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Mechanical Spectral Hole Burning in Glassy Polymers – Investigation of polycarbonate, a material with weak β-relaxation

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Abstract

Mechanical Spectral hole burning (MSHB) has been used to investigate the nonlinear dynamics in polymers, ranging from melts, solutions, block co-polymers, and glasses. MSHB was developed as an analog to the dielectric spectral hole burning method, which is not readily applicable in polymers due to weak dielectric response. While similar holes were observed in both mechanical and dielectric hole burning, the interpretations were different. In the latter case, it has been argued that the holes are related to dynamic heterogeneity as related to an increase in local temperature of molecular sub-ensembles (spatial heterogeneity) while in the former case the holes have been related to the type of dynamics (rubbery, Rouse etc.). Recent work from our labs used MSHB to investigate glassy poly (methyl methacrylate) and showed evidence of hole burning and supported the hypothesis that the origin of holes was related to dynamic heterogeneity as evidenced by the holes being developed near to the strong β-relaxation in PMMA. In the present work MSHB is used to study polycarbonate which has a weak β-relaxation, and the results are compared with those observed in PMMA. We observe that the polycarbonate exhibits weak holes and the nature of the holes with change in pump amplitude and frequency are different than observed in PMMA. These results support the hypothesis that the hole burning observed in amorphous polymers below the glass transition temperature is related to the strength of the β-transition which, in turn, is related to molecular level heterogeneity in the material dynamics.

Key Words: Glass transition, beta-relaxation, dynamic heterogeneity, hole burning spectroscopy, MSHB, polycarbonate, poly(methyl methacrylate)

1) Introduction

Glasses find extensive application in different fields such as optics, pharmaceuticals, electronics and aerospace [1]. Polymeric glasses, in the deep glassy state exhibit excellent mechanical properties and are commonly used in engineering applications. Linear viscoelastic properties of polymers are well characterized by mechanical and dielectric spectroscopies, and going beyond linear response, methods such as large amplitude oscillatory shear (LAOS) provides information about material response under large deformations (non-linear deformation). These LAOS tests have been applied to soft materials such as polymer solutions and polymer melts [2], but only a few works have reported the non-linear dynamics of polymers in the deep glassy state[3-5]. Hence understanding of non-linear response of glassy polymers is important from both fundamental and practical perspectives.

The non-linear measurements in the field of dielectric spectroscopy are similar to LAOS experiments (mechanical counterpart) because of the similar nature for their underlying equations [6]. The non-linear dielectric response of small molecule glass formers (with large dielectric susceptibility) was investigated by Schiener et al[7, 8] through non-resonant spectral hole burning (NSHB). These experiments aimed to investigate dynamic heterogeneity [7-12] in the vicinity of the glass transition temperature. In NSHB, a large sinusoidal electric field (pump) is applied, followed by a short waiting time and then the sample is subjected to a small constant electric field (probe), changing sign in two separate experiments. Then, the after effect on the polarization due to the pump is removed by phase cycling, where a similar pump and probe sequence is applied but with the probe being of the opposite sign. From these two sets of experiments, a modified probe response is obtained which is then compared with the unperturbed linear response of the material not subjected to the large sinusoidal pump. If the difference between the modified and linear responses (either in horizontal or vertical direction) is zero or constant, then it is interpreted as a homogenous response. In the homogenous case, the sample responds uniformly to the pump and the entire spectrum (modified response) shifts uniformly. However, in the case of a heterogenous response, some parts (sub ensembles) are selectively modified by the pump and this leads to a non-uniform shift in response and is evidenced by the presence of holes. Presence of holes in NSHB experiments has been related to thermal energy being dumped in selected regions of the sample upon application of the pump, which causes a

change in local fictive temperature and corresponding dielectric relaxation times. A brief review of NSHB has recently been reported by Chamberlin.[13]

NSHB is not commonly applied to polymers because of their low dielectric response. For such cases, McKenna and co-workers developed mechanical spectral hole burning (MSHB) [14-19] as an analog to NSHB for polymers. Here the sample is subjected to a large sinusoidal pump of either strain or stress (analogous to electric field in NSHB) followed by a waiting time and then by a small step probe (strain or stress). To date, MSHB has been used to investigate several polymeric systems such as polymer melt [14, 15], polymer solutions [15-18], block copolymers [19] and even a polymer in the deep glassy state [20]. These works on MSHB enhance our understanding of dynamic heterogeneity and the possible origin of holes. Shi and McKenna[15] burned holes far above the glass transition in a long chain branched polyethylene (where homogenous dynamics would be expected if the hole-burning requires a local temperature inhomogeneity) and in polystyrene solutions and attributed the presence of holes to spatial heterogeneity (microstructure and concentration fluctuation though space respectively). Further, Shi and McKenna [14, 15] demonstrated that the holes burned were not captured by non-linear models such as the Kaye–Bernstein, Kearsley, and Zapas (K–BKZ) theory[21, 22] and Bernstein–Shokooh stress clock model[23]. These led us to an understanding that holes are not just a manifestation of non-linear viscoelasticity arising from the application of the large pump, at least in the present framework of constitutive equations tested. In addition MSHB on SIS tri-block copolymers (styrene–isoprene–styrene) was performed near the order-disorder transition (ODT) temperature [19]. Holes were burned below the ODT (ordered state) and no holes were observed above the ODT. Qin et al[16] examined a series of polystyrene solutions in different dynamic regimes and varied the length scale of heterogeneity by varying concentration and molecular weight of a series of different molecular weight polystyrenes in solution at different concentrations. Holes were observed in the Rouse regime, rubbery plateau regime, and the rubbery to terminal transition regime, whereas no holes were observed in the terminal regime, independent of the introduced length scales, i.e. the length scale of induced heterogeneity did not influence the hole burning event. From these results it was inferred that the dynamic heterogeneity was not necessarily due to spatial heterogeneity as caused by changing concentration and molecular weight. Qian et al[18] performed MSHB on similar polystyrene solutions[16] but in a stress-controlled domain and made

similar conclusions that the dynamic heterogeneity was related to type of dynamics rather than increase in fictive temperature due to selective heat dumping. MSHB measurements on polystyrene solutions and polybutadiene solutions were compared with other nonlinearity characterizing methods which use LAOS, such as Fourier transform rheology (FTR) and Lissajous–Bowditch (LB) plots[17]. The MSHB provides additional information that is potentially useful in fingerprinting the non-linear response, rather than duplicating the existing results.

Hole burning has been extended to investigate the non-linear dynamics of materials in the deep glassy state. Richert [5] performed NSHB on D-sorbitol near the β-transition temperature. Holes were observed and were attributed to an estimated local temperature change of 0.6 K. Mangalara and McKenna [20] have carried out MSHB on PMMA at room temperature (close to the β-transition). Temperature change during the application of the pump was directly measured and was found to be 0.65 K for a 9% pump deformation. The results were interpreted to imply that the observed temperature change was insufficient to cause the holes. It is of interest to ascertain whether or not the β-relaxation, related to a dynamic heterogeneity is the cause of the burned holes. To this end, in the present work we investigated a polycarbonate material at room temperature. Polycarbonate has a weak β-transition (including at room temperature) which is due to motions of the chain backbone [3, 24] and the results are compared with the prior results [20] for PMMA which shows a strong β-relaxation near to room temperature, which is due to motion of the polymer's side groups.[3, 25]

2) Experimental Methods

Materials:

Polycarbonate rods were obtained from K-Mac plastics and machined into a cylindrical geometry before testing. Details of the experimental setup are given in [20]. The glass transition temperature was determined using Mettler-Toledo DSC 1 where the heating and cooling rates used were 10 K/min. Mass of the sample was 9.92 mg and the T_g for polycarbonate was found to be 144.6 ºC (midpoint).

Rheological Testing:

An RMS 7200 (Rheometrics, Inc.) rotary rheometer was used to perform the MSHB and stress relaxation experiments on the polycarbonate sample. Glasses show memory and aging effects [26] and, hence, prior to each experiment, the sample was heated to 150 ºC and held for 60min to remove prior mechanical and thermal histories. The sample was then quenched to room temperature where aging begins. The sample takes approximately 10 min to cool from 150 ºC to ambient temperature. Struik's protocol [27] was followed to account for the aging effects of polymer glasses. A constant ageing time of 9000 sec was used [20] while the time for the MSHB/stress relaxation experiments themselves were 900 sec. The torsional strain applied on the sample varies linearly with the radius and is given by,[28]

$$\gamma_R = \frac{R\theta}{L} = \psi R$$

Where, R is the outer radius, L is the gauge length and θ is angle of twist in radians. R = 3mm and L = 30mm were the sample gauge geometries in this study. Finite strain rate effects [29] were corrected using $t - \frac{t_1}{2}$ (with $t_1 = 0.07$ sec), which were the same parameters used in [20] to obtain true relaxation time.

Stress relaxation experiments were used in the investigation along with time temperature superposition (TTS) [30] to determine the polycarbonate relaxation response over a wider range of times than the 900 s duration usable within the Struik protocol demanded by the hole burning experiments. As described subsequently, this permitted the data range for the determination of the hole burning behavior to be extended to the full range of the probe time.

MSHB tests were performed at frequencies of 0.0728, 0.036, 0.0189 and 0.0098 Hz. It consists of a series of three experiments as shown in Figure 1(a). In the first experiment a large sinusoidal strain (pump) is applied followed by a small waiting time and then a small (linear deformation) step strain (probe) is applied. Since the experiments are strain controlled, we work in modulus space and the resulting expression for modulus can be written as, [14, 15, 19]

$$G_+(\gamma, t) = G_{pump}(\gamma, t) + G_{mod}(\gamma, t)$$

The second part of the experiment consists of the same sinusoidal pump, waiting time and then probe but in the negative direction (Figure 1(a)). The expression for modulus is given as,[14, 15, 19]

$$G_{-}(\gamma, t) = G_{pump}(\gamma, t) - G_{mod}(\gamma, t)$$

In order to remove the aftereffects caused by the pump, phase cycling was performed, and the modified probe response is given as,[14, 15, 19]

$$G_{mod}(\gamma, t) = \frac{G_{+}(\gamma, t) - G_{-}(\gamma, t)}{2}$$

In the third part of the experiment, only the probe deformation is applied without any prior sinusoidal pump deformation. This is referred to as unmodified or unperturbed response. This unmodified response ($G_{linear}(t)$) is compared with the modified probe response ($G_{mod}(\gamma, t)$) which results in holes. Two types of holes can be seen: (i) in the horizontal direction $\log(t)_{linear} - \log(t)_{mod}$ at a constant modulus; (ii) in the vertical direction $G_{linear}(\gamma, t) - G_{mod}(\gamma, t)$ at constant time. Definition of holes are schematically described below (Figure 1(b)).

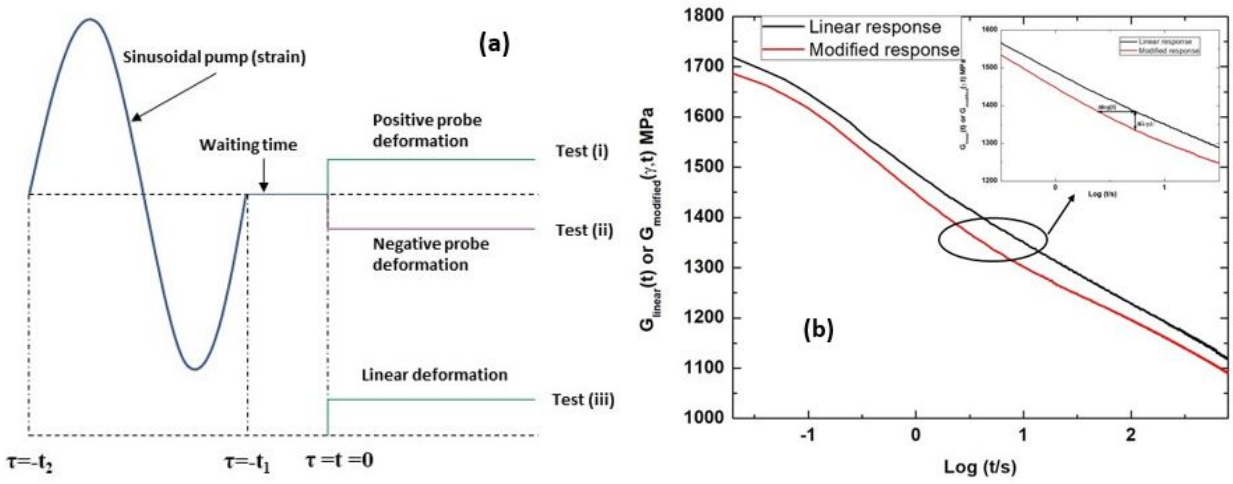


Figure 1. (a) Schematic of mechanical spectral hole burning (Adapted from Schiener et al[7]. Reprinted with permission from AAAS). (b) Schematic of definition of holes for PMMA at 4% pump, 0.6% probe, 0.0728 Hz, 22 ºC (Reprinted from Mangalara & McKenna [20], with the permission of AIP publishing)

3) Results and Discussion

3.1) Establishing the Linear regime

The linear viscoelastic regime was identified by performing a set of stress relaxation experiments at different strain magnitudes at 22 ºC. Figure 2(a) shows shear modulus variation

with time at different strains. The linear regime is established until 1.5% strain and deviation from linearity is seen from 2% strain. Other works have also reported that linear response is observed below 1.5% strain in polycarbonate.[31] from this result we can conclude that the step probe of 0.6% strain used in this study is in the linear regime

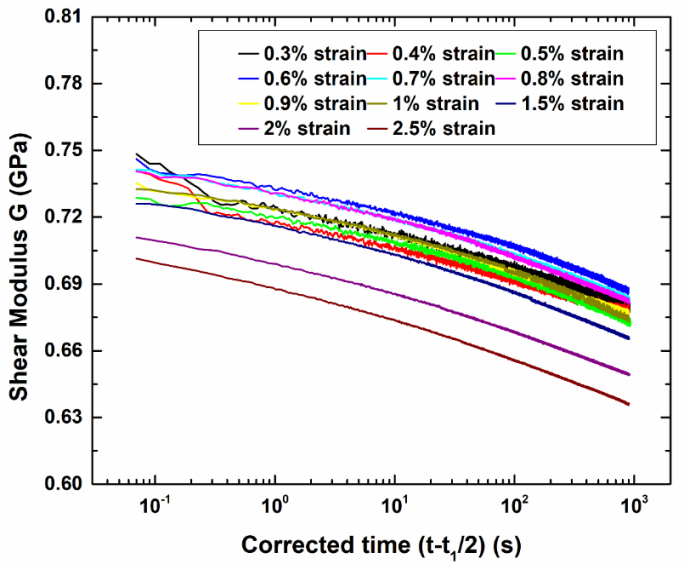


Figure 2: Shear modulus vs. time for polycarbonate at 22 ºC

3.2) Time-Temperature superposition

In order to determine the hole burning response, the long time behavior of the single step stress relaxation response is required, thus we used time-temperature superposition (TTS) to create the required long time relaxation modulus reference response. Polycarbonate shows global thermorheological simplicity due to weak β process[32]. To obtain the master curve using TTS, the polycarbonate was subjected to step shear deformation tests at a strain of 0.6% and for a range of temperatures below the glass transition from 22 ºC to 130 ºC. Prior to each experiment the sample was quenched to the temperature of interest and aged for 9000 sec, which is 10 times the relaxation experiment time of 900 sec. The curves at each temperature were superimposed and the produced master curve is shown in figure 3. The reference temperature used to construct the master curve was 22 ºC. This master curve is useful to obtain horizontal holes over an extended timescale.

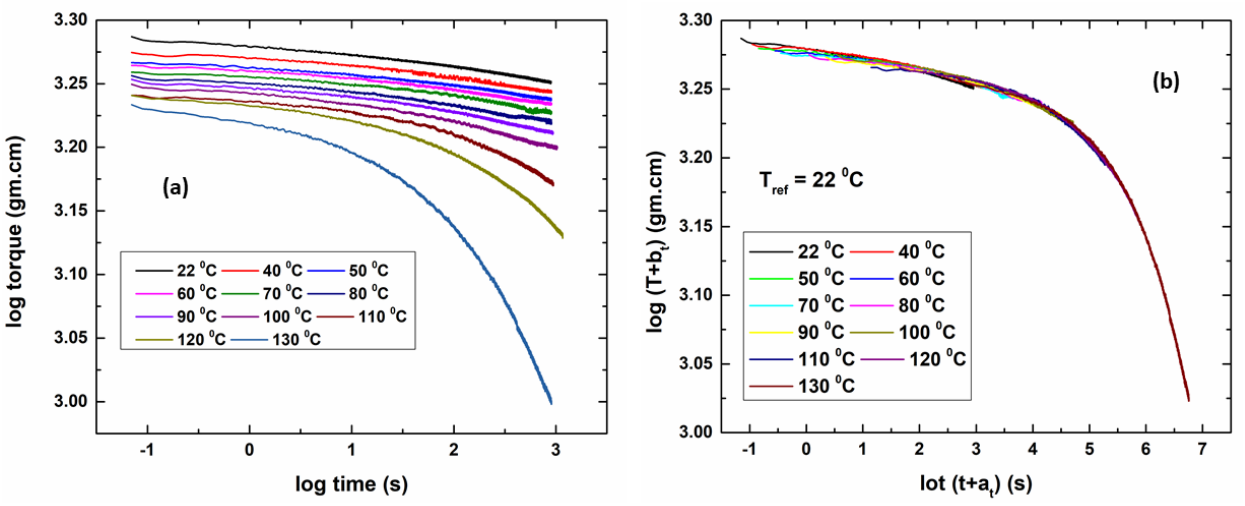


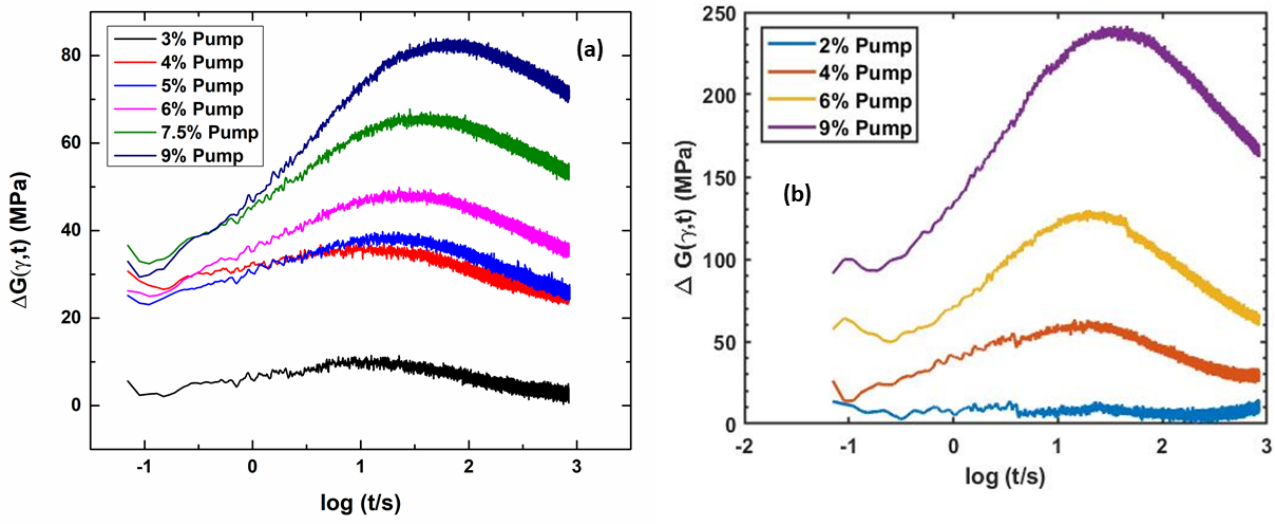
Figure 3: (a) Stress relaxation data for polycarbonate at 0.6% deformation at different temperatures (b) Master curve of polycarbonate at 0.6% strain and reference temperature of 22 ^{o}C

3.3) Hole burning in polycarbonate

3.3.1) Pump Amplitude effects

In the present work, pump amplitudes of 3%, 4%, 5%, 6%, 7.5% and 9% were used at four different frequencies to investigate hole burning effects, if any, in polycarbonate. Figure 4(a) shows clear evidence of vertical holes in the polycarbonate response for a pump frequency of 0.0189 Hz. We have hypothesized that any holes in the polycarbonate response would be weaker than what was observed in PMMA because of polycarbonate having a weaker β–relaxation [33, 34] than does PMMA. For comparison Figure 4(b) shows the corresponding vertical holes for PMMA [20]. For the PMMA the peak intensity can be seen to increase with increase in pump amplitude. On the other hand, we see in Figure 4(a) that the polycarbonate exhibits relatively low amplitude holes. It is important to note that the highest intensity hole for PMMA was ΔG_{max}~275 MPa (9% pump, 0.0098 Hz), whereas for the polycarbonate the highest intensity hole obtained was ΔG_{max}~95 MPa for the same pump-probe conditions. These results strongly support the hypothesis that the holes in the deep glassy state are related to dynamic heterogeneity as reflected in the occurrence of a strong β-transition (as seen in PMMA). On the other hand, horizontal holes were observed for polycarbonate unlike the case of PMMA for

which only segments of potential holes were evidenced. Though the horizontal holes in the polycarbonate shifted to much longer time scales (greater than experimental time scale), the availability of the master curve enabled us to obtain the complete horizontal holes. This was not possible for PMMA because of the presence of a strong β-relaxation at room temperature which precludes the use of time temperature superposition to construct a master curve[35, 36]. In the case of the PMMA, incomplete horizontal holes were seen in the accessible experimental time scale. For the polycarbonate and the 3% and 4% pump amplitudes, clear horizontal holes were not observed and in further analysis of the horizontal holes, these pump amplitudes are not considered. Horizontal holes for polycarbonate at 0.0189 Hz are shown in Fig 4(c). The intensity of the holes is seen to increase with pump amplitude and are shifted to longer time scales similar to the case of the vertical holes. Horizontal and vertical holes both help to distinguish a heterogenous response from a homogenous one. Temporal shifts are more easily recognized in horizontal holes as they represent a direct shift in relaxation times Horizontal holes are more decisive than vertical holes as they can directly distinguish homogenous and heterogenous response based on the data even for a single pump frequency. But with vertical holes, a frequency varying response is needed in order to conclude a heterogenous response.[7, 13]



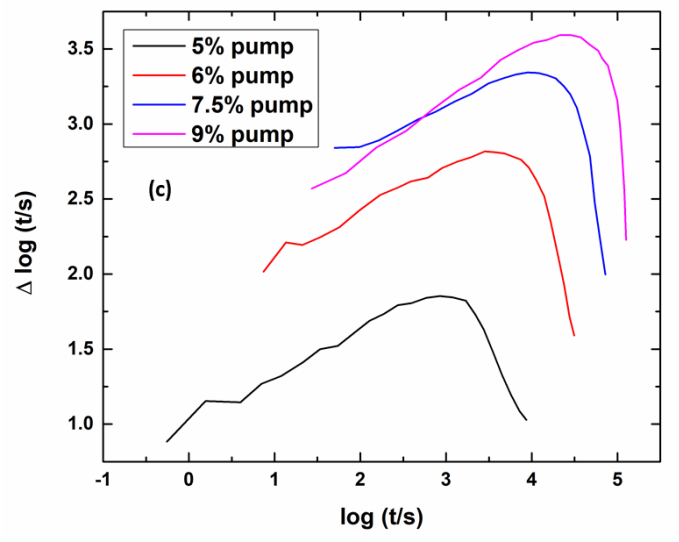


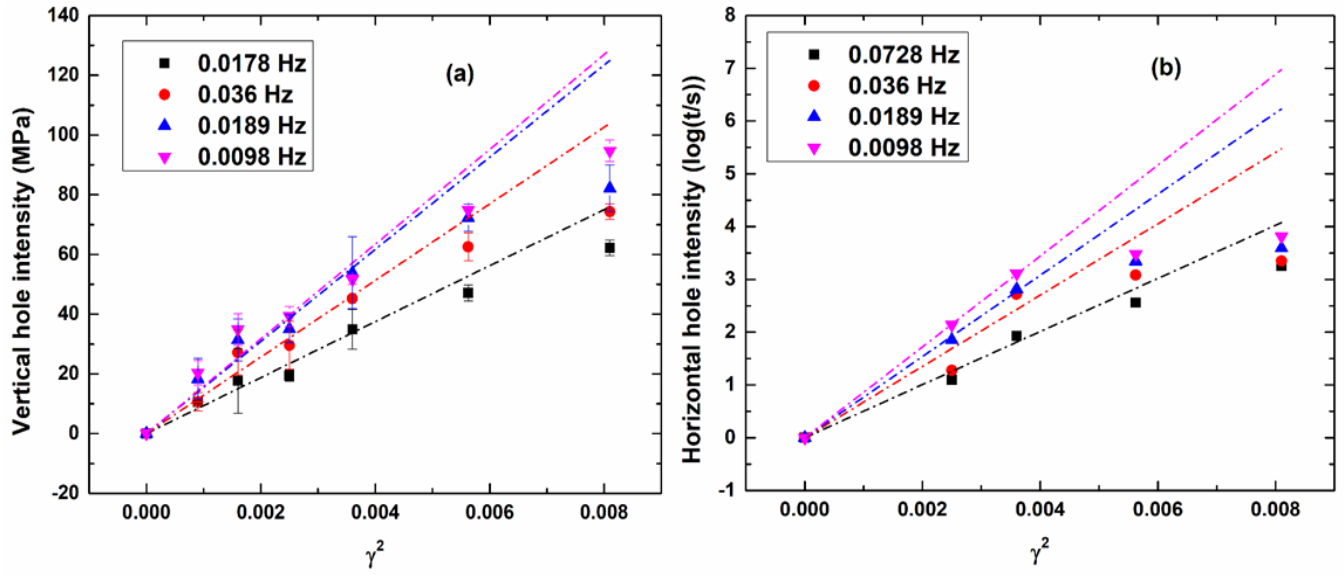
Figure 4: Vertical holes at different pump amplitude at 0.0189 Hz & 22 ºC (a) Polycarbonate (b) PMMA (Reprinted from Mangalara & McKenna [20], with the permission of AIP publishing) (c) Horizontal holes for Polycarbonate at 0.0189 Hz & 22ºC

The intensity of the vertical holes varied linearly with the square of the applied pump strain in PMMA[20], except at the lowest frequency. On the other hand, polycarbonate did not show the same behavior. Figure 5 (a) shows a plot of vertical hole intensity with square of strain amplitude. A linear correlation for vertical hole intensity with square of pump amplitude was observed up until 6% pump and deviation from this behavior can be seen for results above the 7.5% pump amplitude (PMMA showed the quadratic dependence on the pump amplitude up to the highest pump tested of 9%). For lower frequency, vertical hole intensity started to deviate at even lower pump amplitude as seen in the case of 0.0098 Hz. These deviations could be due to shear softening. Similar deviations from linear behavior were observed in dielectric hole burning of a spin glass [37] and titanium-modified lead magnesium niobite ceramic [38]. Similarly, the horizontal hole intensity also deviated from the linear dependence on square of pump amplitude from 6% pump strain (Figure 5 (b)). These deviations are more significant at lower pump frequencies. Of interest here is that, although it was expected that the polycarbonate hole-burning response would be weaker than that of the PMMA, it is surprising that the polycarbonate response also deviates from the expected [8, 12, 15, 17, 18, 20] scaling behavior that the hole intensity should vary with the square of the deformation for the range of pump amplitudes investigated. In order to investigate the shear softening behavior in polycarbonate, a plot of peak shear stress

(sinusoidal deformation) vs. strain (Figure 5(c)) was constructed. The strain applied on a cylindrical sample is a function of radius and the total stress at the edge of the sample is calculated by the equation from Nadai & Wahl [39]

$$S_{r=R} = \left(\frac{1}{2\pi R^3}\right)\left(\theta\frac{dM}{d\theta} + 3M\right)$$

Where M is the torque on the sample and θ is the angle of twist. Polycarbonate begins to soften from around 5% - 6% strain amplitude (Figure 5(c)). The softening behavior is consistent with the deviations seen in the vertical and horizontal hole intensities with applied strain squared. Similar softening was observed at other frequencies investigated in the study.



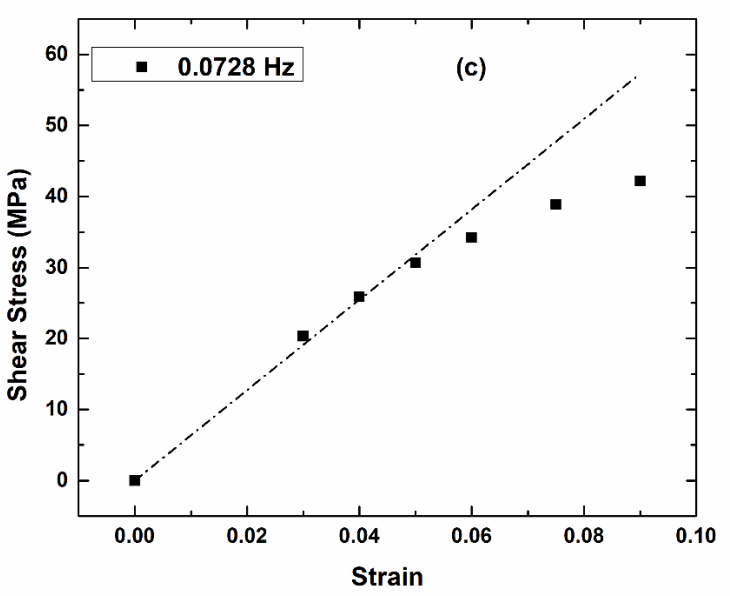
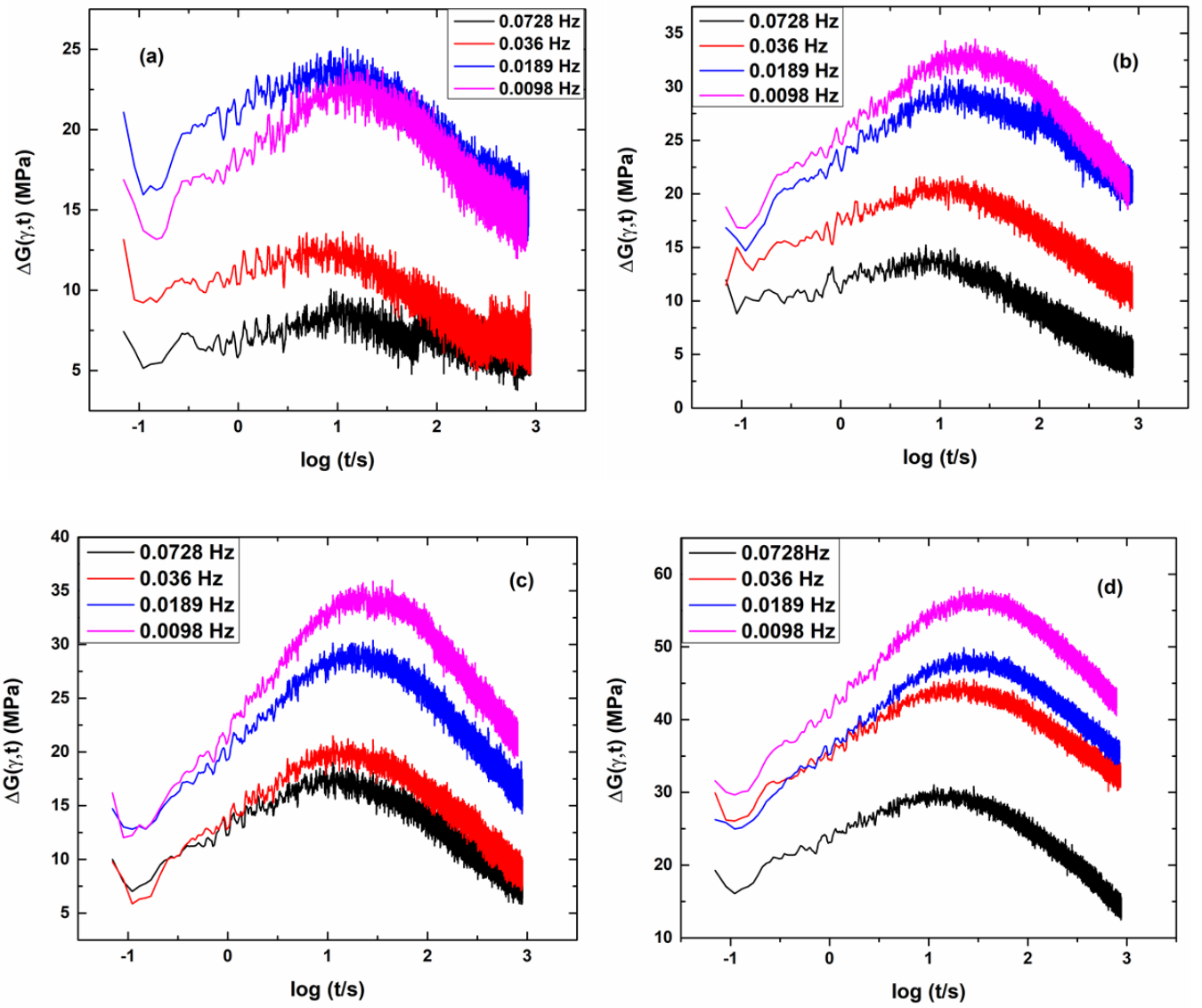


Figure 5: Pump amplitude dependence of the hole burning response in polycarbonate. (a) vertical hole intensity with pump amplitude squared (b) horizontal hole intensity with pump amplitude squared (c) Peak shear stress vs. strain amplitude at 0.0728 Hz

3.3.2) Frequency effects:

In addition to the amplitude dependence of the hole burning event, it is also of interest to examine how the hole amplitude changes with pump frequency. The vertical holes obtained at different frequencies at each pump amplitude studied are shown in Figure 6. Low intensity vertical holes were obtained for the polycarbonate at 3% pump amplitude (figure 6(a)). In this case, the applied non-linear deformation (3%) was not enough to spectrally modify the response and create a clear vertical modification in the polycarbonate under the instrument limitation and experimental time scale investigated. As the pump amplitude was increased, a clear vertical modification in the form of holes was observed at different frequencies. Peak intensity increased with decrease in pump frequency and the position of the holes shifted to longer times. In the glassy state molecular mobility is low and relaxation times become very long. Thus, the lower pump frequencies (higher time period) can modify a greater number of molecules (long relaxation time) and hence higher intensity holes are observed at the lower pump frequencies. The variation of vertical hole intensity with frequency is shown in Figure 7. For the polycarbonate the hole intensity varies as $\omega^{-0.39} - \omega^{-0.13}$(table 1), while for PMMA the

variation was as $\omega^{-0.52} - \omega^{-0.2}$(Figure 7(b)) when the pump amplitude increased from 4% to 9%. The results indicate that PMMA shows a larger dependence of vertical hole intensity on frequency when compared to polycarbonate reflecting that the underlying dynamics in PMMA are more heterogenous and, deep in the glassy state as here, related to the stronger β–relaxation in PMMA at room temperature than that of polycarbonate which is quite weak[33, 34].



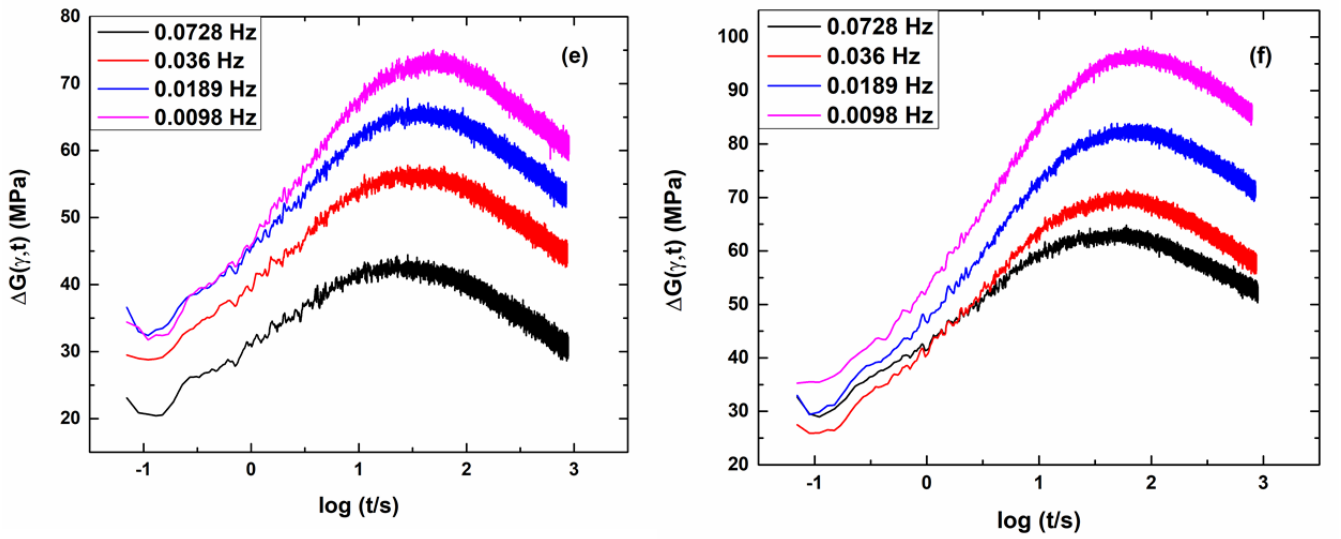


Figure 6: Vertical holes for polycarbonate at 22 C (a) 3% (b) 4% (c) 5% (d) 6% (e) 7.5% (f) 9% pump amplitude

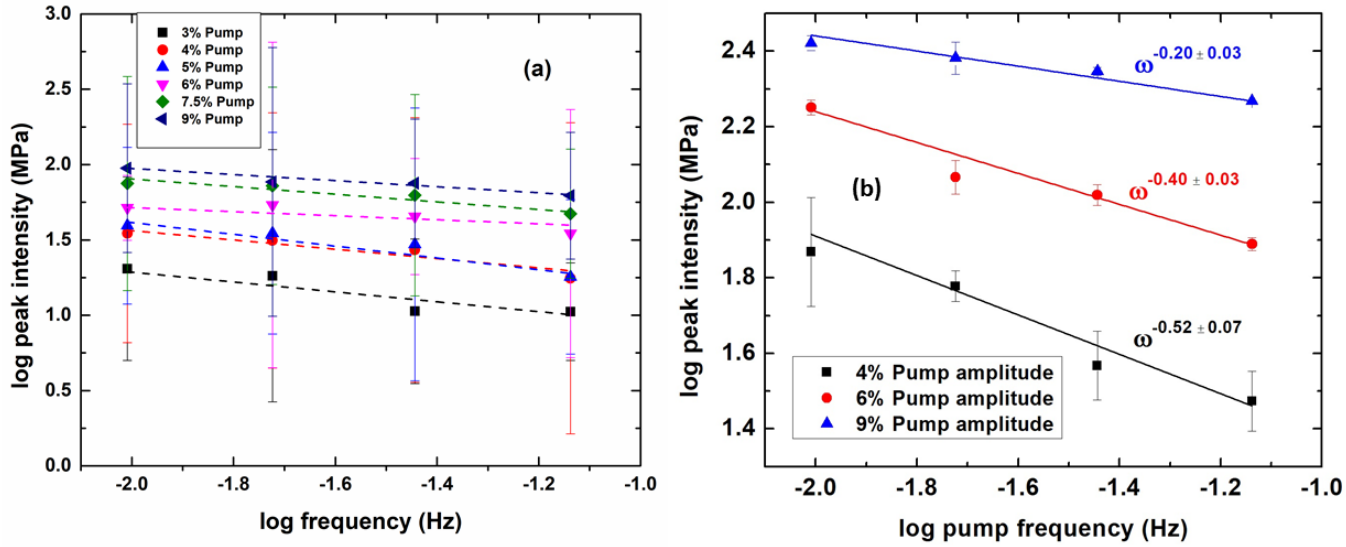


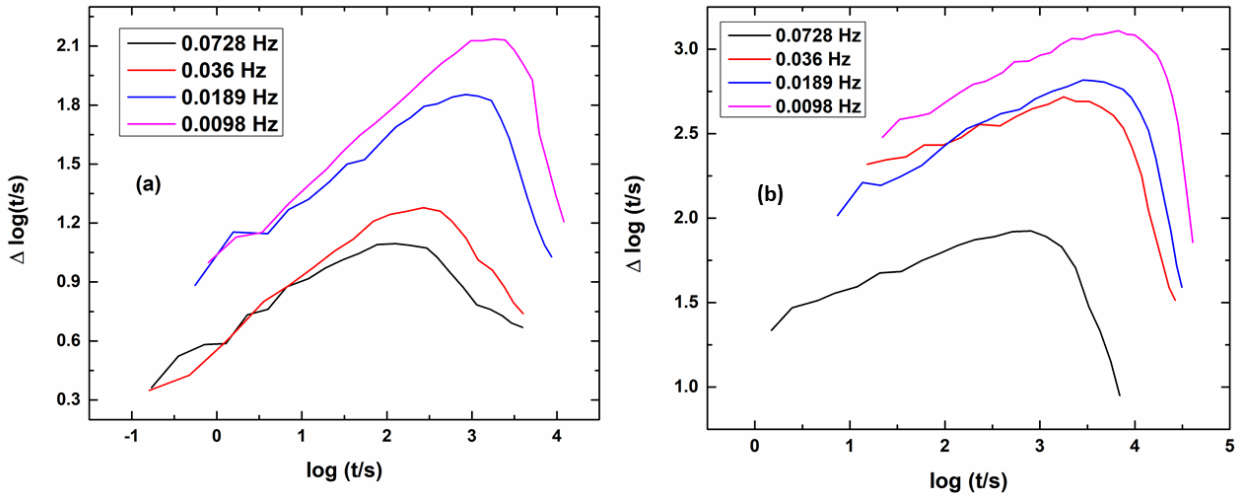
Figure 7: Vertical hole intensity dependence on frequency (a) Polycarbonate (b) PMMA [20]

Pump amplitude	Frequency dependence
3%	$\omega^{-0.33\pm0.1}$
4%	$\omega^{-0.31\pm0.07}$
5%	$\omega^{-0.39\pm0.07}$
6%	$\omega^{-0.13\pm0.043}$

7.5%	$\omega^{-0.25\pm0.05}$
9%	$\omega^{-0.2\pm0.03}$

Table 1: Vertical hole dependence on frequency for polycarbonate

Horizontal hole intensities at different pump amplitudes are shown in figure 8 for the polycarbonate. Hole intensity was found to increase with decrease in pump frequency and the holes shifted to longer times. Clear horizontal holes were not observed for the 3% and 4% pump amplitudes and are not reported. Horizontal holes varied with frequency as $\omega^{-1.27} - \omega^{-0.66}$ when the pump amplitude varied from 5% to 9% (Figure 9). In the case of PMMA, complete horizontal holes were observed only at 4% and 6% pump. From the results obtained for PMMA and polycarbonate, we do not observe any correlation between frequency variation of horizontal and vertical holes, and this precludes a comparison of polycarbonate with PMMA.



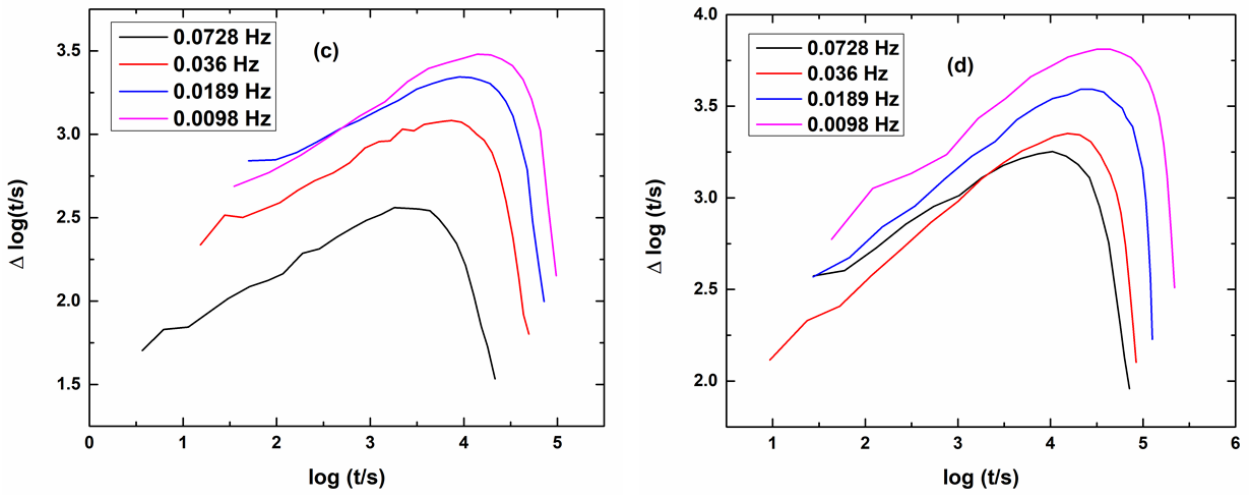


Figure 8. Horizontal holes in polycarbonate at different frequency levels (a) 5% pump (b) 6% pump (c) 7.5% pump (d) 9% pump

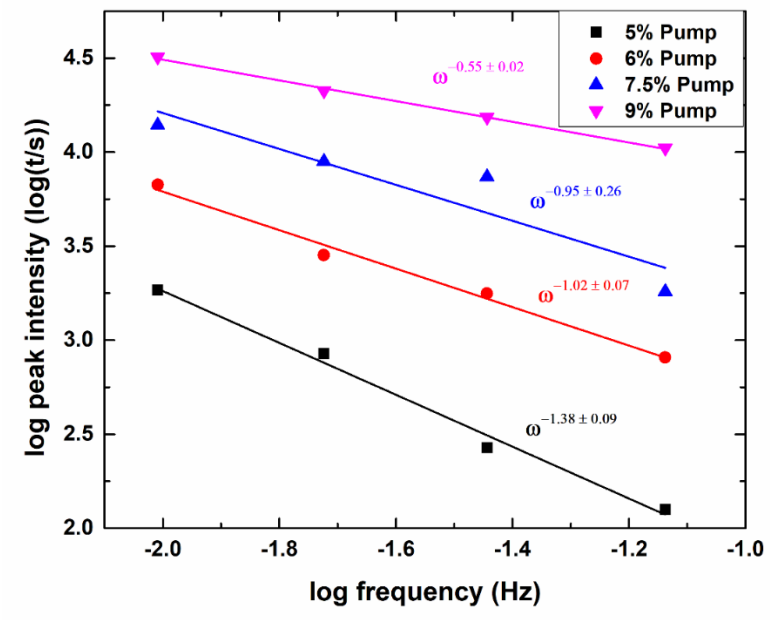


Figure 9: Horizontal hole intensity dependence on frequency for polycarbonate

3.3.3) Lissajous loops and pump energy dissipation

Lissajous loops at different sinusoidal pump strain are shown in figure 10(a). The energy dissipated through the application of sinusoidal pump was calculated from the Lissajous-Bowditch plot and is compared with PMMA (Figure 10(b)). The energy dissipated in a Lissajous loop for a strain amplitude in the linear regime can be calculated from the following equation:

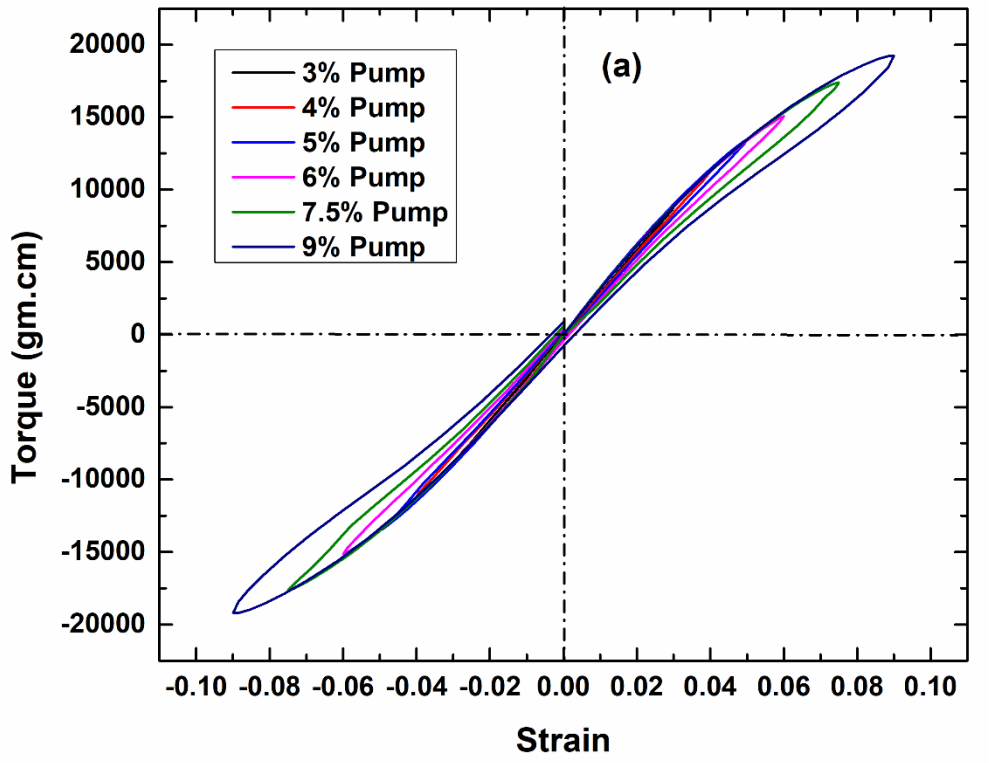
$$E = \pi(\gamma^2)\ (G'')$$

Where γ is strain amplitude and G'' is loss modulus. But in the current work the strain amplitudes reached were in the non-linear regime. Hence the energy loss was calculated from the measured Lissajous figures by calculating the area enclosed by the Lissajous loops. For smaller strain amplitudes (3%, 4% and 5%), a quadratic fit was made to the torque vs strain data and the area enclosed was calculated. For higher strains (6%, 7.5% and 9%), a cubic fit was used to obtain a better fitting for the torque vs strain data and the corresponding area enclosed was obtained. This area gives the energy dissipation in a Lissajous loop. Similar calculations were performed in our previous work on PMMA.[20] Energy dissipated per unit cycle for 9% pump amplitude at 0.0728 Hz for polycarbonate (area enclosed by the Lissajous loop) was found to be 455.24 x $10\text{^}(-4)$ J. The volume of the polycarbonate sample was 8.48 x $10\text{^}(-7)$ $m\text{^}3$. Therefore, the energy dissipated per cycle per unit volume is 53680 J/$m\text{^}3$. Density and heat capacity for polycarbonate are 1178 Kg/$m\text{^}$ [40]and 1200 $\frac{\text{J}}{Kg.K}$ [41] respectively and this would result in a local temperature change of ~ $38\ mK$. Mangalara and McKenna [20] performed similar energy calculations on PMMA and reported an expected temperature change of ~ $96\ mK$ from the Lissajous loop for a 9% pump amplitude and 0.0728 Hz. In fact, the temperature change in PMMA due to application of 9% strain deformation was found to be 0.65K experimentally. Such temperature change magnitude (0.6 K) was estimated by Richert [5] for D-sorbitol near the β-transition temperature to cause the observed holes using NSHB. Mangalara and McKenna [20]concluded that the local temperature change due to energy input itself was not enough to burn holes, while works on dielectric NSHB attributed holes to the rise in local temperature caused by application of a pump. A comparative study of temperature change in both NSHB and MSHB was made [20] and the estimated temperature change [5] required to burn holes could not be reached through the hysteretic loss during the pump application. Therefore, they [20] interpreted the results to support the hypothesis that the dynamic heterogeneity that causes holes is a result of the dynamic regime being probed rather than a local fictive temperature change. The energy dissipated and corresponding rise in temperature calculated from the Lissajous loops for different pump amplitudes are summarized in table 2.

Pump amplitude	Energy dissipated (J/m^3)	ΔT (mK)
3%	2438.44	1.72

4%	5408.49	3.82
5%	12113.63	8.57
6%	20681.7	14.63
7.5%	37880.24	26.78
9%	56167.41	39.73

Table 2. Energy dissipated and corresponding temperature rise calculated from the measured Lissajous loops for different pump amplitudes.



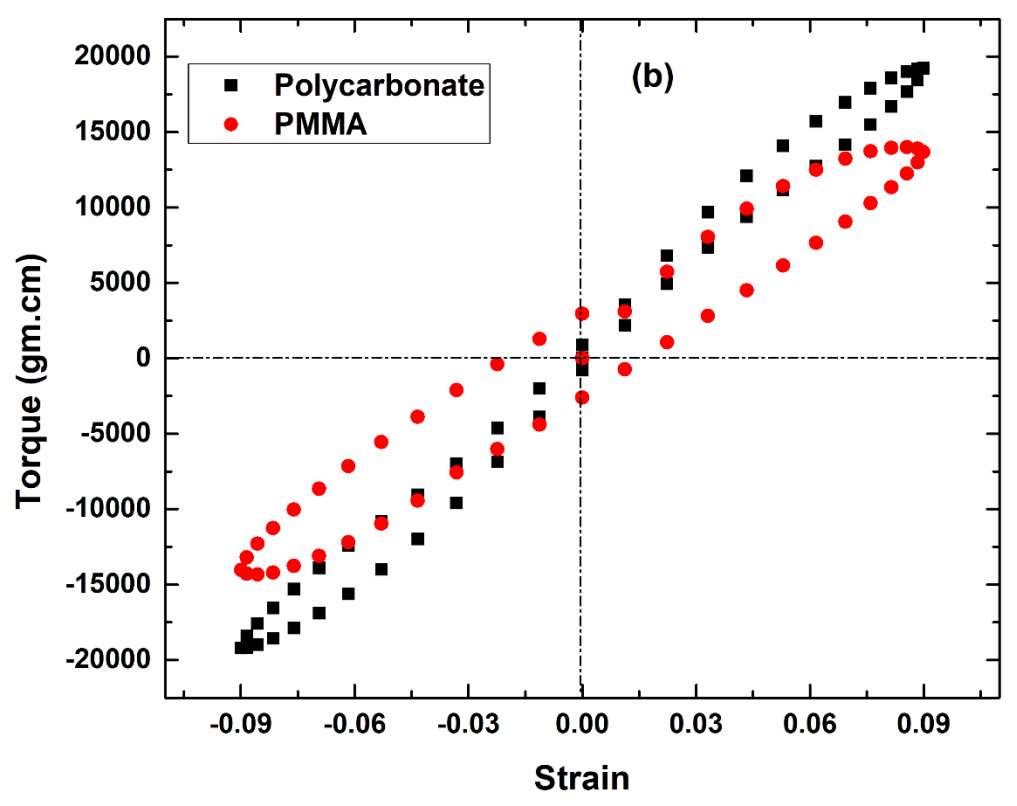


Figure 10. Torque Vs Strain (Lissajous plot) (a) at different pump amplitudes for polycarbonate (b) at 9% pump amplitude and 0.0728 Hz for polycarbonate and PMMA. PMMA data from [20]

Hole intensity variations with energy dissipation due to application of pumps at 0.0728 Hz were also obtained and the results are shown in Figure 11. Both vertical and horizontal hole intensities varied linearly up to 6% strain and started to deviate at higher pump amplitude. These results are consistent with the previous findings on variation of peak intensities with square of pump amplitude.

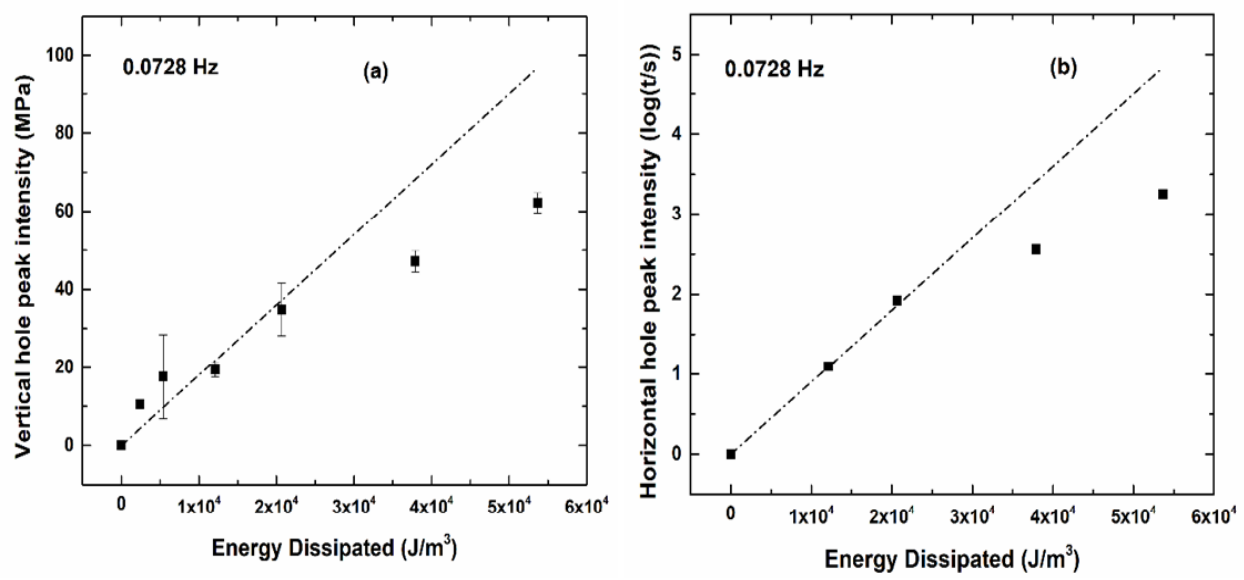


Figure 11. Hole intensity variation with energy dissipated in a Lissajous loop at 0.0728 Hz. (a) vertical hole intensity (b) horizontal hole intensity

Summary and Conclusions

Mechanical spectral hole burning experiments have been performed using polycarbonate material and the results are compared with those for PMMA. Unlike the case for PMMA in the deep glassy state, the polycarbonate shows weaker holes and the peak intensity (horizontal and vertical) show a linear dependence on square of applied strain but deviates at higher strain amplitudes which was not seen in the case of PMMA. This latter result is unexpected and requires further exploration. These findings suggest that a weaker β-transition would result in weaker holes which supports the hypothesis that the hole burning observed in amorphous polymers below the glass transition temperature is related to dynamic heterogeneity related to the strength of the β-transition rather than the dynamic heterogeneity as related to selective heat dumping. Finally, energy dissipation due to application of the sinusoidal pump has been calculated and compared with that of PMMA and the calculated local temperature change is insufficient to burn holes. Hole intensities varied linearly with energy dissipated but started to deviate above 6% pump amplitude. These deviations are consistent with the hole intensity variation with applied strain squared. Further experiments at different temperature and different materials (based on their β-transition strength and position) are to be performed to obtain more

insights into how the nature of β-transition in the deep glassy state is related to dynamic heterogeneity which causes the hole burning rather than change in local fictive temperature.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

1. Kearns, K. L.; Swallen, S. F.; Ediger, M. D.; Wu, T.; Sun, Y.; Yu, L., Hiking down the energy landscape: Progress toward the Kauzmann temperature via vapor deposition. *The Journal of Physical Chemistry B* **2008,** *112* (16), 4934-4942.
2. Hyun, K.; Wilhelm, M.; Klein, C. O.; Cho, K. S.; Nam, J. G.; Ahn, K. H.; Lee, S. J.; Ewoldt, R. H.; McKinley, G. H., A review of nonlinear oscillatory shear tests: Analysis and application of large amplitude oscillatory shear (LAOS). *Progress in Polymer Science* **2011,** *36* (12), 1697-1753.
3. Davis, W.; Macosko, C., Nonlinear dynamic mechanical moduli for polycarbonate and PMMA. *Journal of Rheology* **1978,** *22* (1), 53-71.
4. Lee, H. N.; Paeng, K.; Swallen, S. F.; Ediger, M.; Stamm, R. A.; Medvedev, G. A.; Caruthers, J. M., Molecular mobility of poly (methyl methacrylate) glass during uniaxial tensile creep deformation. *Journal of Polymer Science Part B: Polymer Physics* **2009,** *47* (17), 1713-1727.
5. Richert, R., Spectral selectivity in the slow β-relaxation of a molecular glass. *EPL (Europhysics Letters)* **2001,** *54* (6), 767.
6. Wilhelm, M., Fourier-transform rheology. *Macromolecular materials and engineering* **2002,** *287* (2), 83-105.
7. Schiener, B.; Böhmer, R.; Loidl, A.; Chamberlin, R., Nonresonant spectral hole burning in the slow dielectric response of supercooled liquids. *Science* **1996,** *274* (5288), 752-754.
8. Schiener, B.; Chamberlin, R.; Diezemann, G.; Böhmer, R., Nonresonant dielectric hole burning spectroscopy of supercooled liquids. *The Journal of chemical physics* **1997,** *107* (19), 7746-7761.
9. Chamberlin, R.; Schiener, B.; Böhmer, R., Slow Dielectric Relaxation of Supercooled Liqutos Investigated by Nonresonant Spectral Hole Burning. *MRS Online Proceedings Library Archive* **1996,** *455*.

10. Duvvuri, K.; Richert, R., Dielectric hole burning in the high frequency wing of supercooled glycerol. *The Journal of chemical physics* **2003,** *118* (3), 1356-1363.
11. Jeffrey, K. R.; Richert, R.; Duvvuri, K., Dielectric hole burning: Signature of dielectric and thermal relaxation time heterogeneity. *The Journal of chemical physics* **2003,** *119* (12), 6150-6156.
12. Blochowicz, T.; Rössler, E., Nonresonant dielectric hole burning in neat and binary organic glass formers. *The Journal of chemical physics* **2005,** *122* (22), 224511.
13. Chamberlin, R. V.; Böhmer, R.; Richert, R., Nonresonant spectral hole burning in liquids and solids. In *Nonlinear Dielectric Spectroscopy*, Springer: 2018; pp 127-185.
14. Shi, X.; McKenna, G. B., Mechanical hole burning spectroscopy: Evidence for heterogeneous dynamics in polymer systems. *Physical review letters* **2005,** *94* (15), 157801.
15. Shi, X.; McKenna, G. B., Mechanical hole-burning spectroscopy: Demonstration of hole burning in the terminal relaxation regime. *Physical Review B* **2006,** *73* (1), 014203.
16. Qin, Q.; Doen, H.; McKenna, G. B., Mechanical spectral hole burning in polymer solutions. *Journal of Polymer Science Part B: Polymer Physics* **2009,** *47* (20), 2047-2062.
17. Shamim, N.; McKenna, G. B., Mechanical spectral hole burning in polymer solutions: Comparison with large amplitude oscillatory shear fingerprinting. *Journal of Rheology* **2014,** *58* (1), 43-62.
18. Qian, Z.; McKenna, G. B., Mechanical spectral hole burning of an entangled polymer solution in the stress-controlled domain. *Physical Review E* **2018,** *98* (1), 012501.
19. Qin, Q.; Shi, X.; McKenna, G. B., Mechanical hole burning spectroscopy in an SIS tri-block copolymer. *Journal of Polymer Science Part B: Polymer Physics* **2007,** *45* (24), 3277-3284.
20. Mangalara, S. C. H.; McKenna, G. B., Mechanical hole-burning spectroscopy of PMMA deep in the glassy state. *The Journal of Chemical Physics* **2020,** *152* (7), 074508.
21. Kaye, A. *Non-Newtonian flow in incompressible fluids*; College of Aeronautics Cranfield: 1962.
22. Bernstein, B.; Kearsley, E.; Zapas, L., A study of stress relaxation with finite strain. *Transactions of the Society of Rheology* **1963,** *7* (1), 391-410.
23. Bernstein, B.; Shokooh, A., The stress clock function in viscoelasticity. *Journal of Rheology* **1980,** *24* (2), 189-211.
24. Yee, A.; Smith, S., Molecular structure effects on the dynamic mechanical spectra of polycarbonates. *Macromolecules* **1981,** *14* (1), 54-64.
25. Heijboer, J., Secondary loss peaks in glassy amorphous polymers. *International Journal of Polymeric Materials* **1977,** *6* (1-2), 11-37.
26. McKENNA, G. B., Glass formation and glassy behavior. *Pergamon Press plc, Comprehensive Polymer Science: the Synthesis, Characterization, Reactions & Applications of Polymers.* **1989,** *2*, 311-362.
27. Struik, L., Physical aging in polymers and other amorphous materials. Elsevier, Amsterdam: 1978.
28. McKenna, G.; Kovacs, A., Physical aging of poly (methyl methacrylate) in the nonlinear range: Torque and normal force measurements. *Polymer Engineering & Science* **1984,** *24* (14), 1138-1141.
29. Flory, A.; McKenna, G., Finite step rate corrections in stress relaxation experiments: a comparison of two methods. *Mechanics of Time-Dependent Materials* **2004,** *8* (1), 17-37.
30. Ferry, J. D., *Viscoelastic properties of polymers*. John Wiley & Sons: 1980.
31. O'Connell, P.; McKenna, G., The non-linear viscoelastic response of polycarbonate in torsion: An investigation of time-temperature and time-strain superposition. *Mechanics of Time-Dependent Materials* **2002,** *6* (3), 207-229.
32. Cerrada, M. L.; McKenna, G. B., Physical aging of amorphous PEN: isothermal, isochronal and isostructural results. *Macromolecules* **2000,** *33* (8), 3065-3076.

33. Flory, A.; McKenna, G. B., Microscopic origins of the normal force responses of glassy polymers in the subyield range of deformation. *Macromolecules* **2005,** *38* (5), 1760-1766.
34. Flory, A.; McKenna, G. B., Physical aging behavior of the normal force and torque in polymer glasses. *Mechanics of Time-Dependent Materials* **2010,** *14* (4), 347-357.
35. Guerdoux, L.; Duckett, R.; Froelich, D., Physical ageing of polycarbonate and PMMA by dynamic mechanical measurements. *Polymer* **1984,** *25* (10), 1392-1396.
36. Guerdoux, L.; Marchal, E., Physical ageing of PMMA and polycarbonate in the region of secondary relaxation. *Polymer* **1981,** *22* (9), 1199-1204.
37. Chamberlin, R., Nonresonant spectral hole burning in a spin glass. *Physical Review Letters* **1999,** *83* (24), 5134.
38. Kircher, O.; Diezemann, G.; Böhmer, R., Nonresonant dielectric hole-burning spectroscopy on a titanium-modified lead magnesium niobate ceramic. *Physical Review B* **2001,** *64* (5), 054103.
39. Nádai, A.; Wahl, A. M., *Plasticity*. McGraw-Hill Book Company, inc.: 1931.
40. Ho, H.; Gibson, I.; Cheung, W., Effects of energy density on morphology and properties of selective laser sintered polycarbonate. *Journal of Materials Processing Technology* **1999,** *89*, 204-210.
41. O'Reilly, J. M.; Karasz, F. E.; Bair, H. E. In *Thermodynamic properties of lexan polycarbonate from 110–560 k*, Journal of Polymer Science Part C: Polymer Symposia, Wiley Online Library: 1964; pp 109-115.