Mechanical hole-burning spectroscopy: Demonstration of hole burning in the terminal relaxation regime

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We have developed a mechanical spectral hole-burning (MSHB) scheme that is analogous to dielectric and magnetic spectral hole-burning techniques. Previous dielectric nonresonant spectral hole-burning experiments have been performed close to the glass temperatures of glass-forming materials and interpreted in terms of dynamic heterogeneity. The present study focuses on polymeric systems far above the glass temperature and in the terminal (reptation) regime. Theoretically, we examine Kaye-Bernstein-Kearsley-Zapas and Bernstein-Shokooh nonlinear viscoelastic constitutive models, which do not invoke an explicit heterogeneous dynamics for the relaxation response, to study MSHB, and find that both models fail to capture the subtle mechanical holes observed in the experiments. Experimentally, we successfully burned mechanical holes and show that the hole intensities vary as a function of "waiting time" and pump amplitude. The results suggest that MSHB is a potentially powerful tool with which to examine the dynamics of complex fluids.

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I. INTRODUCTION

Considerable effort has been expended in the past half century to understand the nature of glass-forming liquids, including polymers.[1,2] Of particular recent interest has been the ongoing discussion of the dynamic heterogeneity of these systems.[3–10] While it is widely accepted that the dynamics can be represented by a broad distribution of relaxation times or other nonexponential decay function, such as the Kolrausch-Williams-Watts (KWW)[11,12] stretched exponential, it is less clear whether this dispersion exhibits a uniform relaxation mechanism (homogeneous), or the net broadened relaxation is heterogeneous due to the response of slow and fast subensembles with independent mechanisms, which might be spatially distributed in the material.[3,13–15] There has been a range of techniques used to test the heterogeneity of the relaxational dynamics, such as multidimensional nuclear magnetic resonance,[16] optical deep bleaching,[17] nonresonant spectral hole burning (NSHB) conducted in dielectric and magnetic fields,[5,14,15,18–22] and recently, mechanical spectral hole burning (MSHB).[10] The fundamental assumption behind these spectral hole-burning techniques is that the spectrum of relaxation times can be locally altered rather than uniformly shifted by a strong impulse of given frequency. The striking feature is the capability of selecting virtually all the subensembles from the overall relaxation time spectrum by appropriate selection of experimental conditions. This selectivity forms the fundamental basis that justifies the heterogeneous scenario in the stretched slow dynamics.

Importantly, because many organic materials and especially polymers have very weak dielectric or magnetic responses, it is of interest to develop other means to investigate nonresonant spectral hole burning. In our previous study,[10] a mechanical spectral hole-burning testing scheme was established and conducted to study the heterogeneous relaxation dynamics in a branched low-density polyethylene (LDPE) melt and a concentrated linear polystyrene (PS) solution. Experimentally, we successfully burned the distinguishable mechanical holes well above the glass transition temperatures in their terminal relaxation (reptation) regimes of the materials. We further showed that an analysis based upon the Kaye-Bernstein-Kearsley-Zapas (KBKZ)[23–25] nonlinear viscoelastic constitutive model, which does not explicitly include a built-in heterogeneity concept, failed to capture the mechanical hole observed in the experiments.

In the present work, as an elaboration of the previous one,[10] we summarize the literature concerning NSHB methods and the motivation of the current study. We then describe the MSHB testing scenario and consider two nonlinear viscoelastic constitutive models in the context of the MSHB approach. This is followed by experimental results: (1) mechanical holes; (2) hole refilling; (3) pump amplitude effect on vertical holes; (4) energy dissipation and comparison with the model predictions.

II. BACKGROUND AND MOTIVATION

In 1996 Schiener and co-workers[14,15] showed the nonhomogeneous nature of the relaxation spectrum in two glass-forming liquids, propylene carbonate and glycerol, in the vicinity of their glass transition temperatures, i.e., the primary or α relaxation. In their dielectric NSHB experiments, a large, intense sinusoidal electrical wave with frequency ω is applied to a supercooled liquid near its glass transition temperature. This oscillation is called the "pump." Some underlying local mechanism(s) which is more favorable to this pump frequency is selectively excited or modified and this local modification can be monitored by a subsequent step probe; for details of the experimental methods the reader is referred to the original[14,15] and subsequent works.[19] Basically, a pair of experiments are conducted in which the pumps are identical but the probes are of opposite sign; the "linear aftereffect" caused by the pump is removed by subtracting the negative probe from the positive probe. The analysis examines how this modified response deviates from the linear, i.e., unmodified, response. They quantified the de-

viation by taking a vertical difference and a horizontal difference and plotting against logarithmic time. These vertical and horizontal modifications exhibited peaks in the response that were referred to as holes. And these holes have been interpreted to imply that only a certain band in the spectrum is triggered by the strong input energy pulse rather than that the whole spectrum is altered uniformly. Consequently, it justifies the interpretation that the relaxation is heterogeneous in nature.

While NSHB is a means to explore the inhomogeneous dynamics that can be thought of as a manifestation of the spatial heterogeneity, the NSHB technique does not explicitly have the capability of relating dynamic heterogeneity to spatial heterogeneity.[26–28] The initial explanation of the hole-burning event was pictured as serial heat baths characterized by different fictive temperatures. Certain "dielectric degrees of freedom that absorb energy at the pump frequency are dielectrically heated" (Chamberlin[4]) and this spectrally selected heating alters the local rate of relaxation. "Alternative models have associated the changes with population densities that are driven far away from thermal equilibrium conditions, e.g., within asymmetric double-well potentials."[5] This gives rise to the observed modifications of the dielectric response and the vertical and horizontal holes.

Some time prior to Schiener and co-workers' NSHB work, and for different reasons, McKenna and co-workers[29,30] and others[31,32] had performed related mechanical experiments, in which small deformations were superimposed on large deformations or after large deformations. In these works it was found that homogeneous nonlinear constitutive models such as the KBKZ model[23–25] can often explain, at least qualitatively, the observed anomalous behaviors. In 2000, Cugliandolo and Iguain[33] (CI) claimed to reproduce similar results to the NSHB experiments using a model of glass-forming liquids that represents infinite-range interactions, viz., no heterogeneity is involved. Hence, it is of interest to establish whether or not the hole-burning phenomenon can be reproduced using nonlinear models that contain no explicit heterogeneity.

In the field of glassy dynamics, the NSHB experiment has become a classic in a short period of time and materials such as propylene carbonate that are good glass formers and have very large dielectric permittivities are ready candidates for this method. In the case of polymers, the use of dielectric spectroscopy is commonplace, but few dielectric NSHB experiments have been successfully performed in polymeric materials. One possible reason for this is the low dielectric constants (usually 3–10) that most polymers have compared to that of propylene carbonate (~70). As a specific example, in Blochowicz and Rössler's recent work,[34] binary systems composed of tristyrene (M_n=370 g/mol) oligostyrene (M_n =2140 g/mol) were well studied using dielectric hole-burning spectroscopy and they required great care to avoid dielectric breakdown as voltages increased as the dielectric response decreased with composition. Hence, an alternate experiment such as doing the mechanical analog (mechanical spectral hole burning[10]) to the dielectric experiment becomes attractive. In addition, dielectric spectroscopy provides a different set of information about molecular dynamics (viz., that of the local dipole moments) than does mechanical spectroscopy.[35]

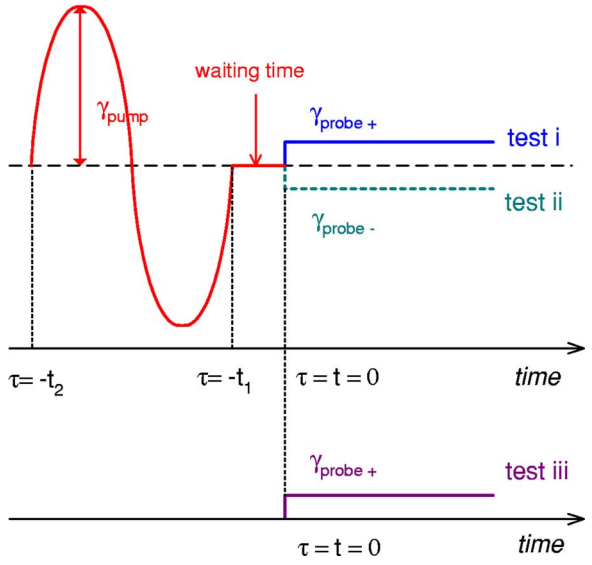

FIG. 1. (Color online) Schematic of the large-strain sinusoidal pump followed by positive or negative small-strain probes in the mechanical hole-burning experiment. The waiting time is inserted to study the transient character of the holes.

In the regime of higher temperature and faster dynamics, for small-molecule glass formers, the relaxation is generally reported to be exponential, which implies that it is intrinsically homogeneous. In a polymeric system the dynamic heterogeneity in the reptation regime, i.e., well above the glass temperature has not been investigated by hole-burning types of studies and heterogeneous dynamics are not generally invoked because mechanisms are perceived to be explicitly molecular, e.g., reptation. The current research examines the usefulness of a mechanical spectral hole-burning method as a tool to investigate the dynamics of polymeric systems well above their glass temperatures and to establish the existence of a hole-burning event. The plausibility that these dynamics are heterogeneous originates from the combined effects of the long chain entanglements (spatial heterogeneity), different rearrangement or reptation mechanisms along the chain (dynamic heterogeneity), local concentration fluctuation in the polymer solutions, or branching in the case of branched polymers.

In the following sections, we first describe the mechanical hole-burning experiment in a conceptual fashion. We then discuss two nonlinear constitutive models that do not explicitly contain heterogeneity and that we use to examine the hole-burning event experimentally. This is followed by a description of experimental details, a results section, and a discussion section. We complete the paper with conclusions and discussion of future work.

III. MECHANICAL HOLE BURNING

The dielectric or magnetic hole-burning scenarios can conceptually be extended to viscoelasticity. Referring to Fig. 1, the mechanical hole-burning scenario is as follows. A large sinusoidal deformation with a specific frequency ω is applied to the sample as the "pump" stimulation. Then per-

form two experiments with the same pump modification but with positive and negative small constant probes, respectively. The relevant procedure is to subtract the second experiment from the first as illustrated in Eq. (1). This subtraction is referred to as "phase cycling." By doing so the linear aftereffect due to the pump is eliminated.[5,14,15] For the purposes of comparison, we follow the same procedures used in the NSHB work to obtain the *modified* shear modulus $G_{\mathrm{mod}}(\gamma,t)$, which is analogous to the dielectric response in NSHB:

$$\text{(i)} \quad G_{+}(\gamma,t) = G_{\mathrm{pump}}(\gamma,t) + G(\gamma,t)_{\mathrm{mod}}, \tag{1a}$$

$$\text{(ii)} \quad G_{-}(\gamma,t) = G_{\mathrm{pump}}(\gamma,t) - G(\gamma,t)_{\mathrm{mod}}, \tag{1b}$$

$$\text{(i)} - \text{(ii)} \quad G_{\mathrm{mod}}(\gamma,t) = \frac{G_{+}(\gamma,t) - G_{-}(\gamma,t)}{2}. \tag{1c}$$

Here, $G_{+}(\gamma,t)$ and $G_{-}(\gamma,t)$ are the measured overall response due to pump±probe; $G_{\mathrm{pump}}(\gamma,t)$ is the aftereffect due to the pump history only; γ is the shear strain; and t is the probe time. $G_{\mathrm{mod}}(\gamma,t)$ is compared to the small undisturbed or linear probe response $G_{\mathrm{eq}}(t)$.

In the plot of modulus versus logarithm of probe time, the mechanical vertical hole is defined as the vertical difference between $G_{\mathrm{linear}}(t)$ and $G_{\mathrm{mod}}(\gamma,t)$:

$$\Delta G(\gamma,t) = G_{\mathrm{linear}}(t) - G_{\mathrm{mod}}(\gamma,t), \tag{2}$$

and the horizontal hole is defined as the horizontal difference between $G_{\mathrm{linear}}(t)$ and $G_{\mathrm{mod}}(\gamma,t)$ at the same modulus level:

$$\Delta \log_{10}(t) = \log_{10}(t)_{\mathrm{linear}} - \log_{10}(t)_{\mathrm{mod}} \quad \text{(at the same } G\text{)}. \tag{3}$$

One point that needs to be clarified is that in the above the mechanical driving force for the pump and probe is the strain, which leads to a stress relaxation type of testing scenario. In the case where one substitutes stress for strain the MSHB is a creep type of testing scenario.

IV. NONLINEAR VISCOELASTIC MODELS

A. Modulus calculations via KBKZ nonlinear constitutive model

Long-chain branched polymers, i.e., LDPE, seem to follow BKZ-type behavior in reversing flow histories, at least at moderate deformations as used here.[36–38] 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[38,39] 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,[40] to future work.

For a simple shearing history, the KBKZ theory gives

$$\sigma(t) = \int_{-\infty}^{t} -K^{*}[\gamma(t) - \gamma(\tau), t - \tau]d\tau, \tag{4}$$

where $\gamma(t) - \gamma(\tau)$ is the relative strain and K^{*} is the partial derivative of the shear stress relaxation function, which can be calculated using the material function [Eq. (9) below] and the correlation of $\alpha(\gamma,t) = G(\gamma,t)\Delta\gamma$.

The response of a small step strain after a large, arbitrary form of strain for a given time can be predicted using the following shear history, where

$$\gamma(\tau) = \begin{cases} 0, & \infty \leqslant \tau < -t_1, \\ \gamma_{\mathrm{pump}} \sin \omega\tau, & -t_1 \leqslant \tau < 0, \\ \gamma_{\mathrm{probe}}, & 0 \leqslant \tau, \end{cases} \tag{5}$$

where τ is the elapsed time, γ_{pump} is the amplitude of the sinusoidal pump strain, ω is the frequency, and γ_{probe} is the small probe strain. When $\tau \geqslant 0$, $\gamma(t) = \gamma(\tau) = \gamma_{\mathrm{probe}}$. Then Eq. (4) can be further simplified to

$$\sigma(t) = \int_{-\infty}^{0} -K^{*}[\gamma(t) - \gamma(\tau), t - \tau]d\tau. \tag{6}$$

Following the same procedure used by Waldron, McKenna, and Santore,[29] defining $\xi = t - \tau$ and numerically integrating the sinusoidal prestrain history, Eq. (6) can be rewritten as

$$\sigma(t) = \int_{\infty}^{t+t_0} K^{*}[\gamma_{\mathrm{probe}} - 0, \xi]d\xi + \int_{t+t_0}^{t+t_1} K^{*}[\gamma_{\mathrm{probe}} - \gamma_0, \xi]d\xi + \cdots + \int_{t+t_{n-1}}^{t} K^{*}[\gamma_{\mathrm{probe}} - \gamma_{n-1}, \xi]d\xi \tag{7}$$

where n is the number of steps in the simulation of the sinusoidal strain. Since the integrands are exact differentials Eq. (7) becomes

$$\begin{aligned} \sigma(t) = {} & \sigma[\gamma_{\mathrm{probe}} - 0, t + t_0] - \sigma[\gamma_{\mathrm{probe}} - 0, \infty] \\ & + \sigma[\gamma_{\mathrm{probe}} - \gamma_0, t + t_1] - \sigma[\gamma_{\mathrm{probe}} - \gamma_0, t + t_0] + \cdots \\ & + \sigma[\gamma_{\mathrm{probe}} - \gamma_{n-1}, t + t_n] - \sigma[\gamma_{\mathrm{probe}} - \gamma_{n-1}, t + t_{n-1}]. \end{aligned} \tag{8}$$

Note that the stress at a sufficiently long time relaxes to zero ($\sigma[\gamma, \infty] = 0$) for liquid or polymer melt states.

The single-step stress relaxation response for LDPE at 120 °C can be described by a time-strain separable function with the form of Eq. (9):

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

$$h(\gamma) = 1/(1 + 0.1068\gamma^2), \tag{9}$$

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

In the results section, we compare the KBKZ model calculation result with the experimental data and show the failure in the model prediction of the subtle hole-burning event although it can qualitatively describe each individual pump and probe response.

B. Compliance calculations via Bernstein-Shokooh nonlinear constitutive model

In the dielectric NSHB work, the response is equivalent to a mechanical creep response. Therefore, a nonlinear constitutive model for calculating the creep response in the scenario of MSHB, where the mechanical driving force is stress instead of strain, is of interest. Some experimental observations suggest the possibility that the intrinsic time can be altered by the instantaneous stress.[41] This is analogous to the notion of a temperature-dependent intrinsic time of Leaderman.[42] Bernstein and Shokooh[43,44] developed the concept of the stress clock function in the context of extending the KBKZ theory. The concept of a clock function can be rephrased by saying that the material senses a clock, which runs at a stress-independent rate and is different from the laboratory time.

For a simple shear case, the Bernstein-Shokooh nonlinear constitutive model[43,44] gives

$$\epsilon(t) = \frac{1}{2}\sigma(t)J(0) + \frac{1}{2}\int_{-t_0}^{t} \dot{J}[\beta(t,\tau)]\sigma(\tau)b[\sigma(\tau)]d\tau,$$

$$b[\sigma(t)] = 1 + ae^{|\sigma_{\text{pump}}/\sigma_{\text{probe}}|},$$

$$\beta(t,\tau) \equiv \int_{\tau}^{t} b[\sigma(s)]ds, \tag{10}$$

where $\dot{J}$ is the time derivative of the creep response; $b[\sigma(t)]$ is a positive scalar quantity called the stress clock function.

Conceptually, the "clock" idea has been widely accepted, but practically, it requires significant experimental work to obtain the form of such a clock. In addition, the form of a clock highly depends on the individual material. Only limited work can be found in the literature.[45] We did not perform the creep version of the MSHB experiment in the current study because the rheometer we used is a strain-controlled instrument. Here, we only present calculational results for the Bernstein-Shokooh model to illustrate that such a model without explicit heterogeneity is not able to capture, even qualitatively, hole burning.

V. EXPERIMENT

A. Materials and instrument setup

Two polymeric systems were studied: (1) a low-density polyethylene (LDPE146, ExxonMobil Co., M_w=166 000, PDI=4.22, T_m=107 °C) in its melt state at 120 °C; (2) 30 wt % polystyrene (PS, Sigma-Aldrich Co., M_w=1.02 $\times 10^6$, PDI=1.03) solution in diethyl phthalate (DEP) at −10 °C. An ARES (Rheometric Scientific, now TA Instruments) torsional rheometer with a cone-plate geometry was used in the study. The geometry parameters were as follows: 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. Nitrogen was always used as a protecting atmosphere as well as a cold source to lower the sample temperature. Temperature was found to fluctuate within ±0.02 °C. All the hole-burning experiments on LDPE were carried out using a strain-gauge transducer[46] and the experiments on the PS solution were carried out using the original force rebalance transducer (2KFRT) that is supplied with the ARES.

The LDPE used in the present study is a long-chain branched polyethylene and work in this laboratory[37] has shown that the behavior of this material follows time-strain separability[47] and behaves as a KBKZ fluid in reversing flows. These results agree with the previous findings by Chodankar *et al.*[48] and Wagner *et al.*[36] 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.*[14,15]) that the holes are associated with the microscopic heterogeneity in the nonexponential relaxation mechanism. We chose the KBKZ model for these calculations though others could arguably be considered. For the polystyrene solution, we only show results because we know that linear polymer chains do not follow the KBKZ behavior and more elaborate models are required to describe their behavior.[40,49–51]

B. Description of mechanical experiments

Strain sweep experiments were performed on both polymeric systems to ensure nonlinear strain amplitude in the pump and linear strain in the probe. The amplitude of the sinusoidal pump strain for both polymeric systems was 300% and the probe strain was ±10% for the LDPE and ±30% for the PS solution. The slow pump frequency was varied from 0.1 to 0.005 Hz. Depending on the duration of the individual hole-burning experiment, a waiting time of 25–60 min was always taken between two runs to ensure the sample relaxes back to its initial equilibrium state. A good confirmation is that the response curve during the large and slow pump period after a set of hole-burning tests overlapped onto each other within the experimental error. Multiple hole-burning runs under the same pump and probe were repeated and the data reproducibility was shown to be within 1%. Moreover, a confidence check was always performed by running a single-step relaxation experiment after all the hole-burning tests to assure no chemical degradation of the sample.

One special caution that needs to be pointed out is that the rheometer always takes a finite time t_1 to reach the command strain. It has been well recognized that without a proper "step" correction this can lead to large errors in the short-time ($<10t_1$) data.[52] Here we followed the procedure of Zapas and Craft[47] to correct the time by subtracting $t_1/2$ from the total time. To rule out any artificial manipulation of the short-time data, a rigid criterion that t_1 is determined by the

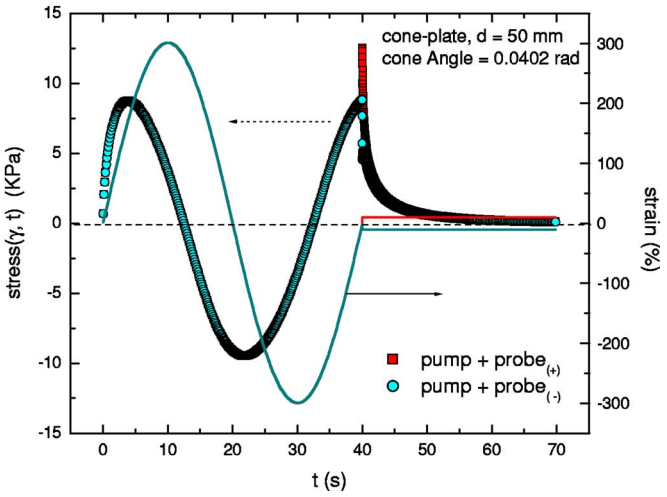

FIG. 2. (Color online) An actual MSHB measurement on LDPE at 120 °C in a 50-mm-diameter cone-plate geometry. The test condition was pump amplitude $\gamma_{pump}=300\%$, probe amplitude $\gamma_{probe}=\pm 10\%$, and pump frequency $f=0.025$ Hz. The overlaid response in the pump period indicates the sample was in the same equilibrium state before each test.

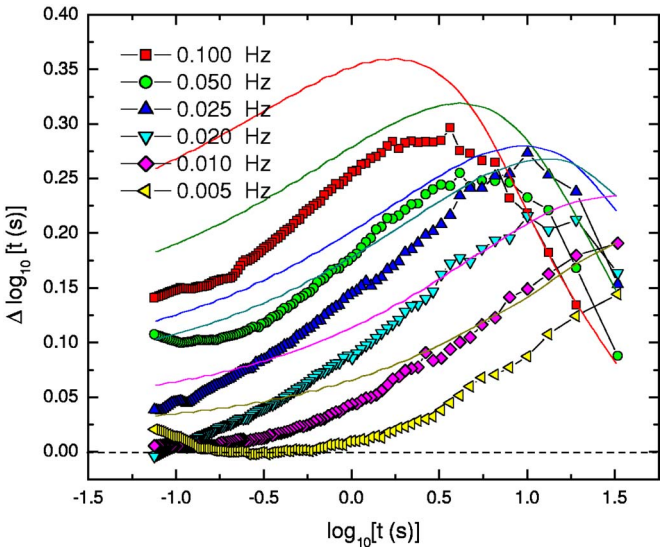

FIG. 3. (Color online) Comparison of horizontal holes for the LDPE experimental data (symbols) with KBKZ theory predictions (solid and dashed curves).

time when the strain reaches 99.9% of command strain is applied. A typical value for t_1 is 0.09 s for $\gamma_{probe}=\pm 10\%$. This would give a correction with $t_1/2=0.045$ s. The effect of this time correction is negligible for the response at long times where the hole-burning event occurs.

VI. RESULTS

A typical MSHB experiment for the LDPE is presented in Fig. 2, where a pair of hole-burning experiments was performed with the same pump (0.025 Hz) but different in the probe direction. The responses during the pump overlaid onto each other very well within the experimental uncertainty. This indicates the sample was always in the equilibrium state, i.e., the prior history had been "forgotten" before the experiments get started.

A. Mechanical holes

As has been demonstrated previously (Figs. 3 and 4 in Ref. 10), the LDPE melt and the PS solution showed how the linear shear moduli were altered by the various frequency-intensive pump modifications. Clear mechanical holes were burned with relatively slow pumps. For faster pumps, a common feature observed previously was a shoulderlike incomplete hole at short times, where shear softening dominates the short-time response. Similar shoulderlike incomplete holes can be found in the magnetic hole-burning experiments by Chamberlin,[22] where a noticeable "magnetic softening" behavior was also observed [his Fig. 3 (Ref. 22)]. The pump with a specific frequency selectively modifies the responding degrees of freedom rather than altering the whole relaxation spectrum.

At this point it is clear that the mechanical hole-burning experiment "works" in that it captures the major features of behavior that were observed in the dielectric NSHB experiments by Schiener *et al.*[14,15] and others.[18,19,21,53] 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 in glass-forming systems. We return to this point at the end of the paper.

The comparisons between the KBKZ predictions and experimental results for the LDPE (Fig. 4 of Ref. 10) show that the KBKZ model fails to capture the mechanical hole-burning event despite giving a reasonable description for each set of data at different pump frequencies. This confirms the conclusion we made previously that the KBKZ model only weakly captures the hole-burning features.[54] Our results as well as calculations with other nonlinear continuum constitutive models provide some justification to the Schiener *et al.* contention that hole burning is indeed due to heterogeneity in the dynamics and not a simple nonlinear history effect. Note that the experimental uncertainty is not an appreciable factor for the mechanical hole burned here. The systematic development of the holes and their intensities of 5–6 % of the linear response itself shows this. Importantly, the hole intensities are considerably greater than what is observed in dielectric measurements[5,15,21] and this implies that the MSHB technique may have advantages when signal-to-noise issues become important in specific experimental conditions. Pump amplitude effects are discussed subsequently.

In the Comment[26] by Chamberlin and Richert on CI's work,[28] they pointed out that these vertical peaks could be misinterpreted and might be due to the nonlinearity of the system. It is crucial to present the horizontal modification $\Delta \log_{10}(t)$ to eliminate this ambiguity, and "only heterogeneous systems can show an increase in $\Delta \log_{10}(t)$."[26] Figure

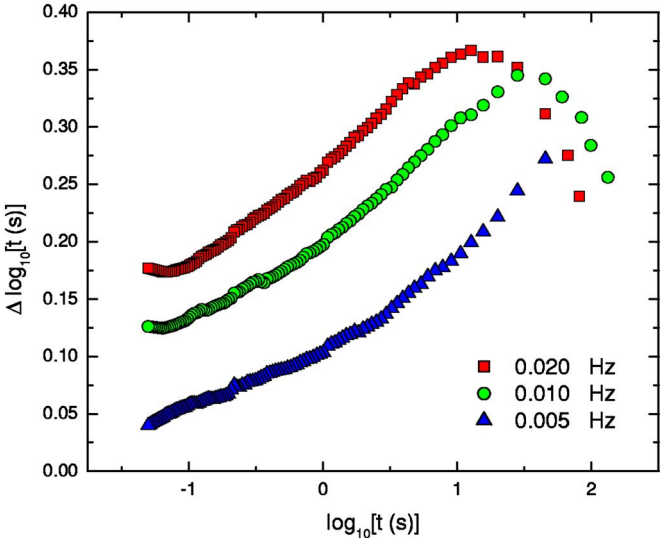

FIG. 4. (Color online) Horizontal holes as a function of pump frequency for the PS solution. As the pump is slower the hole intensity drops and the hole starts to shift out of the experimental window. Note that a uniform modification to the linear response will result in a flat line in this plot.

3 shows the KBKZ model predictions to the horizontal holes $\Delta \log_{10}(t)$ and the actual experimental results for LDPE. Two important features about these horizontal holes are (1) as the pump gets slower, the intensity of the hole decreases; (2) as the pump gets slower, the hole starts to shift to longer times and gradually shifts out of the experimental time window. The hole shape and location are greatly affected by the curvature of the response. Despite the poor prediction for the vertical hole features (steplike incomplete holes; Fig. 2 of Ref. 10), it is interesting to observe that the KBKZ model coincidently gives a "plausible" horizontal hole prediction as shown in Fig. 3, where a "qualitative agreement" between model predictions and actual experimental results can be found. However, when carefully examining the material response (not shown in Fig. 3) at very short times, i.e., $t < 10^{-4}$ s, the KBKZ model calculations predict an infinitely large value in the horizontal holes because of the shear softening, i.e., shoulder rather than complete hole, predicted by the model. Experimentally, although lacking extremely short-time data, the results suggest that the horizontal holes reduce back to zero at very short times (consistent with the vertical holes). Figure 4 shows similar experimental results for the PS solution. A clear mechanical spectral horizontal hole was burned at the slowest pump.

B. Hole refilling

In the NSHB experiments[5,14,15,18,21,53] a waiting time was inserted between the pump and probe (see Fig. 1) to study the hole intensity decay behavior, which was anticipated to be transient in character based on multidimensional NMR.[16] In the present work the hole refilling behavior in the MSHB experiment was also studied by varying the waiting time between the pump and the probe at a fixed pump ($f = 0.025$ Hz) and probe.

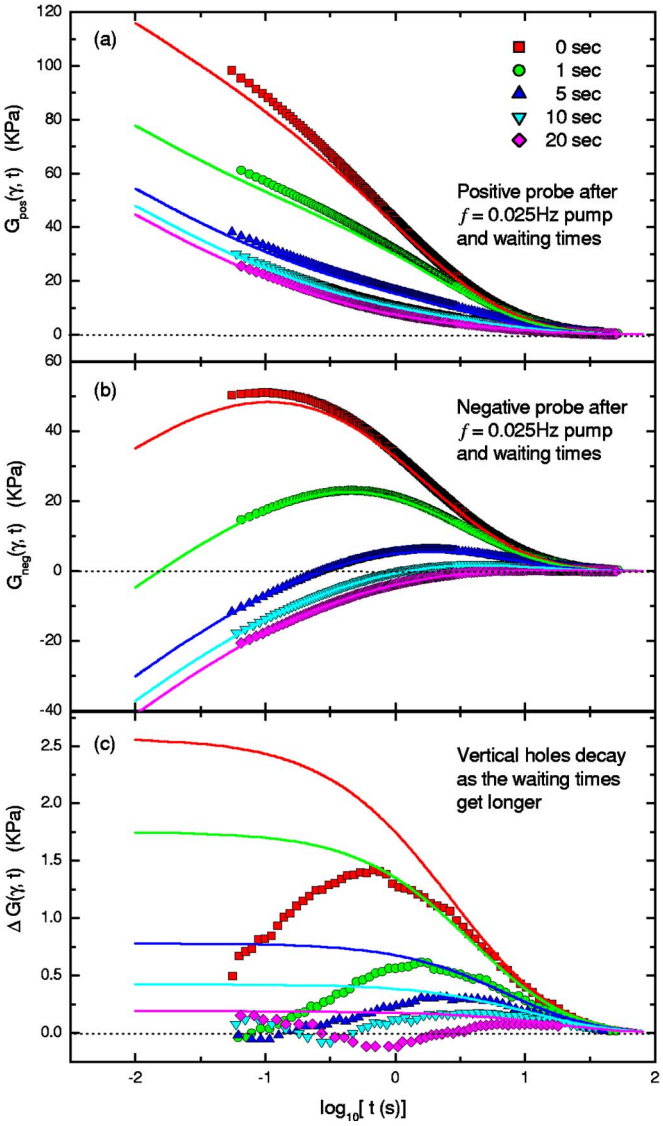

FIG. 5. (Color online) Waiting time effect on vertical hole for LDPE melt. Pump frequency was fixed at 0.025 Hz. (a) and (b) show the response of the positive and negative probes after different waiting times. (c) shows the vertical holes after different waiting times. Symbols are measured response and curves are KBKZ model predictions.

For LDPE, Figs. 5(a) and 5(b) clearly show a systematic changing in the positive and negative probe responses as the waiting time was varied from 0 to 20 s. Systematic weakening in the individual responses as the waiting time gets longer results in a systematic decrease in the vertical hole intensity. Figure 5(c) shows the hole intensity weakening until it has virtually disappeared for waiting times exceeding 20 s. From the nonlinear rheological point of view, this can be referred to as a "fading memory" effect, i.e., as the waiting time gets longer the material loses the previous modifications. The curved lines in Fig. 5 are from KBKZ model calculations. A reasonable agreement between the model prediction and the individual response of positive and negative probe is obtained, but the vertical hole prediction is poor as noted previously for the pump frequency effect.

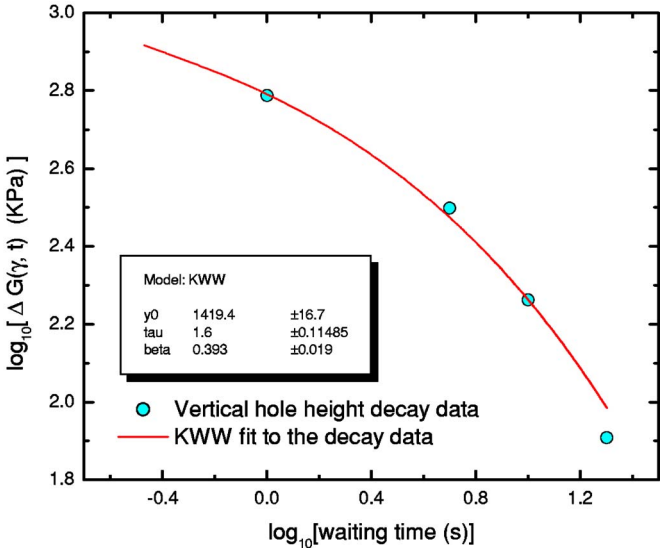

FIG. 6. (Color online) Vertical hole decay as a function of the waiting time for LDPE melt. A KWW function describes the decay behavior with a characteristic refill time 1.6 s.

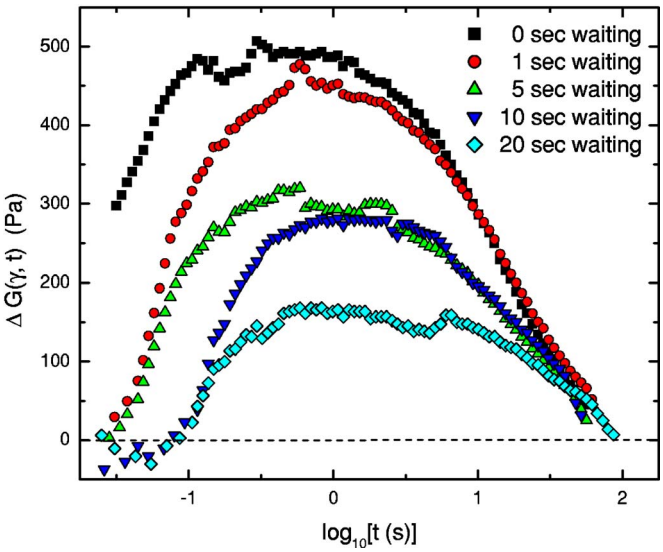

FIG. 7. (Color online) Vertical hole decay as a function of waiting time for PS solution. Pump is fixed at $\gamma_{\text{pump}}=300\%$ and $f=0.005$ Hz.

Another interesting point is to examine how the hole intensity decays as a function of the waiting time. As shown in Fig. 6, the hole decay data can be well characterized by a stretched exponential, i.e., KWW, function with a stretching parameter of 0.39 comparing to $\beta_{\text{KWW}}=0.19$ for the linear stress relaxation response. In the paper by Schiener *et al.*,[15] they reported that "the average primary relaxation time and the reequilibrating time scale are very similar in propylene carbonate as well as in glycerol for a given temperature." They further commented that the "fading memory" effect in nonlinear mechanical experiments in polymeric materials takes a longer time to return to equilibrium than the linear response does. The finding here is consistent with the comment in that the refilling characteristic time $\tau_{\text{refill}}=1.6$ s based on a KWW function fit is significantly greater than the characteristic relaxation time of 0.0018 s for the linear response. In addition, though our current study on polymeric systems is carried out well above the relevant glass transition temperatures, it is of interest to point out that study on supercooled liquid *o*-terphenyl using a deep bleaching technique near its T_g reported that "the distribution of τ in the selected (slow) subensemble returns to the equilibrium distribution on a time scale of about 10^2-10^3 times the average relaxation time."[17] Dielectric hole burning studies on D-sorbitol in the β-relaxation regime[55] and on dipolar reorientation processes in a crystalline relaxor ferroelectric material also show this substantially longer hole refilling process.[56] Similar experimental results for the PS solution are shown in Figs. 7 and 8, where the refilling characteristic time τ_{refill} is about 18 s from a KWW function fit compared to its stress relaxation time of 0.09 s. One interpretation of this[56] is that the pump modifies the sample over at least two orders of magnitude in time. In Figs. 7 and 9, the shift in the position of the peak during the refilling provides a simple explanation for this apparent slow refilling. The fast degrees of freedom get refilled first leaving the slow degrees of freedom at the long times. These slow degrees of freedom, which are typically an order of magnitude slower than the peak modification times, give the apparent slow refilling. The decrease in the mechanical hole intensity shows the transient nature of the subensembles (slow) as well.

C. Pump amplitude effect

Another interesting aspect about these mechanical holes is the relationship between the pump amplitude and the hole intensity. Here we examined the pump amplitude effect using the PS-DEP solutions. A series of experiments was performed by fixing the pump frequency at 0.005 Hz and then varying the pump strain amplitude from 200 to 450 %. In Fig. 9, two complete vertical holes were burned at 200 and

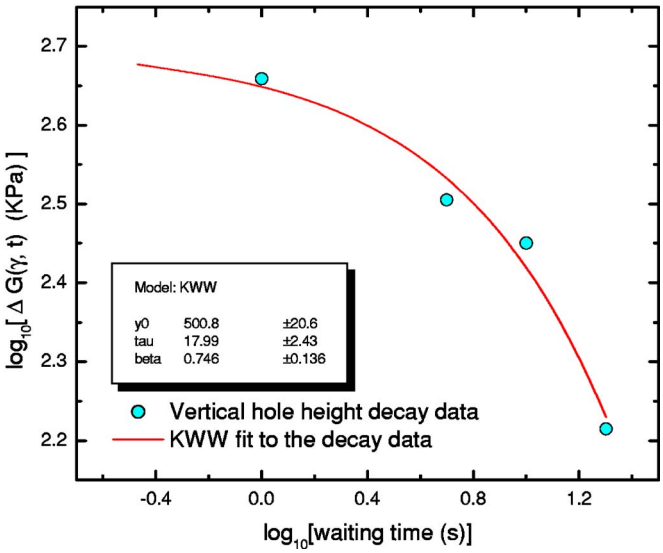

FIG. 8. (Color online) Vertical hole decay as a function of waiting time for PS solution. A KWW function fits the decay behavior with a characteristic refill time 18 s.

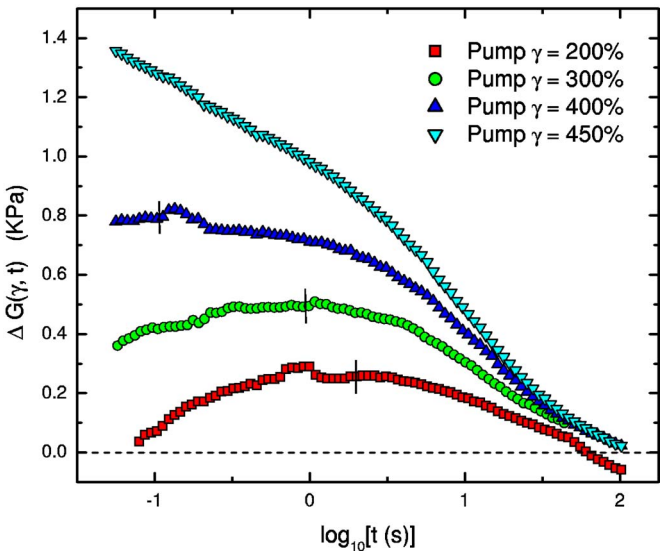

FIG. 9. (Color online) Pump amplitude effect on vertical holes for the PS solution. The vertical holes obtained after different pumps with different pump amplitudes, but with a fixed pump f =0.005 Hz and waiting time=0 s. The short vertical bars indicate the peak positions.

300 % pump amplitudes. Strain amplitudes bigger than 300% lead to tremendous shear softening at short time and bring the holes out of the experimental time window. In the current MSHB study, the correlation between the hole intensity and the pump amplitude does not provide a strong result because of the loss of the well defined hole peak positions in two responses resulting from the pumps with 400 and 450 % amplitudes. Regardless, the intensity was plotted against the square of pump strain amplitude (Fig. 10) for strains to 400% (vertical bars in Fig. 9). We see that a linear relation is observed. This is consistent with the observed quadratic dependence in the dielectric[15] and magnetic[18] NSHB experiments.

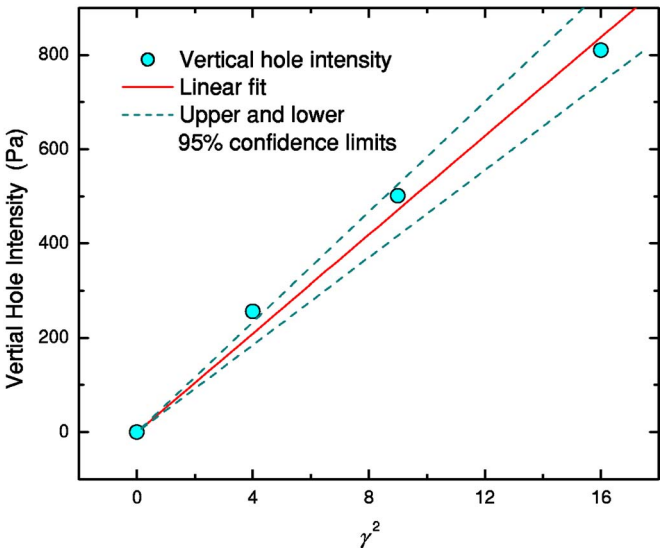

FIG. 10. (Color online) The intensity of the vertical holes from Fig. 9 as a function of the square of the pump strain amplitude. A linear fit shows that the vertical hole intensity is proportional to the square of the pump amplitude. Dashed lines indicate the upper and lower 95% confidence limits.

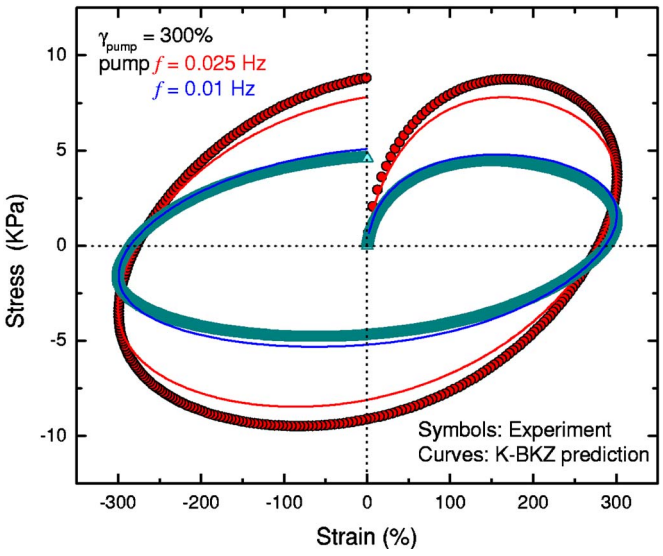

FIG. 11. (Color online) Stress-strain response during the pump for LDPE at a fixed amplitude of 300% and with 0.025 (•) and 0.01 (▲) Hz frequency, respectively. Symbols are experimental data and curves are from KBKZ model predictions.

D. Energy dissipation and hysteresis loop

One question that arises in considering the present work is the general validity of the KBKZ type constitutive model. For the branched PE, as noted, the model seems to produce a good representation of the "reversing" flow histories in the two-step types of experiments.[36,48] Here for completeness we also compare the KBKZ prediction with the response of the branched PE during the sinusoidal pump cycle. We do this as a hysteresis-loop-type of plot in Fig. 11 of two pump frequencies. As can be seen, the KBKZ model captures the response of the highly distorted hysteresis loops for both predictions.

Figure 11 shows the stress-strain response during the pump stage for a fixed $\gamma_{\text{amplitude}}$ with two pump frequencies for LDPE. The distorted hysteresis loop clearly shows a viscoelastic behavior in such a material as expected. Comparing the KBKZ model predictions with the experimental data, interestingly, one can observe that as the pump gets slower the agreement gets better. From the fading memory point of view, the pump history gets forgotten more in the slow pump than that in the fast pump; from the hole refilling point of view, the hole is refilled partially during the pump.

VII. DISCUSSION

We have presented a series of experiments in which the mechanical hole-burning event has been demonstrated for two polymer systems in their terminal relaxation regimes. The importance of the techniques arises because similar nonresonant spectral hole-burning events (dielectric, magnetic) have been interpreted in terms of dynamic and spatial heterogeneity. Because polymers normally have low dielectric

constants and are nonmagnetic, having an alternative hole-burning capability is of interest. The results of the present paper support the contention that dynamic heterogeneity is at the root of the observed hole-burning event. However the origin of the heterogeneity in the polymer systems studied here must be essentially different from that in those glass-forming liquids around their glass transition temperatures. The reasons for these interpretations are threefold.

First, the mechanical holes burned in the experiments are similar to those in dielectric and magnetic hole burning in, i.e., the pump frequency dependence of the mechanical holes, the γ_{pump}^2, and the waiting time dependences of the vertical hole intensities.

Second, the theoretical study in which we find that the KBKZ model fails to predict the hole feature in the branched PE relaxation response supports the consideration that MSHB is a potential technique to study heterogeneity in relaxation dynamics. In spite of some qualitative agreement in the model predictions to the individual probe response, the KBKZ model with a time-strain factorable material function [Eq. (9)] fails to capture the hole-burning event observed in the experiments. In addition, a time-strain nonfactorable material function (with the purpose of introducing stronger nonlinearity) was also investigated and fails to reproduce the main hole features discussed here. The latter attempt also only gave shoulderlike incomplete vertical holes because of the shear softening from the KBKZ model. Details were presented previously.[54]

As mentioned in the previous section, the dielectric NSHB is essentially equivalent to the mechanical creep experiment. For illustrative purposes, we present an infinitesimal step stress linearized Bernstein-Shokooh model calculation result for the MSHB scenario. Details are referred to our previous work.[54] There was no actual experiment conducted. Instead, a calculation for the creep MSHB scenario was performed using a typical material creep function and an arbitrary clock function. Figure 12 shows that the modified response of interest overlaps exactly onto the unmodified response, i.e., the pump effect was eliminated after the phase cycling and no hole-burning feature is captured. The calculated creep behavior does not show any hole-burning evidence because the nonlinearity was canceled out by the phase-cycling procedure. Clearly the Bernstein-Shokooh model, which uses a stress clock to induce nonlinearity cannot capture hole burning and reduces to a superposed linearity because there is no stress-clock effect as the superposed stress becomes infinitesimally small. We remark that the nonlinearity implanted by the KBKZ model is different from that by the Bernstein-Shokooh model in the form used here.

In the NSHB and MSHB, the phase-cycling procedure is essential to eliminate "the large but uninteresting linear aftereffect of the pump field."[14,15] We initially thought that the nonlinear pump effect is the cause of the burned holes. Severe departure from the linear response, which will dramatically affect the final probe response, is a consequence of the nonlinear response inherent in the KBKZ and Bernstein-Shokooh nonlinear viscoelasticity models (or a dielectric equivalent). The failure of these models to capture the hole burning invalidates our initial argument that the hole-burning event is the consequence of nonlinearity. The "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 implications of the results based on the original KBKZ theory are clear and in agreement with much that has been done in the field of NSHB—the continuum approach to molecular dynamics, even when containing strong nonlinearities as in the KBKZ model, does not completely describe the material dynamics. Whether or not this conclusion can be generalized remains to be determined. If the NSHB experiment or the MSHB experiment exhibit holes that arise due to dynamic heterogeneity in the material, then the methods, especially the MSHB method described here, have advantages of simplicity and versatility over some of the other methods mentioned in the introduction.

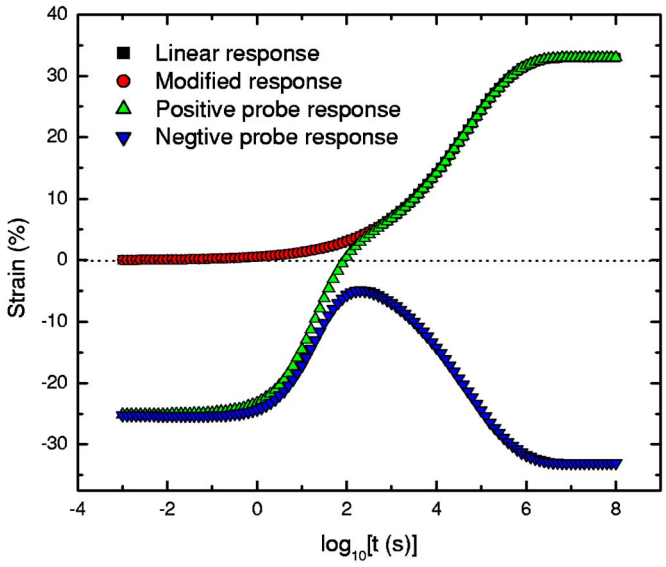

FIG. 12. (Color online) Creep responses obtained from Bernstein-Shokooh model calculation. Symbols triangle and inverse triangle represent the responses after positive and negative probes, respectively. After the phase cycling, the interested modified response (circle) overlaps onto the linear creep response (square).

Third, the mechanical holes burned in the terminal relaxation regimes for entangled polymer (branched) melt and (unbranched) solutions imply a different origin of the dynamic heterogeneity than that involved in the nonresonant holes burned in glass-forming systems near their glass transition temperatures. In the nonresonant hole-burning experiments on simple glass-forming materials,[6,7,14,15,18,19,57] results were interpreted based on the assumption that the absorbed energy increases the local fictive temperature using specific heat of the slow freedom[15] at the molecular level in glass-forming liquids. This dielectric heating effect modifies the highly temperature-dependent relaxation rates in the supercooled liquid. More recent work by Duvvuri, Jeffrey, and Richert[5,21] further developed electric and thermal circuit analogs with distributed relaxation times and the dynamic heat capacity jump at the glass temperature for the model. The model quantitatively captured the dielectric hole burning features. In the study of the dynamic heterogeneity of D-sorbitol

in its β relaxation ($\sim$64 K below its T_g=268 K) Richert[55] showed a small change in the heat capacity, $\sim$1% of that related to the structural relaxation, is responsible for the dielectric hole burned there. Kircher *et al.*[56] used the dielectric hole-burning technique in the study of the dipolar reorientation processes in a relaxor ferroelectric ceramic material that is crystalline in a narrow temperature range ($270 < T < 300$ K) where the heat capacity change is not a very appreciable factor. In the present MSHB study, the work is for polymeric systems well above the glass transition temperature (>100 K), where the dynamic heat capacity shows no frequency dependence, and yet we successfully burned the holes. Hence, the explanations provided by Chamberlin and co-workers[14,15] or Richert and co-workers[5,21] that depend on a high-temperature sensitivity to the relaxations selected by the pump seem unlikely to be at the origins of the mechanical hole-burning response in the entangled polymer systems studied here. We postulate 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.[40] In any case, it appears that the MSHB technique provides a powerful tool to explore further such molecular constitutive models and to investigate the dynamics of complex fluids.

VIII. CONCLUSIONS AND FUTURE WORK

In summary, a mechanical spectral hole-burning technique has been developed and used to examine the behavior of polymeric systems in their terminal relaxation regimes. Distinguishable and systematic mechanical holes were burned in a LDPE melt and in a PS solution at different pump frequencies. These holes are not reproduced by two nonlinear viscoelastic constitutive models (KBKZ and Bernstein-Shokooh models) that do not explicitly include heterogeneity. The latter model gives no evidence of hole burning, while the former gives steplike or shoulderlike incomplete vertical holes. One may ask if other nonlinear models might capture the mechanical holes, and this remains an open question, but the two very different models investigated here do not.

Also, the evolution of the hole intensity with respect to the waiting time and the pump amplitude was investigated. Hole refilling occurs at a different rate than the kinetics of the relaxation (terminal) investigated here. Similar but different observations can be found in Stratton and Butcher's early work,[58] where they reported that the recovery upon cessation of steady flow takes longer than the terminal relaxation time, perhaps due to reentanglement effects. We also found that the pump amplitude γ affects the hole intensity linearly as a function of γ^2, similar to observations of dielectric[15] and magnetic[18] hole-burning intensities.

Though the MSHB shows promise as a tool to explore dynamic heterogeneity, further work is required to fully exploit the potential of this method. Means need to be developed to "calibrate" the length scales of the heterogeneities as they relate to the observed vertical hole $\Delta G(\gamma,t)$ and horizontal hole $\Delta \log_{10} t$. Such work has been initiated in our laboratory using block copolymers and polymer blends of known spatial heterogeneity.

Furthermore, though beyond the scope of the present paper, it is of importance to investigate molecular-based models of polymer chain dynamics to determine whether or not the molecular heterogeneity in such models (as represented by, e.g., convective constraint release,[40] tube fluctuations,[59] and reptation mechanisms[49–51]) can capture the hole-burning event. This would be a possible outcome due not to the linear relaxation spectra but to the effect that the large deformation of the pump cycle "adds" to the probes and consequently influences the probe responses. At present, solutions to the deformation history used in the MSHB experiment are not readily available for these models.

Finally, for MSHB investigations near the glassy state, means need to be found to enable large deformations to be applied to the sample without grip slippage or breakage, sample breakage, etc., occurring in order to perform the experiments. Clearly, such experiments could be performed in the glassy state itself.

ACKNOWLEDGMENTS

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