

## Mechanical Hole Burning Spectroscopy: Evidence for Heterogeneous Dynamics in Polymer Systems

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We have developed a mechanical spectral hole burning (MSHB) scheme that is analogous to non-resonant dielectric spectral hole burning (DSHB). DSHB experiments have been performed close to the glass temperature and interpreted in terms of dynamic heterogeneity. Here we find that holes are burned far above the glass temperature and in the terminal regimes for a branched polymer melt and a polymer solution. The results suggest that MSHB is a potentially powerful tool with which to examine dynamics of complex fluids.

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In 1996 Schiener *et al.* [1,2] developed a novel dielectric spectroscopic technique referred to as nonresonant dielectric spectral hole burning (DSHB). In the technique a strong sinusoidal wave or pump is applied to a material, and this pump is followed by a step probe. By performing two experiments in which the probe is of opposite sign, these authors removed the “nonlinear aftereffect” by subtracting the negative probe from the positive probe and dividing by 2. This “modified” response, if the behavior is linear, is identical to the linear response. In addition, the authors argued that deviations from the linear response even in the case of nonlinear behavior would be null unless there were dynamic heterogeneities in the material response. The deviations of the modified response from the linear response were quantified upon taking a vertical difference and a horizontal difference and plotting on a logarithmic time scale. Both the vertical and horizontal modifications exhibited peaks in the response that were referred to as holes. In that work and subsequent works the cause of the holes was interpreted as due to spatially heterogeneous material regions being heated differently (spectrally selected). This gives rise to the observed modifications of the dielectric response and the vertical and horizontal holes (depicted in Fig. 2 below).

Such results and interpretations are important because much of the present understanding of dynamics of complex glass-forming fluids currently revolves around the ideas of spatial and dynamic heterogeneity. The motivation of the present work is twofold. First, many materials, particularly polymers, do not have strong dielectric responses, and this makes the dielectric hole burning response extremely weak and the DSHB experiment extremely difficult to perform on these materials. Hence, an alternate experiment such as doing the mechanical analogue (MSHB) to the dielectric experiment becomes attractive. The second motivation stems from prior work from McKenna and co-workers [3,4] and by others [5,6] on related nonlinear viscoelastic experiments in which small deformations are superimposed on large deformations or after large deformations. In these works it is found that homogeneous nonlinear

constitutive models such as the Bernstein-Kearsley-Zapas (BKZ) model [7,8] can often explain, at least qualitatively, the observed anomalous behaviors. Hence, it is of interest to establish whether or not the hole burning phenomenon can be reproduced using such a nonlinear model that contains no explicit heterogeneity. Finally, we performed the experiments far above the glass transition, as described below, because mechanical measurements near the glass transition can be plagued by slippage in normal rheological geometries (cone and plate or parallel plate) due to high forces required to deform the high viscosity materials. Although the MSHB experiments performed here do not directly address the heterogeneity of dynamics in the vicinity of the glass temperature, they provide new results concerning dynamic heterogeneity in a branched polymer melt and an entangled linear polymer solution. Our analysis also shows that the hole burning that we observe is not directly attributable to the nonlinearity of the constitutive model considered.

Referring to Fig. 1 we define the MSHB scenario as follows: Apply a large sinusoidal deformation with a specific frequency  $\omega$  to the sample as the “pump” stimulation. This is followed by a positive step “probe.” A second experiment is performed, but now with a negative step probe. The relevant procedure is to subtract the second experiment from the first as illustrated in Eq. (1) (see also Fig. 2). This subtraction is referred to as “phase cycling” and eliminates the “aftereffect” due to the pump [1,2,9]. We follow the same procedure used in the DSHB work to obtain the modified shear modulus  $G_{\text{mod}}(\gamma, t)$ , which is analogous to the dielectric response in DSHB.

$$\begin{aligned} \text{(i)} \quad G_{\text{pos}}(\gamma, t) &= G_{\text{pump}}(\gamma, t) + G(\gamma, t)_{\text{mod}}, \\ \text{(ii)} \quad G_{\text{neg}}(\gamma, t) &= G_{\text{pump}}(\gamma, t) - G(\gamma, t)_{\text{mod}}, \\ \text{(i)} - \text{(ii)} \quad G_{\text{mod}}(\gamma, t) &= \frac{G_{\text{pos}}(\gamma, t) - G_{\text{neg}}(\gamma, t)}{2}. \end{aligned} \quad (1)$$

Here,  $G_{\text{pos}}(\gamma, t)$  and  $G_{\text{neg}}(\gamma, t)$  are the measured overall responses of the  $\pm$  probe after the pump;  $G_{\text{pump}}(\gamma, t)$  is the aftereffect due to the pump history only;  $\gamma$  is the shear

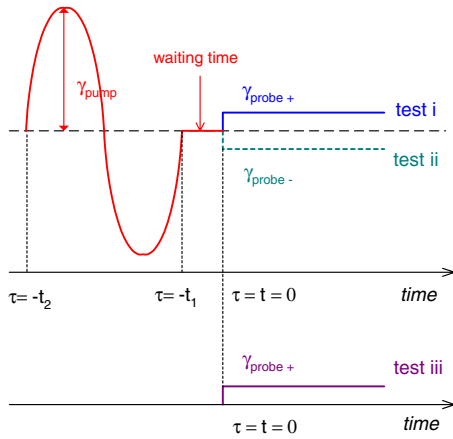


FIG. 1 (color online). Schematic of the sinusoidal pump at a large strain followed by positive or negative small strain probes in the mechanical hole burning experiment. The waiting time is inserted to study the transient characters of the holes.

strain and  $t$  is the probe time.  $G_{\text{mod}}(\gamma, t)$  is compared to the small undisturbed (linear) probe response  $G_{\text{eq}}(t)$ .

The systems studied were (1) low density polyethylene (LDPE 146 ExxonMobil Co.;  $M_w = 166\,000$ , PDI = 4.22,  $T_m = 107^\circ\text{C}$ ); (2) 30% wt. polystyrene ( $M_w = 1.02 \times 10^6$ , PDI = 1.03, Sigma-Aldrich Co.) solution in diethyl phthalate. The LDPE used in the present study is a long chain branched polyethylene, and work in this laboratory [10] has shown that the behavior of this material follows time-strain separability [11] and behaves as a BKZ fluid in reversing flows. These results agree with the previous findings by Chodankar *et al.* [12] and Wagner *et al.* [13] for branched polyethylenes. Motivated by the question of what role the nonlinear pump history plays in the MSHB observation, it is of interest to examine whether or not the features can be qualitatively obtained using a nonlinear continuum constitutive model. If not, it strengthens the arguments of the original workers (Schiener *et al.* [1,2]) that the holes are associated with the microscopic heterogeneity in the nonexponential relaxation mechanism. We chose the BKZ model for these calculations, though others could arguably be considered. For the polystyrene (PS) solution, we show only results because we know that linear polymer chains do not follow the BKZ behavior and more elaborate models are required to describe their behavior [14–17].

An ARES torsional rheometer was used with a cone and plate geometry in the study: For the LDPE, 50 mm diameter and 0.0402 rad cone angle; for the PS solution, 25 mm diameter and 0.1000 rad cone angle. The temperature was found to be stable within  $\pm 0.02^\circ\text{C}$ .

Strain sweep experiments were performed on both polymeric systems to determine the onset of nonlinearity in the pump and the magnitude required to assure a linear strain regime for the probe. The amplitude of the sinusoidal pump strain for the two polymeric systems was 300%, and the probe strain was  $\pm 10\%$  for the LDPE and  $\pm 30\%$

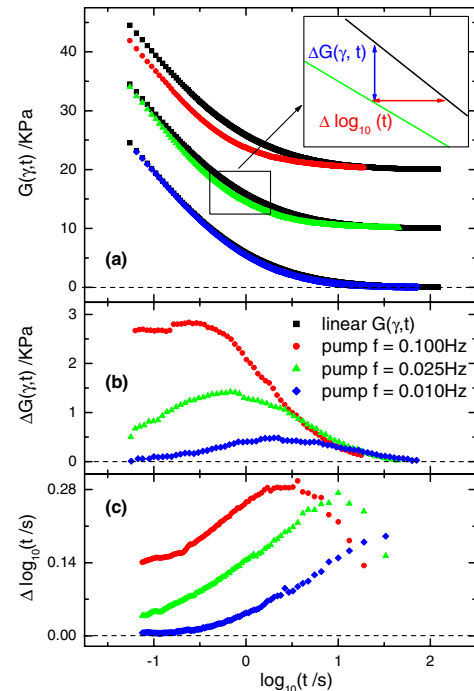


FIG. 2 (color online). (a) Time-dependent shear moduli of LDPE in its melt state at  $120^\circ\text{C}$ . Square symbols represent linear or unmodified single step relaxation data after 10% strain. Circle, triangle, and diamond symbols represent the modified shear moduli after one 300% sinusoidal oscillation at different frequencies as indicated in (b). The inset defines the vertical and horizontal hole. (b) Vertical modifications. (c) Horizontal modifications. Responses are vertically offset for clarity (b). Vertical differences between linear response and modified responses associated with each pump frequency. For 0.1 Hz pump, shear-softening dominates the short-time response resulting in a shoulderlike incomplete hole in the experimental time window.

for the PS solution. The slow pump frequency was varied from 0.1 to 0.005 Hz. Figure 2 shows the time-dependent shear moduli of the LDPE after a single step deformation and after pump modifications with various frequencies. This figure also gives a graphical depiction of the vertical and horizontal modifications. For a relatively fast pump  $f = 0.1\text{ Hz}$ , shear softening dominates the short-time response resulting in a shoulderlike incomplete hole in 2(b) and 2(c); for a slower pump a clear mechanical hole is burned, which is consistent with a heterogeneous dynamics. We note that in magnetic hole burning experiments by Chamberlin, a noticeable “magnetic softening” behavior was also observed (his Fig. 3 [18]), which also leads to a similar incomplete hole at short times. The pump with a specific frequency selectively modifies the responding degrees of freedom rather than altering the whole relaxation spectrum. This can be interpreted more directly when looking at the horizontal modification in 2(c): Responding regions of the relaxation spectrum are selected by the different pump frequencies. The horizontal holes shift out of the experimental window as the pump gets slower. Note

that a uniform shift of the spectrum would result in constant or flat lines in 2(c).

Figure 3 shows similar experimental results for the PS solution in its terminal relaxation regime. A clear mechanical spectral hole was burned at the slowest pump.

At this point it is clear that the mechanical hole burning experiment “works” in that we capture the major features of behavior that were observed in the (DSHB) experiments by Schiener *et al.* [1,2] and others [18–22]. The difference is that we have done the experiments on a branched polymer and a polymer solution, both well above their glass temperatures and in the terminal response regime. Hence, if the holes are due to dynamic heterogeneity, the origins of the heterogeneity are not related to the glass transition phenomenon and the MSHB results could be interpreted more broadly to imply that dynamic heterogeneity is important in the dynamics of entangled polymeric systems as well as to glass-forming systems. We return to this point at the end of this Letter.

As indicated above, long chain branched polymers seem to follow BKZ-type behavior in reversing flow histories, at least at moderate deformations as used here [10,12,13]. Therefore, it is of interest to compare the BKZ model’s predictions of the MSHB scenario with the actually observed results for the LDPE material. This model is known to not work for linear polymers, and we leave full analysis

of molecular models relevant to entangled linear molecules that may inherently contain heterogeneity, such as the convective constraint release model of Marrucci [17] to future work.

We fit the single step stress relaxation data for the LDPE to a time-strain separable function of the form

$$G(\gamma, t) = G(t)h(\gamma), \quad G(t) = G_0 e^{-(t/\tau)^\beta}, \quad (2)$$

$$h(\gamma) = 1/(1 + 0.1068\gamma^2),$$

where  $h(\gamma)$  is the damping function, stretch exponential fit gives  $\tau = 0.0018$  s,  $\beta = 0.193$ , and  $G_0 = 1.73 \times 10^5$  Pa.

Then the hole burning experiment for the LDPE was calculated within the framework of the BKZ model. For a simple shearing history, the BKZ theory gives

$$\sigma(t) = \int_{-\infty}^t -K_*[\gamma(t) - \gamma(\tau), t - \tau]d\tau, \quad (3)$$

where  $\gamma(t) - \gamma(\tau)$  is the relative strain and  $K_*$  is the partial derivative of the shear stress relaxation function with respect to the second argument,  $t - \tau$ .

The response of a small step strain after a large, sinusoidal strain for a given elapsed time can be calculated from Eq. (3) considering the following shear history:

$$\gamma(\tau) = 0, \quad -\infty \leq \tau < -t_e,$$

$$\gamma(\tau) = \gamma \sin \omega \tau, \quad t_e \leq \tau < 0, \quad (4)$$

$$\gamma(\tau) = \gamma_{\text{probe}}, \quad 0 \leq \tau.$$

$\tau$  is the elapsed time,  $\gamma$  is the amplitude of the sinusoidal strain,  $\omega$  is the pump frequency, and  $\gamma_{\text{probe}}$  is the small linear probe strain.

The comparison between the BKZ prediction and experimental results for the LDPE is shown in Fig. 4. Figures 4(a) and 4(b) show that the BKZ model gives a reasonable description for each set of data at different pump frequencies. The model calculations always underpredict the response. As the pump frequency decreases, the agreement between predictions and experiment improves. Figure 4(c) shows that the BKZ model fails to capture the mechanical hole burning event. Rather, the nonlinearity is only weakly imprinted onto the probe response in the form of a shoulder and not a peak. The shoulder is due to the stress softening nonlinearity. This confirms the conclusion we made previously that the BKZ model only weakly captures the hole burning features [23]. Our results as well as calculations with other nonlinear continuum constitutive models provide some justification to the Schiener *et al.* [1,2] contention that hole burning is, indeed, due to heterogeneity in the dynamics and not a simple nonlinear history effect.

In the original DSHB work, results were interpreted based on the assumption that the absorbed energy increases the local fictive temperature at the molecular level in glass-forming liquids. This dielectric heating effect modifies the highly temperature dependent relaxation rates in the super-

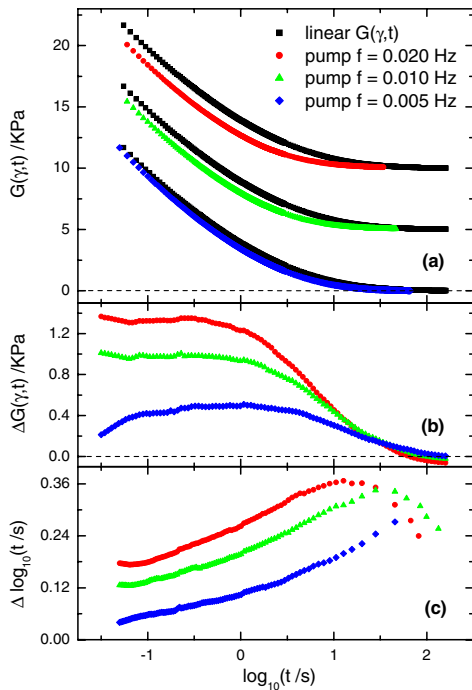


FIG. 3 (color online). (a) Time-dependent shear moduli of 30% wt. PS solution at  $-10$  °C. Square symbols represent linear response. Circle, triangle, and diamond symbols represent the modified shear moduli after one sinusoidal oscillation of 300% strain at 0.02, 0.01, and 0.005 Hz, respectively. Data are vertically offset for clarity. (b) Vertical modifications. (c) Horizontal modifications.

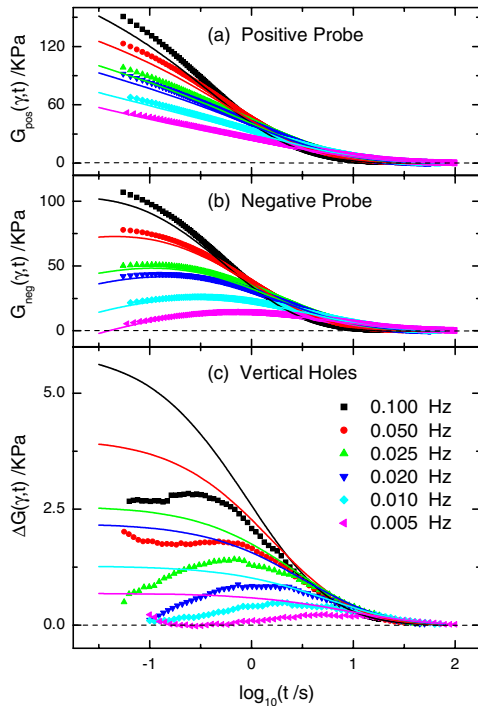


FIG. 4 (color online). (a) In all cases the symbols represent the measurements and the curves represent the BKZ theory predictions. Frequencies corresponding to symbols are given in the legend in (c) and curves represent decreasing frequency going from top to bottom. (a),(b) Responses of the +10% and -10% probe strains after different pumps. (c) Vertical modifications or holes.

cooled liquid. More recent work by Richert and co-workers [9,22] further developed electric and thermal circuit analogs with distributed relaxation times. The model quantitatively captured the dielectric hole burning features.

In the case of the present MSHB study we are working with materials well above the glass transition, but which respond in a heterogeneous fashion. We postulate that the origin of these holes rests in a molecular level heterogeneity, perhaps related to the nature of the entanglement or branching structure of the LDPE. In the case of the PS solution, the heterogeneity may be due to fluctuations in concentration or to heterogeneity in the entanglement distribution due to, e.g., convective constraint release [17]. In either case, it appears that the MSHB technique provides a powerful tool to explore further such molecular constitutive models.

In summary, we have presented results from the first mechanical spectroscopic hole burning experiments (MSHB) using LDPE and a PS solution in their terminal regimes. Distinguishable mechanical holes were burned at different pump frequencies, showing the signature of dynamic heterogeneity and demonstrating the potential power of the MSHB technique in materials with weak dielectric responses.

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