

An approach of modifying poly(aryl ether ketone) to phenol-containing poly(aryl ether) and its application in preparing high-performance epoxy thermosets

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ABSTRACT

Linear poly(aryl ether)s are generally prepared from equal mole of bisphenols and aromatic bishalides in the presence of a base. Therefore, preparing poly(aryl ether)s with a residual phenol group in the repeating unit is a challenge. In this work, we report the synthesis of a phosphinated polyether (**P1**) with a phenol pendent group in the repeating unit from a one-pot reaction of a BPA-based poly(ether ether ketone), poly(oxy-1,4-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylene-isopropylidene-1,4-phenylene (BPA-PEEK), 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and phenol in the presence of sulfuric acid. The moderate-to-high molecular weight of **P1** provides phenol linkages as reacting sites for epoxy resins. Subsequently, flexible and transparent films of epoxy thermosets can be prepared from the curing of **P1** with three epoxy resins. The thermoset based on **P1**/cresol novolac epoxy shows a high T_g value (250 °C), a low dielectric constant (3.08), and flame retardancy (VTM-0). The moderate-to-high molecular weight of **P1** is responsible for the high- T_g and flexibility of the resulting epoxy thermosets.

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1. Introduction

Epoxy thermosets exhibit excellent chemical resistance, dimensional stability, insulation, and adhesion properties [1]. Unmodified epoxy thermosets are relatively brittle and display poor resistance to crack propagation. Four approaches are generally applied to enhance the toughness of epoxy thermosets. The first is incorporating rubber into the epoxy matrix, such as carboxylic acid terminated butadiene acrylonitrile rubber (CTBN), amine-terminated butadiene acrylonitrile (ATBN), epoxy-terminated butadiene acrylonitrile (ETBN), and hydroxyl-terminated polybutadiene (HTPB) [2–5]. The rubber is miscible with the epoxy before curing, but precipitates out gradually during curing. The dispersed rubber particles are thought to be responsible for the increased toughness. However, this modification leads to a reduced tensile modulus and yield strength of the epoxy

thermosets. The second is incorporating amphiphilic block copolymers that self-assemble into vesicles and micelles with the epoxy matrix [6–9]. For example, nanostructures that were dispersed with the epoxy matrix with poly(butylenes oxide) as the epoxy-phobic block and poly(ethylene oxide) as the epoxy-philic block have been reported in the poly(n-butylene oxide)-b-poly(ethylene oxide) diblock copolymer, epoxy, and curing agent system [9]. An increase of nineteen times in the fracture toughness of the epoxy thermoset with relatively small reduction in the elastic modulus was achieved after the addition of 5 wt% PBO-PEO diblock copolymer [9]. The third is blending epoxy with engineering thermoplastics, such as poly(ether sulfones)s [10,11], poly(phenylene oxide)s [12,13], polyamides [14], poly(ether imide)s [15,16], and polycarbonates [17–19]. Homogeneous or heterogeneous morphology has been reported in the literature. This approach avoids the compromise between toughness and thermal stability associated with rubber toughening of epoxy thermosets. However, no significant enhancement in toughness has been noticed due to poor interfacial adhesion between different phases. The fourth is incorporating functionalized thermoplastics, such as amine functionalized poly(aryl sulfone) [20], and amine-terminated poly(aryl ether ketone) [21], which behave as curing agents for epoxy resins and promote interfacial bonding between the thermoplastic and

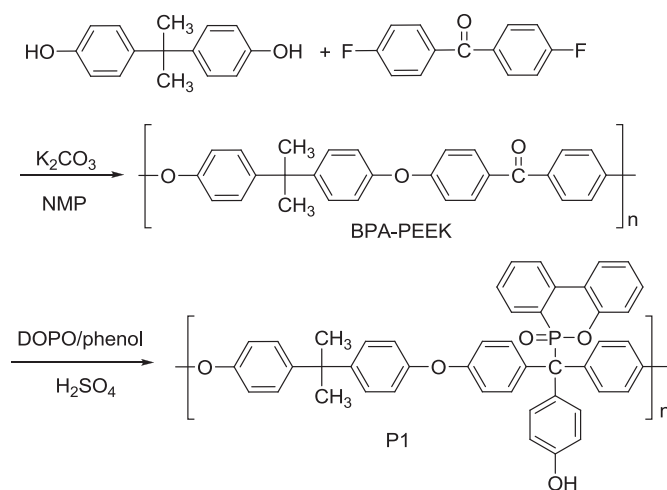
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thermoset through the formation of covalent linkage. In addition, Cicala et al. [22] demonstrated that different molecular weights of polymer modifier possessed significant effect on the rheological and thermomechanical properties of the epoxy/copolyethersulphones blends. They also demonstrated the different end groups, such as amine, chlorine, and hydroxyl moieties on the reaction rate and thermomechanical properties of the resulting resins. However, amine-cured epoxy thermosets usually exhibit higher water absorption than phenol-cured epoxy thermosets, according to the recipe of the industry of copper clad laminate (CCL), in which phenol novolac or bisphenol A novolac are usually used as curing agents. The higher water absorption not only increases the dielectric constant, but also hinders the success of the solder dipping and floating test at 288 °C, which is a critical requirement for CCL manufacturing.

Polymers of the poly(aryl ether)s family, such as poly(ether sulfone)s, poly(ether ketone)s, poly(ether oxazole)s, poly(ether imide)s, poly(ether quinoxaline)s, and poly(ether phosphine oxide)s are typically prepared by nucleophilic displacement polymerization of bisphenols with 4, 4'-dihaloaromatic compounds with electro-negative groups such as sulfonyl, carbonyl, oxazole, imide, quinoxaline, and phosphine oxide that activate the halides to nucleophilic displacement [23,24]. Since poly(aryl ether)s are generally prepared from an equal mole of bisphenols and aromatic bishalides in the presence of a base, preparing poly(aryl ether)s with a residual phenol group in the repeating unit is a challenge to polymer synthesis. Polycondensation of AB₂ or AA'B type monomers has been used to prepare polyethers with phenolic hydroxyl groups [24]. In this approach, B corresponds to an activated aryl halide, and A corresponds to a phenolic hydroxyl group. For example, Hedrick et al. [25] prepared hyperbranched poly(ether quinoxaline)s with phenolic hydroxyl groups from two AB₂ monomers: 2,3-bis(4-hydroxyphenyl)-5-fluoroquinoxaline and 2,3-bis(4-hydroxyphenoxyphenyl)-5-fluoroquinoxaline. Frechet et al. [26] prepared hyperbranched polyethers using an AB₂ type monomer, 5-(bromoethyl)-1,3-dihydroxybenzene. The monomer underwent self-condensation in the presence of potassium carbonate and 18-crown-6 to give hyperbranched polyethers with a large number of phenolic hydroxyl groups located at the chain ends. Hawker et al. used an AB₂ type monomer, 3,5-dihydroxy-4'-fluorobenzophenone, to prepare a hyperbranched poly(ether ketone) with phenolic hydroxyl chain ends. Shu et al. [27] synthesized an oxazole activated ABB' monomer, 2-(4-fluorophenyl)-4,5-di(4-hydroxyphenyl)-1,3-oxazole, to prepare a hyperbranched poly(ether oxazole) with phenolic hydroxyl end groups. Shu et al. [28] also prepared an imide activated AB₂ monomer, N-(4-(1,1-di(4-hydroxyphenyl)ethyl)phenyl)-4-fluorophthalimide, to create a hyperbranched poly(ether imide) with phenolic hydroxyl end groups. Cho et al. [29] prepared a hyperbranched poly(ether ketone) with phenolic hydroxyl end groups based on an AB₂ monomer, 2,4-bis(4-hydroxyphenyl)-6-(4-(4-(4-fluorobenzoyl)phenoxy)phenyl)-1,3,5-s-triazine. Jikei et al. [30] prepared a hyperbranched poly(ether sulfone)s with phenolic hydroxyl end groups based on an AB₂ monomer, 4-(3,5-hydroxyphenoxy)-4'-fluorodiphenylsulfone. Kim et al. [31] prepared an AB₂ monomer, bis(4-hydroxyphenyl)-4'-fluorophenyl-phosphine oxide, and converted it to a hyperbranched poly(ether phosphine oxide) with phenolic hydroxyl end groups. Linear polymers usually exhibit better mechanical properties than hyperbranched polymers due to the entanglement of polymer chains, and should be more suitable for epoxy toughness. However, to the best of our knowledge, no linear poly(aryl ether)s with a phenol pendent in the repeating unit have been reported. In this work, we report a facile and efficient procedure for preparing a phosphinated poly(aryl ether) (**P1**) with a phenol group in the repeating unit from a one-pot reaction of a bisphenol A-based poly(ether ether ketone), poly(oxy-1,4-phenylene-carbonyl-1,4-phenyleneoxy-1,4-phenylene-



Scheme 1. Synthesis of BPA-PEEK and **P1**.

isopropylidene-1,4-phenylene) (BPA-PEEK), 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO), and phenol in the presence of strong acid. Since the phenol linkages can provide reacting sites for epoxy resins, **P1** served as a moderate-to-high-molecular weight epoxy curing agent. Homogeneous, flexible, tough, and transparent films of epoxy thermosets with a high-*T_g* value can be prepared after curing **P1** with three epoxy resins. Detailed structure analysis and the structure–property relationship of the resulting epoxy thermosets are provided in this work.

2. Experimental

2.1. Materials

Bisphenol A (BPA, from Showa), 4,4'-difluorobenzophenone (from Acros), potassium carbonate (from Acros), phenol, 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO, from TCI), *p*-toluenesulfonic acid monohydrate (*p*-TSA, from Showa), sulfuric acid (from Acros), and sodium acetate anhydrous (from Acros) were used as received. Diglycidyl ether of bisphenol A (DGEBA) with an epoxy equivalent weight (EEW) of 187 g/eq and cresol novolac epoxy (CNE) with an EEW of 200 g/eq were kindly supplied by Chang Chun Plastics, Taiwan. Dicyclopentadiene epoxy (DCPDE) with an EEW of 269 g/eq was kindly supplied by Dai-nippon Ink and Chemicals Corporation under the commercial name of HP-7200. *N*-methylpyrrolidone (NMP) was purchased from

Table 1
Effects of reaction conditions on **P1** synthesis.

Run	Catalyst	Catalyst amount (wt%) ^a	Time (h)	Temperature (°C)	Product	Isolated yield (%)
1	Oxalic acid	4	24	130	Unsuccessful	–
2	Oxalic acid	4	24	140	Unsuccessful	–
3	Oxalic acid	4	24	150	Unsuccessful	–
4	<i>p</i> -TSA	4	24	130	Unsuccessful	–
5	<i>p</i> -TSA	4	24	140	Unsuccessful	–
6	<i>p</i> -TSA	4	24	150	P1 ^b	70
7	H ₂ SO ₄	4	24	130	P1	73
8	H ₂ SO ₄	4	24	140	P1	88
9	H ₂ SO ₄	4	24	150	P1 ^c	75

^a Based on the weight of DOPO.

^b **P1** with small impurity signal at 5.3 and 9.2 ppm. The corresponding ¹H NMR spectrum is shown in Figure S1(b).

^c **P1** with some impurity signal at 9.2–9.4 ppm. The corresponding ¹H NMR spectrum is shown in Figure S1(c).

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