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Synthesis and characterization of a novel heat resistant epoxy resin based on N,N′-bis(5-hydroxy-1-naphthyl)pyromellitic diimide

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ABSTRACT

A novel epoxy resin containing imide and naphthyl groups was synthesized, and characterized using NMR, NMR, FT-IR spectra and elemental analyses. The curing behavior was investigated with differential scanning calorimetry (DSC) using 4,4′-diaminodiphenylsulfone (DDS) as curing agent. The physical properties of the cured polymer were evaluated with dynamic thermal mechanical analysis (DMTA) and thermogravimetric analysis (TGA). The results showed that the cured polymer exhibited higher glass transition temperature (T_g) and better thermal stability compared with those commercial available heat resistant epoxy resins.

1. Introduction

Epoxy resins have the combined advantages of excellent chemical and corrosion resistances, good thermal and dimensional stability, and great mechanical and electrical properties, ensuring their wide applications in laminating, adhesive, surface coating and semiconductor encapsulation. However, the conventional epoxy resins are unable to satisfy some applications such as integrated circuit packaging and advanced materials which require higher thermal resistance [1]. Hence it is necessary to design and synthesize novel high heat resistant epoxy resin systems to suit these applications.

Many approaches have been reported to enhance the heat resistance as well as moisture resistance of epoxy resins by changing the structure of the starting resins which influences the properties of final cured epoxy polymers. The incorporation of a naphthalene structure into the epoxy skeleton is an effective way to increase the glass transition temperature and thermal stability [2]. Kaji and Dndo [3], Pan et al. [4], Wang et al. [5] and Castell et al. [6] synthesized the naphthalene-based epoxy resin containing naphthyl and phenyl structures. Xu et al. [7] and Ren et al. [8] reported that the naphthalene-cycloaliphtic moiety linked epoxy resins were prepared and the cured polymers showed higher glass transition temperatures. Liquid crystalline epoxy resins based on naphthalene mesogen were also studied in recent years and exhibited good thermal properties [9]. To design and synthesize epoxy resins containing both naphthyl and aromatic or cycloaliphatic group by chemical bonding in molecular backbone are the trend of recent studies [8,9]. Polyimides are well known for their excellent heat resistant stability due to the thermal stable imide linkage. Polymers, including epoxy resins, made up of aromatic and/or heterocyclic structures have superior thermal properties than the polymers mainly based on flexible aliphatic chains [10]. Considerable attentions have been paid on introducing imide group into epoxy resin network to improve the thermal properties of the cured polymer. Most of the report focused on preparing imide group containing curing agents [10–14] and blending epoxy resins with thermoplastic polyimides or with functionalized polyimides [15]. Few reports were found about modifying the backbone structure of epoxy resins with imide group [16]. Moreover, Tao et al. [17] synthesized a novel imide ring and siloxane-containing cycloaliphatic epoxy resin. Li et al. [18] studied the properties and pyrolysis of a novel siloxane and imide modified epoxy resin from N,N′-bis(4-hydroxylphenyl)-5,5′-bis(1,1,3,3-tetramethyl disiloxane-1,2-diyl)-bis-norborane-2,3-dicarboximide. When cured with siloxane-containing dianhydride, the glass transition temperature of the cured resin was 173.2 °C. Directly blending epoxy resin with polyimide has to focus on the phase separation problem and control the morphology of the cured polymer to obtain the desired performance. Although partial modification of the skeleton of the epoxy rein or curing agent with imide group, including blending with reactive imide compound, could sometimes improve the thermal properties of the cured polymer, the increasing extent is limited. Synthesis of epoxy resin from imide group containing monomers could precisely design and control the backbone structure of the resin, which will retain in the cured

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polymer network and determine the properties of the final product. Furthermore, these imide group containing epoxy resins could be cured with different commercial available hardeners, or even formulated with other epoxy resins to form various cured polymers with desired thermal properties. As a possible approach to advanced thermosets, studies aimed to synthesize a novel heat resistant epoxy resin containing both naphthyl and imide groups have been initiated in our group. The incorporation of naphthyl ring could increase the rigidity of the backbone and the presence of imide linkage could also facilitate the thermal properties of the cured resins. The combination of the special features of the naphthyl/imide structure is expected to offer the epoxy resin great improvement in glass transition temperature and thermal stability to satisfy the requirement in the field of electrical encapsulation and advanced composites.

The goal of this work was to describe the synthesis and structure of a novel heat resistant epoxy resin containing both naphthyl and imide groups. The characteristics of cure and physical properties of the cured polymer were investigated using several measurement methods, and compared with those of commercially available heat resistant epoxy resin.

2. Experimental

2.1. Materials

5-amino-1-naphthol purchased from Acros, Pyromellitic acid dianhydride and p-toluene sulfonic acid (pTSA) from Sinopharm Chemical Reagent Co Ltd., China and epichlorohydrin (ECH) from Tianjin Bodi Chemical Reagent Co Ltd. were used without further purification. Benzyltrimethylammonium chloride from Acros was used as phase transfer catalyst. 4,4′-diaminodiphenysulfone (DDS) obtained from Yinsheng Chemicals Co Ltd., China was used as curing agent. Tactix 556 (Scheme 1a) with epoxy equivalent weight of about 225 g/equiv. was kindly supplied by Huntsman Advanced Materials Americas Inc. Naphthalene-dicyclopentadiene epoxy resin (NDEP) is another heat resistant epoxy resin synthesized in our laboratory in the previous study [8]. The chemical structure is shown in Scheme 1b. All solvents and other chemicals were of reagent grade or better.

2.2. Synthesis

2.2.1. Synthesis of N,N′-bis(5-hydroxy-1-naphthyl)pyromellitic diimide

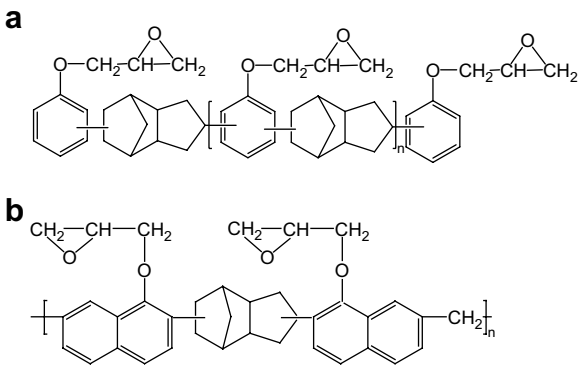
7.95 g of 5-amino-1-naphthol and 100 ml of acetone were put into a 250 ml four-necked round-bottom flask equipped with a heating water bath, a stirrer, a reflux condenser, a dropping funnel and nitrogen inlet. The mixture was heated to 40 °C to let the 5-amino-1-naphthol well dissolve in the acetone. Then solution of 5.45 g pyromellitic acid dianhydride dissolved in 50 ml of acetone was added dropwise over a period of 1 h, and the mixture was maintained at 40 °C for another 5 h. After the reaction was completed, the resultant mixture was filtered and then washed with acetone three times. A lustrous green powder (indicated as **1** in Scheme 2) weighed 9.9 g was obtained.

ESI-MS: $m/z = 534.9$; ^{1}H NMR (DMSO-d_6) δ (ppm): 13.59 (s, 2H, –COOH), 10.49 (s, 2H, aromatic hydroxyl), 8.14 (s, 2H, protons of phenyl), 8.09 (d, 2H), 7.77 (d, 2H), 7.65 (d, 2H), 7.50 (t, 2H), 7.36 (t, 2H), 6.93 (d, 2H) (protons of naphthyl). Elemental analysis: Calc. %: C: 67.16, H: 3.73, N: 5.22; Found %: C: 67.39, H: 3.65, N: 5.63.

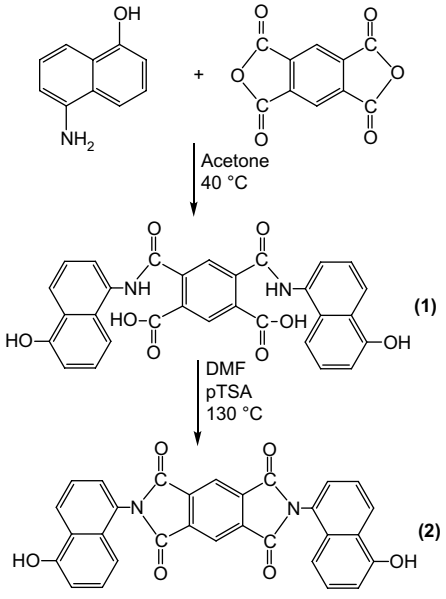
9.9 g of **1**, 45 ml of N,N′-dimethyllfomamide and 15 ml of toluene were added to a 100 ml four-necked round-bottom flask equipped with a heating oil bath, a magnetic stirrer, Dean–Stark condenser and nitrogen inlet. After completely dissolved, 0.1 g of p-toluene sulfonic acid (pTSA) was added, then the mixture was heated to 130 °C and refluxed for 8 h. The generated water was removed from the mixture by azeotropic distillation. After the reaction was completed, the mixture was concentrated to remove some of the solvent and then poured into distilled water at 0 °C and stirrer for 0.5 h. The mixture was filtered and washed with water three times, the solid product was then placed in the vacuum oven to remove the traces of solvent and water. A brown-colored solid product (indicated as **2**) weighed 7.7 g was obtained. The reaction equation is shown in Scheme 2. ESI-MS: $m/z = 499.1$; ^{1}H NMR (DMSO-d_6) δ (ppm): 10.54 (s, 2H, –OH), 8.49 (s, 2H, protons of phenyl), 8.35 (d, 2H), 7.70 (b, 2H), 7.61 (t, 2H), 7.36 (t, 2H), 7.24 (m, 2H), 6.97 (d, 2H) (protons of naphthyl) (Fig. 1) IR (KBr): 3410 cm^{-1} (–OH of naphthyl ring); 1273 cm^{-1} (C–O); 1776 cm^{-1}, 1726 cm^{-1}, 1375 cm^{-1}, 727 cm^{-1} (imide bands); 1630 cm^{-1}, 1598 cm^{-1}, 1519 cm^{-1}, 1581 cm^{-1}, 1416 cm^{-1} (C–C of naphthyl and phenyl) (Fig. 2a). Elemental analysis: Calc. %: C: 72.00, H: 3.22, N: 5.60; Found %: C: 71.98, H: 3.25, N: 5.59.

2.2.2. Synthesis of glycidyl ether of N,N′-bis(5-hydroxy-1-naphthyl) pyromellitic diimide

7.5 g of **2** and 50 ml of epichlorohydrin were put into a 100 ml four-necked round-bottom flask equipped with a heating oil bath, a magnetic stirrer, a syringe pump and a modified reflux condenser. Benzyltrimethylammonium chloride of 0.1 g was added as phase



Scheme 1. Structures of Tactix 556 epoxy resin (a) and NDEP (b).



Scheme 2. Synthesis of N,N′-bis(5-hydroxy-1-naphthyl) pyromellitic diimide.