Meta-phenylenediamine formaldehyde oligomer: A new accelerator for benzoxazine resin

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ABSTRACT

Meta-phenylenediamine formaldehyde oligomer is prepared and used as an accelerator for benzoxazine resin. The structure of the oligomer is characterized by Fourier transform infrared spectroscopy and ^{1}H nuclear magnetic resonance spectroscopy. The molecular weight and distribution are measured by size exclusion chromatography. After mixing the accelerators with benzoxazines, the curing process of the mixtures and thermal properties, including glass transition temperature, thermal stability and char yield of the cured polymers are characterized. Comparing with the materials prepared from pristine benzoxazine and benzoxazine with molecular accelerators, usage of oligomeric accelerator is able to promote the curing and simultaneously enhance the glass transition temperature as well as thermal stability of the cured network.

1. Introduction

Polybenzoxazine, obtained from benzoxazine resin through ring-opening polymerization, constitutes a new series of thermosets. It inherits the advantages and overcomes the drawbacks of phenolic resins [1]. Besides, it also possesses other attractive features, such as low curing shrinkage, low flammability, low water absorption, good molecular design flexibility and no byproduct release during curing [2,3]. These properties satisfy the requirements of high performance resin in various applications, such as aviation composites and electronic packaging [4]. Thus, it becomes one of the rare new polymers which have been industrialized during the last 30 years [5].

However, application of benzoxazine is limited to a certain extent because of several shortcomings. One of them is the high curing temperature. Typical method to obtain polybenzoxazine is to cure benzoxazine monomers at high temperature without accelerators [6]. However, the harsh curing condition is easy to trigger resin degradation [7] and is adverse to process [8]. In response, various accelerators are developed to promote the curing process and decrease the curing temperature [9–11]. In addition, when these accelerators are used, the material properties should at least be retained. However, this prerequisite is frequently overlooked. Accelerators can be introduced in two ways: blending or bonding in resin structures [12]. Blending is convenient to carry out and easy to adjust. However, many accelerators, including transition metal salts [8], metal complex [13], metal-organic

frameworks (MOFs) [14] imidazoles [15] and acids [16–18], do not incorporate into the polymer network after curing. They perform as plasticizers and would migrate to polymer surface and interfere the thermal properties. Other accelerators, including phenols [19,20], thiols [21–23] amines [24–26] and boron derivatives [27,28], are able to bond to polymer chain after curing, but the addition amount needs to be well-controlled. Excessive accelerators would lead to dangling structures to worsen the thermal performances, such as glass transition temperature and thermal stability [19,21]. Bonding the key functional groups of the accelerators in the resin structure is another way to promote benzoxazine polymerization. However, comparing with blending, this method is often sophisticated and the variety of raw materials is less [12,29]. Besides, the amount and species of the functional group is not adjustable once the resin is prepared. In addition, many incorporated groups, such as carboxylic acid, aldehyde, liquid crystal, etc. would release small molecules during curing, therefore sacrifices the processability and material properties [30–32].

Accelerators in oligomeric form can succeed the merits while the large molecular weight and incorporable groups can get over the weakness of the blending approach.. In past, linear phenolic resin was applied to fabricate electronic packaging materials [33]. The active protons in the accelerator can promote benzoxazine polymerization through cationic ring-opening mechanism. Meanwhile, the aryl rings in the accelerator can bond with polybenzoxazine network by Mannich bridge [9]. After copolymerization, the thermal stability is greatly

improved, however, the glass transition temperature decreases observably [33–35]. Thus, more work on developing oligomeric accelerators is needed.

This study reports the synthesis of an oligomer from meta-phenylenediamine and formaldehyde, and its application as an accelerator for benzoxazine polymerization. Two other mixtures, which are benzoxazine monomer/molecular accelerator and benzoxazine oligomer/molecular accelerator are simultaneously investigated for comparison. The structure of the oligomers and the influence of the oligomers on polymerization and thermal performances are studied and discussed. The advantages of using oligomeric accelerator are highlighted.

2. Experimental

2.1. Materials

Aniline (99%), 4,4′-dihydroxyldiphenyl isopropane (BPA, 99%), paraformaldehyde (96%) and meta-phenylenediamine (mPDA, 99%) are obtained from Aladdin Reagent Co., Ltd., Shanghai, China. 4,4′-diaminodiphenyl methane (DDM, 97%), sodium carbonate anhydrous (Na_2CO_3, 99%), sodium sulfate anhydrous (Na_2SO_4, 99%), formaldehyde solution (37%) and deuterated chloroform ($CHCl_3$-d) with tetramethylsilane (TMS) as standard are received from Sigma-Aldrich, St. Louis, US. Toluene is purchased from VWR, Radnor, US. A typical benzoxazine 2,2′-bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxaizn-3-yl) isopropane (BA-a) is achieved based on the solventless method reported before [36]. The synthesis route is sketched in Scheme 1.

2.2. Synthesis of meta-phenylenediamine formaldehyde oligomer O(mPDA-f)

Meta-phenylenediamine formaldehyde oligomer is prepared based on the reported method [37]. Specifically, mPDA (0.1 mol, 10.8 g) is completely dissolved in 40 mL of water before cooling down to below 10 °C. 7.8 mL of formaldehyde solution is rapidly added when the solution is vigorously stirred. Precipitates generate immediately during this time and are collected in a Teflon beaker and dried under vacuum at 200 °C. A transparent, amber resin is obtained after cooling. Yield = 40%. FT-IR (KBr, cm^{-1}): 3403, 3331 ($-NH_2$), 3008 (Ar−H), 2826 ($-CH_2-$), 1622, 1512 (Ar), 1450 ($-CH_2-$), 1212 (C−N), 847 (Ar). ^1H NMR (DMSO-d_6, ppm): 5.70–6.40 (Ar−H), 4.20–4.50 ($-NH_2$), 3.23(Ar−CH_2−Ar).

2.3. Synthesis of main-chain benzoxazine oligomer MCBO(BPA-ddm)a

Main-chain benzoxazine oligomer (MCBO) is synthesized from BPA, DDM and aniline. The preparation process is similar to a cardanol-capped MCBO which we have reported before [38]. Specifically, BPA (0.05 mol, 11.4 g), DDM (0.025 mol, 4.95 g), aniline (0.05 mol, 4.65 g) and toluene (100 mL) are added into a round bottom flask. The mixture is completely dissolved at a temperature around 80 °C before adding paraformaldehyde (0.21 mol). The mixture is then heated and refluxed. After 10 min, a white gel appears in the solution and completely disappears after refluxing for > 4 h [39]. After reaction for 24 h, the solution is cooled down, washed by 1 N Na_2CO_3 solution and water for several times. Once the solution becomes neutral, the organic phase is separated and dried by anhydrous Na_2SO_4 and evaporated under vacuum at a temperature above 100 °C to achieve yellow product. Yield = 42%. FT-IR (KBr, cm^{-1}): 3027 (Ar−H), 2963 ($-CH_3$), 1600, 1497 (Ar), 1231, 1030 (C−O−C), 945(Ox). ^1H NMR ($CHCl_3$-d, ppm):

6.50–7.30 (Ar−H), 5.33, 5.27 (N−CH_2−O), 4.57, 4.52 (N−CH_2−Ar), 3.79 (Ar−CH_2−Ar), 1.56 ($-CH_3$).

2.4. Preparation of the cured benzoxazine/accelerator mixtures

All mixtures are prepared by mixing benzoxazine and accelerators with equimolar amounts of oxazine ring and amino group [24]. The BA-a/mPDA, MCBO(BPA-ddm)a/mPDA and BA-a/O(mPDA-f) mixtures are cured through stepwise heating at 125 °C/1 h, 140 °C/1 h, 160 °C/1 h, 180 °C/2 h and 200 °C/2 h in air. The samples are cooled down freely before property evaluation.

2.5. Characterization methods

The molecular structure is characterized by a Fourier transform infrared spectrometer (FT-IR) Bruker Tensor 27 at a 4 cm^{-1} resolution in 400–4000 cm^{-1} range and a nuclear magnetic resonance spectroscopy (NMR) using a Varian Mercury VX300 equipment. The molecular weight of the oligomers is measured by size exclusion chromatography (SEC) using a Wyatt Technology Dawn Heleos-II gel permeation chromatography (GPC) system. The samples are dissolved in N,N-dimethylformamide (DMF) and measured under room temperature. The polymerization behavior and the glass transition temperature (T_g) are examined using a differential scanning calorimetry (DSC), Q200 TA Instrument. The heating and cooling rates are maintained at 10 °C/min. The thermal stability and char yield are evaluated through a thermogravimetric analyzer (TGA), Q5000, TA Instrument. The tests are carried out under nitrogen atmosphere at a heating rate of 10 °C/min and a temperature range from room temperature to 800 °C.

3. Results and discussion

3.1. Preparation of oligomeric accelerator O(mPDA-f) and oligomeric benzoxazine MCBO(BPA-ddm)a

Oligomeric accelerator O(mPDA-f) is synthesized from mPDA and formaldehyde at low temperature, as shown in Scheme 2. Formaldehyde undergoes an electrophilic attack on the aryl ring of mPDA due to the high electron density, which is caused by the synergetic donating effect of the amino groups. Meanwhile, water is generated during the condensation reaction. The chemical structure of the obtained product is verified by FT-IR and ^1H NMR. Fig. 1 shows the FT-IR spectrum of O(mPDA-f). To facilitate peak assignment, the FT-IR spectrum of mPDA is plotted as well. Specifically, the peaks at 3403 and 3331 cm^{-1} of O(mPDA-f) and mPDA are corresponding to the primary amino groups. The shifted absorbance from 1495 cm^{-1} (mPDA) to 1512 cm^{-1} (O(mPDA-f)), and the peak at 847 cm^{-1} indicates the tetra-substituted benzene ring. The peaks at 2826 and 1450 cm^{-1} are assigned to the methylene groups in between the aryl rings.

The structure of O(mPDA-f) is further verified by ^1H NMR (Fig. 2). The resonance peaks at 5.7–6.4 ppm are assigned to the protons on the benzene ring. The broad resonance peaks between 4.20 and 4.50 ppm are corresponding to the protons of the amino groups in different chemical environment. Most importantly, the resonance at 3.23 ppm is assigned to the protons of the methylene groups in between the two aryl rings.

The molecular weight and distribution are also important features of the oligomeric O(mPDA-f). The SEC profiles are shown in Fig. 3, from which the number-average (M_n) and weight-average (M_w) molecular weights of the oligomers are estimated. The prepared O(mPDA-f) has an
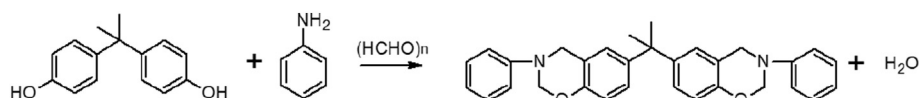
Scheme 1. Synthesis of BA-a, a classical benzoxazine monomer.