Materials Letters 105 (2013) 155–158

Contents lists available at SciVerse ScienceDirect

Materials Letters

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

Ameliorating property gradients in photocured polymer lattices via thermal curing

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ARTICLE INFO

Article history:
Received 11 February 2013
Accepted 14 April 2013
Available online 30 April 2013

Keywords:
Lattice
Polymer
Compressive strength
Thermal curing

ABSTRACT

An experimental study has been performed to assess the efficacy of thermal curing in ameliorating the property gradients that ensue from photo-curing of thiol-ene lattices. Through measurements of glass transition temperatures and complex moduli of the constituent thiol-ene as well as strain distributions during compression testing of the lattices, we show that the lattice can be homogenized with a 24 h curing treatment at 160 °C. In addition to homogenization, the treatment yields an elevated glass transition temperature (to 50 °C) relative to that of the pristine material or that after a lower temperature (130 °C) cure. The resulting elastic response of the lattice at ambient temperature is essentially rate-independent over a strain rate range spanning four orders of magnitude. Finally, comparisons of the measured strengths with model predictions indicate that, through modest changes in either the slenderness ratio or the material properties, the mode of failure (yielding- vs. buckling-dominated) and hence the strain rate sensitivity of the lattice strength could be readily tailored.

1. Introduction

A process for rapid, low-cost fabrication of thiol-ene polymer lattices based on photo-curing has been developed [1,2]. The lattice is created by placing a mask with a periodic array of circular apertures on top of a monomer bath and directing collimated ultraviolet (UV) light at prescribed angles through the mask. The process has proven to be versatile in creating a wide range of lattice geometries with feature sizes ranging from tens of micrometer to several millimeter and with macroscopic dimensions of several centimeter [3]. But, because of finite attenuation of the UV beam [4], the efficacy of the beam in polymerizing the thiol-ene monomer progressively diminishes as it penetrates deeper into the monomer bath. This results in undesirable property gradients, especially in thick lattices [5]. The objective of the present study is to assess the efficacy of subsequent thermal curing in ameliorating the property gradients and their impact on lattice performance [6,7]. The study builds on our recent work showing that the property gradients compromise the compressive properties of such lattices [5].

2. Material and methods

The lattices were fabricated by HRL (Malibu, CA). Following UV curing, the lattice was removed from the bath, washed with toluene to remove remnants of the monomer, and cured for 8 h at 80 °C in air. It was then subjected to an additional 24 h treatment at either 130 °C or 160 °C in vacuum. The former curing temperature (T_C) was selected on the basis of earlier studies on bulk thiol-ene sheets [1–3,8]. The lattice geometry was characterized by X-ray computed tomography (CT). The glass transition temperature of small segments of individual thiol-ene struts was measured by differential scanning calorimetric (DSC). Single struts were tested in an EPLEXOR® dynamic mechanical analysis (DMA) apparatus by forced oscillatory tensile loading at a frequency of 1 Hz, over a temperature range of 0 to 125 °C, with heating rates of 1 °C/min. The lattice mechanical properties were characterized using uniaxial compression tests, augmented by measurements of strain distributions using 3D digital image correlation (DIC, Vic-3D® Software, Correlated Solutions Incorporated, http://www.correlatedsolutions.com). Details of the test methods and specimen preparation techniques employed in this study are described elsewhere [5]. Representative images of the lattices are shown in Fig. 1.

3. Results

The through-thickness variation in the glass transition temperature T_g of individual lattice struts is plotted in Fig. 2. As reported elsewhere [5], T_g exhibits a gradient both in the pristine lattice and in that after curing at 130 °C. In contrast, after curing at 160 °C, T_g is uniform throughout. Additionally, the

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http://dx.doi.org/10.1016/j.matlet.2013.04.048

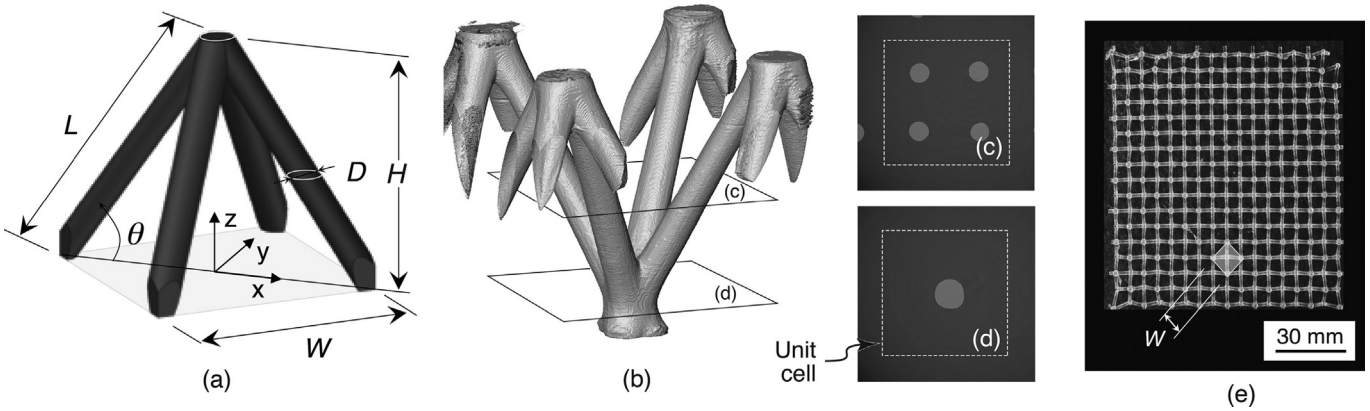

Fig. 1. (a) Schematic of unit cell. (b) 3D rendering based on X-ray computed tomography and (c, d) corresponding cross-sections through a unit cell. (e) Photograph of a lattice in plain view. (Lattice dimensions: $L=13.8$ mm, $D=1.5$ mm, $\theta=60^{\circ}$).

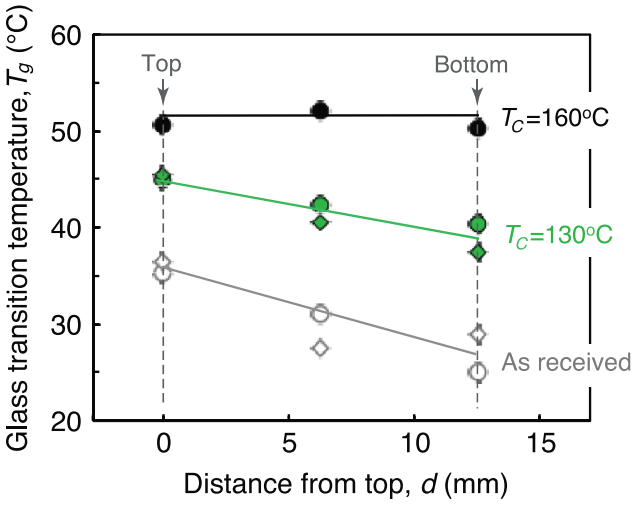

Fig. 2. Though–thickness variation in T_g measured by DSC on small (ca. 1 mm long) specimens.

average value of T_g rises with curing temperature, from about 30 °C to 50 °C. As shown below, this change dramatically alters the mechanical properties because, at ambient, the homologous temperature T/T_g falls from nearly unity to 0.9. Supporting evidence of the increase in T_g is found in the DMA measurements (Fig. 3(a)). Notably, a change in curing temperature from 130 °C to 160 °C yields an increase in T_g of about 10 °C. The rubbery modulus also increases whereas the glassy modulus appears unaffected. The increases in both the rubbery modulus and the glass transition temperature indicate that further cross-linking occurs during the thermal cure.

The effects of curing on the compressive stress–strain response of lattice specimens are shown in Fig. 3(b). When cured at 130 °C, the lattice stiffness and strength exhibit a strong rate sensitivity. This sensitivity is characteristic of glassy polymers at temperatures near T_g. When cured at 160 °C, the parent thiol-ene is in its glassy state (further from T_g when tested ambient temperature). Consequently, its stiffness is higher and it exhibits lower rate sensitivity in its mechanical response. Since the stiffness is proportional to the modulus of the parent material [9], this *rate-insensitivity* is consistent with the *temperature-insensitivity* of the storage modulus measured via DMA [10] (Fig. 3(a)).

A further assessment of lattice properties and their uniformity after curing at 160 °C was made using the DIC measurements [5]. Fig. 4 shows strain measurements at two stress levels within the elastic domain and the resulting computed Young's modulus E and Poisson's ratio ν. Here the strains were computed with respect to a local Cartesian coordinate system in which the y-direction is aligned with the strut axis. The shear component of strain ε_{xy} is found to be negligible, confirming that, although inclined, the struts are stressed in essentially uniaxial compression along their longitudinal axis. Thus, the Young's modulus of the parent material can be determined from the axial strut strain ε_{yy} and the applied load. Similarly, the Poisson's ratio is obtained from the ratio of the transverse and longitudinal strains. Over the central portion of the struts, both E and ν appear to be quite uniform.

4. Modeling

An assessment of the measured strengths of the lattices cured at 160 °C was made using models of yielding and buckling of periodic lattices [4,6]. Here a standard statics analysis is used to obtain the axial stress borne by the struts, assuming that the loads are transmitted via axial compression. The stress σ_{sy} for strut yielding is then obtained by setting the strut stress equal to the material yield strength. For a lattice comprising struts of circular cross-section with diameter D in the plane of the mask, this procedure gives [4]

$$\frac{\sigma_{sy}}{\sigma_0}=\frac{\pi}{2s^2\cos^2\theta} \tag{1}$$

where σ_0 is the material yield strength and s is the slenderness ratio, L/D. If, as in the present lattices, the cross-sectional area of the nodes is less than that of the struts (Fig. 1), strut yielding would be preceded by node yielding, at a stress

$$\frac{\sigma_{sy}}{\sigma_0}=\frac{\beta\pi}{2s^2\cos^2\theta} \tag{2}$$

where β is the node-to-strut area ratio. Using CT scans of the type shown in Fig. 1(b)–(d), $\beta\approx0.5$. Alternatively, setting the stress in the strut equal to the Euler buckling stress yields the macroscopic stress σ_{sb} for buckling, given by

$$\frac{\sigma_{sb}}{E}=\frac{\pi^2\sin^3\theta}{32s^4K^2\cos^2\theta} \tag{3}$$

where K is a non-dimensional coefficient dictated by constraints at the strut ends. When both ends are constrained from lateral displacement and rotation, $K=0.5$.

Fig. 5 shows the variation in the measured peak stress with slenderness ratio. Also shown for comparison are the predictions