Viscoelastic effects on the free retraction of rubber

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Wave propagation and retraction velocities were measured for two elastomers, a 1,4-polybutadiene and a polyurea, freely retracting from large tensile strains ($\leqslant 2$). From these data the stress-strain response was calculated. The achievable strain rate depends on the initial strain and the viscoelasticity of the material, with values exceeding 1800 s^{-1} attained herein. Thus, the method can be used to characterize the mechanical behavior at high strain rates, as well as high strains. A drawback is that the strain rate is not constant during the retraction. The kinetic energy of retraction reflects the unrelaxed stress, providing a straightforward determination of strain energy and its dissipation. The two elastomers represent extremes of viscoelastic behavior, as reflected in the retraction response at both low and high strain rates. © *2007 American Institute of Physics*.
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I. INTRODUCTION

Obtaining accurate mechanical characterization of elastomers at high strain rates is nontrivial.[1] For measurements limited to low strains (linear response), dynamic mechanical spectroscopy extends to about 100 Hz, with specialized instruments able to increase this range by a decade or two. By determining both rate and temperature dependences, measured mechanical data can be extrapolated to higher strain rates using time-temperature superpositioning;[2] however, different modes of molecular motion (chain modes versus the local segmental dynamics) have different time-temperature shift factors, potentially leading to large errors in master curves of mechanical properties.[3–5] A popular method of high strain rate mechanical testing is the split Hopkinson bar device.[1,6,7] Typically a disk-shaped sample is positioned between the ends of two metal bars and compressed by impact from a third bar. From the reflected and transmitted stress pulses the mechanical response of the sample can be determined. The split Hopkinson bar method was originally developed for hard materials, but has been employed for rubbers, with strain rates as high as 10^4 s^{-1} achieved.[8] Various methods to rapidly stretch rubber have been explored over the years, but with limited success.[1,9–14] Some recent work employed a falling weight to accelerate rubber samples, yielding strain rates >100 s^{-1}.[15–18]

A high speed mechanical method that is limited to small strains is the measurement of wave propagation. When a material is subjected to a mechanical perturbation, stress propagates as a pressure wave with a velocity, c, that for a large test specimen depends on the longitudinal modulus $M = K + \frac{4}{3}G$ of the material according to[1]

$$c = \sqrt{M/\rho}, \tag{1}$$

where K is the bulk modulus, G the shear modulus, and ρ the mass density. Both sonic and ultrasonic frequencies are used in this method, which is popular for biological applications.[1]

A related experiment is the free retraction of thin rubber strips from a stretched state. The idea of analyzing the retraction of rubber to determine its mechanical properties has been around for many decades, but is largely unexploited. Early experimental and theoretical studies were carried out by Mrowca *et al.*,[19–21] Stambaugh *et al.*,[22] and James and Guth.[23] These investigators relied on either a recording stylus or photographic methods to quantify the retraction dynamics. Subsequently, Mason[24,25] developed a more rigorous theoretical treatment, which accounted for the nonlinear stress-strain behavior typical of elastomers. More recently, Gent and Marteny[26] compared the pulse velocity in strained samples to the free retraction velocity in natural rubber, both neat and containing carbon black filler.

Modern high speed digital cameras and image analysis software enable the free retraction experiment to be performed with high temporal and spatial resolution. In the present work we explore the utility of the free retraction method for determination of the high strain (>1), high strain rate mechanical response of elastomers. Pulse velocities can reach hundreds of meters per second, corresponding to strain rates of $\sim 10^3$ s^{-1}. However, as we show herein, the transient nature of rubber retraction means that the strain rates are never constant, with the distribution of rates governed by the dissipative properties of the rubber. Along with the fact that the effects of strain and strain rate are convoluted, it becomes difficult to extract stress-strain curves from the data. Nevertheless, the retraction experiment can yield material properties, such as energy dissipation, which are difficult at best to obtain otherwise at high strain rates. Two materials were studied: 1,4-polybutadiene (PB), which exhibits relatively elastic behavior (i.e., high, recoverable elongation with minimal energy loss), and a polyurea (PU), which has pronounced viscoelasticity, manifested in the retraction experiment as broadening of the stress pulse.

II. THEORY AND BACKGROUND

The instantaneous Young modulus of a strip of unstretched length l_0 is

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$$E = \frac{\partial \sigma}{\partial e}, \tag{2}$$

where σ is the engineering stress and the strain $e=(l-l_0)/l_0$. The simple retraction theory of James and Guth[23] assumes Hooke's law, $\sigma=Ee$, to be valid and that the response is elastic (negligible energy dissipation). The sudden release of one end of a strip initially stretched to strain e_0 causes an unloading pulse to arise at the free end and propagate along the strip as a stress wave with a velocity relative to the fixed end given by

$$v_p = (e_0 + 1)\sqrt{\frac{E}{\rho}}. \tag{3}$$

Since the lateral dimensions of the sample are small, the wave propagates as an extensional wave, with longitudinal compression accompanied by lateral expansion of the rubber. The relevant modulus for the wave velocity in Eq. (3) is the tensile modulus, E. This should be distinguished from the "usual" sound velocity in an infinite three-dimensional medium [Eq. (1)], where the bulk modulus dominates. For example, in 1,4-polybutadiene the bulk sound velocity by ultrasonic measurements[27,28] is on the order of 1500 m/s, in contrast to the pulse velocities measured herein, which are a factor of ~25 smaller.

The material ahead of the unloading pulse remains at e_0, while the material behind it is completely relaxed and in uniform motion at a velocity equal to that of the free end

$$v_{\text{tip}} = e_0\sqrt{\frac{E}{\rho}}. \tag{4}$$

In this case, Eqs. (3) and (4) give a simple relation between the tip velocity and the velocity of the unloading pulse, v_p,

$$v_{\text{tip}} = \frac{e_0}{e_0 + 1} v_p. \tag{5}$$

When the wave reaches the opposite (fixed) end, the strip is no longer in tension, the original potential energy (strain energy) having been converted to kinetic energy of the moving rubber. The impedance mismatch of the rubber and its holder causes the wave to reflect backward; this is invariably accompanied by buckling of the thin test piece.

James and Guth[23] extended this simple description to the case of a real elastomer, for which the internal friction is not negligible. Thus, the material does not undergo instantaneous unloading when traversed by the wave; the approach to the unstretched state is time dependent. Reflection of the wave from the fixed end can occur before the sample has completely retracted, interfering with the process and obfuscating the analysis. There are two additional effects in real elastomers. Their deviation from Hooke's law broadens the unloading pulse, as the pulse front propagates through material at the original strain, for which the modulus and thus the wave speed are usually highest, while the trailing end traverses partially unloaded material, typically associated with lower modulus and wave speed. Another complication comes from the finite mass of the sample tip. Upon release of the constraining clamp, this mass limits the acceleration, smoothing the transition from zero to some finite pulse velocity. These combined effects lead to a complex situation, including the fact that the initial potential energy is not completely converted into kinetic energy, whereby Eq. (5) is no longer valid.

To accommodate the dispersion of the wave caused by deviations from the Hooke's law, Mason[25] considered the unloading as an integral of infinitesimal contractions de. The velocity of the material points within the pulse, $u \equiv dY/dt$, where Y represents the distance along the test specimen relative to the fixed end, is a function of the strain, $u=u(e)$, and

$$\frac{du}{de} = -\sqrt{E/\rho}, \tag{6}$$

where E is the (strain-dependent) differential modulus defined by Eq. (2) for any e. In principle, if $u(e)$ can be determined with sufficient resolution, Eq. (6) can be used to obtain the stress-strain relationship by integration

$$\sigma(e) = \sigma_0 + \rho\int_{e_0}^{e}\left(\frac{du}{de'}\right)^2 de', \tag{7}$$

where σ_0 is the stress immediately prior to initiation of the retraction. The modulus can be expressed as

$$E = \rho\left(\frac{du}{de}\right)^2. \tag{8}$$

This approach neglects any viscoelastic energy dissipation. If the strain is relaxed entirely during the unloading wave, the material velocity of all points behind the pulse attains the maximum value given by Eq. (4). On the other hand, if the material is viscoelastic, the velocity of the trailing material is reduced. This can be used to quantify the energy dissipation during the retraction between two points separated by a distance x according to

$$\Delta E_{\text{loss}}(x) = \tfrac{1}{2}\rho[v_1^2 - v_2^2], \tag{9}$$

where v_1 and v_2 are the final material velocities attained by the two points. Calculated for the entire strip with length $l=(1+e)l_0$ the energy loss per unit volume is

$$E_{\text{loss}} = \frac{l}{x}\Delta E_{\text{loss}}(x), \tag{10}$$

which is a (strain- and strain-rate dependent) material property.

III. EXPERIMENTAL

The PB was a random terpolymer of 38% cis-1,4, 51% trans-1,4, and 11% 1,2 (vinyl) butadiene units (Diene 40NF, Firestone Polymers), to which 0.5% by weight of N660 carbon black was added to improve the clarity of the camera images. The polymer was mixed with 0.05% organic peroxide (Varox DCP-R, R.T. Vanderbilt Co.) and cured by molding under pressure at 150 °C for 45 min. The polyurea was a 4:1 (stoichiometric) mixture of Isonate 143L (Dow Chemical, Midland, MI) and Versalink P-1000 polyamine (Air Products and Chemicals, Allenton, PA). The densities of the PB and PU were 0.900 and 1.105 g/cm^3, respectively.

Samples were cut into rectangular strips ($150\times13\times1.5$ mm^3 except where noted); this geometry gives longitudinal waves. Fiducial marks were placed equidistantly along the strip, with both ends then held vertically in the pneumatic grips of an Instron 5500R (Instron Industrial Products, Grove City, PA). An initial strain and the corresponding (relaxed) initial stress were then measured prior to release of lower end. The motion of the specimen was recorded using a PHANTOM V.7 charged coupled device (CCD) camera (Photo-Sonics International Ltd., Oxon, England) at 50,000 frames per second. The camera was positioned ~2 m from the sample, giving 800 pixels along the axis of retraction. Depending on lens, the resolution was 2–3 pixels/mm. From the recorded video, motion of the fiducial marks was digitized using IMAGE EXPRESS VISION V.5.6C (Sensors Applications Inc., Utica, NY) software. The duration of the retraction was material dependent and typically less than 3 ms, corresponding to more than 150 frames per retraction experiment.

Measurements of pulse velocity were also carried out on samples maintained in the stretched state, but otherwise identical to the retraction specimens. A pulse was excited on one end of the strip by striking the clamp, with the consequent pulse propagation observed in the same manner as the retraction experiments.

IV. RESULTS AND DISCUSSION

Results for a representative retraction experiment are shown in Fig. 1 for the PB with an initial strain equal to unity. Each point is stationary until arrival of the unloading wave, which induces rapid acceleration during the retraction. After this initial response, the material retracts at an approximately constant rate, indicated by the constant slope in the distance versus time plot in Fig. 1(a). Near the end of the experiment, the reflected wave becomes visible. Figure 1(b) shows the strain evolution for the material nearest the free end. The transient pulse relaxes about 70% of the strain, followed by a time-dependent unloading at a much slower rate. Data analysis is truncated when the reflected wave reaches the fiducial marks. The inset shows the strain rate, which varies during the retraction, attaining a transient maximum value of 1320 s^{-1} for $e_0=1.0$. The unloading pulse width (half maximum points) is less than 0.3 ms and is constant during propagation through the test specimen, reflecting the elastic nature of the PB. The PU response is more sluggish, so that notwithstanding its higher modulus, it exhibits a more smoothly varying strain rate during unloading that only reaches a maximum of only 385 s^{-1} for $e_0=1$ [Fig. 1(b) inset].

The velocity of the unloading pulse was determined for the two elastomers, retracting from various initial strains as shown in Fig. 2 (filled symbols). Included in the figure are the velocities measured for a pulse propagating in the PB held at the same strain without retraction (open squares). The coincidence of the data makes clear that the speed of the pulse depends only on the modulus of the material in front of the pulse. Also included in Fig. 2 is a datum obtained on a PB specimen having a substantially smaller cross section

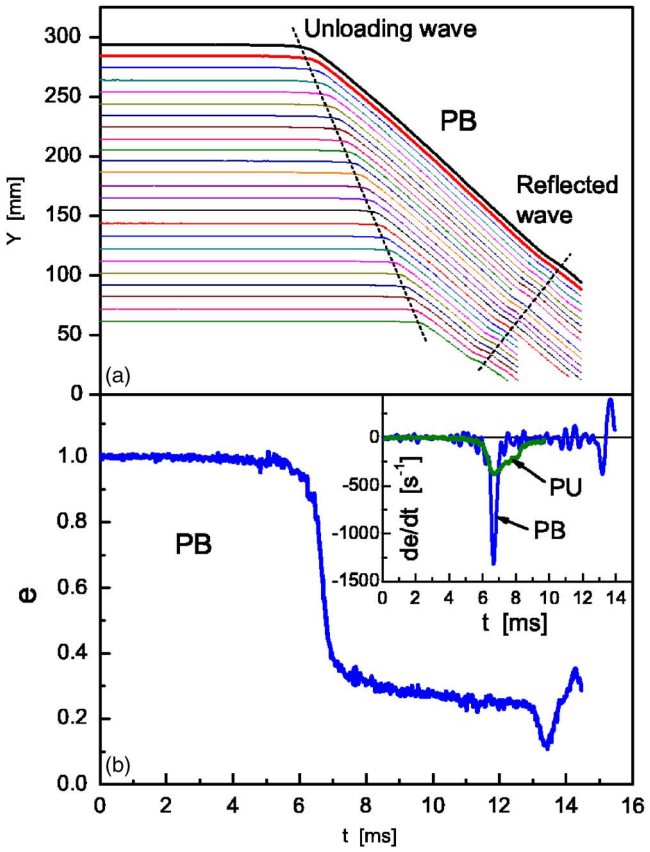

FIG. 1. (Color online) Free retraction of PB from an initial strain of unity; the zero time is arbitrary. (a) Distance from the fixed end of the test specimen, with each line representing one of the 24 fiducial marks, initially spaced 0.5 mm along the strip from the free-retracting end (top) to the fixed end (bottom). The unloading pulse is denoted by the first dashed line, with the reflected wave appearing about 5 ms after retraction commences. (b) Strain for the first pair of fiducial marks. The time derivative of the strain is shown in the inset, with data for PU ($e_0=1$) included.

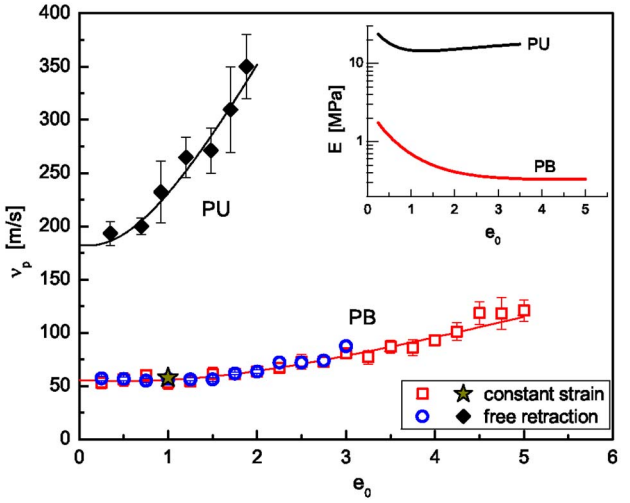

FIG. 2. (Color online) Pulse velocity as a function of initial strain for PU and PB: Unloading pulse during free retraction for PB (open circles) and PU (solid symbols); propagating pulse with strain held constant (open squares), including one measurement at $e_0=1.0$ for specimen with a more than sevenfold smaller cross-sectional area (solid star); solid line is to guide the eyes. Inset: tensile modulus calculated using Eq. (3) and the pulse velocities approximated by the solid line in the main plot.

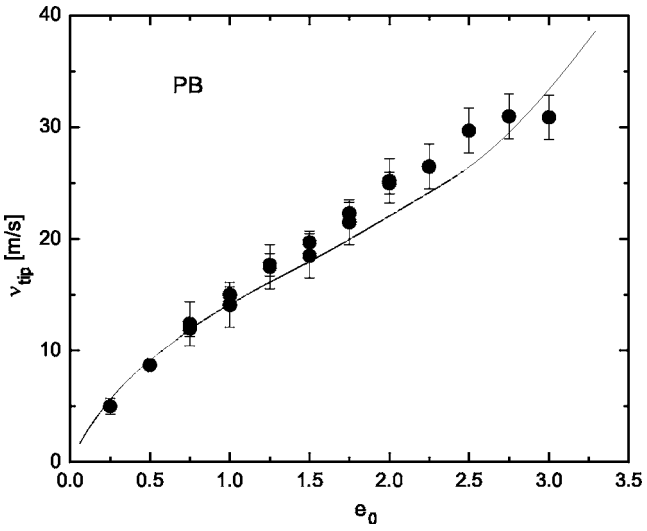

FIG. 3. Retraction velocity of the free end as a function of initial strain. The solid line is calculated using Eq. (4) and the low strain-rate modulus.

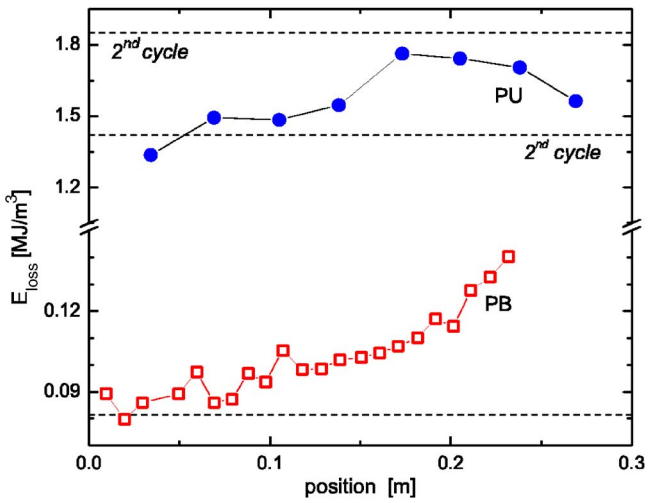

FIG. 4. (Color online) Energy dissipated during free retraction from $e_0=2.0$ for PB (solid circles) and PU (open squares). Note the scale break. The horizontal axis represents the distance from the free end. The dashed lines are the corresponding hysteresis loss measured for an extension/retraction at 0.01 s^{-1}. For the PU there is significant strain softening.

$(150\times1.75\times1.5\ mm^3)$. The unchanged pulse velocity affirms the absence of any bulk modulus contribution to the response; i.e., the wave is simple compression.

For a given e_0 the pulse velocity and the tensile modulus are related by Eq. (3). The inset to Fig. 2 shows the respective moduli for PU and PB calculated from the pulse velocities represented by the corresponding solid lines in Fig. 2. It should be noted that these values differ from the modulus measured by conventional (slow) stretch-retract experiments if viscoelasticity is significant. The modulus governing the pulse velocity is the instantaneous differential modulus, prevailing as material unloads from the initial strain e_0, and this strain history cannot be reproduced in a controlled displacement experiment. The modulus calculated from the pulse velocity during free retraction is closest to the *initial* value for slow unloading from the same strain (as discussed below).

The final retraction velocity of the free end of the retracting strips is shown in Fig. 3 as a function of the initial strain, along with the value calculated from the tensile modulus using Eq. (4). There is good agreement between the predicted and the measured values. This validates the assumption that for the polybutadiene hysteretic losses are minimal, so that the initial potential energy is almost completely converted into kinetic energy of the retracting material; that is,

$$E_{loss} \ll \tfrac{1}{2}Ee^2 \sim \tfrac{1}{2}\rho v_{tip}^2. \tag{11}$$

Equations (9) and (10) were used to determine the energy dissipated during the retraction, with results for PB and PU for the same initial strain, $e_0=2.0$, shown in Fig. 4. The abscissa represents the distance from the free end. The dashed lines indicate the energy loss measured during a low strain rate (Instron) experiment for one loading-unloading cycle. For PB this energy loss is constant $(=0.081\ MJ/m^3)$, while for polyurea the magnitude of the hysteresis decreases during the first few cycles; e.g., from 12.4 to 1.85 to 1.42 MJ/m^3 from the first to third cycles. For comparison, the energy losses measured from the low strain dynamic shear modulus, calculated as $\frac{1}{2}(3G'')e^2$, were 0.08 and 9 MJ/m^3 for PB and PU, respectively. For the PB, the linear viscoelastic value is quite close to the retraction value, in accord with the material's elastic nature. However, the behavior of the PU is viscoelastic and markedly nonlinear and therefore the dynamic shear modulus overestimates the energy loss by almost an order of magnitude.

Experimentally, the main limitation in applying Eqs. (9) and (10) is the mass of rubber behind the fiducial mark acting as an inertial element. This is aggravated by the requirement of long strips, in order to allow attainment of the final velocity at a given position before arrival of the reflected wave. These effects cannot be entirely eliminated; nevertheless, the data in Fig. 4 illustrate the utility of the method for quantifying energy dissipation at high strains and high rates, with differences between the present two materials clearly evident.

Mason[25] has suggested that Eq. (7) can be used to obtain the stress-strain relationship during the retraction. For this purpose the strain was calculated between the pair of fiducial marks (2 mm spacing) closest to the free end of the retracting strip; the results are an average for the material between these two points. Figures 5 and 6 show the stress-strain curve obtained from the unloading data for the PB and PU, respectively. For PB the free retraction is from $e_0=2.0$, and the stress-strain curve is much steeper than the data for slow (strain rate$=0.01\ s^{-1}$) unloading. For PU results for free retraction from two strains ($e_0=1$ and 2) are shown; note that the initial stretching induces significant "plastic" flow, with an apparent yield stress equal to ~6.6 MPa.

There are two limitations to using the free retraction experiment to determine the stress-strain behavior. First, the strain rate varies during the retraction (for the PB passing through a maximum$=1.82\times10^3\ s^{-1}$ as shown in Fig. 5). This means that the measured response is a convolution of strain and strain-rate dependences, since both quantities change over the course of the experiment. Thus, although high strain rates are attained during free retraction, it is an intrinsically transient process that cannot provide constant strain-rate data.

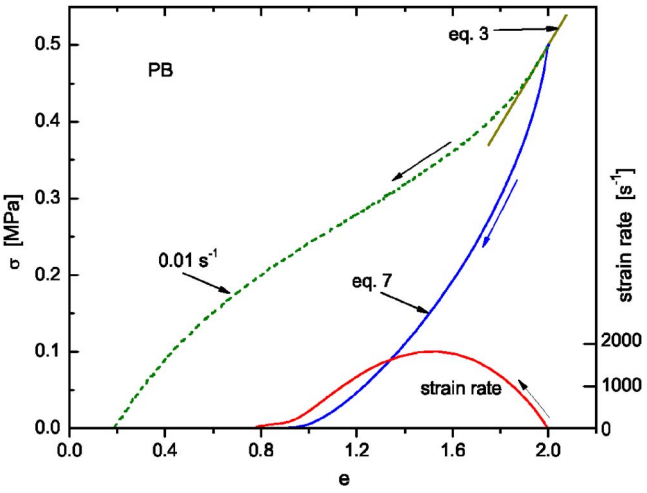

FIG. 5. (Color online) Engineering stress vs strain for PB rubber retracting from $e_0=2.0$ at low rate (dashed line) and freely at high rate (solid line). The strain rate for the latter varies during the free retraction as shown. The tangent line is from Eq. (3).

A second limitation is that Eq. (7) assumes that the strain energy is converted completely to kinetic energy of the retracting material. This assumption is reasonably valid for the PB rubber, which has small energy dissipation. Thus, the curve in Fig. 5 reflects what is actually happening during free retraction, and unloading curves calculated for different sections of the strip vary only slightly, reflecting the small energy loss as the unloading progresses. (The most accurate result is obtained by analyzing sections closest to the free end.) In contrast, the free retraction stress-strain curve for PU (Fig. 6) reflects only that portion of stress converted to kinetic energy, with neglect of the substantial dissipated component ignored in Eq. (7). Consequently, calculating the stress-strain response for different sections of the PU strip yields different results, with any stress calculated via Eq. (7) representing only the portion still available for conversion to motion of the material. The modulus values extracted from the data are lower than obtained directly from high strain-rate experiments. For example, from Fig. 6 for $e_0=1$, we obtain $E=1.7$ MPa at $e=0.5$, whereas direct high speed stretching measurements at a strain rate equal to the maximum during the retraction test (383 s^{-1}) yield a value of the modulus equal to 10.6 MPa for $e=0.5$.[8,17] As noted above, the sluggish response of the PU dampens the strain-rate variation over the course of the retraction. The maximum strain rate increases with initial strain, for example, from 385 s^{-1} for $e_0=1$ to 505 s^{-1} for $e_0=2$.

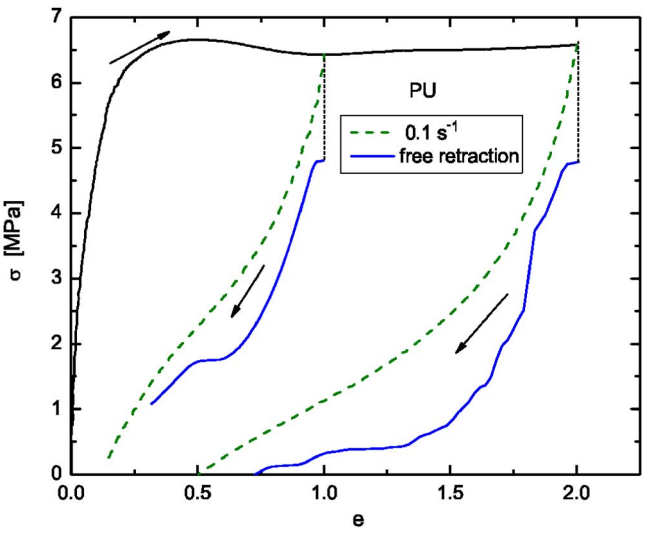

FIG. 6. (Color online) Engineering stress vs strain for PU extended at 0.01 s^{-1} to $e_0=1$ and 2, followed by immediate retraction at the same rate (dashed lines) or free retraction after cessation of stress relaxation, typically after ~30 s hold (solid lines). The free retraction curve, calculated using Eq. (7), represents only the elastically unloaded stress. The maximum strain rates are 385 and 505 s^{-1} for $e_0=1$ and 2, respectively.

V. CONCLUSION

Free retraction is a method to characterize the mechanical behavior of elastomers at high strain rates, as well as at high strains. The retraction speed reflects the amount of energy elastically retained, providing a means to quantify energy dissipation in the rubber; such information is not easily obtained by other methods for simultaneous high strains and high rates. The strain rate achieved by the method increases with the retraction strain, but depends on the transient response of the rubber. The higher modulus of the PU results in higher pulse velocities than for the PB, but the former's longer retardation times (more viscoelastic nature) result in lower strain rates. The major drawback of the technique is that the strain rate varies during the retraction, so that the effects of strain and strain rate are convoluted in the stress-strain data.

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[1] C. M. Roland, Rubber Chem. Technol. **79**, 429 (2006).
[2] J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed. (Wiley, New York, 1980).
[3] D. J. Plazek, I.-C. Chay, K. L. Ngai, and C. M. Roland, Macromolecules **28**, 6432 (1995).
[4] P. G. Santangelo and C. M. Roland, Macromolecules **31**, 3715 (1998).
[5] C. M. Roland, K. L. Ngai, P. G. Santangelo, X. H. Qiu, M. D. Ediger, and D. J. Plazek, Macromolecules **34**, 6159 (2001).
[6] B. Hopkinson, Philos. Trans. R. Soc. London, Ser. A **213**, 437 (1914).
[7] H. Kolsky, Proc. Phys. Soc. London, Sect. B **62**, 676 (1949).
[8] S. S. Sarva, S. Deschanel, M. C. Boyce, and W. Chen, Polymer **48**, 2208 (2007).
[9] G. J. Albertoni, Rubber Chem. Technol. **10**, 317 (1937).
[10] F. L. Roth and W. L. Holt, Rubber Chem. Technol. **13**, 348 (1940).
[11] D. S. Villars, J. Appl. Phys. **21**, 565 (1950).
[12] K. G. Hoge and R. J. Wasley, J. Appl. Polym. Sci. **12**, 97 (1969).
[13] J. A. Rinde and K. G. Hoge, J. Appl. Polym. Sci. **15**, 1377 (1971).
[14] A. Gale and N. J. Mills, Plast. Rubber Process. Applic. **5**, 101 (1985).
[15] I. Bekar, M. S. Hoo Fatt, and J. Podovan, Tire Sci. Technol. **30**, 45 (2002).
[16] M. S. Hoo Fatt and I. Bekar, J. Mater. Sci. **39**, 6885 (2004).
[17] C. M. Roland, J. N. Twigg, Y. Vu, and P. H. Mott, Polymer **48**, 574 (2007).
[18] P. H. Mott, J. N. Twigg, D. F. Roland, H. S. Schrader, J. A. Pathak, and C. M. Roland, Rev. Sci. Instrum. **78**, 045105 (2007).
[19] B. A. Mrowca, S. L. Dart, and E. Guth, Phys. Rev. **66**, 30 (1944).
[20] B. A. Mrowca, S. L. Dart, and E. Guth, Phys. Rev. **66**, 32 (1944).
[21] B. A. Mrowca, S. L. Dart, and E. Guth, J. Appl. Phys. **16**, 8 (1945).
[22] R. B. Stambaugh, M. Rohner, and S. D. Gehman, J. Appl. Phys. **15**, 740 (1944).

[23]H. M. James and E. Guth, Phys. Rev. **66**, 33 (1944).
[24]P. Mason, J. Appl. Phys. **31**, 1706 (1960).
[25]P. Mason, Proc. R. Soc. London, Ser. A **272**, 315 (1963).
[26]A. N. Gent and P. Marteny, J. Appl. Phys. **53**, 6069 (1982).
[27]D. Fioretto, L. Palmieri, G. Socino, and L. Verdini, Phys. Rev. B **50**, 605 (1994).
[28]A. Aouadi, M. J. Lebon, C. Dreyfus, B. Strube, W. Steffen, A. Patkowski, and R. M. Pick, J. Phys.: Condens. Matter **9**, 3803 (1997).