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Greatly improved thermal properties of polybenzoxazine via modification by acetylene/aldehyde groups

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ABSTRACT

A novel benzoxazine resin (PHB-apa) with low curing temperature, high T_g and excellent thermal stability was developed. Be different from other benzoxazines, PHB-apa contains both aldehyde group and acetylene group on the phenol ring and the aniline ring, respectively. Other benzoxazine monomers contain only one aldehyde group or one acetylene group were chosen for comparison. Their chemical structures were proved by ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). The polymerization reaction monitored by Differential Scanning Calorimetry (DSC) and FTIR suggests that the presence of the aldehyde group in PHB-apa leads to a low curing temperature that is benefit for processing. Besides, it is noticeable that this new polybenzoxazine has outstanding thermal property due to the cooperative reaction of the aldehyde group and the acetylene group. Its T_g from Dynamic thermo mechanical analysis (DMA) and char yield at 800 °C under N_2 from Thermogravimetric Analysis (TGA) are as high as 459 °C and 77.2%, respectively. Such kind of high values is a breakthrough for thermosetting resins, which will allow its application as a heat-resistant material at a much high temperature.

1. Introduction

Thermosetting resins are an important part of fiber reinforced composites. Phenolic resin, as the first thermosetting resin, has a wide range of application because of its good heat resistance. Especially, high char yield and good ablative performance make it to be an excellent material for thermal protection systems. However, the application of the phenolic resin is limited due to the release of small molecules during the curing process. Polybenzoxazines, as a kind of high performance thermosetting resin, not only keep good heat resistance of the phenolic resin but also overcome its drawback on processing [1–3]. Benzoxazine monomers are synthesized *via* the Mannich reaction based on phenols, primary amines and formaldehyde. The choice for using varied starting materials allows structure design flexibility of benzoxazine monomers, which will make polybenzoxazines exhibit different performance. No small molecule is released during its curing because of the ring-opening polymerization of benzoxazines. The production of a number of hydrogen bonds determines its nero-zero volumic shrinkage during the curing. Thus they are expected to replace traditional phenolic and epoxy resins in some fields [4]. The usage temperature of polybenzoxazines is usually around 180 °C that is higher than epoxies but lower than bismaleimide resins. To extend their application area, many studies have been done to improve the thermal performance of polybenzoxazines.

By taking advantage of the extraordinary molecular design flexibility, some reactive functional groups can be easily introduced into the structures of benzoxazine monomers, and their corresponding polybenzoxazines show improved thermal properties [5–11]. These self-polymerized functional groups can provide extra cross-linking sites during the curing process and lead to higher thermal stability. It has been reported that the T_g of maleimide containing mono-benzoxazines can reach 204 °C, and its char yield at 800 °C under nitrogen increased to 50% after curing at 240 °C [12]. When the benzocyclobutene groups were appended to benzoxazine monomer, the cured resin showed a very high T_g of 366 °C after curing at 260 °C [13]. Recently, Ohashi et al. prepared a monofunctional benzoxazine with cyanate ester group. When it was cured at 220 °C, its polymer showed a T_g of 265 °C and a high char yield of 65% [5]. It can be seen that their thermal properties are

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much better than ordinary polybenzoxazines.

Acetylene resin is well known for its extraordinary thermal stability because of the polymerization of the acetylene groups. Therefore, the introduction of the acetylene groups absolutely can play an active role in improving the thermal property. Researches on preparing acetylene functional benzoxazines have also been done. Ishida et al. prepared a series of acetylene functional benzoxazine [6,14]. Due to extra polymerization of the acetylene groups, the corresponding phenol or bisphenol-A based polybenzoxazines after curing at 220 °C showed very high char yields of 81% and 74% at 800 °C under N_2, and the T_gs of 329 °C and 356 °C, respectively [6,14]. Actually, a few mono-benzoxazine polymers can have such a high char yield above 75%. In addition, Agag and Takeichi reported a propargyl ether functional mono-benzoxazine, its polymer showed a char yield of 66% and a T_g of 251 °C after 240 °C [15]. Chernykh et al. prepared a series of main-chain type diacetylene functional polybenzoxazines that exhibited the char yields from 59% to 72% [16]. So, we can find that the involvement of the acetylene groups indeed greatly improves the thermal resistance of polybenzoxazines.

Based on the truth that one functional group can improve the thermal properties of polybenzoxazines, introducing two or more functional groups into mono-benzoxazines may obtain higher thermal stability theoretically. However, reported results do not seem to support this hypothesis. For example, when acetylene and maleimide groups were introduced into a mono-benzoxazine, a char yield of 61% and a T_g of 348 °C were obtained after 250 °C [17]. Additionally, a cured cyano and maleimide functional mono-benzoxazine just showed a char yield of 63% and a T_g of 230 °C even after curing at 250 °C [18]. For a multifunctional benzoxazine containing allyl and maleimide groups, a char yield at 700 °C and T_g of its polymer after curing at 280 °C are less than 60% and 300 °C (from a DSC test), respectively [19]. Therefore, increasing the number of reactive functional groups may not mean great improvement of the thermal resistance of polybenzoxazines. The possible reason is that the crosslinking reaction of one functional group increases the viscosity of the bulk, which makes the reaction of other functional groups much difficult. So, to get a better consequence, two functional groups involved must have synergistic effect.

Besides the enhancement of the thermal property, good curing processing is also required. For those functional benzoxazines mentioned above, it should be noted that high curing temperatures at least 220 °C are needed to ensure the polymerization of the functional groups. In previous research, we found that the presence of the electrophilic aldehyde group attached to the phenolic ring of benzoxazine monomer can effectively decrease the curing temperature [20,21]. Moreover, the thermal stability of the corresponding cured product was also improved because of the cooperative crosslink reactions based on oxidation and decarboxylation of the aldehyde groups [21,22]. So, the introduction of the aldehyde group plays two roles in decreasing the curing temperature and increasing the thermal stability.

In this case, considering from improving the curing processing and thermal property, it will be a good choice to incorporate both acetylene and aldehyde groups into a mono-benzoxazine. On the one hand, besides respective crosslink reactions of the acetylene and aldehyde groups during the curing process, the alkene groups generated from the acetylene groups can further react with the carboxyl group generated from the aldehyde group. This reaction named as the Heck-like coupling reaction can greatly improve the thermal stability [23,24]. On the other hand, the existence of the aldehyde group can decrease the curing temperature. At the same time, mono-benzoxazine makes itself low melting viscosity because of its small molecular weight. Based on this idea, a novel benzoxazine monomer was synthesized in this work *via* introducing an aldehyde group and an acetylene group into phenol and amine structures, respectively. Its chemical structure, curing behavior, polymerization reaction and thermal properties of its polymer were studied. For comparison, some typical benzoxazine monomers (Fig. 1) were chosen and studied simultaneously.

2. Experimental

2.1. Material

All chemicals were used as received. 3-Aminophenylacetylene (98%) was obtained from Shandong Jiaozhou Fine Chemicals Co. *p*-hydroxybenzaldehyde (99%) was obtained from Shanghai Jiacheng Fine Chemicals Co. Paraformaldehyde (≥96%), phenol (99%), aniline (99%), ethanol (99%), sodium hydroxide (99%), N, N-dimethylacetamide (98%) and toluene (99%) were bought from Chengdu Kelong Fine Chemicals Co.

2.2. Synthesis of benzoxazine monomers

The synthesis route of PHB-apa is shown in Scheme 1. Paraformaldehyde (3.03 g, 0.1mol) and 3-aminophenylacetylene (5.86 g, 0.05mol) were stirred in toluene (30 ml) at 80 °C for 2 h under N_2 atmosphere. Then, *p*-hydroxybenzaldehyde (6.11 g, 0.05 mol) was added into the reaction system. The mixture was stirred at 80 °C for another 3 h. After that, the solution was cooled to room temperature, and washed with 1N NaOH solution followed by distilled water several times. Then, the organic layer was dried over anhydrous Na_2SO_4. The solution was dried under vacuum to afford a viscous solid. The light pink crystal can be obtained after recrystallization several times from the mixtures of toluene and ethanol. Yield: 9.84 g, 75%; Mp 107 °C (from DSC). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): σ = 9.82 (s, 1H, CHO), 4.15 (s, 1H, ≡CH), 4.80 (s, 2H, Ar-CH_2-N), 5.61 (s, 2H, O-CH_2-N), 6.91–7.74 (m, 8H, Ar-H). FTIR (KBr, cm^{-1}): 3276 (stretching of ≡C-H), 1681 (stretching of C=O), 1236 (asymmetric stretching of, Ar-O-C), 938 (out of plane C-H stretch of benzene attached to oxazine).

PHB-a was prepared according to our previous report [21]. The sample was recrystallized from toluene. Mp: 97 °C (from DSC). ^{1}H NMR (400 MHz, $CDCl_3$, 298K): σ = 9.83 (s, 1H, CHO), 4.70 (s, 2H, Ar-CH_2-N), 5.45 (s, 2H, O-CH_2-N), 6.90–7.66 (m, 8H, Ar-H). FTIR (KBr, cm^{-1}): 1687 (stretching of C=O), 1238 (asymmetric stretching of, Ar-O-C), 940 (out of plane C-H stretch of benzene attached to oxazine), 693, 754 (out of plane C-H stretch of monosubstituted benzene).

PH-apa was synthesized according to the reference [25] and recrystallized from toluene. Mp: 67 °C (from DSC). ^{1}H-NMR (400 MHz, DMSO-d_6, 298K), ppm: δ: 4.14 (s, 1H,≡CH), 4.67 (s, 2H, C-CH_2-N-), 5.46 (s, 2H, N-CH_2-O-), 6.72–7.26 (m, 8H, Ar); FTIR (KBr, cm^{-1}): 3280 (stretching of ≡C-H), 2104 (stretching of C≡C), 1230 (asymmetric stretching of C-O-C), 1160 (asymmetric stretching of

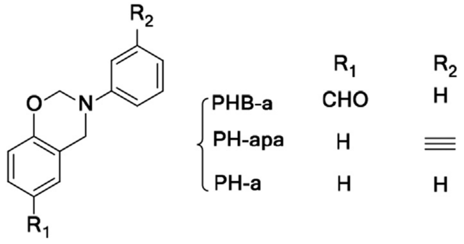

Fig. 1. The chemical structures of benzoxazine monomers.