European Polymer Journal 73 (2015) 94–104

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Synthesis, morphology, and thermal stability of nanoporous cyanate ester resins obtained upon controlled monomer conversion

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ARTICLE INFO

Article history:
Received 31 July 2015
Received in revised form 30 September 2015
Accepted 8 October 2015
Available online 8 October 2015

Keywords:
Cyanate ester resins
Controlled conversion
Nanoporous thermosetting films
Thermal stability

ABSTRACT

This paper focuses on the development of a straightforward and effective method for producing nanoporous thermosetting Cyanate Ester Resins (CERs) with controlled conversion of the reactive groups of cyanate monomer by varying polymerization temperature and duration of CER synthesis, followed by a simple extraction procedure. Using Fourier transform infrared spectroscopy, the conversion degree ranging from about 79% up to 96% was determined. DSC-based thermoporometry and scanning electron microscopy analyses evidenced the generation of nanoporous structures in the cross-linked CER films produced. The pore size distribution varied from ~10 to 220 nm with an average pore diameter of around 20–45 nm and the porosity ratio was comprised between 2.8% and 7.4% for all the nanoporous CERs studied. It was established that the thermal stability of nanoporous CERs remained high enough and depended on the final conversion of cyanate groups in the partly cured CER networks.

1. Introduction

Cyanate Ester Resins (CERs) – also known as polycyanurates (PCNs) – are high-crosslink density polymers resulting from the polymerization of dicyanate esters and represent a unique family of high-performance thermosets possessing an attractive combination of excellent dimensional and thermal stability ($T_d > 400\,^{\circ}\mathrm{C}$), high glass transition temperatures ($T_g > 220\,^{\circ}\mathrm{C}$), high adhesion to different substrates, low dielectric constants ($\varepsilon \sim 2.6$–3.2), low water uptake, low inflammability as well as chemical inertness to aggressive media [1–6]. Like most of thermosets, the main drawback associated with CERs is their inherent brittleness. To cope with this problem, physical modifications with thermoplastics or rubbers via the elaboration of semi-Interpenetrating Polymer Networks or chemical embedding of some reactive soft oligomers into network structures are usually used [5,6]. Such strategies lead to the generation of hybrid thermosets with improved toughness; nonetheless, their dielectric characteristics and thermal stability are generally depleted. In contrast, the formation of porous structures constitutes an original means to improve mechanical properties of CER-based materials while lowering their dielectric constants and maintaining high thermal stability [7].

To the best of our knowledge, only a few reports on the design of porous CERs have hitherto been published [7–9]. In view of the scarcity of comprehensive studies on the generation of porous CER-based thermosets, engineering (nano)porous CER

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http://dx.doi.org/10.1016/j.eurpolymj.2015.10.009

films still remains challenging. Such materials may be promising candidates for membrane technology requiring especially high dimensional and thermal stability and related processes, including transport phenomena and diffusion through nanopores.

Recently, we have reported on several novel approaches for producing nanoporous CER films via selective alkaline hydrolysis or partial extraction of reactive poly(ε-caprolactone) (PCL) sub-chains from CER/PCL hybrid networks [10,11]. During the synthesis of PCL-modified CER films, partial incorporation of the reactive modifier into CER crosslinked structures was found through condensation reactions of terminal hydroxyl groups from PCL with cyanate groups of growing CER networks [12]. Nanoporous frameworks were then derived from such CER/PCL-based hybrid networks by hydrolysis of a significant part of PCL sub-chains under mild conditions [10]. Since a non-negligible part of PCL oligomers was not chemically incorporated into the network structure, we developed an alternative and easier route to generate nanopores in films of CER/PCL hybrid networks by mere removal of free unreacted PCL through acetone extraction [11]. We also successfully created nanoporous CER-based frameworks through the track-etching technique, i.e. irradiation of thin films by α-particles, followed by chemical etching [13]. Lately, we have implemented an unprecedented methodology for the formation of nanoporous pure CER films by using inert high-boiling temperature liquids as porogens, e.g. dimethyl-, dibutyl-, or dioctyl phthalate, during network formation, followed by their quantitate extraction [14,15].

The stimulus for the present work lies in the development of a straightforward and effective route toward nanoporous CER films without using any oligomeric modifier or porogenic liquid. In this context, we have investigated the production of nanoporous CER film materials by controlling conversion of cyanate groups during the synthesis of CERs through the variation of polymerization temperature and time. Further extraction of unreacted monomer along with CER fragments non-embedded into the growing network should result in (nano)pore generation in the CER films obtained. The scope and limitations of one such approach are discussed through the careful examination of the resulting porous systems by several physico-chemical techniques, including Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Differential Scanning Calorimetry (DSC)-based thermoporometry, thermogravimetric analysis (TGA), and classical DSC.

2. Experimental

2.1. Materials and sample preparation

4,4′-Ethylidenediphenyl dicyanate (dicyanate ester of bisphenol E, DCBE), under the trade name Primaset™ LECy, was kindly supplied by Lonza (Lonza Ltd, Switzerland), and was used as received. A mixture of cobalt acetylacetonate (0.017 phr) and nonylphenol (2 phr) was used as a catalytic metal complex; these compounds were supplied by Sigma–Aldrich and were used as received. DCBE was mixed with the catalytic metal complex (ratio of nonylphenol equivalents to cyanate ester equivalents equal to 1/84), poured into a PTFE-coated mold, and then heated through different step-by-step schedules. The code of samples prepared and the corresponding temperature–time schedules are given in Table 1.

The thickness of the as-obtained CER films was around 150 μm.

Porous structures were generated via acetone extraction of partially cured CER films using a Soxhlet apparatus for 16 h, followed by drying under vacuum up to constant weight. In the rest of the manuscript, index “e” in sample code will refer to the extracted samples.

The experimental values of gel fraction, w_g, were determined as the insoluble contents of totally extracted samples using Eq. (1):

$$w_g\ (\text{wt.\%}) = m_2/m_1 \cdot 100 \tag{1}$$

where m_1 and m_2 stand for the mass of the dried samples before and after extraction, respectively.

2.2. Physico-chemical techniques

FTIR spectra were recorded on a Bruker Tensor 27 DTGS spectrometer between 4000 and 450 cm^{-1} using the Attenuated Total Reflection (ATR) mode. For each spectrum, 32 consecutive scans with a resolution of 4 cm^{-1} were averaged.

Table 1
Temperature–time schedule for synthesis of CERs with controlled monomer conversion.

Sample code	Temperature step, T_i (°C)	Duration of curing at T_i (h)	Total polymerization time (h)
CER1	150 + 180	5 + 0.5	5.5
CER2	150 + 180	5 + 1.5	6.5
CER3	150 + 180	5 + 3	8.0
CER4	150 + 180 + 210	5 + 3 + 1	9.0
CER5	150 + 180 + 210 + 230	5 + 3 + 1 + 1	10.0
CER6	150 + 180 + 210 + 230 + 250	5 + 3 + 1 + 1 + 1	11.0
CER7	150 + 180 + 210 + 230 + 250 + 270	5 + 3 + 1 + 1 + 1 + 0.5	11.5