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Synthesis and characterization of difunctional benzoxazines from aromatic diester diamine containing varying length of aliphatic spacer group: Polymerization, thermal and viscoelastic characteristics

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ABSTRACT

A series of four novel diamine-based benzoxazines containing aliphatic spacer groups in their structures were synthesized by the condensation of formaldehyde, phenol and aromatic diester diamine obtained by reduction of their precursor dinitro compounds. The four aromatic diamines synthesized are ethane-1,2-diyl bis (4-aminobenzoate), butane-1,4-diyl bis (4-aminobenzoate), hexane-1,6-diyl bis (4-aminobenzoate), and octane-1,8-diyl bis (4-aminobenzoate). The chemical structures of diamine benzoxazines are confirmed by Fourier-transform infrared (FTIR) and nuclear magnetic resonance spectroscopy (^{1}H and ^{13}C NMR). The curing properties with respect to the basic benzoxazine structure of the monomer were studied by differential scanning calorimetry (DSC). The softening points, onset of cure temperatures and the heat of polymerization have all decreased with increasing spacer length. DSC of polybenzoxazines indicated decrease of glass transition temperature (T_g) with increasing spacer length. The thermal behavior of polybenzoxazines was studied by thermo gravimetric analysis (TGA). Higher T_{d5} and T_{d10} values were obtained by polybenzoxazines with longer spacer groups but an inversion in thermal stability was observed after T_{d10}. The derivative thermo gram of polybenzoxazine indicated a two stage degradation process due to chain cleavage at Mannich bridge as well as breakdown of polymer chain respectively. The char yield at 700 °C has decreased with increasing spacer length from 47% to 27%. The mechanical properties of glass cloth coated polybenzoxazines were evaluated with dynamic mechanical analysis (DMA). The storage modulus of the composite laminate of polybenzoxazine has increased with increasing spacer group which could be due to improvement in adhesion between fibers and resin with increasing flexibility of the resin.

1. Introduction

Benzoxazines are six-membered heterocyclic compounds synthesized via Mannich condensation reaction from phenols, amines, and formaldehyde [1]. However, the usefulness of benzoxazines as precursors for a class of thermosetting phenolic resins with excellent mechanical and thermal properties has not been recognized until recently [2]. Benzoxazines polymerized by a thermally induced ring-opening reaction to form a new thermosetting resin [3]. Polybenzoxazines possess

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several outstanding properties such as high thermal stability, high glass transition temperature, near-zero shrinkage after curing, exhibit good dielectric properties and low water absorption. Because of these properties they used as high performance materials in various fields, such as automotive, aerospace, construction industries and electronic packaging applications [4–9].

Initially benzoxazines were synthesized using monophenols, monoamines, and formaldehyde, but they could not form polymers with high molecular weight. Most difunctional benzoxazines were synthesized from bisphenol, monoamines, and formaldehyde. The large varieties of aromatic bisphenol and monoamines allow for considerable molecule-design flexibility of benzoxazines [10–15]. The properties of polybenzoxazine materials mainly depend on the molecular structure of the corresponding benzoxazines.

A second approach to synthesize dibenzoxazines is to use aromatic diamines, monofunctional phenols and formaldehyde in a suitable solvent. Recently, a series of novel diamine based benzoxazine monomers has been successfully synthesized by using high boiling nonpolar solvent in a three-step synthetic method. They exhibit increased thermal stability of polymers relative to conventional polybenzoxazines due to inter nitrogen linkage with other repeating unit [16,17]. Allen and Ishida have recently developed a series of aliphatic diamine-based benzoxazine monomers [18,19]. These monomers were easily synthesized using a monofunctional phenol with linear aliphatic diamines by varying the length of the linear aliphatic chain. The diamine-based benzoxazine with a short aliphatic chain demonstrated the ability to polymerize at lower temperatures to give the polymer with a comparable glass transition temperature (T_g) and improved mechanical properties to the traditional polybenzoxazines.

Aromatic diamine-based polybenzoxazine have been reported in literature which can provide higher glass transition temperature and thermal stability than the conventional bisphenol-A-based polybenzoxazine and this kind of benzoxazine resin can be polymerized in the same manner as the bisphenol-based polybenzoxazines [20]. High curing temperature and brittleness of the cured network as a consequence of the short molecular weight of the network structure are limited to the application of benzoxazine. Addition of a flexible component, often reactive, into the thermosetting matrix have been attempted in order to improve the toughness of polybenzoxazines [21–25]. Polybenzoxazines containing substituted cyclohexyl moieties have been synthesized to impart better processibility, low peak cure temperature and a wide cure controllable window [26].

Earlier we have prepared cardanol based benzoxazine, which can act as replacement of petro based bisphenol-A benzoxazine resin as reactive diluents and toughening agent of conventional benzoxazine [27]. The high molecular weight cardanol monomers have low percentage of reactive groups and as result displayed low heat release during cure and correspondingly lower T_g values. Hydroxy benzoxazoline was copolymerized with cardanol benzoxazine to improve the glass transition temperature [28]. Cardanol based epoxy resin was reacted with cardanol benzoxazine in a bid to develop a bio based curing system. Synergistic effect of improvement in properties over pure homopolymers was observed [29].

High strength and high temperature applications of benzoxazines are met with high aromatic content in the back bone. However, they are more difficult to process and the polymers are tending to be brittle. Thermal stability and processing of benzoxazines can be balanced by the use of flexible spacer groups in between aromatic rings of benzoxazine monomers. The present work takes the advantage of benzoxazines rich molecular design to develop matrix materials with inherent flexibility in the molecular structure that is less brittle than typical benzoxazines (Fig. 1). A series of aromatic diamine-based benzoxazines were designed and synthesized by incorporating a flexible diol component as ester groups in between the benzene rings of the aromatic diamine according to the Scheme 1. The diamine portion contained aliphatic chain of 2–8 carbons in between their ester linkages. The ester linkage increases opportunities for bond rotation and structural disorder in the polymer chain improving processibility. The structures of these monomers are characterized by Fourier transform infrared (FTIR) spectroscopy, ^{1}H – and ^{13}C – Nuclear magnetic resonance spectroscopy (NMR). It is of interest to establish structure property relationships in these diamine benzoxazines, particularly the effect of aliphatic chain length, with respect to curing behavior, thermal stability and viscoelastic properties. The ring-opening polymerization of dibenzoxazines monomers was studied with Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). The thermal stability of polybenzoxazine was studied by thermo gravimetric analysis (TGA) whereas their viscoelastic behavior was investigated by dynamic mechanical analysis (DMA).

2. Experimental

2.1. Materials

Phenol, Para formaldehyde, 4-Nitro benzoic acid, hydrazine hydrate (99%), xylene (mixture of isomers) and 1,4-butane diol were purchased from S.D. Fine Chemicals Ltd. India; 10% Pd/C was obtained from Spectrochem, India; 1,2-ethanediol and 1,6-hexane diol were procured from Sigma–Aldrich, Bangalore, India; 1,8-ocatane diol was obtained from Hychem, India. The starting reagents were used directly without further purification. P-nitro benzoyl chloride was prepared according to a text book procedure [30]. The recrystallized product (m.p. 72–73 °C) was used in all synthesis of dinitro compounds.

2.2. General procedure for synthesis of dinitro compounds (1–4)

To a 500 ml three-neck round bottom flask equipped with a magnetic stirrer, reflux condenser and nitrogen inlet was introduced a solution of the corresponding diol (13.47 mmol) and triethyl amine (3.734 ml; 26.94 mmol) in anhydrous