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Preparation and cure kinetics of epoxy with nanodiamond modified with liquid crystalline epoxy

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ABSTRACT

A novel epoxy composite with liquid crystalline epoxy resin modified nanodiamond (ND-LCER) was prepared by grafting diglycidyl ether of 4,4′-bisphenol (DGEBP) monomers onto the surface of acid treated nanodiamond (ND-COOH). Untreated nanodiamond (UND), ND-COOH and ND-LCER were composited with epoxy/4,4′-diamino diphenyl sulfone (DDS) in various weight ratios, respectively. The cure behavior of the prepared composite systems was investigated with dynamic differential scanning calorimetry (DSC) technology at different heating rates. The NDs exhibited acceleration effects on the curing reaction with increase of content amounts, which might attribute to the special structure of the nanodiamond (ND) particles itself and the functional groups of the ND. The modified ND particles showed the lowest activation energy value due to the diminution to the diffusion control process caused by liquid crystalline epoxy resins molecules. The two-parameter (m, n) autocatalytic model of Sestak-Berggren based on the Malek method is in-line with the epoxy/ND composites.

1. Introduction

Nanodiamond (ND) has attracted much attention in recent researches. ND is an outstanding nanoparticle which not only has the advantage of nanoparticle, like high specific surface area, high active surface, quantum effects, small size effect, but also expresses outstanding properties, like remarkable thermal condition, distinguished optical performance. Besides, ND is non-toxic, which makes ND well suit for biomedical applications [1–8]. ND particle was first produced by detonation technology in 1960s by Russian scientists [9]. From the early of 21st century, ND has shown great application in the areas of nanocomposites, biomedicines, polishing grinding and many others since we can get the particle much easier [10–12].

Many studies have shown that ND has significant positive effects on epoxy nanocomposites [13,14]. Guo et al. [15] reported that the storage modulus of epoxy composites with 0.5 wt% amine functioned ND is higher than that with 5 wt% raw ND and the storage modulus with only 1 wt% modified ND loading leads to 105% increase compared with that of neat epoxy. Zhai et al. [16] discovered that with 0.3 wt% of filled ND, the Vicker's hardness, tensile strength and tensile modulus of the ND/epoxy nanocomposites were 24.7%, 52.7% and 54.2% higher than those of pure epoxy, respectively.

Liquid crystalline epoxy resins (LCREs) is an important branch of thermosetting polymer which shows the well-aligned of liquid crystal structures and the three dimensional crosslinking networks with outstanding heat stability and high strength. The rigid rod epoxy monomers exhibit excellent properties of high modulus, high glass transition temperature and superior toughness [17–22]. As a consequence, many liquid crystalline epoxy monomers or polymers were synthesized, characterized and applied to acquire composite materials.

The cure kinetics of thermosetting polymer nanocomposites is very important to explore the curing behavior and thus get the optimal curing process to reach the desired properties for the resulted structures. The research work dedicated to the mechanical, thermal properties and curing kinetic of epoxy/ND, nanoparticle/LCREs and epoxy/LCREs composites have increasingly appeared in recent years [21,23–27]. The dispersion of nanoparticle in matrix is related with the surface functionalization, and the surface functionalization which is essential to achieve nanocomposites with desired structure and properties. The influence of nanoparticles on the cure kinetic of epoxy resins have been addressed [28–30]. It is reported that both the content and the surface functionalizing groups of multi-walled carbon nanotubes had a significant influence on reaction rate and the activation energy. The accelerating effect of functionalized CNTs also antedates the vitrification and turns the reaction to diffusion control driven, and the cure kinetics have been deeply influenced by the type, content, and

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surface of the nanoparticles [31,32].

However, to the best of our knowledge, there are few reports on LCREs modified ND and epoxy/ND-LCREs nanocomposite has not been reported, either. We are interested in conducting further research about the microstructure with respect to the epoxy/ND-LCREs nanocomposite.

In this study, we investigated the cure kinetics of epoxy resins composited with LCER modified ND (ND-LCER) by using dynamic DSC, and the iso-conversional method was utilized to analyze the process of curing reaction [33].

2. Experimental

2.1. Material

The untreated ND (manufactured by detonation technique, purity > 95%) with average diameter of 50 nm used in this study were purchased from Henan Hengxiang Diamond Abrasive, Zhengzhou, China. Sulfuric acid (H_2SO_4, 95%–98%) and nitric acid (HNO_3, 65%–68%) were obtained from Tianjin Hongyan Chemical Co., Tianjin, China. 4,4′-Dihydroxybiphenyl (98%) and 4,4′-diaminodiphenyl sulfone (DDS, 98%) were supplied by Zhengzhou Alfachem Co. Ltd., Zhengzhou, China. Epichlorohydrin (AR) and Tetrabutylammonium bromide were bought from Tianjin Chemate Chemical Technology Co. Ltd., Tianjin, China. Benzyltrimethylammonium chloride and dimethyl sulfoxide-d_6 (DMSO-d_6) were purchased from Shanghai Titan Scientific Co. Ltd., Shanghai, China. Sodium hydroxide (99%). Methylbenzene and acetone were purchased from Tianjin Fu Chen Chemical Reagent Factory, Tianjin, China. N,N-Dimethylformamide (DMF) and dimethylcarbinol were bought from Tianjin Fengchuan Chemical Reagent Co. Ltd., Tianjin, China. The epoxy resin E-51, with epoxy equivalent weight of 184–200 g/eq, was supplied by Nantong Xingchen Synthetic Material Co. Ltd., Nantong, China.

2.2. Synthesis of DGEBP

The synthetic procedure of DGEBP was based on the previous report by Li et al. [34]. 4,4′-Dihydroxybiphenyl (0.05 mol), epichlorohydrin (0.5 mol), dimethylcarbinol (21.2 g) and benzyltrimethyl-ammonium chloride (0.5 mmol) were mixed in a 250 ml three-neck round-bottom flask and the mixture was refluxed for 1 h at 60 °C. Then aqueous sodium hydroxide solution (80 ml, 10 wt%) was added to the flask dropwise over a period of 1 h under reflux. The mixture was stirred for another 2 h at room temperature. The final product was obtained from vacuum filtration and then washed with excessive water and methanol (yield: 13.8 g, 92.6%). IR (KBr, cm^{-1}): 2926, 1607, 1496, 1236, 1041, 817. ^1H NMR (400 MHz, DMSO-d_6, ppm): δ, 7.55 (d, $J = 8.8$ Hz, 4H, CH of biphenyl), 7.02 (d, $J = 8.8$ Hz, 4H, CH of biphenyl), 4.36 (dd, $J_1 = 11.6$ Hz, $J_2 = 2.4$ Hz, 2H, CH_2 of glycidyl), 3.85 (dd, $J_1 = 11.6$ Hz, $J_2 = 6.4$ Hz, 2H, CH_2 of glycidyl), 3.35 (m, 2H, CH_2 of epoxy), 2.85 (dd, $J_1 = 4.8$ Hz, $J_2 = 2.8$ Hz, 2H, CH_2 of epoxy), 2.72 (dd, $J_1 = 4.8$ Hz, $J_2 = 2.8$ Hz, 2H, CH_2 of epoxy). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ, 156.0, 131.1, 125.8, 113.4, 67.5, 48.3, 42.3.

2.3. Preparation of ND-COOH

UND particles were dispersed in the mixture of concentrated sulphuric acid and concentrated nitric acid (volume 3:1). The mixed solution was sonicated at 80 KHz ultrasonic for 2 h and then magnetically stirred at 70 °C for 3 days. The mixture was diluted with lots of water and vacuum filtered. The resulted solid was collected and dried under vacuum for 12 h at 60 °C to obtain the ND-COOH.

2.4. Preparation of ND-LCER

The synthetic route to obtain ND-LCER is shown in Scheme 1. A 100-mL three-necked flask was charged with 0.50 g of ND-COOH and 60 ml of DMF and ultrasonicated for 3 h. DGEBP (1.00 g) and tetrabutylammonium bromide (0.01 g) were added into the flask with stirring and heated at 100 °C under reflux for 1 day. After cooled to room temperature, the final product was vacuum-filtered and washed with excess amounts of DMF which was removed with water. The filtrate solution was vaporized by rotation to make sure no residual of LCER at the bottom. The powder was vacuum dried at 60 °C for a day and labeled as ND-LCER.

2.5. Preparation of epoxy/ND nanocomposites

In acetone 1 wt% of UND was dispersed and ultrasonicated for 1 h. Subsequently, epoxy resin and DDS were added to the mixture with mechanical stirring at room temperature for 20 min. Thereafter, the mixture was exposed to vacuum with magnetic stirring to remove the acetone. The same procedures were used to prepare epoxy composites with ND-COOH (END-COOH, 1 wt%) and ND-LCER. And 1 wt%, 3 wt%, 5 wt% and 7 wt% of ND-LECRs filled epoxy resins were labeled as ENDL-1, ENDL-3, ENDL-5 and ENDL-7, respectively. The samples were stored in a freezer.

2.6. Characterization techniques

Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) were employed to analyze and characterize DGEBP and the surface groups of ND particles. FTIR was recorded with a resolution of 2 cm^{-1} from 400 to 4000 cm^{-1} using a Bruker Vector 22 FTIR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were obtained with a Bruker AV400 nuclear magnetic resonance (NMR) spectrometer at a proton frequency of 400 MHz and 100 MHz, respectively, using deuterated DMSO as solvents. Thermogravimetric analysis (TGA) was carried out on a TA Q600 thermogravimetric analyzer from 50 °C to 1000 °C with a heating rate of 10 °C/min under the nitrogen flow of 100 cm^3/min.

DSC analysis were performed on a DSC214 polyma (NETZSCH) under dynamic conditions. The sample controlled between 5 mg and 8 mg were placed in an aluminum pan and heated up to 380 °C from room temperature at rates of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min, respectively. Nitrogen at a rate of 50 ml/min was used as the purging gas.

3. Result and discussion

3.1. Characterization of monomer and surface groups of ND

The NMR and FTIR analyses were employed to characterize the structure of DGEBP at room temperature. The ^1H NMR and ^{13}C NMR spectra of DGEBP are exhibited in Fig. 1 which proves the structure of DGEBP. As shown in the ^1H NMR, two doublets at 7.55 and 7.02 ppm are assigned to the phenyl protons on the aromatic rings with coupling constant of 8.8 Hz. Two doublets of doublets at 4.36 ppm and 3.85 ppm are attributed to the two protons of methylene adjacent to the epoxy group, respectively. The multiple peak at 3.35 ppm was observed for proton number 2 because of coupling effects with proton number 1 and proton number 3, while two doublets of doublets at 2.85 and 2.72 ppm are assigned to the two methylene protons of the epoxy group. In the ^{13}C NMR spectra the resonances at 156.0, 131.1, 125.8 and 113.4 ppm are attributed to carbons on the phenyl rings with peaks at 67.5, 48.3 and 42.3 ppm for carbons of the glycidyl group. The data of ^{13}C NMR is in line with that of ^1H NMR analysis, which proved the structure of DGEBP.

The FTIR spectra of UND, ND-COOH, ND-LCER and DGEBP are compared in Fig. 2. As seen, the strong absorption peaks at 1607 cm^{-1} and 3006–3063 cm^{-1} are corresponding to C═C and C─H stretching of benzene rings, respectively. The prominent peaks at 817 cm^{-1} and