Polymer 82 (2016) 87–92

Contents lists available at ScienceDirect

Polymer

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

Digital image correlation analysis of strain recovery in glassy polymer network isomers

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ARTICLE INFO

Article history:
Received 10 September 2015
Received in revised form
6 November 2015
Accepted 12 November 2015
Available online 19 November 2015

Keywords:
Digital image correlation
Strain recovery
Polymer deformation

ABSTRACT

Digital image correlation techniques were applied to compressive strain recovery experiments of glassy network isomers to study architectural contributions to deformational response. Strain recovery experiments provided a direct comparison of network isomer structure on viscoelastic deformation. Diglycidyl ether of bisphenol-A (DGEBA) was cured with 3,3′- and 4,4′-diaminodiphenyl sulfone (33DDS and 44DDS). The comparison revealed the networks have similar elastic and plastic strain components, but differ in anelastic strain response. DGEBA cured with 44DDS developed pre-yield anelastic strain at a significantly higher rate attributed to increase in free volume, molecular motions and energy dissipation. In contrast, DGEBA cured with 33DDS displayed lower pre-yield energy dissipation attributed to lower free volume and molecular motions, but exhibited a higher degree of post-yield strain-softening due to larger segmental rearrangements.

1. Introduction

Understanding deformation responses of polymers is essential for engineered structures. Epoxy polymers used for matrices in fiber reinforced composites are subjected to high loading in applications which emphasize an understanding of strain response for design allowables. Cross-linked epoxy networks can realize relatively high strain values prior to yield and plastic deformation. However, pre-yield deformations of epoxy networks undergo elastic and viscoelastic deformations making them susceptible to fatigue failures. Since the deformations of amorphous polymer glasses follow nonlinear viscoelastic behavior prior to yield, the prediction of their strain behavior is complicated. Extensive research has been conducted to study the pre- and post-yield nonlinearity of cross-linked polymer glasses, however a general model that applies to all materials has not been realized [1,2]. The difficulties in model predictions are associated with deformations occurring through three distinct strain components: elastic, anelastic and plastic. In order to improve the resolution of each strain component to the general event, strain recovery techniques are applied [3]. During recovery, the elastic deformation instantaneously disappears, the plastic deformation is frozen in, and only the anelastic strain recovers at a time-dependent manner which accounts for the nonlinearity of the polymer glass. Time-dependent recovery experiments are thus uniquely capable of isolating and quantifying elastic, anelastic, and plastic strain components of polymer glass deformation [4,5].

Research on the strain recovery of amorphous glassy polymers has shown complete anelastic strain recovery occurs at a temperature of approximately 20 °C below T_g, and all strain is recovered above T_g [6–9]. Most strain recovery research has been conducted on linear amorphous polymer glasses such as PC, PMMA, and PS, but glassy polymer networks have been reported to behave in a similar manner [10]. This work seeks to investigate the strain recovery aspects of different glassy epoxy networks through the application of digital image correlation (DIC) techniques to measure strain during loading and recovery. Strain recovery measurements will be used to elucidate individual strain component contributions to develop a clear understanding of how strain develops during loading. These methods will be employed to compare the pre- and post-yield deformation of two epoxy networks of identical chemical composition but different curative isomer structure. The isomeric networks are cross-linked epoxies fully cured at 1:1 stoichiometric equivalents of diglycidyl ether of bisphenol A (DGEBA) with 3,3′-diaminodiphenyl sulfone (33DDS) or 4,4′-diaminodiphenyl sulfone (44DDS), hereafter referred to as 33A and 44A, respectively. The isomer positioning on the diamine curatives have a profound influence on thermomechanical properties leading

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http://dx.doi.org/10.1016/j.polymer.2015.11.026
0032-3861/

to observed differences in modulus and T_g. Studying the isomeric networks provides insights into architectural contributions to strain behavior since variation in chemical composition is eliminated. DIC methods provide a pathway to compare glassy network strain component differences due to architectural variances.

2. Experimental

2.1. Materials

Bisphenol A diglycidyl ether (DGEBA, EPON 825, 175 g per equivalent, Hexion Specialty Chemicals Co.) and 3,3′- and 4,4′-diaminodiphenyl sulfone (33DDS and 44DDS, 97%, Aldrich Chemical Co.) were used as received.

2.2. Glassy polymer network preparation

In a typical reaction, 200.0 g (571.4 mmol) DGEBA was charged to a 500 ml Erlenmeyer flask equipped with a vacuum fitting and magnetic stirring device. The epoxy prepolymer was heated to 100 °C when 70.9 g (285.7 mmol) DDS ground powder was slowly added over a 10–15 min period to avoid agglomeration. Upon addition, vacuum was slowly applied to a level of ~10^{-3} Torr when the temperature was increased to 120 °C and the mixture was stirred until dissolution of amine was observed. Vacuum was removed. The clear solution, called the b-stage resin, was poured into preheated (100 °C) molds and was cured for 5 h at 125 °C and 2 h at 200 °C. Upon cooling the cured glassy polymer was precision lathed into three 12.70 mm diameter × 25.40 mm length compression test cylinders with parallel loading surfaces. Specimens were conditioned for 48 h at 28 °C and 50% RH prior to physical testing.

2.3. Thermal and morphological characterization

The thermal properties of the epoxy networks were determined from dynamic mechanical analysis (DMA). DMA specimens were formed by casting b-stage resins into silicone molds with rectangular cavities of 60.0 mm length × 5.0 mm width × 1.5 mm depth. Curing was conducted under the same prescriptions as described above. Cured samples were machine cut into two approximately 30 mm long rectangular bars, and DMA experiments were conducted on a Thermal Analysis (TA) Q800® Dynamic Mechanical Analyzer using a tensile fixture. Strain amplitudes of 0.05% and frequencies of 1 Hz were applied over a temperature range of −140 °C to 250 °C at a ramp rate of 3.0 °C/min. T_g values of 33A and 44A as indicated by the tan-δ peaks are 180 and 220 °C, respectively (Table 1).

Hole-size free volumes of the epoxies were measured by positron annihilation lifetime spectroscopy (PALS) as reported in our previous publication [11]. The average hole-size free volumes of 33A and 44A at room temperature are77 Å^3 and82 Å^3, respectively (Table 1).

Table 1
The T_g, hole-size free volumes, and mechanical properties of the isomer networks.

	DMA T_g (°C)	V_h (Å^3)	Compression modulus (MPa)	Yield strain (%)
33A	180	77	3914	9.07
44A	220	82	3691	11.51

2.4. Yield measurements

The yield points of epoxy networks were determined following uniaxial compression testing procedures prescribed in ASTM 695-02a. Cylinders were compressed at a displacement controlled test rate of 1.27 mm/min on a MTS Systems Corporation Model 810 servo-hydraulic universal test frame equipped with a low friction compression sub-press (Wyoming Test Fixtures Model CU-SP). Linear variable differential transformer (LVDT) compression data was recorded from MTS Testworks® software using a MTS 100 kN load cell at a sampling rate of 10 Hz. Compression strain measurements were recorded simultaneously using digital image correlation methods. The yield point of each network was taken from the LVDT derived “knee”, or stress drop, in the stress–strain curve. The strain corresponding to this yield point, ε_y, was used to develop the strain recovery protocol for each system.

2.5. Strain recovery measurements

Strain recovery experiments were conducted on the epoxy matrices at unloading strains both pre- and post-yield. The unloading strain increments for compression samples were based on the LVDT yield point of the epoxy polymer in order to develop a test matrix of unloading strains in increments of $0.1\varepsilon_y$ from $0.1\varepsilon_y$ to $2.0\varepsilon_y$. LVDT displacement control was used to assure measurement consistency between yield points and unloading strains. Cylinders were compressed at a LVDT displacement controlled rate of 1.27 mm/min up to the desired strain, at which point the specimen was unloaded at the maximum machine displacement rate. Strain recovery for all samples was measured using digital image correlation.

2.6. Digital image correlation measurement

Digital image correlation (DIC), developed in the early 1980's at the University of South Carolina as a method for full-field analysis of surface strain, was used to capture the strain recovery of the glassy networks [12–14]. DIC measures specimen deformation by tracking random surface patterns in gray-scale image sets from the undeformed to deformed states. Strain analysis using DIC was conducted using a GOM Optical Measuring Techniques ARAMIS 3D Deformation Analysis System (Trilion Quality Systems). Specimens were “speckle coated” to create a non-uniform surface pattern to be tracked by the ARAMIS software. Speckle patterns were created on compression cylinders using white and black aerosol paints with a white solid basecoat and black speckles in the appropriate size range of 2–5 pixels [15]. Digital gray scale images were captured via two 2 M digital CCD cameras equipped with 50 mm lenses. Camera calibration was performed using a 25 mm × 20 mm standard to obtain a resolution deviation of less than 0.03 pixels. A capture sequence was written to provide the optimum frame (capture) rate for each portion of the strain recovery test. The frame rate was set at 1 frame per second (fps) for the loading segment of the strain recovery test. Just prior to unloading, the frame rate was increased to 10 fps to capture elastic strain recovery until 30 s post-unloading when the rate was reduced to 1 fps after 30 s and then further reduced to 1 frame per minute for approximately 10 min.

Digital images were taken through a series of processing steps to increase the accuracy of surface strain maps. These steps included the definition of analysis areas, assignments of a start points, and masking of improperly speckled/illuminated areas. Strain maps were developed by computer computation of the gray scale image sets. Deformations were measured through the tracking of random speckle patterns from “image-to-image” and three-dimensional displacement gradient tensor fields were calculated. From these