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Influences of template concentration and epoxy functionality on porous epoxy systems: Characteristics of thermal stability, optical, dielectric, and mechanical properties

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ABSTRACT

Two different multi-porous epoxy thermosets (MPETs), bi-functionality of DGEBA and tri-functionality of TGTPM, were prepared foremost for the interaction of template concentration and epoxy functionality under several physical properties. By performing an automated mercury porosimeter test, we found out template concentration was critical to the amount of voids/pores. Meanwhile, epoxy functionality decided the formation of porous structure through SEM. Comparing with TGTPM MPETs system, the DGEBA MPETs system with 20 wt% template displayed appreciable T_g and tan δ properties while the phenomenon exhibited higher thermal stability property. Additionally, thermal conductivity patterns show the DGEBA MPETs system is a remarkable material of thermal resistance. However, it reduces optical clarity, dielectric permittivity and mechanical strength according to the UV–visible spectroscopy, LCR meter, and DMA, normally. Therefore, we can understand that template concentration and epoxy functionality are key factors of physical degradation and stability in porous epoxy materials.

1. Introduction

Recently, neat porous polymeric materials have received much attention due to their important characteristics which can be applied in versatile fields, such as electrolysis in fuel cells [1,2], electronic devices [3], separation membranes [4,5], thermal insulation [6], acoustic insulation materials [7] and scaffolds for tissue engineering [8–10]. Upon screening a considerable amount of porous polymer-related literatures, six approaches can be concluded or summarized to prepare various porous materials. For example, chemically and/or thermally induced phase separation [11–13], fiber bonding [14], solvent evaporation [15], gas foaming [16–18], freeze drying [19], electro-spinning [20,21] and so on. Therefore, design of porous polymeric materials is continuously developing for such applications and entails controlling the permeability by tailoring the pore size, structure, and interface chemistry. Versatile synthesis methods have been developed for the preparation of porous polymeric materials. Basically, these approaches can be broadly classified into three categories including (i) methods that involve no pore-generating agents, (ii) methods that use templates, and (iii) methods that associated with the use of a solvent as porogen, where the porous morphologies are formed due to phase separation mechanisms induced in a system of polymer-solvent [22,23].

For a thermoplastic materials, porosity is often introduced through a "thermally induced phase separation" (TIPS) method. Typically, the foaming strategy applied on common thermoplastics was usually carried out by chemical foaming [24,25] or physical foaming [26–28] process. Generally, foams with inclusion voids under investigation for potential applications are mainly based on the porous structure within the thermoplastic polymers [29,30]. On the other hand, porous structures of thermoset-based polymers containing epoxy, cyanurate and dicyclopentadiene thermosets were usually obtained using a "polymerization induced phase separation" (PIPS) method [12,13,31]. In these cases, porous thermosets are synthesized by reactive encapsulation of suitable solvents using a cross-linking polymerization reaction carried out to completion phase separation.

The epoxy system was selected because of its good thermal and dimensional stability, excellent chemical and corrosion resistance, and superior mechanical and electrical properties [32]. Porous epoxy monolith will have more potential applications as thermal and vibration barriers. In the previous works, an attempt on the porous epoxy monoliths was made to extend the process in presence of organic solvents [22,23,33–36]. In this study, we will describe the choice of a polymer additive (poly(ethylene glycol),

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PEG) which is subjected to be removed by extraction, leaving behind porous structures.

The objective of this work is to establish a general methodology to synthesize porous cross-linked polymers with controlled porosity and pore size. The strategy we sought to employ is based on the generation of two porous epoxies via PEG extracted afterwards. Two epoxies were selected so that bi-functionality of DGEBA and tri-functionality of TGTPM can be cross-linked with PEG in order to vary the pore morphology. The contribution of the present paper is the analysis of high-performance porous epoxy process in model systems and of the resulting physical changes depending on the amount of PEG and epoxy functionalities. Furthermore, potentially, curing of both epoxies with hardener (T-403) and template (PEG) has yielded three-dimensional porous structures that multi-porous DGEBA system displayed superior properties of thermal stability and heat resistibility.

2. Experimental section

2.1. Materials and instrumentations

Diglycidylether bisphenol-A (DGEBA), and triphenylolmethane triglycidyl ether (TGTPM) that was purchased from Aldrich, were used as bi-functionality and tri-functionality of epoxide monomers to prepare series of epoxy resins. Trimethylolpropane tris[poly (propylene glycol), amine terminated]ether (T-403) (Aldrich) was used as hardener to cure epoxy thermosets. Poly(ethylene glycol) (PEG, M_w = 1500, Janssen Chimica) technically acted as pore-forming template and acetone were used as received without further purification.

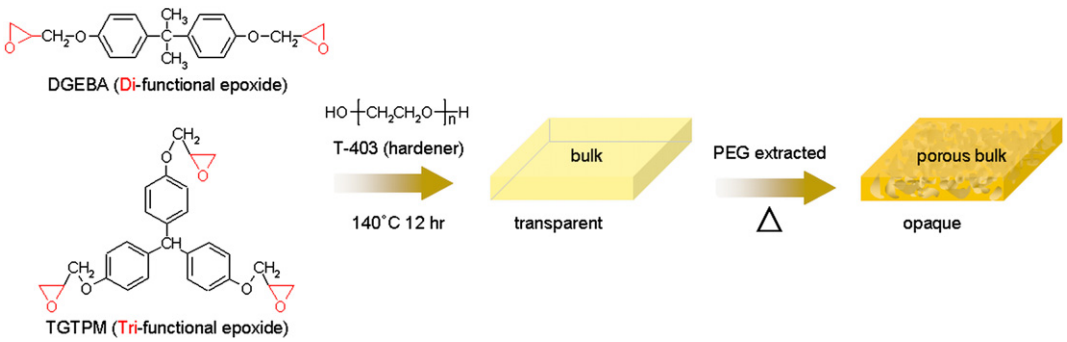
Infrared spectra were recorded on the bulky form of as-prepared porous materials using a Perkin–Elmer Spectrum one FTIR spectrometer. Determinations of the pore size distribution by mercury intrusion were carried out using an automated mercury porosimeter, Model PoreMaster 60 (Quantachome Instruments). This equipment was computer controlled and supplied directly the cumulative and incremental intrusion volumes as a function of the pore diameter, derived from the applied pressure. Micro-image of cross-sections of porous polymers were first gold plated and then were imaged using SEM (Hitachi S-4100). Thermal transport parameters were recorded on a Hot Disk Thermal constants analyzer with Hot Disk sensor (Design No. 5465) with a radius of 3.200 mm with Kapton insulation connected to a Keithley 2400 voltmeter constant current source system. Sample was prepared in the bulky form with dimensions of 4 × 4 × 0.5 cm^3. Dielectric permittivity was measured by an Agilent Precision LCR Meters with model Hewlett Packard 4291B at various frequencies (1.0 MHz to 1.8 GHz) under room temperature. A vacuum-evaporated aluminum electrode was deposited on both sides of the bulky porous epoxy thermosets. The samples were typically with dimension of 1 × 1 × 0.3 cm^3. UV–visible transmission spectra were obtained using a JASCO V-530 UV–visible spectrometer. Differential scanning calorimeter was performed on DuPont TA Q10 at a heating or cooling rate of 10 °C/min in nitrogen atmosphere. Operational temperature was performed at 30–150 °C. Mechanical behavior of porous epoxy thermosets were measured on a dynamic mechanical analyzer in Dual Cantilever mode which fulfilled with a DuPont TA Q800 from 30 °C to 200 °C at a heating rate of 3 °C/min and a frequency of 1 Hz.

2.2. Template-assisted synthesis of bulky multi-porous epoxy matrices

A typical procedure was given as follows: two different functionalities of epoxy monomers used in this work were 5 g of DGEBA and TGTPM, respectively. Subsequently, the variable ratio template molecules, PEG, were dissolved into pre-mixing uncured epoxy resin solution to yield a homogeneous transparent blending solution containing epoxy and PEG. The as-prepared solutions were then casting into molds and followed by processing thermal cross-linking ring-opening reactions of epoxy resin at operational temperatures of 140 °C for 12 h and post-cured at 160 °C for 1 h inside a vacuum oven to give a series of epoxy-PEG hybrid bulk materials. The as-prepared bulk hybrid materials were subsequently soaking in the distilled water, which maintained at 60 °C for a month to effectively remove the template molecules. Eventually, a series of template-assisted synthesis of bulky porous epoxy thermosets were obtained. Controlled experiments were also performed under identical conditions in the absence of template molecules. Typical flowchart for the porous epoxy thermosets prepared from non-surfactant templating route was shown in Scheme 1.

2.3. Heat transport property measurements

Based on the theory of the transient plane source (TPS) technique, the Hot Disk Thermal Constant Analyzer utilized a sensor element in the shape of a double spiral. This Hot Disk sensor acts both as a heat source for increasing the temperature of the sample and a resistance thermometer for recording the time dependent temperature increase. In most cases the sensor element is made of a 10 μm thick nickel-metal double spiral, with precisely designed dimensions. The encapsulated Ni-spiral sensor is then sandwiched between two halves of the solid samples. During a pre-set time, 200 resistance recordings are taken, and from these the relation between temperature and time is established. A few parameters, like the "Output of Power" to increase the temperature of the spiral, the "Measuring Time" for recording 200 points and the size of the sensor are used to optimize the settings for the experiment so that



Scheme 1. Chemical structure of multifunctional epoxy monomer and flowchart for the template-assisted synthesis with two kinds of bulky porous epoxy resins.