HIGH-THROUGHPUT MEASUREMENTS OF VISCOELASTIC PROPERTIES USING SURFACE INDENTATION

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Introduction

Relaxation processes in viscous liquids and glasses have been studied extensively, but the underlying causes of glassy behavior in polymeric systems remains as a major unsolved area of condensed matter physics [1,2]. These processes are critical in the development of polymers for constant or cyclical load applications, where relaxation processes can lead to permanent deformation or the eventual failure of the specimen. Experiments to measure these properties either use long time scale experiments or time-temperature superposition to determine mechanical responses over the required application time.

Time-temperature superposition is difficult to implement in thermorheologically complex formulations, involving new models or unknown shift factors [3]. In these cases, a viscoelastic analysis of the system is required to calculate the shift factors and the resulting time-shifted creep compliance curve. This issue commonly arises in polymer blends and composite materials which may have viscoelastic responses that occur from multiple effects in distinct time domains. This complexity is caused by interfacial regions, blend composition, and filler characteristics which in turn contribute to changes in creep compliance and other 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 indentations. This system can be easily adapted to analyze combinatorial libraries with composition or temperature gradients.

Experimental

Photopolymer systems were polymerized from a mixture containing isobornyl methacrylate (IBoMA), lauryl methacrylate (LMA), and the photoinitiator 2,2-dimethoxy acetophenone (DPMA) [4]. The mass fraction of photoinitiator was 0.5% in all samples, while the composition of the two monomers varied. The monomer formulation was cured between glass slides and then separated, resulting in ≈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. After curing, samples were left for 48 h in the dark before experiments were performed. Styrene-ethylene/butylene-styrene block copolymer (Kraton 1650) samples were solvent cast in toluene and later left under vacuum to eliminate any remaining solvent, making 0.5 mm thick films.

An array of 1.19 mm radius chrome steel spheres are lowered to the polymer surface, and each sphere indented the polymer surface due to the force load from gravity. This type of indentation is described by Hertzian mechanics and depicted in Figure 1. The measured contact radii for this sphere size ranged from 15 μm to 60 μm, 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 [5]. The creep compliance, *J(t)*, for a step load stress response is calculated by:

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

where *a* is the contact radius, *R* is the indenting sphere radius, *v* 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 an infinitely thick sample.
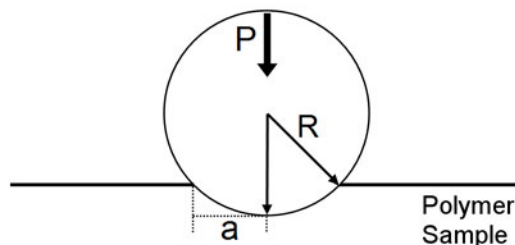

Figure 1. Schematic of indentation on a polymer sample under a gravity load, *P*. Indentation depth is not to scale.

Images were collected using an inverted microscope (Leica DMIRE2) with a computer controlled XY-translation 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 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 in each image in the sequence. The drift of the center point was less than 2 μm over the entire time span

of the experiment, and the spheres released from the surface upon tilting the sample.

A temperature gradient was used for time-temperature superposition experiments, with a quartz substrate to allow for imaging of the contact area [6,7]. 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 the samples were saved from indentation experiments and utilized for tensile creep experiments. Tensile creep measurements were measured using a Texture Analyzer (model TA.XT2i, Texture Technologies Corp., Scarsdale, NY) in tension mode.

Results and Discussion

Creep compliances of Kraton 1650M films were collected to compare the high throughput technique to other methods for viscoelastic response measurement. These results were converted to a creep tensile modulus using a Poisson's ratio of 0.49 when needed. Results from the high-throughput technique were statistically equivalent to the tensile tests performed on the same polymer. Creep compliance is also comparable to literature time-temperature superposition experiments performed by Rek and coworkers [8]. 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 ranging from a mass fraction of 45 % LMA to 60 % 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 is reduced and the samples should show a higher rate of creep due to the loss of glassy polymer regions. 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 the expected theory, and this range of creep compliance encompasses the analysis range of most polymers.

In addition to composition gradients, a temperature gradient experiment was performed using the Kraton 1650 film. A temperature gradient from 18 °C to 37 °C was analyzed at multiple positions to confirm that time-temperature superposition is possible using this technique. Elevated temperatures and a 22 °C temperature scan which matched the prior creep compliance experiments were tested to confirm 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. The shifted creep compliance curves matched the results from the room temperature sample and the prior Kraton film test. Shifted creep compliance at similar time points to the room temperature data confirms statistically equivalent creep compliance.

Currently, we are developing more complex polymer composites for viscoelastic analysis and measurement techniques for substrate/polymer film interface effects which occur in confined geometries. Both of these are important factors to quantify and measure accurately for better predictions of complex thermorheological systems.

Conclusions

A high-throughput method to measure creep compliance in polymer films was developed and validated. Good agreement to other experimental methods was found, and the measurement technique is accurate to long times. The systems analyzed demonstrate that both glassy and rubbery polymer systems are within the measurement range of this technique. Time-temperature superposition was also validated and provides the ability to determine shift factors for a polymer sample within a single high-throughput experiment.

Acknowledgements

References

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