



Hybrid dual-curable cyanate ester/boron phosphate composites via sequential thiol-ene photopolymerization and thermal polymerization



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ABSTRACT

The aim of this study was to improve hybrid dual-curable cyanate ester/boron phosphate composites via sequential thiol-ene photopolymerization and thermal polymerization for high performance applications such as aerospace and electronic devices. A novel 2,2'-diallylbisphenol A dicyanate ester (DA-BADCy) which is the allyl group containing cyanate ester was synthesized and characterized. DA-BADCy, silicon containing monofunctional thiol compound, trifunctional thiol compound and boron phosphate were cured using both ultraviolet (UV) and thermal methods. Using thiol-ene system, cyanate ester formulations, which are normally prepared at high temperatures, were prepared at room temperature. This study maintains ease of application for cyanate esters. Thermal stability, flammability and thermal conductivity of the samples were evaluated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), limiting oxygen index (LOI) and laser flash method, respectively. The samples were characterized with the following analysis; gel content, water absorption capacity and stress-strain test. Hydrophobicity of the samples was determined by the contact angle measurements. Moreover, the surface morphology of the samples was investigated by a scanning electron microscopy (SEM-EDS). The obtained results prove that the composites have good thermal and mechanical properties and with the help of easier preparation techniques, they can be used in many applications such as aerospace, electronic devices, materials engineering.

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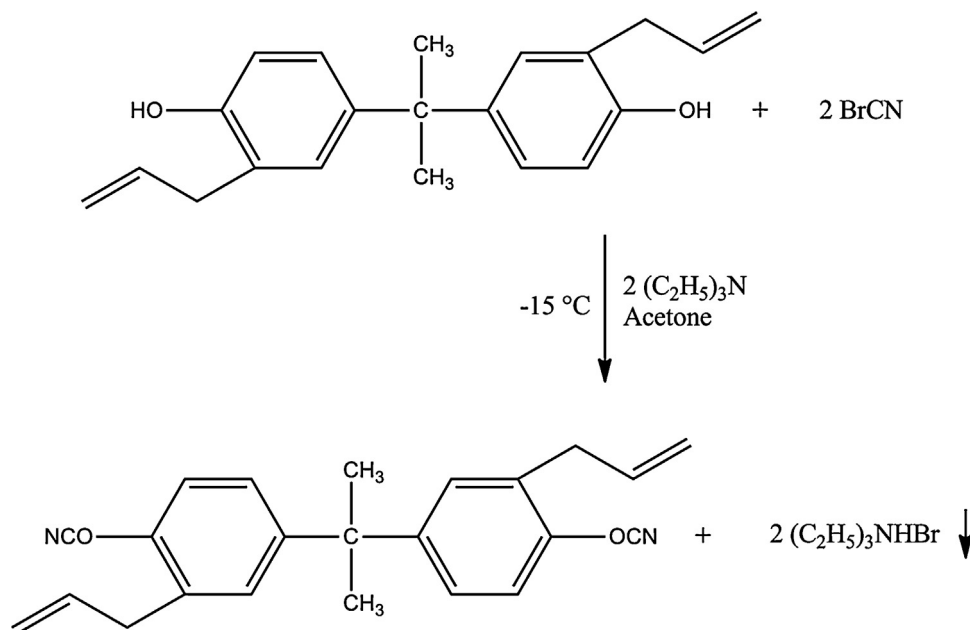
1. Introduction

UV curing technology has been used because of its many advantages, including fast reaction rates, solvent-free curing at room temperature, low energy consumption, and low capital investment. The applications of this technology include electronic, printing, optical and electro-optical materials, as well as the use as adhesives, sealants, coatings and surface modification components. Recently, the application of UV-curing technology has been extended to the assembly of various electronic devices for the purpose of encapsulation, adhesion, and protection. However, the UV reaction does not take place in the shadow area, so another method is necessary for curing the uncured area. Thus, a dual curing technology, typically UV and thermal curing, has been developed to address this problem [1].

Although thiol-ene reaction was first suggested by Posner in 1905 [2] and thiol-ene polymerization was put forward by Kharasch et al. in 1938 [3], the unique features of this useful reaction/polymerization began to interest both the academic and the industrial community in the last decades. Recently, thiol-ene click reaction which is also called as thiol-ene coupling has gained a lot of interest due to its ease of application and desirable properties for a click type of reaction [4,5]. Thiol-ene click reaction tolerates many functional groups and the reactions take place in mild conditions. Thiol-ene click reactions can be conducted in the absence of solvent and catalyst and the products can be easily purified in high yields [6]. This reaction is also an efficient tool for the functionalization of several surfaces, molecules, and polymers [7–9]. Generally, thiyl radicals are generated under UV irradiation and these radicals add to double bonds (enes) to give anti-Markownikoff products in high yields [10,11].

Dual-cure systems combining UV irradiation and thermal treatment have been recently developed. For instance; in one study, dual-cure thermoset amide and acrylate functionalized latexes were prepared for waterborne coatings. It has been reported

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Scheme 1. Synthesis of DA-BADCy.

that prepared latexes films showed high mechanical and thermal properties [12]. In other study, dual-curing of waterborne urethane–acrylate coatings were prepared. It has been reported that these water borne dual-cured coatings proved to be more resistant to accelerated weathering than thermoset melamine/acrylate clearcoats which are commonly used as automotive finishes [13].

Cyanate esters have attracted considerable attention due to their unique properties such as low water absorption, low dielectric constant and heat release rate, good strength, excellent adhesion to metals, glass and carbon fibers, low out gassing in curing and high environment resistance [14]. Because of these properties, cyanate ester based resins have been widely used as adhesives and matrixes for composites. They have many properties that are highly required in electronics, aerospace and adhesive industries. The aryl–cyanate (Ar–O–CN) compounds undergo thermal cyclotrimerization to form cyanurates with the help of phenol. The cyclotrimerization leads to highly crosslinked aryl cyanurates which have three-dimensional networks. The physical, mechanical and thermal properties of the cured cyanate resins (polycyanurates) depend on their backbone structures, which can be defined by proper selection of the phenol and cyanate monomers [15].

In the recent years, various studies have been done in order to improve the properties of cyanate ester nanocomposites. In one study, cyanate ester/graphane oxide nanosheet composites were prepared and the composites exhibited better thermo-stability in comparison with the cyanate ester resin matrix [16]. In other study, rod-like silicate/cyanate ester nanocomposites were prepared and the mechanical properties of nanocomposites increased in the range of 40–55% relative to the neat cyanate ester resin [17]. In another study, a cyanate matrix was modified by the incorporation of an organically modified layered silicate (Nanofil 919) and/or polysulfone (PSF) and thermogravimetric analyses indicated that the thermal stability of the modified matrices were improved respect the onset decomposition temperature [18].

Boron and phosphorus containing substances are often used in the composite materials due to their superior properties. One of these materials is boron phosphate. In one paper, conductivity and characterization of acid/base polymer blend membranes and their composites containing solid boron phosphate has been presented. The acid–base blend membranes showed very good

thermal stability, moderate swelling and good proton conductivity thanks to boron phosphate [19]. In another article, composite membranes of poly(ether ether ketone)/BPO₄ with improved thermal and electrochemical properties were prepared by introducing boron phosphate [20].

With this article, both 2,2'-diallylbisphenol A dicyanate ester (DA-BADCy) synthesis and its composites are reported for the first time. In this study, the DA-BADCy was prepared from the 2,2'-diallylbisphenol A and cyanogen bromide (CNBr) in the presence of triethylamine. DA-BADCy, silicon containing monofunctional thiol compound, trifunctional thiol compound and boron phosphate were cured using both UV and thermal methods. Using thiol–ene system, cyanate ester formulations, which are normally prepared at high temperatures, were prepared at room temperature. This study has given ease of application for cyanate esters. Thermal stability, thermal conductivity, mechanical properties and hydrophobicity of the samples were determined. Gel content and water absorption capacity of the samples were also measured. The surface morphology of the samples was investigated by SEM–EDS.

2. Experimental

2.1. Materials

2,2'-Diallylbisphenol A, CNBr, trimethylolpropane tris(3-mercaptopropionate) (TPTMP), (3-mercaptopropyl)trimethoxysilane (MPTMS), boron phosphate, camphorquinone (2,3-bornanedione) were purchased from Aldrich. Irgacure 184 (1-hydroxy-cyclohexyl-phenyl-ketone) was purchased from CIBA. Triethylamine and acetone were purchased from Merck and used as received.

2.2. Synthesis of 2,2'-diallylbisphenol A dicyanate ester (DA-BADCy)

The DA-BADCy was prepared from the 2,2'-diallylbisphenol A and cyanogen bromide (CNBr) in the presence of triethylamine. A 250 ml three-necked round bottomed flask equipped with a magnetic stirring device, a nitrogen inlet and dropping funnel was loaded with 10 g (0.0324 mol) of 2,2'-diallylbisphenol A which was previously dissolved in 50 ml acetone. The flask was maintained at -15°C and then 6.86 g (0.0648 mol) of CNBr was added while

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