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High-performance thermosets derived from acetovanillone-based reactive polyethers

Chien-Han Chen [a, b], Wei-Feng Shiao [a], Mathivathanan Ariraman [a], Ching-Hsuan Lin [a, b, *], Tzong-Yuan Juang [c]

[a] Department of Chemical Engineering, National Chung Hsing University, Taichung 402, Taiwan
[b] Advanced Research Center for Green Materials Science and Technology, National Taiwan University, Taipei 10617, Taiwan
[c] Department of Cosmeceutics, China Medical University, Taichung 402, Taiwan

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To achieve high-performance thermosets from renewable resources, six acetovanillone-derived poly(aryl ether)s (two with the acetic moiety, two with the phenyl methacrylic moiety, and two with the vinyl benzyl ether moiety) were prepared. The poly(aryl ether)s with acetic- or phenyl methacrylic moiety were applied as epoxy curing agents to cure with a phenol-dicyclopentadiene epoxy resin (HP7200). The T_g values of the resulting epoxy thermosets range from 228 to 252 °C (DMA data) and the dielectric constants range from 2.78 to 3.01 U (at 3 GHz). The two poly(aryl ether)s with vinyl benzyl ether moiety were self-cured to high-performance thermosets with T_g values of 255 and 293 °C (DMA data) and with a dielectric constant of 2.89 and 2.68 U (at 3 GHz), respectively. This work successfully demonstrates a strategy to achieve high-performance thermosets from reactive polyethers, which are derived from renewable acetovanillone.

1. Introduction

Because of the limited quantity of petroleum, research on sustainable resources such as cellulose and lignins have been extensively done [1–11]. Vanillin, a phenolic aldehyde, is the major component of the extract of the vanilla bean. Vanillin production from lignin has been reported by Caillol et al. [12] They also have reported vanillin as a promising building-block for monomer synthesis [13]. Acetovanillone, also known as apocynin, is a phenolic acetophenone which is structurally similar to vanillin. It has been isolated from a variety of plant sources [14], and has been studied for its variety of pharmacological properties. Vanillin and acetovanillone are monofunctional phenol, which makes it difficult to prepare polymers from them. To prepare vanillin- or acetovanillone-based polymers, difunctional monomers are required. Cramail et al. prepared a vanillin-based biphenol, divanillin, through the dimerization of vanillin using a green process, and then prepared renewable (semi)aromatic polyesters [15]. Pearl prepared a vanillin-based biphenol, 4,4′-dihydroxy-3,3′-dimethoxystilbene, using a four-step method [16,17]. Caillol et al. prepared a biphenol, methoxyhydroquinone, by the Dakin oxidation [13,18,19]. Lin et al. prepared two phosphinated bisphenols from vanillin and acetovanillone, respectively, by a one-pot reaction of DOPO, vanillin (or acetovanillone), and phenol in the presence of p-TSA [20]. The experimental data shows that only the acetovanillone-derived bisphenol (**DAVP**) is alkaline-stable for nucleophilic substitution. A phenol-functionalized polyethersulfone (DAVP-S-OH) was prepared from a nucleophilic substitution of **DAVP** and difluorodiphenyl sulfone, followed by demethylation (the structure of DAVP-S-OH is shown in Scheme 1). DAVP-S-OH, with phenolic OHs, can react with a phenol-dicyclopentadiene epoxy resin (HP7200) to get a flexible and transparent of epoxy thermosetting film with a high T_g value and flame retardancy. However, the highly-polar secondary alcohols, resulted from the reaction of epoxy group and phenol of DAVP-S-OH, hinder the resulting epoxy thermosets to be low dielectric. Since the signal propagating speed in an integrated circuit is inversely proportional to the square root of dielectric constant (D_k). Thus, a material with a low D_k is desired for the field of printed circuit boards.

Active ester-type epoxy curing agents (curing agent with Ph-O-

* Corresponding author. Present address: Department of Chemical Engineering, National Chung Hsing University, 250 Kuo Kuang Road, Taichung, 402, Taiwan. Tel.: +886 4 22850180; fax: +886 4 22854734.
E-mail address: linch@nchu.edu.tw (C.-H. Lin).

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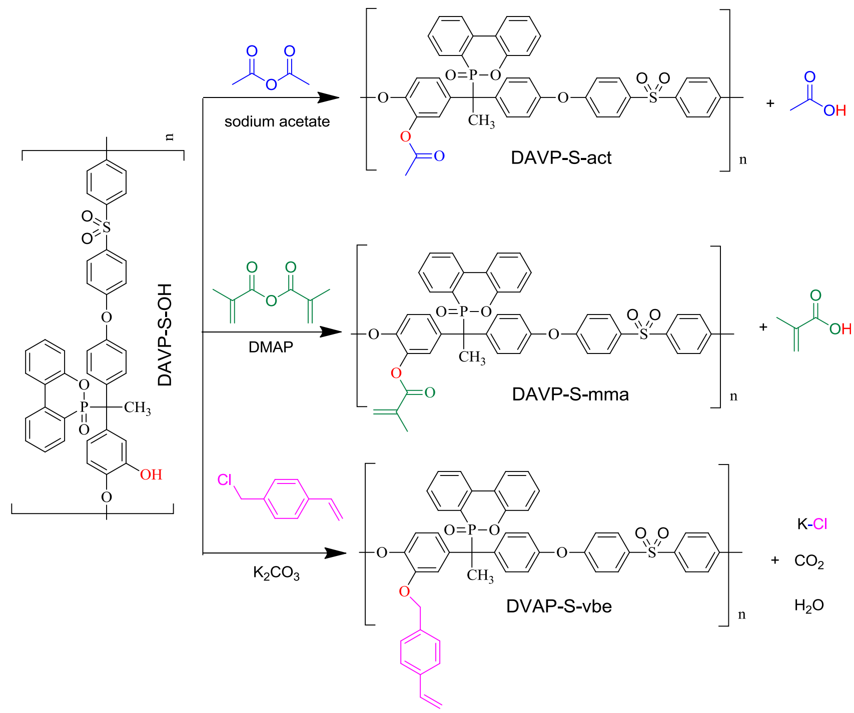

Scheme 1. Synthesis of DAVP-S-act, DAVP-S-mma and DAVP-S-vbe.

(C=O)- structure) is an approach to prepare secondary alcohol-free epoxy thermosets. Nishikubo et al. cured active ester-containing polymers with polyfunctional epoxy to obtain secondary alcohol-free, low-dielectric epoxy thermosets [21,22]. Similar to the reaction of active ester and epoxy, we have demonstrated the curing reaction of phenyl methacrylate and epoxy in a previous work [23]. To prepare epoxy thermosets with good dielectric properties, we modify the phenolic OH of DAVP-S-OH to acetic- and phenyl methacrylic moiety. Therefore, DAVP-S-act (with acetic moiety), DAVP-S-mma (with phenyl methacrylic moiety) were modified from DAVP-S-OH in this work. Except for phenyl methacrylate end capping, MGC (Mitsubishi gas chemical) has developed a vinyl benzyl ether end-capped oligo (2,6-dimethyl phenylene oxide), OPE-2st. The thermoset of OPE-2st exhibit a low dielectric constant of 2.65 U and a very low dissipation factor of 0.005 U [24,25]. To prepare low-dielectric epoxy thermosets, we modify the phenolic OH of DAVP-S-OH to vinyl benzyl ether moiety, and DAVP-S-DAVP-S-vbe (with vinyl benzyl ether moiety) was prepared in this work. To further reduce the polarity of polymer chains, a perfluorobiphenyl structure was incorporated to the replace diphenylsulfone structure. A phenol-functionalized polyetherperfluorobiphenyl (DAVP-PF-OH) was prepared from a nucleophilic substitution **DAVP** and perfluorobiphenyl, following by demethylation (the structure of DAVP-PF-OH is shown in Scheme 2). Three derivatives of DAVP-PF-OH: DAVP-PF-act (with acetic moiety), DAVP-PF-mma (with phenyl methacrylic moiety), and DAVP-PF-vbe (with vinyl benzyl ether moiety) were prepared. The polyethers with acetic or phenyl methacrylic moiety were applied as epoxy curing agent for HP7200 to obtain secondary hydroxyl-free epoxy thermosets. The polyethers with reactive vinyl benzyl ether moiety, were self-cured to high-performance thermosets. The detailed synthetic strategy, thermal and dielectric properties of the resulting thermosets are provided in this work.

2. Experimental section

2.1. Materials

The acetovanillone-derived bisphenol (DAVP) was prepared in a one-pot procedure by the reaction of DOPO, excess phenol, and acetovanillone using *p*-TSA as a catalyst [20]. The phenol-functionalized polyethersulfone (DAVP-S-OH) was prepared from a nucleophilic substitution of DAVP and difluorodiphenyl sulfone in the presence of potassium carbonate, followed by demethylation in the presence of pyridine hydrochloride [20]. Sodium acetate (from TCI), acetic anhydride (from TCI), methacrylic anhydride (from Acros), 4-dimethylaminopyridine (DMAP, from TCI), 4-chloromethyl styrene (from Acros), *t*-butyl cumyl peroxide (TBCP), potassium carbonate (from Acros), perfluorobiphenyl (from TCI), and pyridine hydrochloride (from Alfa Aesar) were used as received. Dicyclopentadiene epoxy (HP7200, DIC) with an EEW of 269 g/eq was kindly supplied by Dainippon Ink and Chemicals Corporation under the commercial name of HP-7200. N-methyl pyrrolidone (NMP; HPLC grade from Showa) and N,N-dimethyl acetamide (DMAc, HPLC grade from Showa) were purified by distillation under reduced pressure over calcium hydride (from Acros), and stored over molecular sieves.

2.2. Characterization

NMR measurements were performed using a Varian Inova 600 NMR in DMSO-d_6, and the chemical shift was calibrated by setting the chemical shift of DMSO-d_6 as 2.49 ppm. Thermogravimetric analysis (TGA) was performed by a Perkin-Elmer Pyris 1 in a nitrogen or air atmosphere and heat from 40 °C to 800 °C with a rate of 20 °C/min. Dynamic mechanical analysis (DMA) was performed with a Perkin-Elmer Pyris Diamond DMA with a sample size of 5.0 cm × 1.0 cm x 0.2 cm. The storage modulus E′ and tan δ were