Reactive and Functional Polymers 131 (2018) 156–163

Contents lists available at ScienceDirect

Reactive and Functional Polymers

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

Copolymerization of mono and difunctional benzoxazine monomers with bio-based phthalonitrile monomer: Curing behaviour, thermal, and mechanical properties

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ARTICLE INFO

Keywords:
Eugenol based phthalonitrile
Benzoxazine
Copolymerization
Thermal properties
Thermomechanical properties

ABSTRACT

The eugenol based phthalonitrile (EPN) monomer was successfully copolymerized with mono and difunctional benzoxazine (P-a and BA-a) monomers *via* concerted catalysis polymerization. The loading of EPN in benzoxazine monomers was varied from 10 to 40 wt% and impacts of loading on thermal, thermomechanical and mechanical properties were studied. The FTIR analysis confirmed that both poly(P-a/EPN) and poly(BA-a/EPN) copolymers can be completely cured without the addition of curing additive. The addition of the bio-based EPN monomer enhanced the curing peak temperatures and reduced the curing reaction enthalpies. Initially, −OH groups were produced from the oxazine ring opening polymerization of benzoxazine and they enhanced the curing of EPN. The thermal stabilities, as well as the stiffness and T_g of the copolymers, were much higher as compared to the neat polymers. Highest values were seen on the 40 wt% loading of EPN monomer in the copolymers. Moreover, the difunctional benzoxazine based copolymer showed higher enhancements in the properties as compared to the mono-functional benzoxazine based copolymer. The decline was seen in the flexural properties as EPN monomer contains the flexible chain in the structure. The morphological changes supported all the claims for the copolymers. The prepared copolymers can be used as a high performance thermosetting resin.

1. Introduction

The rise has been recorded in the research on the bio-based polymers due to the decline in the fossil fuel resources and increased awareness on the environmental pollution. The highest turnaround in the research of biobased polymers has been recorded since the start of 21st century. A significant number of biobased polymers have been synthesized from various sources of the natural materials including furfurylamine, octadecanamide, decanediamine, eugenol, guaiacol, and cardanol [1–3]. The eugenol based phthalonitrile (EPN) and guaiacol based phthalonitrile (GPN) are very high performance phthalonitrile polymers synthesized from the biobased sources [4].

The polybenzoxazine thermosetting resins are considered as an alternative to the conventional phenolic and epoxy thermosets due to their good mechanical properties, high thermal stabilities and glass transition temperatures (T_g), good flame-retardancy and electric insulation, and very low water absorption [5–7]. The benzoxazine precursors (phenols, primary amines, and formaldehyde) are characterized as inexpensive and can be obtained from renewable sources [8]. Moreover, they are cured without using any catalyst or curative *via* the cationic oxazine ring-opening of the corresponding monomer, and form intermolecular and intramolecular hydrogen bonding, and does not release by-products [9]. These resins have been widely applied in the field of electronics and aerospace industries due to their excellent properties [10–12]. However, the application of these resins in various industries can be enhanced by reducing the brittleness and increasing the thermomechanical and thermal properties.

On the other hand, the phthalonitrile (PN) resins are well known for their flame retardancy, high thermal stabilities, lower water absorption, and shielding potential against radiations. Furthermore, the higher melting points (> 200 °C), an initiator for curing, and narrow processing window are the major associated problems of the PN resins [13–16]. The phenolic, organic amines, organic acid, and amine salt are used as the curing initiator for successful curing of PN monomers,

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https://doi.org/10.1016/j.reactfunctpolym.2018.07.022
Received 9 April 2018; Received in revised form 11 July 2018; Accepted 27 July 2018
Available online 01 August 2018
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which also reduced the crosslink density of PN polymers [17, 18].

The studies confirmed that the thermal stabilities and T_g of benzoxazines can be enhanced by the blending of reactive nitrile groups containing PN [19, 20]. However, the addition of the PN in the benzoxazine monomer was limited to 30 wt%, due to the higher melting temperatures of the PN monomers.

In the current study, amino groups containing bio-based PN monomer (EPN) has been added to the mono functional phenol–aniline based benzoxazine (P-a) and difunctional bisphenol A–aniline based benzoxazine (BA-a) monomers to form the copolymers. The curing behaviours of the P-a/EPN and BA-a/EPN monomer blends with different mass ratio blending were studied. Moreover, the thermomechanical, thermal, and mechanical properties of the prepared copolymers were studied. The SEM analysis of the copolymers was conducted to understand the morphological changes.

2. Experimental

2.1. Materials

The *p*-formaldehyde (AR) was provided by Shanghai Reagent Factory Co. Ltd. (Shanghai, China). The eugenol (> 99.0%) and 4-nitrophthalonitrile (99.5%) were supplied by Aladdin Reagent Co. Ltd. (Shanghai, China). The P-a (98.5%) and BA-a (98.0%) monomers were kindly gifted by the Jiangxi Huacui Advanced Materials Co. Ltd. (Jiangxi, China). All AR grade solvents were kindly donated by the Chengdu Kelon Chemical Reagent Factory (Chengdu, China).

2.2. Synthesis of eugenol based PN (EPN) monomer

The eugenol based PN monomer was synthesized by the reaction of eugenol with 4-nitrophthlonitrile in the presence of potassium carbonate according to the literature [4]. ^{1}H and ^{13}C NMR tests of the EPN monomer were conducted for the purity analysis (Fig. S1).

2.3. Preparation of P-a/EPN and BA-a/EPN copolymers

The appropriate masses according to the mass ratios of P-a and EPN were taken into a beaker and mixed for 2 h at 110 °C by using a mechanical stirrer, to have an identical mixture. After that, the homogeneous monomers mixture was transferred to the appropriate test sample steel mould. The entrapped gases were removed by degassing the monomers mixture in a vacuum oven at 100 °C for 3 h. Afterwards, the mould was kept in an air circulating oven for the isothermal curing of the sample. Following procedure was following for curing at 180, 200, 220, and 240 °C for 2 h at each heating stage. The BA-a/EPN blends and copolymers were prepared by the similar way, only BA-a monomer was used instead of P-a monomer. The proper labeling was used to determine the difference between the blends and copolymers. The monomer blends were labeled as P-a/EPN-A:B and BA-a/EPN-A:B, while copolymers were labeled as poly(P-a/EPN)-A:B and poly(BA-a/EPN)-A:B, here A and B represent the mass ratio of benzoxazine and EPN monomer, respectively.

2.4. Characterization

The Bruker AVANCE-500 NMR spectrometer with tetramethylsilane ($Si(CH_3)_4$) as the internal standard was used to record the ^{1}H and ^{13}C NMR characterizations of the EPN monomer. EPN monomer was dissolved in $CDCl_3$ at room temperature prior to the test and immediately tested at room temperature at 500 and 125 MHz for ^{1}H and ^{13}C NMR, respectively. The neat monomers and blended monomers were studied for understanding the curing behaviour on the differential scanning calorimetry (DSC), Q200, TA Instruments (USA), under a constant nitrogen flow (50 mL/min), from 30 to 400 °C at a heating rate of 20 °C/min. The 4–5 mg samples were placed in a hermetic aluminum pan, while an empty aluminum pan was used as a reference. The chemical studies of the pristine monomers, blends, and copolymers were studied by the Fourier transform infrared (FTIR) spectra, from 4000 to 450 cm^{-1} at 4 cm^{-1} resolution. Thin films of the sample powders were casted after blending with KBr powder and immediately tested on the PerkinElmer Spectrum 100 spectrometer. The 30 × 5 × 2 mm^3 rectangular sample was evaluated in a nitrogen atmosphere from 20 to 400 °C at 3 °C/min heating ramp and 1 Hz frequency in single cantilever mode on the dynamic mechanical analyzer (DMA) model Q800, TA Instruments, (USA) for the study of the thermomechanical properties of produced neat polymers and copolymers. The flexural tests were conducted to understand the mechanical properties behaviour of the copolymers, mean value of the three samples was reported as result. The flexural test on 50 × 10 × 2 mm^3 samples was carried out on the Instron 5569 instrument at 2 mm/min crosshead speed. The thermal stabilities of pristine polymers and copolymers were evaluated under a nitrogen atmosphere (50 mL/min flow) in a thermogravimetric analyzer (TGA). Nearly 10 mg of the sample was placed in a platinum crucible and heated from 50 to 820 °C at a heating rate of 20 °C/min in a TGA, Q50 model from TA Instruments, (USA). The scanning electron microscope (SEM) of Oxford Instruments, UK, model CamScan MX2600FE was employed to understand the morphological changes. The 10 mm height sample was removed from the flexural tests surfaces by using the diamond saw, and 3–5 nm (thick) gold coated to reduce the charging and tested at 20 kV accelerated voltage *via* a tungsten wire.

3. Results and discussion

3.1. Curing behaviour of benzoxazine/EPN monomer blends

The DSC tests were performed to comprehend the curing behaviour of P-a/EPN and BA-a/EPN blends on different blending ratio of benzoxazine and EPN monomers, results are illustrated in Fig. 1 and DSC parameters are presented Table 1.

The melting temperature peak (endothermic, T_m) was not observed for the P-a benzoxazine monomer, but meting peaks were recorded for the BA-a benzoxazine and eugenol based PN at 60 and 102 °C, respectively. This suggests that the homogenous monomer blend can be easily formed at 110 °C.

The transition peak temperature (exothermic, T_p) for the neat mono and difunctional benzoxazine monomers were observed at 249 and 245 °C, respectively, which confirms the oxzine ring opening reaction of benzoxazine for the polymerization [21]. Moreover, the T_p for the EPN was recorded at 364 °C, which confirms that the EPN monomer can be polymerized in absence of any initiator. The T_p of the EPN monomer is very high due to the −CN groups, which needs high energy for activation.

After blending of EPN in the benzoxazine monomers, two exothermic peaks were recorded one for the benzoxazine and second for the PN curing. However, the T_{p1} representing the benzoxazine polymerization moved to the higher temperature as the mass ratio of EPN increased, and the decline was recorded in the curing reaction enthalpy (ΔH). This suggests the reduced reactivity of the oxazine rings due to the dilution. Moreover, as the loading of EPN raised from 10 to 40 wt% the T_{p2} representing the PN polymerization reaction moved to the lower temperature and ΔH was increased. The higher amount of the ΔH, on similar composition, for P-a/EPN monomer as compare to the BA-a/EPN blend suggest that the BA-a monomer is more reactive as compare to the P-a monomer in EPN blend. These DSC results confirmed that the hydroxyl groups produced on the oxazine ring opening can catalyze the curing of amino groups of the EPN monomer [22].

3.2. FTIR analysis of benzoxazine/EPN monomer blends

The benzoxazine/EPN monomer blends under 7:3 mass ratio were studied at each curing stage for the understanding of copolymerization

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