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Enhanced thermal conductivity of fluorinated epoxy resins by incorporating inorganic filler

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ABSTRACT

Electronic and circuit components become smaller but easier to produce heat nowadays. Finding a kind of materials with high thermal conductivity to dissipate the heat is greatly needed. In this work, a fluorinated epoxy monomer, 3-trifluoromethyl phenylhydroquinone epoxy resin (3-TFMEP) with good mobility was synthesized. The fluorinated epoxy resins also show low dielectric constant and hydrophobic nature. Then a kind of inorganic filler, boron nitride (BN), with high thermal conductivity was chosen to make the hybrid resin mixture. The epoxy resins' mixture both showed the advantages of simple epoxy resins and considerable thermal conductivity. The good mobility of 3-TEMEP allows a larger addition of filler BN by the maximum mass fraction at 70 wt% in the epoxy resin, thus enhancing the thermal conductivity of 3-TEMEP up to 1.2 W/mK, which is about 10 time higher than the pristine 3-TFMEP epoxy resin. These properties ensure these fluorinated hybrid epoxy resins to have great potential in the application of thermal transfer in the area of electronic and circuit components.

1. Introduction

The development of electronic and circuit technology has been significantly promoted in recent decades, so the electronic instruments have transformed from house-size to palm-size, even much smaller. However, as the electronic components in those instruments grow smaller, the problem of high heat influence becomes prominent, thus making amounts of damage to the components [1–4]. Therefore, the development of new strategy to dissipate heat of electronic components has been focused by many scientists and technical corporations nowadays. Finding a kind of materials that is suitable for heat dissipation is the most direct way to deal with this problem.

Epoxy resins, due to their great stability, rigidity and flexibility, have been considered as a kind of versatile material since 1930s. Recently, the application of epoxy resins in the area of electronic components production has attracted much attention of scientists and researchers [5–9]. Epoxy resins are often used as the bonding components and the fixing circuits in different parts of instruments. However, traditional epoxy resins always have a diathermancy according to their epoxy structure. As reported in the literatures [10,11], the thermal conductivity of traditional epoxy resins is usually in the range from 0.17 to 0.25 W/m·k (Table 1). Besides the thermal conductivity of metal materials and some inorganic salts, whose magnitude is between 10 and 10^2, these numerical values are quite insignificant.

The introduction of fillers with very high thermal conductivity into epoxy resins is a simple and convenience method for enhancing the thermal conductivity of epoxy resins [12–14]. The filled heat-conducting composites, which we called the hybrid mixture, have many advantages such as thermal stability, insulation and flexibility. These advantages could be applied in the production of electronic components. To avoid decreasing the insulation of the composites and reduce their cost, we usually choose the inorganic salts fillers rather than metal fillers. The fillers should have not only the low price and insulation property but also good compatibility with the epoxy resins.

In a view of the normal structure of epoxy resins, the crosslinking in epoxy resins polymer leads to high viscosity, which usually makes the fillers difficult to be mixed into epoxy resins. To the best of our knowledge, the application of epoxy resins needs the curing craft. Under the function of curing agent, the viscosity of epoxy resins will decrease temporarily, thus leading the mixing craft to be more easily. However, many kinds of epoxy resins for application in heat conduction are solid and thermosetting. Therefore, the temperature range from the melting to solidification of epoxy resin is quite narrow, which brings some difficulty for the curing process. To broaden the temperature range, we chose and used an epoxy resin which has high mobility at room temperature [15–17].

In this paper, we prepared a fluorinated epoxy resin monomer with the biphenyl structure, 3-trifluoromethyl phenylhydroquinone epoxy resin (3-TFMEP). It has high thermal stability, low dielectric constant and reduced moisture absorption simultaneously [18]. Low moisture

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Table 1
Thermal conductivity of various polymers at room temperature.

Material	Thermal conductivity (W/mK)
PVDF	0.19–0.23
ABS	0.25
PVC	0.12–0.17
PVA	0.2
Epoxy	0.17–0.21
PMMA	0.17–0.25
PPS	0.31

absorption is an important factor for advanced electronic packaging materials because the absorbed H_2O influence electrical-insulating and dielectric performance. Besides these advantages, 3-TFMEP is viscous liquid and still has mobility at relatively lower temperature (25–35 °C), which is the most attractive property to us. By using methylhexahydrophthalic anhydride (MEHHPA) as the curing agent and 2-methylimidazole (2-MI) as the curing accelerator, the cured fluorinated epoxy resins could be obtained.

Among those inorganic salts as the thermal fillers of polymers, boron nitride (BN) is well considered by many researchers due to its low density, high mechanical strength, chemical stabilities, and intrinsic electrical insulating properties, good electrical/dielectric properties, thermal stability, oxidation resistance, toxicity and cost, especially good thermal conductivity (290 W/m·k) [19–24]. It has analogous hexagonal crystal structure to graphite. After adding into the polymer system, BN crystal will transform into sheet structure and then enhance the thermal conductivity of the hybrid composites significantly. However, during the blending process, the BN filler usually cohere at high temperature of melting polymers because of its little size and low interface energy, thus decreasing the thermal conductivity of composites obviously. Furthermore, the content of thermal filler in the common hybrid composites could only reach around 30 wt% [25,26].

In our paper, BN filler will be mixed with liquid 3-TFMEP at temperature around 30 °C, which leads to no coherency and allows adding much more fillers to the mixture up to 70 wt%. The high content of thermal filler will make the curing epoxy resins possess really high thermal conductivity of 1.2 W/m·k. And the fluorinated structure also provides the solidified epoxy resins with low dielectric and good hydrophobic property. These properties ensure the epoxy resin with BN filler to be potential in the area of electronic component packaging.

2. Experimental section

2.1. Materials

(3-Trifluoromethyl)aniline monomer and 1, 4-benzoquinone was purchased from Beijing Chemical Company (Beijing, China). Epichlorohydrin (ECH) was obtained from TCI Shanghai Development Co., Ltd. MEHHPA and 2-MI were obtained from Energy Chemical. Co., Ltd. Sodium hydroxide (NaOH), sodium nitrite ($NaNO_2$) and tetrabutylammonium bromide were purchased from Sinophram Chemical Reagent Co., Ltd. Hexagonal BN powder with micrometer size was obtained from Xinnai Chemical Reagent Co., Ltd. All other reagents and solvents were obtained commercially and used without further purification.

2.2. Synthesis of (3-trifluoromethyl) benzoquinone monomer

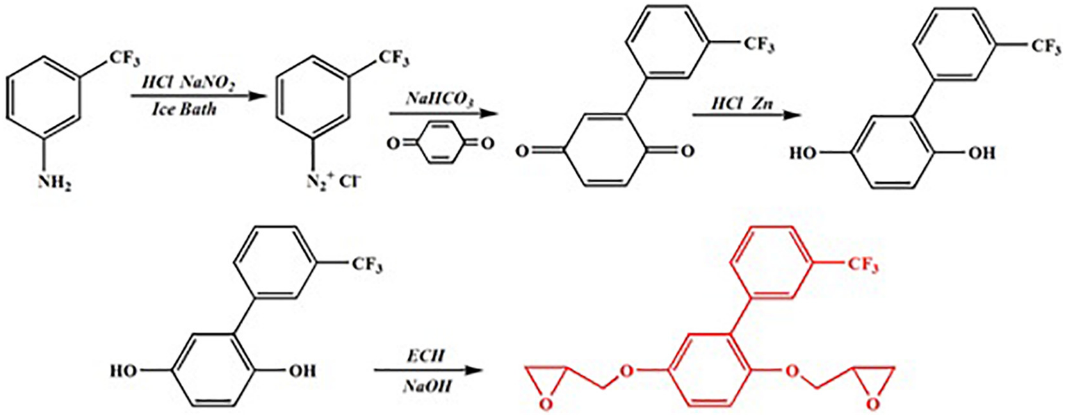
3-Trifluoromethylaniline (63.5 mL, 0.5 mol) and deionized water (200 mL) were added into a 2000 mL beaker equipped with a mechanical stirrer, a dropping funnel, and a thermometer. The mixture was kept stirring at a temperature under 5 °C by chilling in ice-salt bath. Then, hydrochloric acid (168 mL, 11.8 M) was added into the mixture dropwise to avoid the temperature growing fast. The sodium nitrite (36.25 g) was prepared into an aqueous solution of 27.7%. And then it was added from a dropping funnel to a well stirred mixture into the beaker. The mixture was stirred at 0–5 °C for 20 min and a transparent solution was obtained. The resulting solution was filtered and added dropwise into a mixture of 1,4-benzoquinone (43.2 g, 0.4 mol), sodium bicarbonate (50 g, 0.6 mol) and deionized water (200 mL). The reaction mixture was stirred in a big bucket at 8–10 °C for 4 h, and then kept at room temperature overnight. The resulting mixture was filtered and the precipitate was washed with deionized water for 7–8 times. Then, the final 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 (30 g), Zn powder (23.22 g), and deionized water (180 mL) were added into a 1000 mL, three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a condenser. In the atmosphere of nitrogen, the mixture was heated to 90 °C under stirring, followed by the addition of hydrochloric acid (30 wt%, 126 mL) at the speed of 1 drop per second. After that, the reaction system was allowed to reflux for 2 h under nitrogen atmosphere. Then, the hot mixture was filtered. After cooling the filtrate under 0 °C, the white precipitate would crystallize. Finally the precipitate of white needle crystals was filtered and dried in a vacuum oven.

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

As shown in Scheme 1, a mixture of 23.32 g (3-trifluoromethyl)



Scheme 1. The synthetic route of 3-TFMEP.