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Application of photothermal methods to the measurements of glass transition and viscoelasticity of polymers

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Abstract: The glass transition temperature T_g can be identified with a sharp increase of the thermal expansion coefficient χ . We present photoacoustic and constrained photodeformation measurements of the glass transition in polystyrene in conditions of weak optical absorption. Since the thermoelastic contribution to the signal prevails in those conditions, we show both theoretically and experimentally that the signal amplitudes exhibit a sharp increase near T_g , allowing its clear identification and the observation of a viscoelastic behavior.

1. INTRODUCTION

Numerous theories exist for the glass transition, but none of them explains that phenomenon completely. Moreover, a glass transition seems to be a kinetic process rather than a pure phase transition. This is supported by theoretical works [1] on nonlinear volume and temperature relaxation in the vicinity of the glass transition temperature T_g in polymers. A method of measurement allowing a better understanding of that physical phenomenon would be important for theoretical advances as well as for technical applications of polymers. On the other hand, from a thermodynamic point of view, the thermal expansion coefficient χ is an important material property to measure since, according to Sharma [2], various parameters describing the thermoacoustic and anharmonic properties can be calculated employing only χ near T_g (viz. Sharma and Gruneisen parameters). Thus, there exists an interest in a nondestructive measurement of χ .

Photothermal methods allow the measurement of thermal properties such as the heat capacity c_p and the thermal conductivity k . For this reason, interesting works have been published on phase transitions using those techniques after the pioneering work of Florian *et al.* [3]. To our knowledge, the first and main work on glass transition in polymers using photoacoustics is due to Korpiun *et al.* [4]. Their measurement was made in conditions of strong optical absorption and relatively large cell gas volume. The amplitude of the acoustic signal, measured as a function of temperature, showed a variation essentially due to the increase of c_p in the vicinity of T_g .

In recent work Lévesque *et al.* [5] theoretically showed, solving the coupled thermoviscoelastic equations using the finite element method, that both the glass transition and the viscoelastic relaxation in polystyrene could be clearly observed. The glass transition is associated with a sharp increase of the signal amplitude at T_g , resulting from a sharp increase of χ at that temperature. The viscoelastic behavior

is associated with a characteristic decrease of the signal amplitude, which is a function of frequency, for $T > T_g$. Their theoretical results showed the importance of the thermoelastic contribution to the photoacoustic signal for the measurement of phase transitions, as previously stressed by Junge *et al.* [6].

2. NUMERICAL SIMULATIONS OF PA AND CPD SIGNALS

The details concerning the numerical solution of the coupled thermoviscoelastic equations are given elsewhere [5,7]. Those equations, in the Laplace transform domain, are

$$k \nabla^2 \theta^* - \rho s c_v^* \theta^* = K^* \chi T_0 s \nabla \cdot \mathbf{u}^* - Q^* \quad (1)$$

$$\mu^* \nabla^2 \mathbf{u}^* + (\lambda^* + \mu^*) \nabla (\nabla \cdot \mathbf{u}^*) - \rho s^2 \mathbf{u}^* = K^* \chi \nabla \theta^* - \rho \mathbf{g}^* \quad (2)$$

where the temperature deviation from T_0 , θ^* , and the displacement vector, $\mathbf{u}^*$, are the variables; k is the thermal conductivity; ρ , the mass density; χ , the thermal expansion coefficient; c_v^* , the complex specific heat at constant volume; λ^* and μ^* , the complex Lamé coefficients; $K^* = \lambda^* + 2\mu^*/3$, the complex bulk modulus; $\mathbf{g}^*$, the body forces and s , the Laplace parameter. Q^* is the internal heat source, due to the optical absorption of a sinusoidally modulated gaussian laser beam (diameter of 2 mm approximately).

For the case of the photoacoustic (PA) method, equations (1) and (2) are solved for both sample (polystyrene) and gas (air) and the signal is given by the amplitude of the modulated pressure $p^* = K^* (\chi \theta^* + \nabla \cdot \mathbf{u}^*)$ [5]. Figure 1 shows the signal amplitude for an atactic polystyrene sample (diameter 10 mm, length 27 mm), a gas length of 0.5 mm and a modulation frequency of 10 Hz. Following previous work [5], we assumed typical temperature dependence for the material parameters. For the needs of the numerical simulation, the sharp increase of χ near T_g is set at 373 K.

The normalized signal amplitude shown in figure 1 is the ratio of the signals at a given temperature and at $T_g = 373$ K. PA response was calculated for various optical absorption coefficients β . The numerical simulation clearly shows that the increase in the signal amplitude near T_g is proportionally much more important for low optical absorption. A drop in the signal occurs for $T > T_g$, a conjugated effect of the increase of c_p and the rapid change of the mechanical properties of polystyrene near T_g . However, this effect is much more obvious for low optical absorption. This last result enables the observation of the thermoelastic contribution to the signal (in opposition to the thermoacoustic contribution mainly observed in [4]); therefore, we chose to make our measurements at low optical absorption.

We also conducted simulations for constrained photodeformation (CPD). In this experimental scheme (presented for the first time to our knowledge), a membrane is used to constrain the surface of the sample in photothermal deformation. There are three main reasons for that. The first is experimental: near T_g , the position of the surface of the heated sample highly fluctuates; the membrane thus stabilizes the surface. Secondly, thermoelastic effects do not compete with thermoacoustic ones (heat diffusion in the coupling gas in PA) in photodeformation experiments. Finally, a mechanical work is executed by the sample in periodic thermal expansion against the constraining membrane in CPD, allowing the observation of the collapse of the mechanical properties near T_g . This is similar to the work done by the sample against the closed gas volume in a PA cell.

Figure 2 shows results for a simulated CPD experiment. The conditions are similar to the case of PA, except that equations (1) and (2) are solved for the same polystyrene sample and a 12 μm thick Kapton® membrane (exhibiting very stable mechanical and thermal properties in the range of temperature of interest [8]). In particular, thermal expansion is negligible in comparison to polystyrene. The circular membrane is clamped and continuity of normal displacement and stress is assumed at the

sample-membrane boundary. The general behavior of CPD signal amplitude (taken as the normal displacement u_z at the center of the constraining membrane) is clearly similar to PA signal (compare figures 1 and 2 for an optical absorption $\beta=0.5 \text{ cm}^{-1}$ and a modulation frequency of 10 Hz). That figure also shows, based on the Vogel-Tammann-Fulcher relaxation law [5], that the drop in the signal for $T > T_g$ occurs at a higher temperature for an increasing modulation frequency, which is typical of a viscoelastic behavior. The same behavior was observed for PA simulations at low optical absorption. For high values of β , we observed that the important drop in the signal amplitude is much less striking, and is due to the increase of c_p near T_g .

Figure 1 Simulated PA signal as a function of temperature for different values of β

Figure 2 Simulated CPD signal for $\beta=0.5 \text{ cm}^{-1}$ and for different modulation frequencies

3. EXPERIMENT

PA and CPD experimental measurements have been carried out in conditions of low optical absorption ($\beta \approx 0.5 \text{ cm}^{-1}$ for $\lambda=0.6328 \text{ }\mu\text{m}$ (HeNe laser) and $\lambda=1.064 \text{ }\mu\text{m}$ (Nd³⁺-YAG laser)). The PA cell has been designed to reduce the residual volume (the microphone is attached to the CaF₂ window), to enable the expansion of the gradually heated sample (air gas length: 3 mm) and to keep the ambient pressure at the atmosphere. Details of that special PA cell will be given elsewhere. The experimental setup for CPD measurements is illustrated in figure 3. The schlieren detection method we used to measure the periodic displacement of the membrane was inspired by the laser schlieren microphone of Choi *et al.* [9], and first presented for photodeformation measurements by Saito *et al.* [10]. In that technique, the insertion of an iris in front of the detection photodiode transforms the divergence induced in the probe beam by the deformation of the constraining membrane into an intensity variation, proportional to the photodeformation.

Results are shown in figure 4. The sample was a Polysar 204[®] atactic polystyrene (Vicat softening point $T_v=107 \text{ }^\circ\text{C}$). PA measurement was made with a 40 mW Nd³⁺-YAG pump laser (beam diameter: 2 mm). For CPD measurements (two sets of data in identical conditions show the reproducibility of the experiment), HeNe lasers were used for pump (20 mW, diameter of 100 μm) and probe (4.5 mW, diameter of 700 μm). It is clearly shown that the main features of figures 1 and 2 are experimentally observed. PA and CPD measurements are very similar, but since the PA signal was noisy, we had to average it, while the CPD signal presents a high signal-to-noise ratio. In both cases, a jump in the signal amplitude occurs at $107 \text{ }^\circ\text{C}$, which is consistent with T_v . The maximum of the signal is shifted toward higher temperatures for increasing variation rate of the ambient temperature, which is typical of glass transition.

Finally, a decrease of the signal is observed for $T > T_g$, a characteristic of the viscoelastic behavior of polymers.

Figure 3 CPD experimental setup for the measurement of T_g

Figure 4 PA and CPD signals for polystyrene at the vicinity of $T_g \approx 107$ °C

4. CONCLUSION

PA and CPD experiments support the evidence that thermoelastic effects are dominant at low optical absorption, allowing the identification of T_g . A quantitative measurement of χ and viscoelastic properties of polymers should be possible after calibration of the optical probe and comparison with absolute values for the membrane deformation from the numerical simulations (not shown here). The simple CPD technique is also demonstrated to be a more efficient method than PA. Work is in progress to study the influence of modulation frequency on the measurement of the glass transition.

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