Composites Communications 10 (2018) 52–56

Contents lists available at ScienceDirect

Composites Communications

journal homepage: www.elsevier.com/locate/coco

Improved performance of dual-cured organosolv lignin-based epoxy acrylate coatings

Ru Yan[a], Yangyang Liu[a], Baijun Liu[b], Yumei Zhang[a], Qi Zhao[a], Zhaoyan Sun[c], Wei Hu[a,*], Niaona Zhang[a,*]

[a] College of Chemical Engineering, Changchun University of Technology, 2055 Yan'an Street, Changchun 130012, PR China
[b] College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, PR China
[c] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China.

ARTICLE INFO

Keywords:
Organosolv lignin
epoxy acrylate
UV-cured
dual-cured
coatings

ABSTRACT

Organosolv lignin (OL) was used to synthesize organosolv-lignin-based epoxy acrylate (OLBEA) coatings. The reaction process was determined by epoxy and acid values. OLBEA coatings were prepared by dual (Ultraviolet (UV) and thermal) curing to achieve a deep and complete process. The structures of lignin-based epoxy (OLBE) and OLBEA were characterized by Fourier transform infrared spectroscopy (FTIR). The properties of the dual- and UV-cured coatings were then compared by measuring gel content and mechanical properties. Results revealed that the dual-cured films had higher cross-linking degree and better mechanical properties than the UV-cured films. The chemical resistance of the dual-cured coatings was also examined. The properties of OLBEA coatings obtained by dual curing were shown to be excellent and promising for wide-ranging applications.

1. Introduction

Lignin is a three-dimensional phenylpropanoid polyphenol macromolecule in which phenylpropane units are connected to p-coumaryl, coniferyl, or sinapyl alcohol units by ether bonds [1]. It is one of the most abundant renewable natural polymers composed of aromatic rings, and it is expected to be an excellent raw material that is an excellent alternative to petroleum-derived chemicals [2]. In recent decades, the applications of lignin to prepare coatings, composites, and prepolymer components in polymeric systems have become a research hotspot in the field of bioproducts.

At present, the development of coatings tends to be ecologically friendly and healthy [3,4]. Many researchers utilized renewable lignin to prepare raw materials of coatings, such as polyurethane and waterborne polyurethane. The addition of lignin into PU can not only reduce the cost, improve the performance, but also protect the environment. Shahabadi applied the lignin to modify graphene [5]. Then, the modified graphene was added into the waterborne polyurethane to produce self-healable, UV-resistant, and electrically conductive nanocomposite Coatings. Li applied lignin to prepare polyurethane. For polyurethane with 40% of lignin, the Young's modulus, tensile strength, and strain at break reached 176.4 MPa, 33.0 MPa, and 1394%, respectively [6].

The epoxy acrylate (EA) backbone endows excellent toughness, flexibility, and chemical resistance to films through carbon-carbon and ether bonds. And EA has thus been widely applied in UV-cured systems [7]. Currently, UV-cured EA resin is one of the most extensively applied commercial materials for printing inks, anticorrosive coatings, printable coatings, sealant, electronic components, and optical devices [8].

UV-curing technology is attracting extensive attention because of its advantages of energy conservation, low costs, and solvent-free formulation curing at ambient temperature [9]. This technology applies UV light to induce polymerization, which can convert a liquid, low-viscosity oligomer into a cross-linking network [10]. The obtained coatings have very good physical, mechanical, and chemical properties because of the highly cross-linked network produced by UV curing. However, UV-cured coatings still have problematic aspects. For pigmented systems, pigment particles usually absorb part of the UV light and affect the penetration of photons through deep layers, which leads to decreased cross-linking density and poor physical and mechanical properties of cured films [9]. Thus, some researchers have attempted to solve the problem by modifying photoinitiator systems, formulations, and curing methods. Zhang [11] successfully prepared electrically conductive adhesives with both excellent mechanical property and electrical conductivity through dual-curing methods, i.e., UV-thermal treatments.

Studies on EA in-situ synthesized with lignin as a monomer are very few. In the present study, organosolv lignin was chemically added into EA as a reinforcing agent. Organosolv lignin based EA (OLBEA) with

* Corresponding authors.
E-mail address: hw7527@sina.com (W. Hu).

https://doi.org/10.1016/j.coco.2018.04.006
Received 3 January 2018; Received in revised form 12 April 2018; Accepted 17 April 2018

Table 1
The reaction conditions to prepare OLBE and OLBEA.

Sample	OLBE		OLBEA
	Reaction time at 80 °C (min)	Reaction time at 100 °C (min)	Reaction time at 80 °C (min)
EA	–	–	640
OLBEA-5	120	300	120
OLBEA-10	120	105	95
OLBEA-15	120	80	80
OLBEA-20	140	–	70
OLBEA-25	50	–	60

different content of organosolv lignin was initially prepared by etherification between organosolv lignin and epoxy to produce organosolv lignin based epoxy (OLBE), followed by the esterification between OLBE and acrylate. Finally, the OLBEA coatings were obtained by UV-thermal dual curing. The properties of the coatings were evaluated in detail.

2. Materials and methods

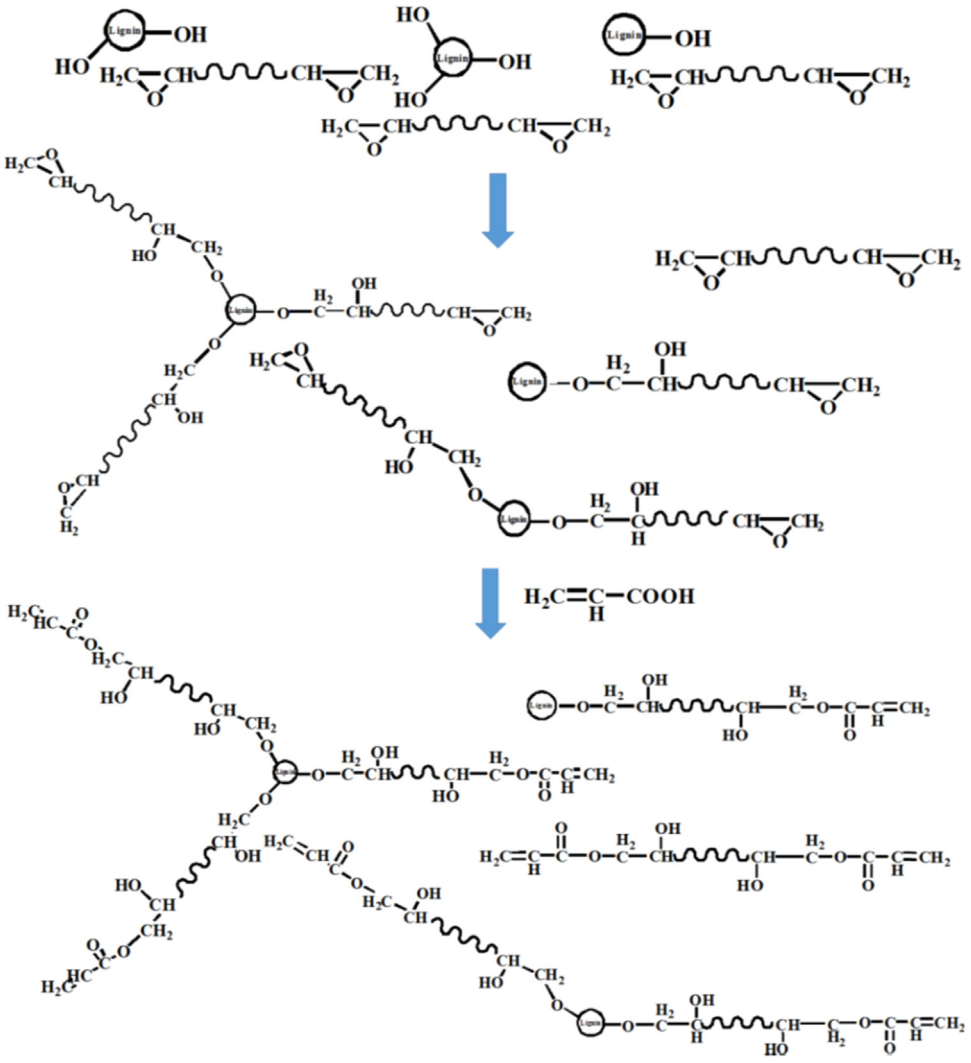
2.1. Materials

The industrial grade organosolv lignin was purchased from Jinan Yanghai chemical. Its purity was 88% according to acid-alkali purification method. The industrial grade Epon827 epoxy resin was obtained from shell oil company; hydroquinone was supplied by Aladdin reagent (Shanghai) (99.0%); dimethylformamide (DMF) and acrylate (AA) was obtained from Recovery of Tianjin Guangfu chemical with the purity of 99.5% and 99.0%, respectively. Pyridine was purchased from Tianjin Damao chemical reagent (99.5%).

2.2. Synthesis of OLBEA

The synthesis of OLBEA can be divided into two steps. The first was the synthesis of etherification by reaction of organosolv lignin with different percentages (0, 5, 10, 15, 20 and 25%, w/w) and epoxy in the presence of DMF to prepare OLBE. The mixture was placed into 3-neck flask, which was equipped with mechanical stirrer and water condenser. The reaction mixture was kept at 80 °C~100 °C for 1~7 h. The reaction conditions of the first step are shown in Table 1. The reaction route is shown in Scheme 1.

The second step was the synthesis of OLBEA by the esterification between OLBE and acrylate in the presence of 0.2% hydroquinone and 0.2% pyridine. The required amount of acrylate was dropped in over a period of 30 minutes with stirring. The reaction mixture was kept at 80 °C for 1~10 h to obtain the OLBEA. The reaction conditions are shown in Table 1. The reaction route is shown in Scheme 1.



Scheme 1. The synthesis route of OLBE and OLBEA.