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Preparation and characterization of ultralow dielectric and fibrous epoxy thermoset cured with poly(arylene ether ketone) containing phenolic hydroxyl groups

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ABSTRACT

Poly(arylene ether ketone) containing naphthalene and phenolic hydroxyl groups (HPAEK) was prepared by polycondensation and demethylation reaction. Polymer cured epoxy resin with high-*Tg* was obtained through reactions between oxirane ring of epoxy and phenolic hydroxyl groups of HPAEK. Electrospinning technology was used to fabricate porous film. The porous film shows a high *Tg* value (262 °C), a low dielectric constant (1.9 at 1 MHz), and a low coefficient of thermal expansion (52 ppm $°C^{-1}$). The thermal stability and water contact angle were also measured. The naphthalene and phenolic hydroxyl containing poly(arylene ether ketone) provides us with a new strategy to achieve ultralow dielectric constant materials via electrospinning.

1. Introduction

Epoxy resins have been used as insulation materials for dielectric devices due to their good balance of properties such as superior electrical and mechanical properties, excellent solvent and chemical resistance and good adhesion to many substrates [1,2]. However, unmodified epoxy thermosets are relatively brittle, thus displaying poor resistance to crack propagation [3]. One of the widely used approaches for improving the toughness of epoxy resin is to modify it by liquid rubbers [4–7]. The dispersed rubber particles could enhance the toughness of epoxy resin significantly. Nevertheless, a decrease in thermal stability and tensile modulus was observed for the resulted thermosets. Another approach is to incorporate engineering polymers into epoxy matrix [8,9]. The thermal stability of thermosets was also greatly improved. However, poor interfacial adhesion between different phases leads to a decrease in the improvement effect of the fracture toughness. To improve interfacial adhesion, functionalized polymers containing epoxy [10,11], amine [12,13] and phenolic hydroxyl groups [14,15] are used as the modifier or curing agent to form covalent linkage. Low molecular weight poly(phenylene oxide) (PPO) with terminal phenolic hydroxyl groups was utilized to modify epoxy resin, and the thermosets showed good thermal stability and improved dielectric property (2.6–3.1 at 1 GHz) [16]. Lin et al. prepared poly(aryl ether ketone) with phenol pendent group in every repeating unit. Flexible and transparent films were obtained, which showed high *Tg* and thermal stability [17].

To meet the requirements of modern electronic industry, numerous investigations have been carried out to prepare kinds of modified epoxy resins, such as the incorporation of fluorine [18,19], nanoparticles [20,21] and porous structures [22]. Since the design of molecule structure is complicated and time-cost, the strategy of incorporation of voids ($k \approx 1$) into epoxy resins has been an attractive approach to decrease the dielectric constant.

Over the years, electrospinning has been considered as an efficient technique to fabricate fibrous films, due to its potential for industrial-scale processing and repeatability in control of fiber dimension [23,24]. It has been demonstrated that electrospun polymer films exhibit ultralow dielectric constant (usually below 2.2) compared with as-cast films [25–28]. However, it is more difficult to fabricate high quality fibrous films using epoxy solution with low concentration. Thus, beads and defects are inevitable. Adding polymers into solution is an efficient way to increase viscosity and obtain electrospun epoxy film at a low concentration.

In this work, we synthesized fluorinated poly (arylene ether ketone) containing naphthalene and phenolic hydroxyl groups (HPAEK) and presented a simple and effective approach for the fabrication of epoxy films with ultralow dielectric constant through electrospinning technique. 4,4′-Diglycidyl (3,3′,5,5′-tetramethylbiphenyl) epoxy resin (TMBPER) is a kind of liquid crystal epoxy resin possessing high thermal and mechanical properties.[29–31] Fluorinated HPAEK was

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used as a suitable macromolecule curing and toughness agent due to its linear structure and phenolic hydroxyl groups in the repeating unit. Flexible and tough films were prepared through cast and electrospinning. The detailed characterization including thermal stability, dielectric constant and water contact angle was also provided.

2. Experimental

2.1. Materials

1,5-Bis(4-fluorobenzoyl)-2,6-dimethoxynaphthalene (DMNF) and 4,4′-diglycidyl (3,3′,5,5′-tetramethylbiphenyl) epoxy (TMBPE) were synthesized according our previous work [32,33]. 2-Methylimidazole, 4,4′-(hexafluoroisopropylidene)diphenol and boron tribromide (BBr_3) were purchased from Alddin chemistry Co. Ltd and used as received. Toluene, sulfolane, N-methyl-2-pyrrolidinone (NMP), dichloromethane, potassium carbonate were purchased from Beijing chemical company and used as received.

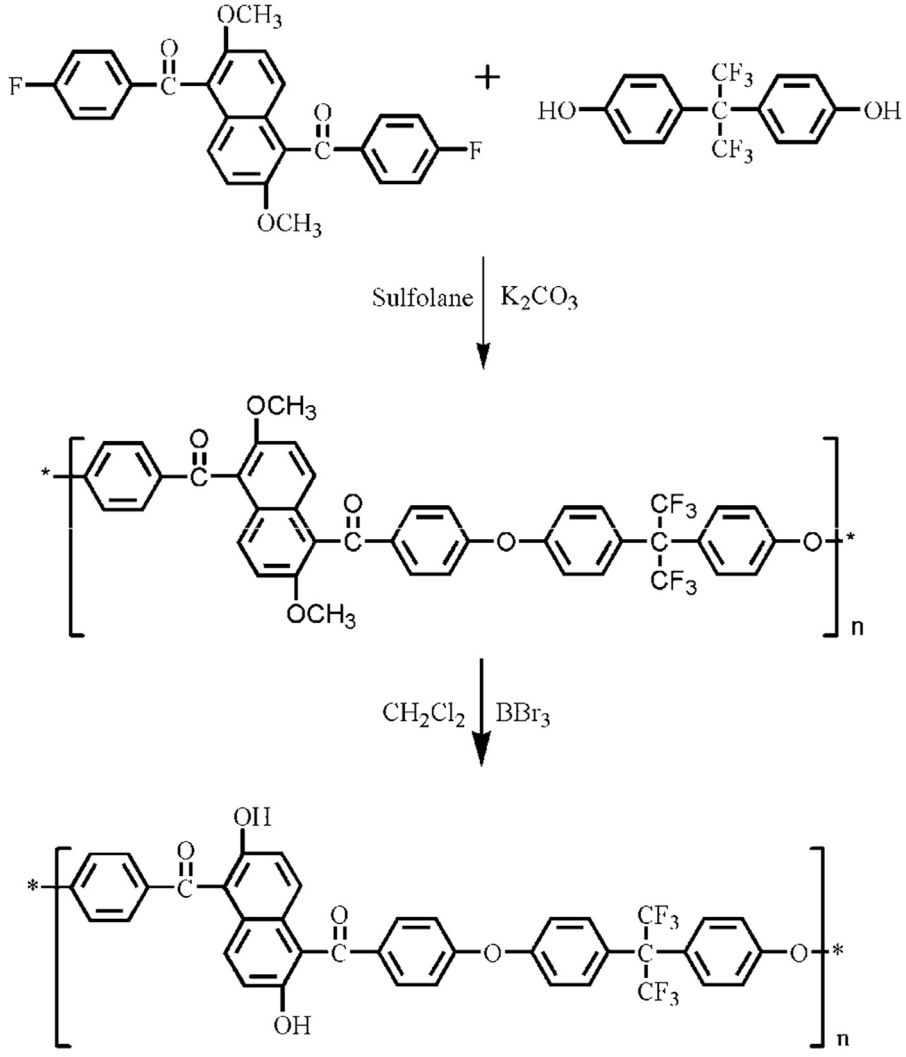
2.2. Synthesis of poly(arylene ether ketone) containing naphthalene and phenolic hydroxyl groups (HPAEK)

HPAEK was synthesized through polycondensation of DMNF and 4,4′-(hexafluoroisopropylidene)diphenol, and demethylation reaction, as shown in Scheme 1. A mixture containing DMNF (6.48 g, 0.015 mol), 4′-(hexafluoroisopropylidene) diphenol (5.04 g, 0.015 mol) and K_2CO_3 (2.277 g, 0.0165 mol), sulfolane (24 mL) and toluene (8 mL) was added to a three-necked flask equipped with a nitrogen inlet, a mechanical stirrer and a Dean-Stark trap. The mixture was heated at 140 °C for 3 h to remove the water by azeotropic distillation with toluene. Then the reaction was heated to 200 °C and stirred for 2 h. The high viscosity mixture was coagulated into a large excess of deionized water. The precipitation was washed with deionized water several times and dried under vacuum at 80 °C for 24 h.

The demethylation of obtained polymer was performed as follows: 1.0 g of polymer was dissolved into 40 mL anhydrous dichloromethane. The solution was cooled to 0–3 °C, and 5 mL solution of BBr_3 in dichloromethane (1 mol L^{-1}) was added dropwise. The mixture was stirred at room temperature under nitrogen atmosphere for 24 h. The mixture was poured into ice water to hydrolyze the BBr_3 and the boron complexes. The HPAEK was washed with deionized water. The resulting polymer was dried at 80 °C for 24 h.

2.3. Preparation of macromolecule cured TMBPER resin

HPAEK (2.62 g) and TMBPE (1.34 g) were dissolved in 15 mL DMF. After all contents were dissolved, 2-methylimidazole (0.04 g) was added into the solution. The solution was poured onto glass plate and heated at 60 °C for 24 h to dry the film. And then the film was cured at 100 °C for 2 h, 150 °C for 2 h, at 200 °C for 2 h in a convection oven.



Scheme 1. The synthesis of HPAEK.