

Surface Indentation Arrays for High-Throughput Analysis of Viscoelastic Material Properties

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INTRODUCTION

Relaxation processes in viscous liquids and glasses have been studied extensively as these processes dictate polymer reliability in applications where a constant or cyclical load is applied. These relaxation processes may lead to permanent deformation or the ultimate failure of the sample, yet the underlying causes of glassy behavior in polymeric systems remains a major unsolved area of condensed matter physics.^{1, 2} Relaxation processes are generally studied using long time scale experiments or time-temperature superposition; both approaches allow for the measurement of these responses over the required application time. Creep compliance is one measurement of these relaxations, using a fixed shear stress to measure strain relaxations over time.

Time-temperature superposition is difficult to implement in thermorheologically complex formulations, often involving new models or unknown shift factors. If shift factors cannot be predicted, viscoelastic experiments on the polymer at multiple temperatures are required to calculate the shift factors and the resulting time-shifted creep compliance curve.³ This issue commonly arises in polymer blends and composite materials which may have viscoelastic responses arising from multiple mechanisms in distinct time domains. These formulations commonly contain a mix of soft and hard domains to impart unique material properties difficult to develop in single component systems. This complexity is caused by interfacial regions, blend composition, and filler characteristics that change the viscoelastic response and mechanical properties. In this work, we demonstrate a simple, high-throughput method to measure creep compliance of polymer films using an array of independent spherical indenters. This indentation array can be easily adapted to produce a high number of unique conditions through the use of composition or temperature gradients.

EXPERIMENTAL

Materials. Equipment, instruments or materials are identified in the paper in order to adequately specify the experimental details. Such identification does not imply recommendation by National Institute of Standard and Technology (NIST), nor does it imply the materials are necessarily the best available for the purpose. Styrene-ethylene/butylene-styrene block copolymer (SEBS - Kraton G1650M) samples were solvent cast in toluene and later left under vacuum to eliminate any remaining solvent, making 0.6 mm thick films. Additional experiments used photopolymer samples which were polymerized from a mixture containing isobornyl methacrylate (IBoMA), lauryl methacrylate (LMA), and the photoinitiator 2,2-dimethoxyacetophenone (DPMA). The mass fraction of photoinitiator was 0.5 % in all samples, while the composition of the two monomers varied. Uncertainties in this paper are presented as standard error with 95 % confidence intervals.

The monomer formulation was cured between glass slides producing ≈ 1 mm thick samples for analysis. Samples were polymerized for 3600 s using an Acticure 2000 mercury arc lamp (EXFO Systems) with a 365 nm bandpass filter at a light intensity of 10 mW/cm^2 . To produce a step composition gradient, after curing the spacers were moved to create an opening between the slides, and a different monomer formulation was then polymerized next to the cured sample. Cured samples were covered from the light to prevent differences in exposure time. After curing, samples were left for 48 h in the dark before experiments were performed.

Experimental Design. An array of 1.19 mm radius chrome steel spheres was lowered to the polymer surface, and the force load due to

gravity from each sphere indented the polymer surface according to Hertzian mechanics (Figure 1). The measured contact radii for this sphere size ranged from $15 \mu\text{m}$ to $70 \mu\text{m}$, well within the limits for the Hertz contact model. This mechanical problem has been solved in prior work by Lee and others for a viscoelastic substrate.⁴ The creep compliance, $J(t)$, for a step load stress response is calculated by:

$$J(t) = \frac{8a(t)^3}{3RP(1-\nu)} \quad (1)$$

where a is the contact radius, R is the indenting sphere radius, ν is the Poisson's ratio, and P is the indenter load. All variables except for the contact radius are fixed and constant for each experiment. Only bulk viscoelastic properties are considered, since the film thickness is large enough to be considered as infinitely thick.

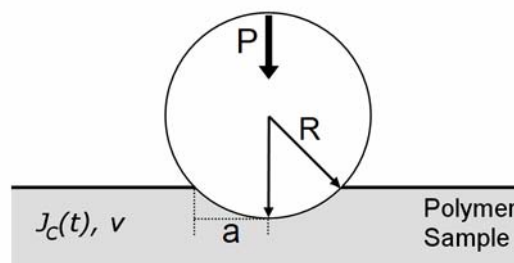


Figure 1. Schematic of indentation on a polymer sample under a gravity load, P . Indentation depth is not to scale.

Images were collected using an inverted microscope (Leica DMIRE2) with a computer controlled XY stage. LabView (National Instruments) software was developed to control stage positioning and image sequence timing, with image collection through Image Pro (Media Cybernetics) software. Nine indenters arranged in a square array were imaged sequentially over the time period analyzed, up to 68 h depending on the rate of creep in the sample. All images were processed using threshold and edge detection techniques to determine the contact area of the sphere. A circular Hough transform was then used to calculate the center point and contact radius (a) of the contact area for each image in the sequence.

A temperature gradient was used for time-temperature superposition experiments, with a quartz substrate to allow for imaging of the contact area. Temperature gradients have been well-characterized previously and used in a variety of high-throughput metrologies.⁵ Temperature was validated using sensors at the polymer surface to ensure stability of the temperature gradient. Time-temperature superposition for the Kraton system was fit for each temperature and not calculated from theory.³

Portions of each sample were saved from indentation experiments and utilized for tensile creep experiments to validate the technique. Tensile creep measurements were measured using a texture analyzer (model TA.XT2i, Texture Technologies Corp.) in tension mode. Samples were measured for up to 24 h using a constant load force at a temperature of $21 \text{ }^\circ\text{C}$, using new samples for each experiment.

DISCUSSION

Creep compliances of Kraton G1650M films were measured to compare the high-throughput technique to other measurement methods for viscoelastic responses. The surface indentation technique required a single scan, obtaining nine compliance measurements simultaneously. Tensile creep measurements were converted from a tensile creep modulus to $J(t)$ using a Poisson's ratio of 0.49. Creep compliances for Kraton films tested using tensile and surface indentation is shown in Figure 2.

Both tensile and surface indentation techniques show statistically equivalent creep compliance measurements. Creep compliance measurements at 5 s show a compliance value of $6.52 \times 10^{-8} \text{ Pa}^{-1} \pm 1.9 \times 10^{-9} \text{ Pa}^{-1}$ for surface indentation compared to $6.41 \times 10^{-8} \text{ Pa}^{-1} \pm 1.3 \times 10^{-9} \text{ Pa}^{-1}$ from tensile creep measurements. Both data sets were statistically equivalent throughout the entire time range tested, with a

higher standard error for surface indentation technique. Creep compliance was also comparable to literature time-temperature superposition experiments performed by Rek and coworkers on SEBS.⁶

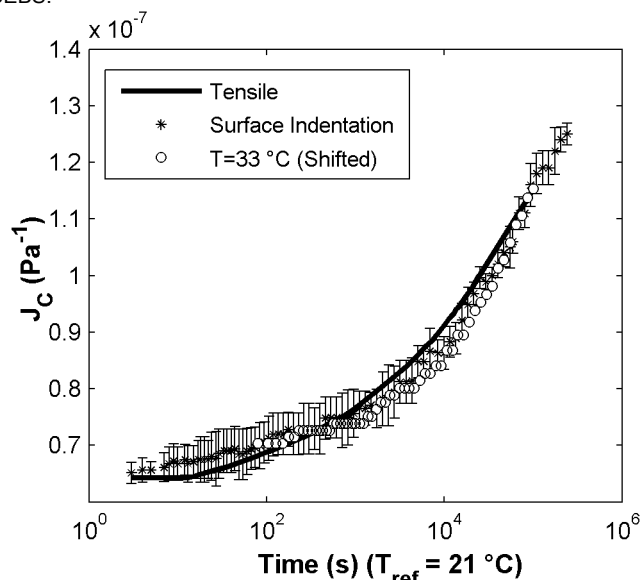


Figure 2. Creep compliance measurements for a Kraton G1650M [poly(styrene-ethylene/butylene-styrene)] polymer measured using surface indentation and tensile creep measurements at 21 °C. Compliance at 33 °C was shifted using time-temperature superposition, shifting the compliance in time to a reference temperature of 21 °C. Error bars are standard error with 95 % confidence intervals.

A temperature gradient experiment was performed using the SEBS substrate. A temperature gradient from 20 °C to 40 °C was analyzed at multiple positions to confirm that time-temperature superposition is possible using this technique. A sample scan of the SEBS system on the temperature gradient at 21 °C was statistically equivalent to the prior experiments and confirmed the stability of the temperature gradient over long times. Experiments were ended at 4800 s, and creep compliance curves were shifted to room temperature using time-temperature superposition. One temperature scan from this result is shown in Figure 2, shifted to the reference temperature of 21 °C.

This elevated temperature scan was statistically equivalent to room temperature compliance curves when shifted using time-temperature superposition. Additional creep compliance curves at other temperatures were shifted and matched the results from the room temperature SEBS experiments. By developing a temperature gradient within the polymer sample, multiple temperature scans were simultaneously sampled. In addition, it is possible for each polymer substrate to be indented multiple times in sequence by shifting the sphere array to a new region since the stress from a contact point is limited to a small region. The shift factors obtained at each temperature in the array allow for the calculation of shift factors as a function of temperature and ultimately the development of a time-temperature master curve.

Since creep compliance in Kraton films varies less than an order of magnitude at room temperature, photopolymer samples were used to generate systems with a much broader range of creep compliance. Photopolymer samples of LMA and IBoMA were cured to form a sample with a step gradient of composition with mass fractions of 45 % LMA, 50 % LMA, and 55 % LMA. This gradient of composition was chosen as these compositions would have a glass transition temperature near room temperature and therefore show a wide range of creep compliance. As the LMA concentration increases, the glass transition temperature was reduced and the samples should show a higher rate of creep due to the decrease in modulus and increase chain mobility. The compositions tested were statistically equivalent at

very short times but were all significantly different after 60 s. Creep compliances ranged from 10^{-9} Pa⁻¹ to 10^{-6} Pa⁻¹ and showed a clear trend of a reduction in creep with the reduction of LMA. This effect is consistent with theory, and this range of creep compliance encompasses the analysis range of most polymers in the viscoelastic regime. Photopolymer systems containing fillers of various size scales demonstrate time-temperature viscoelastic shifts from multiple domains, and the combination of composition and temperature gradients will be demonstrated to elucidate the effects of multi-component hybrid systems.

CONCLUSIONS

Through the use of simple contact geometry with independent probes, a high-throughput methodology for viscoelastic properties has been developed using surface indentation. This technique shows good agreement with other experimental techniques and allows for the measurement of multiple material properties dependent on polymer substrate design and environmental conditions. Further changes to the substrate geometry and environment are possible to expand the metrology to measure buried interfaces or degradation effects on viscoelastic responses. Time-temperature superposition was also validated for this technique and offers a facile route to the determination of shift factors for a variety of polymer samples using a single high-throughput experiment.

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