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Synthesis and characterization of a renewable cyanate ester/polycarbonate network derived from eugenol

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ABSTRACT

A homogenous polycarbonate/cyanate ester network has been prepared from a renewable, eugenol-derived bisphenol. The pure polycarbonate exhibited a T_g of 71 °C, $M_n = 8360$, and polydispersity of 1.88. An 80:20 blend of cyanate ester: polycarbonate was prepared and thermally cured. The presence of the polycarbonate had no significant effect on the cure behavior of the cyanate ester. Small Angle Laser Light Scattering (SALLS) and DSC were used to analyze the blend and no phase separation was observed either during or after cure, suggesting that a homogenous network was generated. TMA of the resulting composite material revealed a single T_g of 132 °C (tan δ), roughly 55 °C lower than the T_g of the pure polycyanurate and 60 °C higher than the polycarbonate. A solvent extraction study showed that the polycarbonate could be quantitatively separated from the thermoset matrix after cure. This result proved that no chemical grafting occured under the cure conditions employed. The excellent miscibility of the polycarbonate and cyanate ester coupled with the efficient cure of the blend to a homogenous network suggests that these types of blends may have applications for fabrication of toughened composite structures.

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1. Introduction

Sustainable thermoplastics and thermosets derived from renewable phenols have a number of potential advantages over those derived from petroleum sources. These materials can be considered carbon sinks that are generated from CO_2 by a combination of photosynthesis (by plants) and chemical manipulation. Petroleum-based polymers can also be considered carbon sinks, but there is no net benefit to the overall carbon balance as one carbon sink (crude oil) is merely replaced with another. In contrast, increased utilization of sustainable polymers has the potential to actually reduce the amount of atmospheric carbon dioxide in the short term and to be carbon neutral in the long term. Another unique aspect of renewable polymers lies in their structural diversity. For example, the presence of various functional groups in renewable phenols may provide opportunities to reduce the number of synthetic steps required to generate a final polymer [1] and has an impact on the properties of resins without subjecting the monomers or polymers to additional chemical processes. These structural features can affect important parameters including water uptake, hydrophobicity, thermal stability, and glass transition temperature.

Over the last few years our group has studied a variety of cyanate esters derived from sustainable phenols [2–5]. Most recently, we described the synthesis and characterization of a cyanate ester resin derived from the renewable phenol eugenol [6]. To expand the potential applications of this resin it became of interest to investigate blends of the cyanate ester with a thermoplastic that was also prepared from eugenol. In this manner a 100% bio-based composite material would be realized. Although cyanate esters have a number of physical properties that make them desirable in high performance applications, one of their drawbacks and thermoset materials in general, lies in their modest fracture resistance. Toughening approaches for thermosets date back to the late 1960s, where rubber was shown to improve the fracture strength of epoxy resins [7]. More recent studies have explored the use of reactive rubbers to improve the toughness of cyanate esters, however, the use of these materials led to significant reductions in

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both the T_g and mechanical strength [8]. In general, elastomeric modification has been shown to decrease elastic modulus, yield strength, and creep resistance. Furthermore, elastomer modification of highly crosslinked thermosets, such as cyanate esters, is not an effective approach since matrix yielding is the dominant toughening mechanism. To mitigate these issues, the effects of blending cyanate esters with various thermoplastic resins, including poly(ethylene phthalate) [9], poly (ether imide) [10], polysulfones [8,11–13], and polycarbonates [14,15] have been studied. In most cases the thermoplastic phase separates during cure of the cyanate ester with toughening of the bulk material dependent on the resulting morphology. The morphology of the material is affected by the composition and molecular weight of the thermoplastic, cure temperature, kinetics, and pressure, among other factors.

The formation of a micro-sized particulate phase having a majority composition of the modifying agent is widely considered to be the most effective morphology for imparting toughness to thermosets. However, this approach to toughening relies on reaction-induced phase separation which is sensitive to cure temperature. During the production of composite parts from highly exothermic cure, significant temperature gradients cannot be avoided and practical control of morphology is difficult to achieve. In contrast, morphologies that allow alternative toughening mechanisms and are not dependent on cure temperature may be useful for composite part fabrication. For example, sub-micron phase separation that results in domains smaller than optical wavelengths of light or interpenetrating networks have also been shown to provide augmented fracture strength. In one study, polycarbonates blended with epoxy resins were shown to be completely miscible upon cure at loadings of up to 12% [16]. Homogenous formulations of this type had improved flexural modulus compared to related heterogeneous blends. Another study on phenoxy/epoxy blends showed that at high epoxy cure rates, homogeneous networks were produced that demonstrated higher fracture toughness compared to heterogeneous morphologies, at some expense to blend T_g [17]. This effect has also been observed with polycarbonate/cyanate ester blends. Loadings of up to 50% polycarbonate with cyanate esters have been shown to form single phase interpenetrating networks with improved toughness [15]. From a design standpoint, there are two keys to achieving this morphology. First, the modifying polymer's structure should closely match that of its intended thermoset host. Second, the molecular weight of the thermoplastic should be kept relatively low [18], both to generate a homogenous network and to limit viscosity increases, thus having minimal effects on fiber reinforced composite processing. With the goal of developing a compatible thermoplastic toughener for the eugenol derived cyanate ester, the current work explores the synthesis and characterization of a low-molecular weight polycarbonate and cyanate ester/polycarbonate network derived from eugenol.

2. Experimental

2.1. General

4,4′-(butane-1,4-diyl)bis(2-methoxyphenol) (**1**) and 1,4-bis(4-cyanato-3-methoxyphenyl)butane (**2**) were prepared as previously described [6]. Triphosgene and pyridine were obtained from Aldrich and used as received. NMR spectra were collected on a Bruker Avance II 300 MHz NMR spectrometer. Samples were prepared in $CDCl_3$ and spectra were referenced to the solvent peaks ($\delta = 7.26$ and 77.16 ppm for ^1H and ^{13}C spectra, respectively). Fourier Transform Infrared Spectroscopy (FTIR) was carried out using a Thermo Nicolet Nexuus 6700 FTIR equipped with the Smart iTr attenuated total internal reflection (ATR) accessory, single bounce diamond crystal. The detector type was a liquid nitrogen cooled MCTA. FTIR spectra are an average of 32 scans, at 4 cm^{-1} resolution, and have been baseline and background corrected.

2.2. Polycarbonate synthesis

In a typical synthesis **1** (1.006 g, 3.3 mmol) was dissolved in 8 mL pyridine and the solution cooled to −20 °C with stirring. Triphosgene (0.384 g, 1.3 mmol) was added and the solution was allowed to warm to room temperature. An additional 4 mL of pyridine was then added to dissolve residual solids. Stirring overnight yielded a thick gray mixture which was poured into 200 mL of water to give a white precipitate. The aqueous supernatant was decanted and replaced with methanol. The mixture was heated to ~50 °C and the solid was dispersed with vigorous stirring for 30 min in the methanol solution. The supernatant was decanted off and the solid was dried first under a stream of nitrogen and then in a vacuum oven at 50 °C overnight to yield 0.622 g (57%) of an off-white powder. The polymer was further purified by dissolving in a minimum amount of methylene chloride followed by reprecipitation in methanol. ^1H NMR ($CDCl_3$) δ 7.12 (d, $J = 8.0$ Hz, 2H, Ph), 6.80–6.70 (m, 4H, Ph), 3.87 (s, 6H, OMe), 2.63 (bs, 4H, CH_2), 1.67 (bs, 4H, CH_2).

2.3. Polycarbonate endcapping

This procedure was conducted as described in the literature [19]. 100 mg of polycarbonate was dissolved in 6 mL of pyridine. *t*-Butyldimethylsilyl chloride (0.468 g, 3.1 mmol) was dissolved in triethylamine (1 mL) and this solution was then added to the pyridine solution. The reaction was stirred under nitrogen at 50 °C for 24 h. The solvent was removed under reduced pressure to yield a resinous solid. The solid was then dissolved in a minimum of dichloromethane and precipitated in methanol. After a second precipitation, the resulting solid was collected, washed with methanol, and dried in a vacuum oven. The molecular weight of the endcapped polymer was determined by comparing the ^1H NMR integrals for the *tert*-butyl group from the endcap to the methoxy group from the repeat unit. The M_n calculated by this method was 9575 Da.

2.4. Solvent extraction of cyanate ester/polycarbonate network

An intimate mixture of 160 mg of **2** and 38 mg of the polycarbonate was added to a circular silicone mold with a diameter of 20 mm and a depth of 2 mm. The mold was heated to 150 °C under a slow flow of nitrogen and then held at that temperature for 30 min. All of the solids melted to form a clear, homogeneous mixture. The temperature was then increased 10 °C every 10 min until it reached 210 °C and was then held at that temperature for 24 h. After cooling to room temperature, the puck was removed from the mold, broken into several large pieces, and then transferred to a glass vial. 5 mL of dichloromethane was added to the vial and the sample was gently heated to 35 °C for 15 min. The dichloromethane solution was then decanted and any loose pieces of material were collected on a frit. The dichloromethane extraction was repeated 5 times and then the glass vial and frit were placed in a vacuum oven to dry. The dichloromethane aliquots were combined and the solvent removed under reduced pressure to leave a yellow residue. After drying, the insoluble fragments of the puck weighed a total of 153 mg. The soluble residue from the dichloromethane fractions weighed 42 mg. A total of 195 mg of sample (98.5%) was accounted for in the experiment.