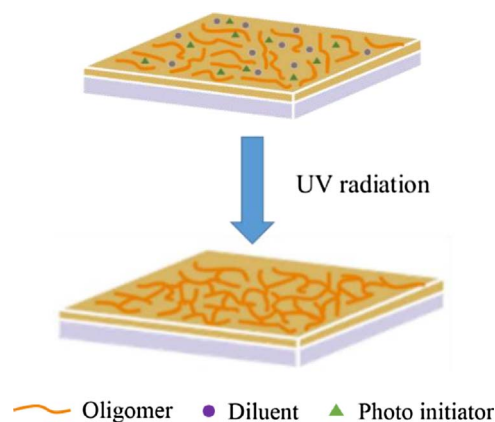


Fig. 1. Curing schematic diagram of LBEA.

Before coating, the tinplate substrates were polished with abrasive paper and rinsed with acetone and ethanol, and dried in the oven at 80 °C. The LBEA oligomers were casted on a tinplate with a wiper. The thickness of the coating membrane was about 20 μm.

UV chamber (UVLED light curing machine, Shanghai Maixin photoelectricity technology) was used to cure the membrane. The curing time was 60 s and the wavelength range of 300–545 nm was applied. The power of the UV light was 100 W, and the distance between sample and light bulb was 10 cm. Fig. 1 shows the curing process.

2.4. Characterization

The epoxy value of LBE was determined according to Chinese Standard GB/T1677-2008. The epoxy group content of residual epoxy after the reaction was determined by the method of hydrochloric acid-acetone method.

The acid value of the reaction system to synthesize LBEA was determined according to Chinese Standard GB2895-82. The measurement method was KOH-ethanol solution titration method.

The FTIR spectra were recorded using NEXUS-670 (Nicolet, USA) equipped with an attenuated total reflectance (ATR) accessory. The resolution of the spectra recorded was 4 cm⁻¹. 256 scans were performed for each sample in the range of 4000–400 cm⁻¹ at room temperature.

Gel content was determined by the following equation.

$$\text{Gel content (\%)} = (m_2/m_1) \times 100\%$$

where m_1 is the weight of the cured film sample; m_2 is the residual weight of the cured film. The cured film was immersed in a beaker filled with acetone, and was kept for 48 h. The film was then dried at 60 °C until its weight was constant to get the weight m_2 .

Thermogravimetric analysis (TGA) was performed on a TGA/DSC1 STAR^e System over the temperature range of 50–600 °C under the nitrogen atmosphere with a heating rate of 10 °C/min. The weight of samples were 5–10 mg.

The pencil hardness was measured using a Pencil coating hardness tester (Shanghai PuShen chemical machinery, China) according to the Chinese Standard GB/T 6379-1996. The film flexibility was measured according to the Chinese Standard GB/T 1731-93 with the coating film iron panels. The adhesion was measured according to the Chinese Standard GB/T 9286-1998 using the lattice notch method (Shanghai PuShen chemical machinery, China).

The chemical resistance of UV curing coatings was studied by immersing the cured membrane into 5% HCl, 5% NaOH solutions and ethyl alcohol for a period of time, respectively. The appearance of film was observed and recorded.

A scanning electron microscope (JSM5600, Japan) was employed to observe the morphology of the lignin powder and the fractured surface

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