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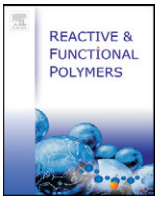

Hexa(eugenol)cyclotriphosphazene modified bismaleimide resins with unique thermal stability and flame retardancy

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ABSTRACT

We have successfully synthesized high performance bismaleimide based hexa(eugenol)cyclotriphosphazene (HECTP) resin which possess good mechanical, excellent thermal stability at high temperature and flame retardant properties. Hexa(eugenol)cyclotriphosphazene (HECTP) were obtained by the reaction of sodium, eugenol (EG) and hexachlorocyclotriphosphazene (HCCP). ^{1}H NMR and ^{31}P NMR were employed to confirm the formation of (HECTP). NMR analysis of the HECTP showed that all chlorine (Cl) atoms of HCCP were successfully substituted by sodium (Na) atom of the sodium eugenol. The 4,4′-bismaleimidodiphenylmethane (BMI) was reacted with EG and HECTP to produce BMI-EG1/1 resin with maleimide/allyl unit ratios of 1/1 and BMI-HECTP resins with maleimide/allyl unit ratios of 1/1, 1.5/1, 2/1, 2.5/1 and 3/1, respectively. The characterization results of TGA showed that HECTP could greatly enhance the thermal stability, the residues of BMI-HECTP 1/1, 1.5/1, 2/1, 2.5/1, 3/1 resins were 61%, 63.9%, 68%, 66.2% and 65% respectively. Besides, their flame retardancy were excellent, and the LOI values of all BMI-HECTP resins were 39%, 48.4%, 50.1%, 49.8% and 48.9% respectively, and the results of all BMI-HECTP resins at UL-94 vertical burning tests reached V-0 level and extinguished at once after removing the flame agitator. The flexural strength (77.77–100.03 MPa) of all BMI-HECTP resins was higher than that of BMI-EG1/1 (73.93 MPa). Furthermore, the impact strength of BMI-HECTP1/1, BMI-HECTP1.5/1 and BMI-HECTP 2/1 were 12.4, 13.3 and 11.94 KJ·m^{-2}, respectively, higher than that of BMI-EG1/1(9.42 KJ·m^{-2}), except for BMI-HECTP 2.5/1 (9.19 KJ·m^{-2}) and BMI-HECTP3/1 (6.14 KJ·m^{-2}).

1. Introduction

Bismaleimide (BMI) resins are high-performance materials endowed with outstanding performance, including low evolution of volatile gases, chemical resistance, low water absorption, dielectric properties, fatigue resistance under conditions of high humidity, high glass transition temperature, superior thermal stability that are relatively constant over a wide range of temperatures et al. [1–6], which make them appealing for a number of applications ranging, for instance, from multilayer printed circuit board, electronic and information sectors, microelectronics packaging, to aerospace industry etc. [7–11]. However, high melting point and poor processing characteristics make them difficult to achieve good formability. Most of all, the aromatic nature and the high crosslink density of the cured BMI resins cause these materials brittle, making it difficult to meet a broader range of application [12]. A number of researchers have investigated a range of methods aimed at improving the processability and the ductility of BMIs, from fillers including engineering thermoplastics [13–15] and elastomers [16], to coreacting bismaleimide with multifunctional reactants containing cyanate [17], amino [18] and allyl [19–20] compounds. Among the investigated approaches, the copolymerization with allyl compounds has become the most reliable method for decreasing brittleness and improving the processing characteristics of BMI resins. The commonly used allyl terminated compound is 2,2′-diallyl bisphenolpropane (DABPA), which was regarded as the most popular allyl compound to modify BMI resin and have obtained some achievements to date [21]. Though the aforementioned toughening techniques can improve the brittleness of the BMI resins, weaken the heat resistance of the materials. Thus, finding a method to balance the toughness and thermal stability of the modified BMI resins is necessary and has given rise to broad attention.

Recently, Mitsuhiro Shibata et al. have reported new bio-based thermosetting bismaleimide resins made with eugenol (EG), bieugenol (BEG: 3,3′-dimethoxy-5,5′-diallyl-1,1′-biphenyl-2,2′-diol), allyl-etherified eugenol (AEG), and allyl-etherified BEG(ABEG) [22–23].The results showed that the cured EG/BMI, BEG/BMI AEG/BMI and ABEG/BMI resins had higher glass transition temperatures (T_g) than DABPA/BMI and significantly lower flexural moduli than cured DABPA/BMI as well. The higher concentration of allyl functionalities within the eugenol structure compared to DABPA, leads to a higher crosslinking density when reacted with BMI, thereby, improving the resin's T_g and

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mechanical properties [23]. Luo et al. reported a cured resin made from allyl-etherified phenol novolac and BMI which can improve the thermal properties [24]. Gu et al. also reported that cured materials made from allyl-etherified polyaralkylphenolic resin (Xylok) and BMI exhibit superior thermal and mechanical properties [25]. However, it is difficult to achieve complete allyl cure, requiring prolonged heating (nearly 6 h) at 250 °C, which degrades other fragile groups in the network [26]. Therefore, it is a required to find an effective approach, which can not only enhance the toughness of the modified BMI resins but also improve its thermal properties.

Phosphazene based family of materials have received greatly interest in recent decades, because they not only have a wide range of thermal and chemical stabilities, but they can also provide improved thermal and flame retardant properties to polymers and relevant materials [27–32]. Several cyclotriphosphazene derivatives with excellent thermal properties and preferable compatibility have been synthesized by replacing Cl atoms of HCCP [33–36]. The derivatives of cyclotriphosphazene have been used as additives or reactants in a variety of fields such as special rubber [37], biomedicine [38] and fire retardancy of resin [39–42].

Herein, we have focused to synthesize a new kind of star-shaped cyclotriphosphazene derivative named hexaeugenolcyclotriphosphazene (HECTP) which contains higher concentration of allyl functional group through the reaction of eugenol (EG) and HCCP. The structure of HECTP was characterized by proton nuclear magnetic resonance (^{1}H NMR), phosphorus nuclear magnetic resonance (^{31}P NMR) and FTIR to verify that we prepared HECTP successfully. And then we obtained the cured resins by the curing of BMI with EG, HECTP, respectively. Meanwhile, the corresponding properties including glass transition temperatures (T_g), thermal resistance, flame retardancy and mechanical properties were investigated systemically for BMI-HECTP resins and compared with BMI-EG. All of the above analysis confirmed that the performances of hexa(eugenol)cyclotriphosphazene modified bismaleimides were enhanced on thermal stability, flame retardants and mechanical properties.

2. Experimental

2.1. Materials

4,4′-bismaleimidodiphenylmethane (BMI) was provided by Northwestern Chemical Engineering Institute (China). The hexachlorocyclotriphosphazene (HCCP) 99.9(t) % trimer was obtained from Lan Yin Chemical Corporation, China. Eugenol (99%) was purchased from Johnson Malthey Co., Ltd. (England). Other solvents and common chemicals were obtained from Beijing Chemical Works (China).

2.2. Preparation of hexa(eugenol)cyclotriphosphazene (HECTP)

The HECTP was synthesized by reacting HCCP with eugenol and sodium in tetrahydrofuran (THF). The whole process was divided into two steps. The first reaction step was carried out as follows: sodium (49.68 g, 2.16 mol), THF (1500 mL) were added in a 2000 mL four-neck round bottom flask attached to a condenser, a thermometer, a constant pressure funnel and a nitrogen port. Then, a mixture of eugenol (389.66 g, 2.376 mol) and THF (250 mL) were added gradually into flask by constant pressure funnel, and reacted under nitrogen atmosphere for 24 h. In the next step a mixture of HCCP (104.4 g, 0.3 mol) and THF (250 mL) were added gradually into solution obtained from the first step. The reaction mixture was stirred at 60 °C for 72 h. After the reaction, the solution of HECTP was washed with alcohol and deionized water successively. The synthesis routes of HECTP are shown in Fig. 1.

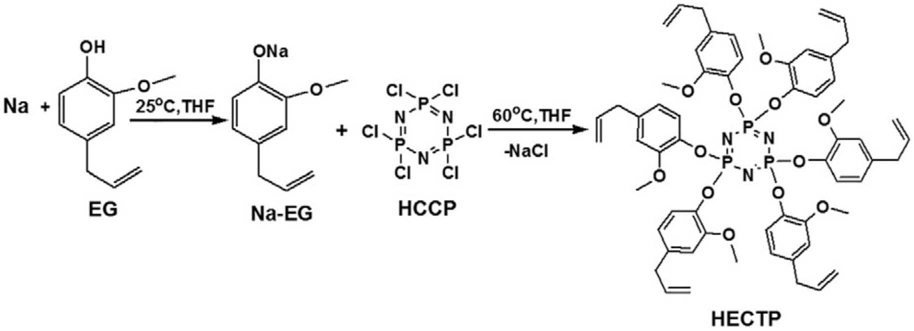

Fig. 1. The detailed synthesis route of HECTP.

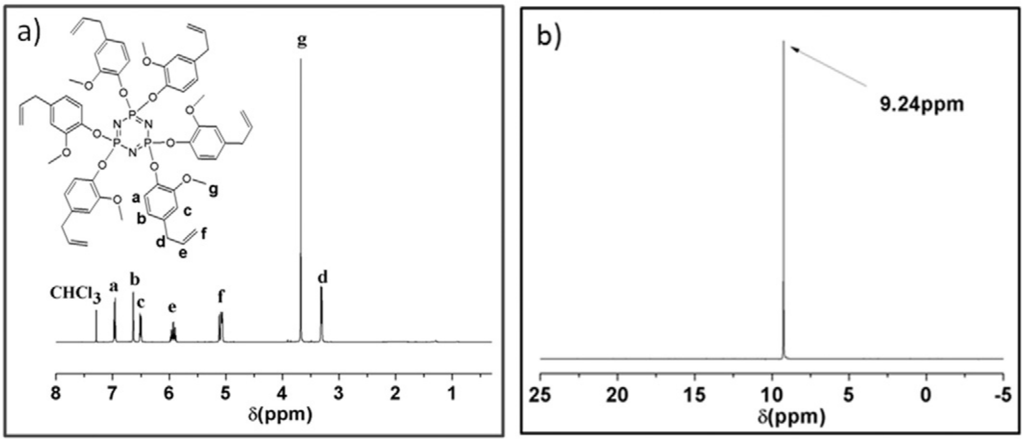

Fig. 2. The ^{1}H NMR (a)and ^{31}P NMR (b) spectra of HECTP.