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Fluid uptake behavior of multifunctional epoxy blends

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ABSTRACT

Profound changes in network architecture from blending trifunctional (*m*-triglycidylaminophenol, *m*TGAP) or tetrafunctional (tetraglycidyldiaminodiphenylmethane, TGDDM) epoxides with diglycidyl ether of bisphenol-A (DGEBA) and a curative amine (3,3′-diaminodiphenylsulfone, 3,3′-DDS) were observed using PVT, DMA, and PALS analyses. Increasing multifunctional content, which increased the crosslink density (with the expected increase in T_g), produced a *decrease* in the average free volume hole size (V_h) accompanied by a counterintuitive *increase* in fractional free volume (FFV). This unusual inverse relationship between FFV and V_h allowed clear resolution of their respective roles in equilibrium moisture uptake vs. the rate of uptake (diffusivity). Equilibrium water uptake increased with increasing multifunctional content, concomitant with the increase in FFV. Water diffusivity, on the other hand, decreased with increasing multifunctional content, concomitant with the decrease in V_h. The decreasing V_h in the epoxy blends also had interesting consequences for organic solvent sensitivity. MEK ingress was substantial in the binary DGEBA/DDS epoxy and completely inhibited for most of the blends, implying hole size selectivity was responsible for the MEK uptake inhibition. MEK uptake was precluded in epoxies whose V_h was below a critical threshold value of ~68 Å^3. A small amount of *m*TGAP or TGDDM was sufficient to reduce the V_h of DGEBA/DDS epoxy below the threshold and prevent MEK uptake.

1. Introduction

Glassy polymer matrix chemistry is an important area of research for advancing fiber-reinforced composite performance. Critical composite properties such as thermal stability, fluid sensitivity, interfacial properties, and deformation characteristics are matrix-dominant. Amine-cured epoxy polymers continue to play a major role in advanced composites due to their high strength, good corrosion resistance, and low shrinkage [1].

The matrix materials for aerospace-grade epoxies are generally formulated from a selection of materials including di- and multifunctional epoxide resins and diamine hardeners. Epoxies based on multifunctional epoxides tend to have higher strengths, stiffnesses, and glass transition temperatures (T_g) than their difunctional analogs due to their higher crosslink densities [2,3]. Binary systems consisting of an epoxide and an amine have been comprehensively studied in the literature. In application, however, blends of two or more epoxies are often used. Combining di- and multifunctional epoxides can produce an epoxy blend with intermediate properties, providing an increase in stiffness without completely sacrificing other properties [4]. Despite the prevalence of epoxy blends in aerospace applications, to the best of our knowledge the relationship between fluid sensitivity and crosslinked glassy polymer network architecture has not been extensively reported.

Fluid sensitivity is a critical area of research in epoxy network science because a high-performance composite structure, such as an aircraft, will be exposed to a number of aggressive fluids during its service life. Examples of aggressive fluids include water, methyl ethyl ketone (MEK), jet fuel, and hydraulic fluids. Exposure to these fluids can precipitate a decrease in key mechanical properties of the matrix [5–7]. Fluid resistance and performance confidence could be improved if the relationships between network chemistry, network architecture, and solvent susceptibility were fully resolved.

Reports of transport kinetics of small molecules through linear polymer glasses have proliferated in the past 30 years. Diffusion of water through polymeric glasses has been extensively studied and shown to follow classic Fickian behavior, in which uptake rate depends on concentration gradient [8,9]. Fickian diffusion is described by the following equation:

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$$\frac{\partial \varphi}{\partial t} = D\frac{\partial^2 \varphi}{\partial x^2}$$

where φ is moisture concentration, t is time, and x is position [10].

Reports on the diffusion of organic solvents through glassy polymers are less common.

Transport of organic solvents through polymer glasses has been shown to follow non-Fickian kinetics; specifically, Case II diffusion is observed [11]. Case II diffusion is defined by linear mass uptake over time due to a constantly moving well-defined flow front, with an unperturbed region of material in the center of the sample persisting until equilibrium.

While the kinetics of moisture and solvent ingress in epoxy networks have been well-reported, a comprehensive understanding of how network morphology and architecture control fluid uptake characteristics is lacking. Recently, free volume arguments have been used to explain the ingress of organic solvents in glassy polymers in terms of the size of the penetrant molecule. Gall [35] and Sahlin [12] observed relationships between penetrant size and uptake rate for various solvents. Researchers have also attempted to explain water ingress in epoxies in terms of free volume hole size (V_h) and fractional free volume (FFV). Li and coworkers noted correlations between free volume characteristics and water uptake in glassy networks; however, the specific contributions of FFV and V_h were not resolved [13,14]. Ramesh et al. recently published a review article describing free volume approaches to diffusivity theory for polymer glasses [15].

Previous work on binary epoxies applied a free volume approach to the study of organic solvent ingress. Jackson et al. determined that average free volume hole size controls solvent ingress in glassy binary epoxies [16]. It was shown that the susceptibility of a cured epoxy to ingress of an organic solvent is dependent on V_h: if the average hole size is less than the hydrodynamic volume of the solvent molecule, a substantial reduction in solvent ingress is observed. Our present work reports the ability to control fluid susceptibility through selective modification of the network architecture and thus V_h and FFV.

2. Experimental

2.1. Materials

The following materials were used as received: diglycidyl ether of bisphenol-A (DGEBA, EPON825, EEW = 177.5, Hexion), 3,3′-diaminodiphenylsulfone (3,3′-DDS, Royce Chemical Corp., >99% pure, 4 μm particle size), N,N,N′,N′-tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM, MY721, EEW = 113, Huntsman), *m*-triglycidylaminophenol (*m*TGAP, MY0610, EEW = 101, Huntsman). Water and methyl ethyl ketone (MEK) (HPLC grade, Fisher) were used as received.

2.2. Sample preparation

Blends of difunctional and tri- or tetrafunctional epoxies were formulated from DGEBA and *m*TGAP (trifunctional) or TGDDM (tetrafunctional) in weight ratios of 75:25, 50:50, and 25:75. All blends were cured with 3,3′-DDS using a 1:1 stoichiometric equivalent of oxirane to amine active hydrogen. Binary samples consisting of DGEBA/DDS, *m*TGAP/DDS, and TGDDM/DDS were prepared for benchmarks. Structures of all starting materials are shown in Scheme 1. In a typical reaction, 75.0 g (0.211 mol) DGEBA and 25.0 g (0.083 mol) of *m*TGAP were charged to a 500 mL Erlenmeyer flask equipped with a vacuum fitting and magnetic stirring device. The epoxide blend was heated to 100 °C and 41.6 g (0.168 mol) 3,3′-DDS was added over a 10 min period. Pressure was slowly decreased to $\sim 10^{-3}$ torr and temperature was increased to 120 °C. The mixture was stirred until the amine fully dissolved. At that point the clear solution was poured into preheated (100 °C) silicone test coupon molds of various dimensions. Samples were cured in two steps: 5 h at 125 °C and 2 h at 200 °C.

Table 1 describes the nomenclature employed within this manuscript for glassy polymer network chemistries. The weight and molar ratios are provided. Weight and molar ratios were similar; hereafter samples will be referred to by their weight ratios for clarity.

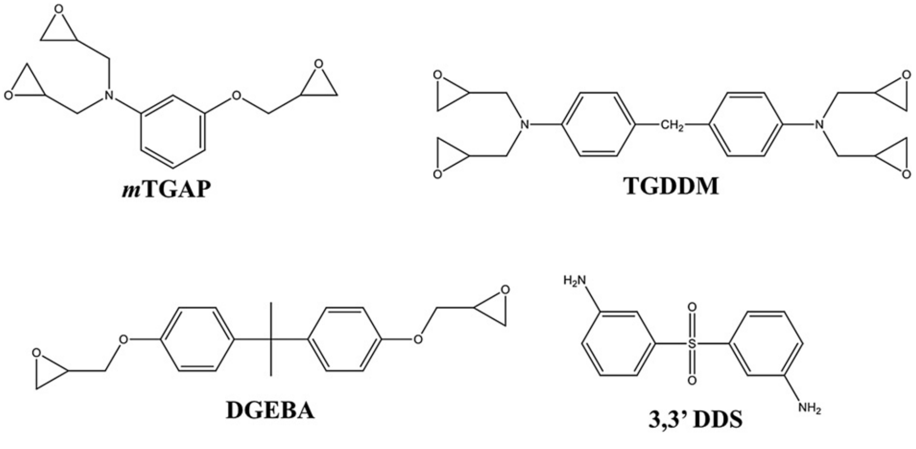
2.3. Characterization

2.3.1. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties, including storage modulus (E′) and thermomechanical T_g, were measured with a Thermal Analysis Q800 DMA in tensile mode with a strain amplitude of 0.05% and a frequency of 1 Hz. Temperature was ramped from 50 °C to 300 °C at a rate of 3 °C/min.

2.3.2. Positron annihilation lifetime spectroscopy (PALS)

Samples for PALS analysis were cast as circular discs with average diameters in the range of 9.5–9.9 mm and thicknesses of ~1–2 mm. Two identical pieces of epoxy sandwiched a 5 μCi ^{22}Na positron source that was sealed between two sheets of 13 μm thick kapton (kapton stops ~ 5% of the positrons but produces no positronium signal). After wrapping in aluminum foil this two-



Scheme 1. Epoxy monomers.