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Hydrolytic degradation kinetics of bisphenol E cyanate ester resin and composite

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ABSTRACT

Cyanate ester resin systems offer promise for many high-temperature polymer applications, but the potential for many applications is limited due to hydrolytic degradation of the cured polymer network, which can blister the resin, decrease its cross-linking density, and reduce the maximum allowable use temperature. This study examines the hydrolytic degradation of a Bisphenol E dicyanate ester (LECY) and a glass-fiber composite of LECY. Equilibrium water sorption, reaction rates, and glass transition temperature changes are monitored. Despite differences in diffusion and sorption, the glass fiber composite is shown to behave similarly to the neat polymer system in terms of degradation. Results were compared to PT-30 triphenolic cyanate ester, and LECY was determined to have lower equilibrium water sorption values, and a lower degradation rate.

1. Introduction

Bisphenol-based cyanate esters [1,2] are rigid thermosetting resins that generally exhibit high glass transition temperature (Tg), good fracture toughness, excellent substrate adhesion, low shrinkage, low dielectric loss, and low moisture uptake [3]. These properties make them attractive replacements for common thermosetting systems such as epoxies or maleimides for applications in the aerospace, communications, and microelectronics industries. In some applications, such as lightweight structures aboard spacecraft [4–6], concerns about moisture uptake in cyanate esters are mainly limited to concerns about outgassing. In others, such as radomes [7,8], the effect of moisture uptake and network hydrolysis on properties such as dielectric loss is a significant concern. In addition to impacts on dielectric performance [9], in microelectronic applications [10,11], hydrolysis also impacts adhesion properties on metal substrates and reduces the glass transition temperature (T_g), which must remain above hot solder temperatures for proper performance. Hydrolysis products can also lead to blistering and component failure [12]. Many of these same concerns can be found in other applications such as photonics [13,14] and radiation-resistant magnets for particle accelerators [15,16] and thermonuclear fusion reactors [17–25].

Both monomers (containing the cyanate ester functional group) and the cured resin (containing triazine rings) are conventionally referred to as cyanate ester resins. They are formed in excellent yields by the reaction of corresponding phenols with cyanogen halide [26]. Upon heat treatment, a polycyclotrimerization reaction occurs that can be accelerated by the use of a metallic and hydroxyl catalysts to form a highly crosslinked network with the cyanurate ring at the crosslink junction [3,26–29].

Early tests showed that multilayer cyanate ester laminate parts failed when stored under high humidity conditions [27]. Although cyanate esters absorb less moisture than epoxies, the blister time for moisture-conditioned cyanate ester boards can be less than that of epoxy boards [12]. Additional studies established a significant reduction in glass transition temperature upon humidity conditioning, limiting the potential of cyanate esters for high temperature applications. Kasehagen et al. demonstrated that both phenomena are related to a chain scission hydrolysis reaction that degrades the network structure when wet material is exposed to high temperature conditions [12]. They proposed a mechanism for the hydrolysis reaction and derived the reaction kinetics from calorimetry. They found that the primary degradation mechanism of cyanate ester resins proceeded via hydrolysis of the aryl ether bonds, followed by decomposition, yielding phenols, carbon dioxide and ammonia as the final hydrolysis products. A schematic representation for the degradation reaction was proposed by Kasehagen et al. and is shown in Fig. 1 [12].

Lin et al. report the same phenomenological observations - water

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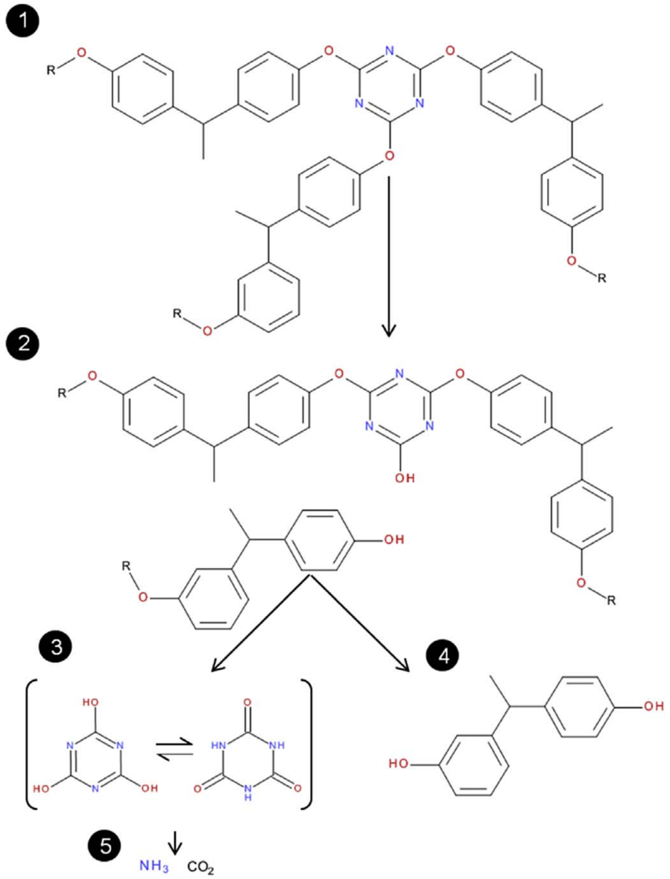

Fig. 1. Full hydrolytic degradation of LECY cured network, featuring the fully formed network (1), after a single hydrolysis event, a triazine alcohol and phenol are created and a single cross-link is removed (2), the tautomeric forms of cyanuric acid (3), the bisphenol degradation product (4), and the final degradation products – ammonia and carbon dioxide (5).

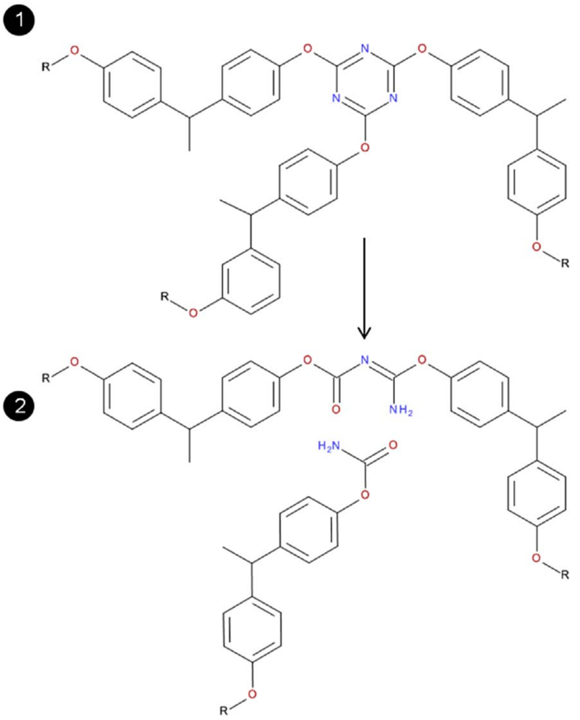

Fig. 2. Alternative degradation scheme following Lin et al. [30] Under this scheme, 2 mol of water hydrolyze the triazine ring, producing a primary carbamate and a dimer linkage.

uptake, hydrolysis, and T_g reduction for cyanate esters conditioned at 60 °C/100% RH [30]. In contrast to Kasehagen, they proposed that water decomposes the triazine ring rather than breaking an aryl ether bond, through a reverse-polymerization reaction that produces an aminated isocyanate. This mechanism is shown in Fig. 2. It should be noted that these network-degradation reactions are distinct from the hydrolytic carbamate formation of uncured cyanate ester groups commonly studied as a cyanate ester degradation pathway [31–33].

This study follows the methods of Marella et al. [34] and aims to understand the mechanism and reaction kinetics of highly cured cyanate ester degradation by studying cyanate ester resins in hot/wet conditions using a combination of reversible and irreversible gravimetric sorption, Fourier-transform infrared spectroscopy (FTIR), and T_g change by dynamic mechanical analysis (DMA). Other studies have identified the final degradation products, as phenol, carbon dioxide and ammonia [35,36]; this investigation concentrates mainly on the formation of intermediate products – phenols, cyanuric acid and bisphenol, by mass uptake and FTIR, as well as on methods to quantitatively link changes in mass, hydrolysis rates, and the decrease in T_g associated with hydrolysis.

2. Materials and methods

2.1. Materials

The dicyanate ester of bisphenol E, which has the chemical name 1,1-bis(4-cyanatophenyl)ethane, and the trade name Primaset® LECY, was supplied by Novoset and stored at 4 °C in a low humidity environment. The as-received bisphenol E dicyanate ester was catalyzed with 2.0 phr of a 30:1 (by weight) mixture of nonlyphenol (Aldrich, 97%) and copper (II) acetylacetonate (Research Organic/Inorganic Chemicals Inc.), with a total copper concentration of 160 ppm by weight. Catalyst batches were formulated by first dissolving the copper (II) acetylacetonate in the nonylphenol at 60 °C by stirring for 1 h, and then storing under ambient conditions for up to 30 days. The chemical structures for nonylphenol, bisphenol E dicyanate ester, and copper (II) acetylacetonate are shown in Fig. 3.

2.2. Methods

2.2.1. Neat resin casting and cure

Just prior to cure, the resin and catalyst were mixed at room temperature and de-gassed under vacuum for 30 min. The de-gassed mixture was then poured into a 75 × 87 mm vertical mold cavity formed by inserting a 1.5 mm thick U-shaped aluminum spacer between two sheets of Teflon-coated aluminum. The pieces were clamped together and held with the long axes of the cavity in the vertical position for the

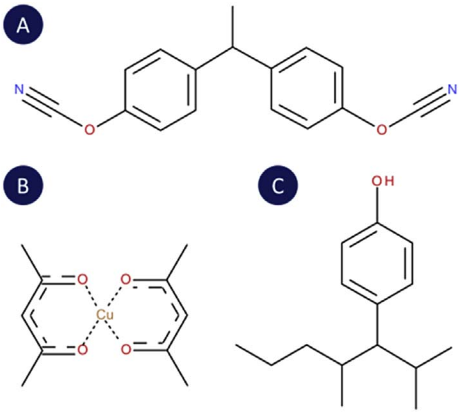

Fig. 3. Bisphenol E dicyanate ester (A), Copper (II) acetylacetonate (B), and nonylphenol (C).