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Preparation and properties of novel fluorinated epoxy resins cured with 4-trifluoromethyl phenylbenzimidazole for application in electronic materials

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ABSTRACT

A novel 3-trifluoromethyl phenylhydroquinone epoxy monomer (3-TFMEP) and a novel 4-trifluoromethyl phenylbenzimidazole (4-TFMBI) curing agent both with trifluoromethyl moieties were synthesized via a multi-step procedure. Their chemical structures were confirmed by FT-IR and ^{1}H NMR spectra. Herein, we employed 3-TFMEP as the epoxy matrix, and 4-TFMBI as the curing agent or the curing accelerator. Next, we prepared a series of epoxy resins with four kinds of different curing system as 3-TFMEP/Methylhexahydrophthalicanhydride (Mehhpa)/2-methylimidazole (2-MI), 3-TFMEP/Mehhpa/4-TFMBI, 3-TFMEP/2-MI and 3-TFMEP/4-TFMBI in order to investigate the variation of the properties with different curing agents and curing accelerators. The result showed that no matter whether 4-TFMBI was used as the curing agent or as the curing accelerator, the epoxy resin cured with 4-TFMBI exhibited high mechanical and thermal stabilities, as well as low dielectric constant and dielectric loss. In particular, 3-TFMEP/4-TFMBI possessed the highest $T_{d5\%}$ (the decomposition temperature of 5% weight loss) of 374 °C, 131 °C higher than 3-TFMEP/Mehhpa/2-MI. Additionally, the storage modulus of 3-TFMEP/Mehhpa/4-TFMBI was 3266 MPa at 25 °C, which was much higher than other kinds of cured epoxy resins. Moreover, 3-TFMEP/4-TFMBI possessed the lowest dielectric constant of 3.38 at 10^7 Hz among these cured epoxy resins. Therefore, we believed that this novel fluorinated epoxy resin cured with 4-TFMBI containing 3-trifluoromethyl moieties have a great potential for application in the electronic packaging material field.

1. Introduction

Advanced electronic materials play the key role in the proper functioning and useful life of the electronic assembly. The requirements for ideal electronic materials include hydrophobic, electrical insulation, mechanical support and environmental protection, as well as thermal stability and dielectric properties [1–8].

Epoxy resin, as one of the most widely used electronic packaging materials has attracted much interest due to its outstanding adhesion, lower density, high strength, good durability and excellent chemical resistance [9–19]. However, the properties of conventional epoxy resins could not satisfy the demand of advanced electronic material including low dielectric constant and loss as well as excellent thermal stability [20]. The current strategy to improve the performance of electronic materials is designing the epoxy resins with novel structures for satisfying the demand of dielectric and thermal properties. According to the literature, introducing fluorine groups into epoxy resin has become the effective way to reduce dielectric constant because the small dipole of C—F bonds makes the molecule difficult to be polarized. Thus, fluorinated epoxy resins are considered to be one of the most potential candidates for electronic packaging material.

Many researchers have reported the incorporation of fluorine into epoxy resins over past few decades. For example, Fan and coworkers [21] prepared a novel fluorinated epoxy resin. They also found the material possessed reduced moisture absorption and low dielectric constant simultaneously. Tao et al. [22] synthesized a novel fluorinated epoxy resin containing CF_3 groups by a four-step procedure. The fluorinated epoxy resin exhibited a high glass transition temperature (T_g), low dielectric constant and low water absorption. Therefore, we believed that the introduction of fluorine into epoxy resin could improve the properties to satisfy the demand of advanced electronic materials. Although the structure of epoxy monomer is crucial to achieve good performance, the structure of curing agents is another important factor that determines the properties of epoxy materials. To the best of our knowledge, there are few reports concerning the development of curing agents with additional fluorine groups. Since the most conventional curing agents have no fluorine in their structures, the cured epoxy resins by using the conventional curing agent possessed the lower

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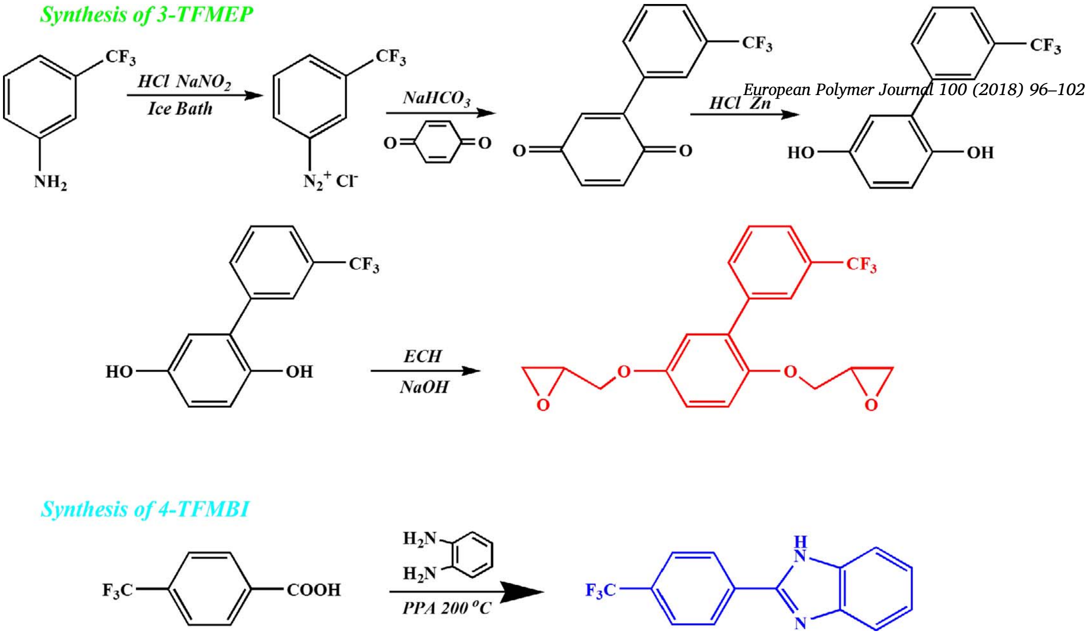

Scheme 1. The synthetic routes of 3-TFMEP and 4-TFMBI monomers.

fluorine moiety in the final production. Therefore, selecting and synthesizing the curing agent with proper structure is a priority among priorities for preparing the high performance epoxy resin materials. Sasaki and Nakamura [23] reported that fluorinate anhydride cured diglycidyl ether of bisphenol A could reduce the water absorption by 75% and showed the low dielectric constants in the range of 2.7–2.8. Liu et al. [24] reported a series of fluorinated epoxy resins with different fluorine contents by selecting different curing agents. The obtained materials showed better thermal stability and lower moisture absorption as the fluorinate content increased. However, they didn't explore the variation of the dielectric properties with the fluorinate content increasing. Thus, the research on the influence of the dielectric properties with different fluorinate content has drawn our attention.

In this study, we synthesized a novel curing agent of 4-trifluoromethyl phenylbenzimidazole (4-TFMBI) with trifluoromethyl moieties to maintain the fluorine content in the final cured fluorinate epoxy resins. 4-TFMBI was also employed as the curing accelerator besides as the curing agents. Meanwhile, the rigid benzimidazole structure in 4-TFMBI could improve the thermal stability of cured epoxy resin and satisfy the demand of the advanced electronic materials. Furthermore, we focused on the relationship between the structure and the properties of the epoxy resins obtained by introducing trifluoromethyl groups into the backbone. For this purpose, the synthesis and characterization of both the epoxy resins and the novel curing agent was firstly described. Then the thermal stability, glass transition temperature and dielectric properties, as well as contact angle of the cured epoxy resins were studied in detail. This study provides a way to obtain a series of epoxy resins by using suitable curing agents for application in electronic materials.

2. Experimental

2.1. Materials

Monomer (3-trifluoromethyl)aniline, 1,4-benzoquinone and polyphosphoric acid (PPA) were purchased from Beijing Chemical Company (Beijing, China). Epichlorohydrin (ECH) and 1,2-diaminobenzene were obtained from TCI Shanghai Development Co., Ltd. Methylhexahydrophthalic anhydride (Mehhpa), 2-methylimidazole and 4-(trifluoromethyl)benzoic acid were obtained from Energy Chemical. Co. Sodium hydroxide (NaOH), sodium nitrite ($NaNO_2$) and tetrabutylammonium bromide were purchased from Sinophram Chemical Reagent Co., Ltd. All other reagents and solvents were obtained commercially and used without further purification.

2.2. Synthesis of monomer 3-(trifluoromethyl) benzoquinone

3-Trifluoromethylaniline (80.5 g, 0.5 mol) and 200 mL of deionized water were added into a 1000 mL three-necked flask equipped with a mechanical stirrer, a dropping funnel and a thermometer. The mixture was kept at a temperature below 5 °C with ice bath. Then, hydrochloric acid (168 mL, 11.8 M) was added into the solution drop by drop. The sodium nitrite solution (124.5 g) with a concentration of 27.7% was added from a dropping funnel to a well stirred mixture in the flask. The mixture was stirred at 0–5 °C for 1 h and a transparent solution was obtained. The resulting solution was filtered and added dropwise into a mixture of 1,4-benzoquinone (54 g, 0.5 mol), sodium bicarbonate (126 g, 1.5 mol) and deionized water (200 mL). The reaction mixture was stirred at 8–10 °C for 3 h, and then kept at room temperature for another 3 h. The resulting mixture was filtered and the precipitate was washed with deionized water five times. Finally, the obtained yellow solid was dried at 50 °C in a vacuum oven for 24 h.

2.3. Synthesis of (3-trifluoromethyl)phenylhydroquinone monomer

The yellow solid 3-(trifluoromethyl) benzoquinone (168 g), Zn powder (130 g), and 500 mL of deionized water were placed into a 3000 mL three-necked flask equipped with a mechanical stirrer, a condenser, and a dropping funnel. The mixture was heated to 90 °C with stirring, followed by the addition of hydrochloric acid (30 wt%, 126 mL) dropwise at a rate of 1 drop per second. After completing the addition, the reaction system was allowed to reflux for 2 h. Then, the hot mixture was filtered. After cooling the filtrate, the white precipitate was filtered, dried and recrystallized from toluene to give white needle crystals.

2.4. Synthesis of 3-trifluoromethyl phenylhydroquinone epoxy monomer (3-TFMEP)

As shown in Scheme 1, a mixture of 32 g (0.126 mol) (3-