



Structural aspects of high temperature thermosets – Bismaleimide/propargyl terminated resin system-polymerization and degradation studies

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ABSTRACT

Bispropargyl ether of bisphenol-A (BPEBPA), 4,4'-bismaleimido diphenyl ether (BMIE) and a blend consisting 60 mol% of BPEBPA and 40 mol% of BMIE are prepared. The materials are structurally characterized by FTIR. The curing characteristics of the monomers are measured by FTIR and DSC. The results indicated that BPEBPA–BMIE blend has low ΔH_{cure} (J g^{-1}) for the thermal polymerization and the whole temperature window for the exothermic curing reaction is shifted to lower temperature compared to BPEBPA. Borchardt and Daniels method is used to study the cure kinetics of the materials. The thermal curing of BMIE requires activation energy of $156.0 \text{ kJ mol}^{-1}$ whereas BPEBPA needs slightly higher activation energy ($177.2 \text{ kJ mol}^{-1}$). From the TG studies, it can be concluded that the cured BPEBPA exhibits higher thermal stability than the cured BMIE due to the more complex network structure that are formed during thermal polymerization of BPEBPA. Dharwadkar and Kharkhanavala equation is employed to calculate the activation energy needed for the thermal degradation of the thermally cured materials. BPEBPA shows much higher activation energy (65.5 kJ mol^{-1}) for thermal degradation indicating the higher thermal stability over the other two materials (BMIE: 42.5 kJ mol^{-1} and BPEBPA–BMIE blend: 46.9 kJ mol^{-1}). The isothermal degradation of cured materials is effected in nitrogen atmosphere for constant time interval (10 min). The detailed analysis of the degradation products by GC–MS revealed the formation of phenols and several substituted phenols. This finding hints that the competitive C–C and C–O scissions of the chromene ring units formed via the Claisen rearrangement of the aryl propargyl ether system present in BPEBPA is operative.

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1. Introduction

High temperature and high performance polymers along with the proper choice of fiber reinforcement lead to composites having superior properties compared to common materials. These properties include stability at temperatures in excess of $300 \text{ }^\circ\text{C}$, low density, high specific strength and stiffness, high toughness, low heat

distortion and good processability. To fulfill the need for the high temperature resistant polymeric materials used in many fields including transportation, electronics, military, space exploration, etc., a great amount of research has been focused in this area. The high thermal stability in organic polymers can be achieved by three different ways viz., (1) by improving the rigidity of the polymeric chain by incorporating aromatic units, (2) by synthesizing polymers with the ability to crystallize and (3) by designing materials that can undergo crosslinking.

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In the field of aeronautics and electronics, the polymers most often used to prepare composite parts are based on epoxy resins but they have limited thermal stability (150–180 °C) depending on the chemical system chosen [1–3]. In order to have materials with higher thermal stability than the epoxy systems several thermosetting materials have been developed. Bismaleimides [4–7], cyanate esters [8,9], benzocyclobutene resins [10,11], acetylene terminated resins [12–14], bisnadimide resins [15,16] and aryl ethynyl resins [17–19] are some of the high performance thermosets. Apart from the above systems, unusual high performance thermosets like styrenyl terminated oligomers [20], propargyl terminated resins [21–23], biphenylene containing resins [24,25], bisphthalonitrile resins [26,27], biscyanamide resins [28,29], bisacenaphthylenyl systems [30] and paracyclophane terminated oligomers [31,32] were being developed for the fabrication of composite materials which can have continuous service at high temperatures.

The commercially available high performance thermosetting materials like epoxy resins and several imides structure bearing resin systems (bismaleimides, bisnadimides, etc.) are hydrophilic in nature owing to the presence of polar groups in these systems. There is a strong need for excellent hydrophobic thermosets without losing high temperature stability for sophisticated applications in electronics and aviation sectors.

Acetylene terminated (AT) resins [12–14,33–39] have been developed for various applications where properties such as excellent thermal resistance, service temperature, reduced defects, low moisture pickup and high strength are important. The curability and processability upon heating without releasing void producing by products are the major advantages of AT resin systems. The relatively expensive complex process to prepare acetylene terminated monomers is the most significant weakness of the AT resins.

In contrast to terminal acetylene or phenyl acetylene functional monomers, propargyl ether derivatives are attractive from the point of view, ease of synthesis and polymerization. Initially, synthetic methods have been developed for the bulk preparation of highly pure bispropargyl monomers from industrially available low cost starting materials [21–23,40–42]. Major advantages of propargyl terminated resins are long self life, good thermal stability, low moisture absorption, excellent adhesion, low dielectric constant and acceptable physico-mechanical properties. The formation of void free materials without the application of high pressures is an added advantage in the case of propargyl terminated resins.

Blends of bismaleimide (BMI) and allyl derivatives of phenols [43,44] were extensively studied. The results indicated that the blend resins showed better toughness and high heat resistance. In the present investigation, the structural resemblance between the allyl and the propargyl groups is used to make bispropargyl ether–bismaleimide blend so as to achieve easy thermal processability and better thermal stability. The structural features clearly indicate that such systems will crosslink on heating without the liberation of any volatile compounds and thus lead to void free materials. In this study, bispropargyl ether of

bisphenol-A (BPEBPA), 4,4'-bismaleimido diphenyl ether (BMIE) and 60:40 blend of BPEBPA and BMIE were prepared and thermally polymerized at 200 °C. The thermal studies were carried out using Differential Scanning Calorimeter (DSC) and Thermogravimetric Analyzer (TGA). Off-line isothermal degradation in nitrogen atmosphere was carried out for the thermally polymerized samples and the pyrolysis products were separated and identified using Gas Chromatograph–Mass Spectrometer (GC–MS). From the results obtained, attempts have been made to understand the structural aspects of the cured materials.

2. Experimental

2.1. Materials

Maleic anhydride, 4,4'-oxydianiline, acetone, anhydrous sodium acetate, bisphenol-A, sodium hydroxide, isopropanol, methanol and tetrabutyl ammonium bromide were obtained from E. Merck India Ltd., Mumbai. All the materials were used as received. Propargyl chloride obtained from Grauer & Weil (India) Limited, Vapi 369 195 was distilled at 57 °C before use. Acetic anhydride (Reachem Laboratory Chemicals (P) Ltd, Chennai 600 098) was dried over calcium hydride for 12 h and freshly distilled (boiling point: 138–140 °C/760 mmHg) and used.

2.2. Synthesis of bisamic acid

4,4'-Oxydianiline (0.15 mol) was dissolved in 500 mL of dry acetone with constant stirring at room temperature. Maleic anhydride (0.33 mol) was added in small portions for 15 min. An exothermic reaction was noted and stirring was continued for 30 min. The pale yellow bisamic acid was filtered in a G4 sintered crucible and washed well with large quantities of ice cold acetone to remove the acetone soluble materials. The material was dried in a vacuum oven (1 mmHg) kept at 50 °C for a period of 24 h.

2.3. Synthesis of 4,4'-bismaleimido diphenyl ether (BMIE)

The pale yellow bisamic acid powder (0.1 mol) was dispersed in dry acetone taken in a two necked round bottom flask fitted with reflux condenser. Anhydrous sodium acetate (2.7 g) and acetic anhydride (20 mL) were added to the solution as the dehydrating agent. The reaction mixture was allowed to reflux gently for 6 h. After this period, yellow solution was obtained. This solution was poured drop wise into large quantities of crushed ice with constant stirring. The bismaleimide separated as a pale yellow powder was filtered and washed with ice cold distilled water to remove all water soluble impurities. The material was dried in a vacuum oven (1 mmHg) at a temperature of 50 °C for a period of 24 h. The synthetic route was shown in Scheme 1.

2.4. Synthesis of bispropargyl ether of bisphenol-A (BPEBPA)

Among the several procedures reported in the literature [21,22,41–43], the procedure developed by Inbasekaran and Dirlikov [42] was used to synthesize BPEBPA (Scheme 2).

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