



# Annealing behavior and thermal stability of nanoporous polymer films based on high-performance Cyanate Ester Resins



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## ABSTRACT

The present study discloses the annealing behavior and thermal stability of nanoporous film materials based on Cyanate Ester Resins (CERs) obtained by the chemically induced phase separation technique through the use of porogenic molecules of different sizes and concentrations. Measurements were performed by means of thermogravimetric analysis in dynamic and isothermal modes as well as by Fourier Transform Infrared Spectroscopy. Isothermal annealing in the temperature range from 50 to 150 °C led to mass losses observed at temperatures far below the glass transition. Such mass losses were associated with desorption of moisture/water and residual porogen molecules trapped in the bulk. Therefore, these processes were described by diffusion laws, and the values of the basic kinetic parameters were determined. The results were correlated to the structure of the nanoporous CER-based networks derived from the extraction of different porogen molecules. Further, thermal-oxidative degradation occurred in the glass transition temperature domain (expected between 220 and 250 °C) during isothermal annealing at 250 °C.

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## 1. Introduction

Thermosetting Cyanate Ester Resins (CER) have received considerable attention among the currently known densely cross-linked polymers, mainly due to their high-performances in terms of thermal and chemical stability, excellent dielectric characteristics and fire resistance, low moisture/water absorption, etc [1–4]. When comparing the basic characteristics of epoxy-, phenolic-, or bismaleimide-based conventional resins with those associated with CERs, a substantial improvement in the dimensional stability, and consequently a higher thermal durability at elevated temperatures without penalizing the processability of the latter, can be found (Table 1) [3–5].

Considering the superior thermal and heat/water resistance of CERs combined with extremely high chemical stability and hydrophobicity, the generation of porous structures in CER networks can be envisioned as a promising way to develop high-performance

efficient membranes serviceable at elevated temperatures for advanced applications in many branches of industry, including microelectronics, airspace technology, and automotive industry [1–5].

Recently, we have developed a method for obtaining nanoporous CER-based thin film materials using the chemically induced phase separation approach [6,7], firstly applied to CERs in 1996 by Hedric, Kiefer et al. [8,9]. Generally, it relies on the generation of two-phase structure morphology during polymerization, starting from a homogeneous mixture of precursory CER monomer with a non-reactive liquid. After curing completion, a highly crosslinked CER matrix containing dispersed liquid droplets is formed. A porous medium is revealed through the removal of the dispersed phase via evaporation, extraction or degradation. Consequently, the size and spatial arrangements of the voids formed is strongly dependent on the morphology generated during the phase separation process [8,9]. Kiefer et al. [9] mainly used mixtures of CER monomers with low molecular mass volatile liquids and sealed capsules to generate CER foam materials. However, such technique disables producing thin film materials based on CER networks.

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**Table 1**  
Basic characteristics for some thermosetting polymers.

Characteristic	Type of resin matrix			
	Epoxy	Phenolic	Bismaleimide	Cyanate ester
Density (g/cm <sup>3</sup> )	1.1–1.4	1.24–1.32	1.2–2.9	1.1–1.4
Curing temperature (°C)	RT <sup>a</sup> –180	150–190	220–300	180–280
Maximum continuous-use temperature (°C)	80–215	70–175	230–320	150–250
Dielectric constant (1 MHz)	3.8–4.5	4.3–5.4	3.4–3.7	2.7–3.2
Tensile modulus (MPa · 10 <sup>-3</sup> )	3.1–3.8	3–5	3.4–4.1	3.1–3.4
Coefficient of thermal expansion at RT <sup>a</sup> (10 <sup>-6</sup> /°C)	45–65	25–60	30–50	54–71
Mold shrinkage (mm/mm)	0.0006	0.0002	0.007	0.004
Onset degradation temperature (°C)	260–340	300–360	360–400	400–420

<sup>a</sup> Room temperature.

Our investigations [7] aiming to produce CER-based porous thin films (thickness up to 150 μm) using such phase separation route have shown that introducing up to 30 wt % of dimethyl phthalate or dibutyl phthalate as porogens possessing boiling temperatures higher than the CER final curing temperature allows for preventing premature evaporation of dispersed phase and probable pore collapse without sealing. Using FTIR spectroscopy, no chemical interactions between the growing CER frameworks and the phthalates used have been found. Further extraction of the porogens from the corresponding CER networks has afforded well-defined nano-sized porous structures, as confirmed by SEM and DSC-thermoporometry. Later on, we have used all the CER/phthalate precursors synthesized with different phthalate contents for the creation of nanoporous CER networks [10,11]. Indeed, along with dimethyl phthalate (DMP) and dibutyl phthalate (DBP), dioctyl phthalate (DOP) was also involved and the concentration range of the latter was varied from 20 to 50 wt %. In order to minimize the possible dilution effect of the phthalates and to accelerate the polycyclotrimerization reaction, thus ensuring the completion of the CER curing process, a well-known catalytic complex comprising cobalt acetyl acetonate and nonylphenol has been used. The removal of the liquids after synthesis *via* extraction in acetone has led to the formation of nanoporous structures in the corresponding CER frameworks, as expected. The effect of type and initial porogen content on the main porosity characteristics of nanoporous CERs produced has been also established. Nevertheless, the presence of catalytic complex has prevented in some cases full removal of the phthalates from the nanoporous CER-based films [11]. In order to reach complete removal of residual porogens from the corresponding densely crosslinked CER matrices further annealing of the samples at 50, 100, 150, or 250 °C has been performed. It is noteworthy that the increase in annealing temperatures generally resulted in the formation of larger pore diameters and higher pore volumes [11].

The present study aims at comprehending the thermal stability of the resulting nanoporous CER samples during isothermal annealing within a temperature range from 50 to 250 °C for 24–48 h. The effect of the structural features and initial amounts of the porogens used on thermal characteristics of the CERs produced is analyzed by thermogravimetry in both isothermal (under air atmosphere) and dynamic (under N<sub>2</sub>) modes. Such physico-chemical investigation allows for a possible prediction of long-term properties of nanoporous CER film materials.

## 2. Experimental

### 2.1. Materials

Cyanate ester monomer, namely 4,4'-ethylidenediphenyl

dicyanate, under trade name Primaset<sup>®</sup> LECy was kindly supplied by Lonza (Bazel, Switzerland) and used as received. All porogens, namely dioctyl phthalate (DOP), dibutyl phthalate (DBP), dimethyl phthalate (DMP), as well as the components of catalytic complex, *i.e.* cobalt acetyl acetonate (II) (Co(AcAc)<sub>2</sub>) and nonyl phenol (NPh), were purchased from Aldrich and used as received. The chemical structures and main characteristics of all the chemicals used are presented in Table 2.

### 2.2. Preparation of CER-based films

LECy was first mixed with 20–50 wt % of porogen (DOP, DBP or DMP) at 80 °C. Then, the catalytic complex (170 ppm of Co(AcAc)<sub>2</sub> + 2 phr of NPh) was added. The reaction mixture was poured into a PTFE-coated mold, and heated using the following step-by-step schedule: 150 °C for 5 h, then 180 °C for 3 h, and finally 210 °C for 1 h. Extraction with acetone in a Soxhlet apparatus for ~24 h, followed by drying of the samples up to constant weight resulted in the generation of nanoporous structures. Table 3 summarizes the main porosity characteristics of the nanoporous CER-based film samples thus produced.

Further isothermal annealing was carried out in a programmable oven at temperatures (*T*<sub>a</sub>) equal to 50, 100 or 150 °C for 48 h as well as at 250 °C for 24 h under air atmosphere. Since significant darkening and brittleness of the samples were observed after 24 h at 250 °C, subsequent annealing was discontinued. To determine the mass evolution with time at a given temperature, the samples were periodically removed from the oven and weighed.

### 2.3. Instrumentation

The effect of thermal annealing on chemical structure of the samples was investigated by means of FTIR spectroscopy. FTIR spectra were recorded using a Bruker Tensor 27 spectrometer between 4000 and 450 cm<sup>-1</sup> with the Attenuated Total Reflection (ATR) mode. For each spectrum, 32 consecutive scans with a resolution of 0.6 cm<sup>-1</sup> were averaged.

DSC investigations were performed on a Perkin Elmer DSC 8500 differential scanning calorimeter under nitrogen atmosphere. The sample masses were varied from 10 to 15 mg. The materials were exposed to a single heating run in a temperature range from 20 to 260 °C at a heating rate of 10 °C min<sup>-1</sup>. The glass transition temperature (*T*<sub>g</sub>) was determined as a midpoint-by-half-height of glass transition region on DSC curves obtained.

Thermogravimetry measurements were performed on a Netzsch TG 209 thermobalance in dynamic mode under nitrogen atmosphere. Sample pellets with masses ranging from 10 to 20 mg were heated at 20 °C min<sup>-1</sup> from 20 °C up to 700 °C.

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