

Hydrolytic degradation of highly crosslinked polyaromatic cyanate ester resins



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ARTICLE INFO

Article history:

Received 9 January 2014

Received in revised form

17 March 2014

Accepted 24 March 2014

Available online 1 April 2014

Keywords:

High temperature

Hydrolysis

Degradation

Cyanate ester

Infrared spectroscopy

ABSTRACT

This work presents a robust method for the study of the hydrolytic degradation of a polyaromatic cyanate ester thermoset. A detailed understanding of the kinetics of formation of phenolic degradation intermediates was determined both by fractional increase in weight and near infrared spectroscopy following exposure to controlled moisture and temperature environments. Evidence of decreased cross-linking density by chain scission degradation was also obtained based on the decrease in glass transition temperature (T_g). The effects of catalyst type and concentration on both reaction kinetics and T_g were also determined, linking hydrolysis events directly to T_g degradation. It was found that low conversion of hydrolyzable bonds can lead to significant decreases in T_g values and that the type of catalyst used significantly influences the rate of hydrolysis. The experimental techniques developed in this work were found to be a reliable and reproducible method to characterize the hydrolysis reaction, and can be extended to other cyanate ester systems.

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1. Introduction

Polyaromatic cyanate esters [1,2] are rigid thermosetting resins that generally exhibit high glass transition temperature (T_g), 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 particular, high temperature service ceiling and low shrinkage make cyanate esters an excellent candidate for lightweight composite rocket nozzles and other high temperature parts [4], while a low dielectric loss makes them the material of choice in radome applications. Additionally, excellent adhesion properties on metal substrates and T_g above hot solder temperatures make them a promising substitute for epoxies in the microelectronics industry.

Both prepolymers (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 [3]. 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 [3,5–7].

Early tests [5] showed that multilayer cyanate ester laminate parts failed when stored under high humidity conditions. Although cyanate esters absorb less moisture than epoxies, the blister time for moisture-conditioned cyanate ester boards is less than that of epoxy boards [8]. 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. demonstrate 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 [8]. They propose a mechanism for the hydrolysis reaction and derive the reaction kinetics from calorimetry.

For this study, the primary degradation mechanism of cyanate ester resins proceeds via hydrolysis of the cyanurate ester bond between phenyl and triazine rings. The reaction then proceeds to produce 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 [8].

Lin et al. report the same phenomenological observations – water uptake, hydrolysis, and T_g reduction for cyanate esters conditioned at 60 °C/100% RH [9]. In contrast to Kasehagen, they find the hydrolysis to affect the triazine ring rather than the cyanurate ester crosslink, with a reverse-polymerization reaction that

Abbreviations: T_g , glass transition temperature; FTIR, Fourier-transform infrared spectroscopy; DMA, dynamic mechanical analysis; NIR, near-infrared spectroscopy.

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produces an aminated isocyanate. This study finds small amine peaks, indicating that while present, this mechanism is secondary to the chain hydrolysis mechanism shown in Fig. 1. It should be noted that the network-degradation hydrolysis studied in this work and that of and Kasehagen [8] and Lin [9] is different from the hydrolytic carbamate formation of uncured cyanate ester groups commonly studied as a cyanate ester degradation pathway [10,11].

This study 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 [12,13]; this investigation concentrates mainly on the formation of intermediate products – phenols, cyanuric acid and a tri-phenolic compound, by mass uptake and FTIR.

2. Materials and methods

2.1. Materials

Oligo(3-methylene-1,5-phenylenecyanate), PRIMASET® PT-30 cyanate ester resin, was obtained from Lonza, Inc. and was used

as received. Copper (II) naphthenate, 6% by weight of metal, was obtained from Shepherd Chemical Company and 95% dibutyltin dilaurate (DBTDL) was purchased from Aldrich Chemicals. These structures are shown in Fig. 2. No proton source was added as a co-catalyst for any of the systems studied.

2.2. Methods

2.2.1. Curing and preparation of samples

As received, the monomer is a yellow, highly viscous liquid ($\eta = 392$ mPa s at 80 °C) with limited room temperature flow. Before preparing polymer blocks of the resin, the monomer was placed in an oven at 60 °C for 30 min to decrease viscosity. Blends of monomer and catalyst at varying concentrations were prepared in 100 ml glass containers and placed in the oven at 100 °C. The resin and catalyst mixture was stirred with a glass rod to disperse the catalyst homogeneously. The metal concentration of catalyst is reported here in parts per million (ppm) by mass. Once a homogeneous mixture was obtained it was poured into a rectangular mold $2.5 \times 7 \times 8.8$ cm and processed in an oven according to the cure conditions given in Table 1.

Curing at elevated temperatures results in the cyclotrimerization of monomers to form a three-dimensional network of cyanurate ester linked cyanurate rings. A scheme for the

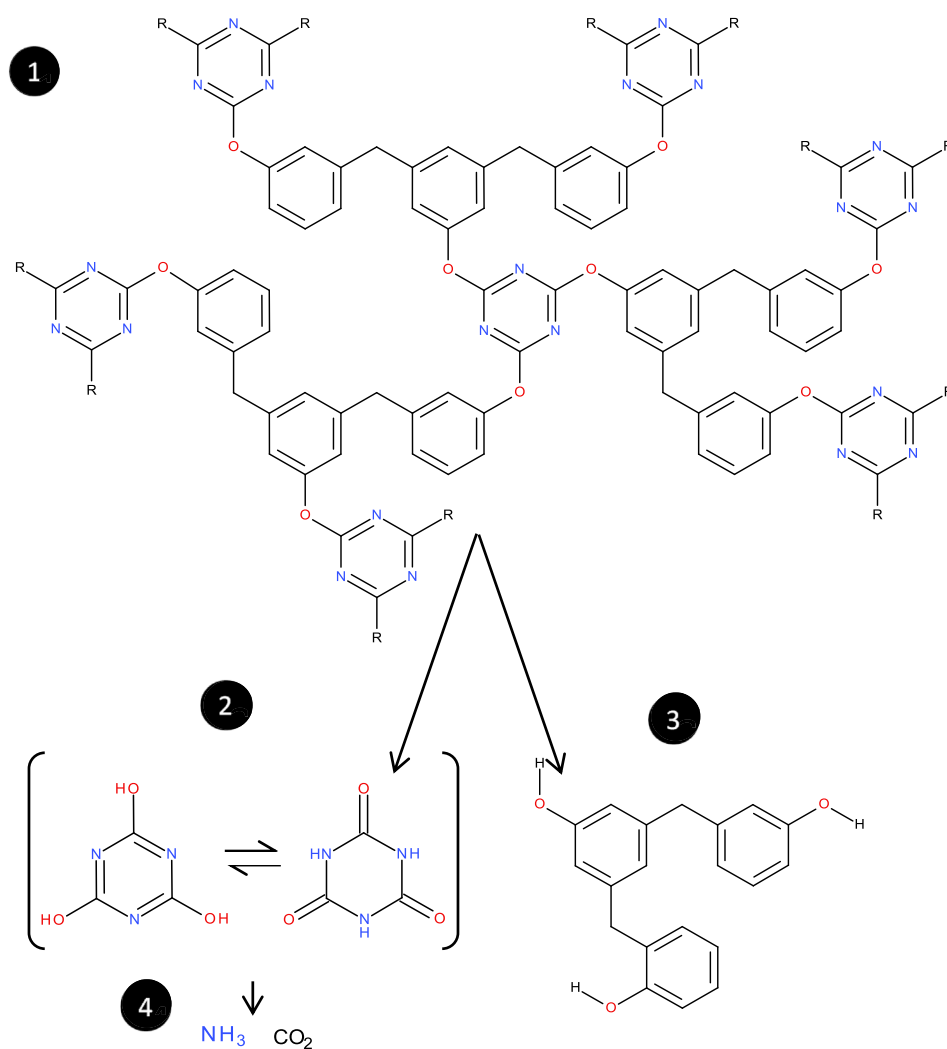


Fig. 1. Full hydrolytic degradation of PT-30 cured network, featuring the fully formed network (1), the tautomeric forms of cyanuric acid (2), the triphenol degradation product (3), and the final degradation products – ammonia and carbon dioxide (4).

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