

Effect of Elastic Properties Modification on the Vibrational Density of States: A Joint Brillouin and Raman Scattering Study

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ABSTRACT: The modification of the vibrational density of states in a reactive epoxy-amine mixture during isothermal polymerization at different temperatures was characterized by Brillouin and Raman scattering measurements. During the reaction, the system underwent the glass-transition passing from the liquid to the glassy phase. The relative variations of the boson peak (BP) and the elastic moduli were investigated. We found that the intensity variation and the shift of the BP could be completely explained in terms of the elastic medium transformation. A master curve of the spectra in the BP region can always

be obtained both as a function of the reaction temperature and as a function of the reaction time. Moreover, the Brillouin light-scattering results gave evidence of the validity of a Cauchy-like relation for the real part of the elastic moduli measured at finite frequencies also in a relaxing regime. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3672–3676, 2011

Key words: resins; viscoelastic properties; degree of polymerization (DP); glass transition; Raman spectroscopy

INTRODUCTION

The glass transition is a general process common to different systems, ranging from polymers,^{1–3} network-forming materials,^{4,5} colloidal suspensions,⁶ and others. As a matter of fact, if the cooling rate is fast enough, a large class of materials is not able to rearrange their microscopic configuration to the equilibrium position before their temperature is further decreased. The systems overcome the crystallization process, and at temperatures lower than the melting point, they remain in a liquid phase (supercooled liquids). When reaching the glass-transition temperature, the microscopic structures appear to be frozen in the liquid configuration, and the system's viscosity increases several orders of magnitude in a few degrees. A decrease in the temperature is the most common route to the glass transition, but an increase in the pressure has a very similar effect. Moreover, one can obtain a glass by exploiting the

chemical vitrification also. In the initially liquid solution of mutually reactive monomers, an increasing number of van der Waals bonds are replaced by stiffer covalent bonds: the molecular diffusion slows down, and ultimately, the system is frozen in a glassy structure.^{7,8} In this case, the control parameter is the chemical conversion, which is defined as the ratio between the reacted functional groups to the total functional groups.^{7,8}

In this study, we examined the chemical vitrification process in a reactive epoxy-amine mixture during isothermal polymerizations. The changes in the vibrational dynamics were investigated by means of Raman and Brillouin light scattering from the liquid to the glassy phase during the chemical vitrification process.

Raman scattering measurements gain access as a function of the frequency, ω , to the reduced vibrational density of states [$g(\omega)/\omega^2$], which in disordered materials presents a characteristic bump over the Debye level, usually known as the boson peak (BP).^{5,9–16} The physical nature of the modes responsible for the BP is still unclear and represents a problem of current interest. As already found in the literature,¹⁰ we found that the changes of the BP during the chemical reaction could be fully explained by the changes of the elastic

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properties of the medium,⁹ and a master curve could be drawn accordingly. In this article, we also show that in the study of the evolution of the reactive mixture at two different temperatures, a single master curve was obtained when the spectra was scaled at the two temperatures.

The Brillouin light-scattering measurements allowed us to monitor the evolution of longitudinal acoustic (LA) and transverse acoustic (TA) modes. The evolution of the Brillouin scattering spectra showed clear evidence for the validity of a Cauchy-like relation for the real part of the elastic moduli measured at finite frequencies.

EXPERIMENTAL

Samples

The epoxy-amine system investigated was a mixture of diglycidyl ether of bisphenol A (DGEBA) and diethylenetriamine (DETA) at a molar ratio of 5 : 2. The reactive mixture was studied during its polymerization at a constant temperature. The reaction proceeded by the stepwise addition of the amino hydrogen of the epoxy group, without elimination of byproduct molecules. Starting from the liquid sample, the final product was a glassy network polymer. The total times of reaction were about 12 h and 2.5 days at temperatures (T) of 22 and 2°C, respectively. In these conditions, the monomers bonded slowly to each other so that the state of the system at any given time of reaction could be seen as a quasi-equilibrium state: no appreciable reaction occurred over a single measurement. In fact, the Brillouin spectra were integrated for about 20 min, whereas the Raman spectra were measured in about 15–30 min, depending on the extension of the frequency range. The eventual spectral variations were inside the experimental errors.

Raman and Brillouin light scattering

A double monochromator spectrometer Jobin-Yvon U1000 (HORIBA Jobin Yvon S.A.S., 231 rue de Lille, 59650 Villeneuve d'Ascq.) was used to perform Raman scattering experiments in a wide frequency range, from -100 to 4500 cm^{-1} , to follow the evolution of the molecular vibration peaks. The measurements were performed both in VV and HV polarization geometries, where V and H indicate the polarization perpendicular and parallel to the scattering plane, respectively. The spectra were collected sequentially, and they did not present any luminescence background. The data treatment did not require any intensity normalization factor.

In the Brillouin scattering experiments, a single-mode, 532-nm laser with a typical power of 100 mW was used as a light source, and light scattered from

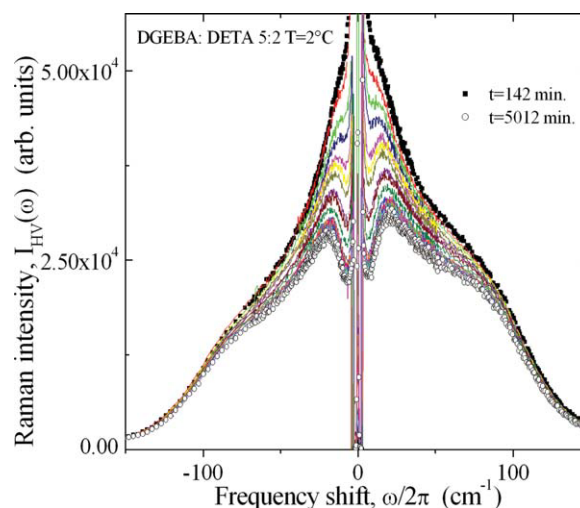


Figure 1 Raman spectra at some selected reaction times (t 's), during the isothermal polymerization of the mixture 5 : 2 DGEBA–DETA at $T = 2^\circ\text{C}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the sample at an angle of 90° was analyzed by means of a Sandercock type 3 + 3-pass tandem Fabry–Pérot interferometer, characterized by a finesse of about 100 and a contrast ratio higher than 10^9 . Scattered light was not further analyzed by polarization (unpolarized geometry). In this configuration, it was possible to detect both the LA mode, which scattered light without a change of polarization, and the transverse mode, which scattered light with a change of polarization.

The measurements were performed *in situ*, and the samples were maintained at a fixed temperature during the whole reaction time by a temperature-controlled system. For the reaction at $T = 22^\circ\text{C}$, the temperature was stabilized by a thermal circulator pump, which allowed the reaction to maintain a constant temperature within 0.1°C during the whole reaction time. In the case of the reaction performed at $T = 2^\circ\text{C}$, a cryostat was used, and the temperature variation was less than 2°C during the 2.5 days needed to complete the reaction.

RESULTS

Figure 1 shows typical Raman spectra for the investigated 5 : 2 DGEBA–DETA mixture, acquired at several times during the isothermal reaction at $T = 2^\circ\text{C}$. The spectra were normalized to the high-frequency molecular peaks, in the 1600-cm^{-1} range, that were invariant during the whole reaction. With regard to the evolution of the low-frequency part of the spectra, two characteristic features were evident: the quasi-elastic signal centered at zero frequency and the BP. The quasi-elastic scattering (QES) dominated in the initially liquid solution and decreased

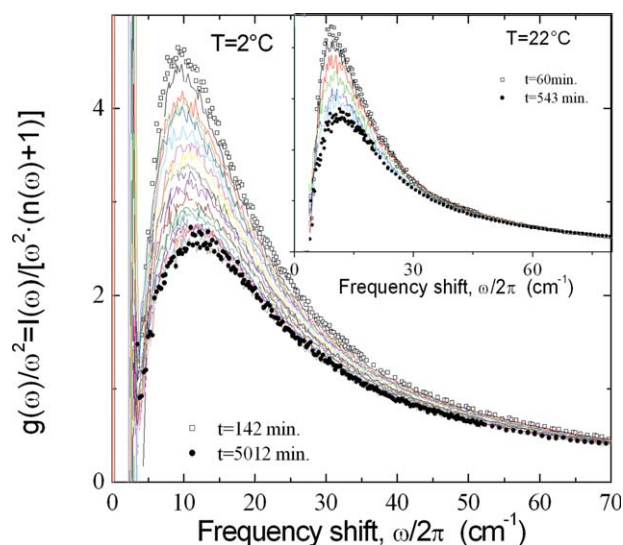


Figure 2 Quantity of $C(\omega) \propto \omega$ obtained from the measured Raman spectra after subtraction of the QES contribution, according to eq. (3), at different reaction times (t 's). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in intensity as the reaction proceeded, whereas the BP became more and more evident, shifting to a higher frequency and decreasing in intensity.

The QES is usually ascribed to a relaxational contribution,¹⁵ whereas the BP is ascribed to vibrations affecting the vibrational density of states [$g(\omega)$]. The Raman intensity [$I_R(\omega)$] can be modeled as a sum of the two contributions:

$$I_R(\omega) = I_{\text{QES}}(\omega) + I_{\text{BP}}(\omega) \quad (1)$$

To investigate the BP variations [$I_{\text{BP}}(\omega)$], we subtract from the total signal the QES contribution [$I_{\text{QES}}(\omega)$], which can be safely approximated with a Lorentzian centered at zero frequency.⁹ In the subtraction procedure, the Lorentzian width is fixed for all of the spectra, and the only adjustable parameter is the intensity. With this procedure, we assumed that the measured spectra were dominated at low frequency by their relaxational component, which evolved in a self-similarity regime. So, changing the amplitude of the Lorentzian curve was equivalent to shifting the frequency position of the relaxation peak in the susceptibility spectrum.

In the final subtracted spectra, there was no intensity left at low frequency. The obtained spectra were proportional to $g(\omega)$:

$$I_{\text{BP}}(\omega) = \frac{C(\omega)g(\omega)}{\omega} [n(\omega, T) + 1] \quad (2)$$

where $n(\omega)$ is the Bose–Einstein population factor and $C(\omega)$ is the light-to-excitation coupling function.

Using the empiric relation $C(\omega) \propto \omega$, found in many systems^{17–20} in the BP frequency range, we can write

$$\frac{g(\omega)}{\omega^2} = \frac{I_{\text{BP}}(\omega)}{\omega} \quad (3)$$

The quantity $g(\omega)/\omega^2$ so obtained is presented in Figure 2 and showed a clear evolution of the BP during the isothermal polymerization at both temperatures.

Typical Brillouin spectra are reported in Figure 3, where the inelastic peak due to the scattering from LA modes is visible at about 10 GHz, together with a second, weaker peak at about 5 GHz, associated with the scattering from TA modes. The LA modes were always present in the spectra during the whole reaction, whereas the TA modes (not present at the beginning of the reaction at 22°C) became visible only at reaction times long enough that the structural relaxation rate became comparable to or smaller than the frequency of the TA modes. This condition started to be valid well before the vitrification or gelation point.

DISCUSSION

The characterization of the vibrational properties in the hypersonic low-frequency region (gigahertz) could be made by the study of the Brillouin spectra. At each time of reaction, the frequency positions of the LA and TA modes (ω_L and ω_T , respectively) could be obtained from a fit of the spectra,² and the density of the sample (ρ) was separately measured. From these data, we calculated the real part of the longitudinal modulus (M') at ω_L and the real part of the transversal, or shear, modulus (G') at ω_T , as $M'(\omega_L) = \rho\omega_L^2/q^2$ and $G'(\omega_T) = \rho\omega_T^2/q^2$, where \mathbf{q} is the exchanged wave vector in the scattering

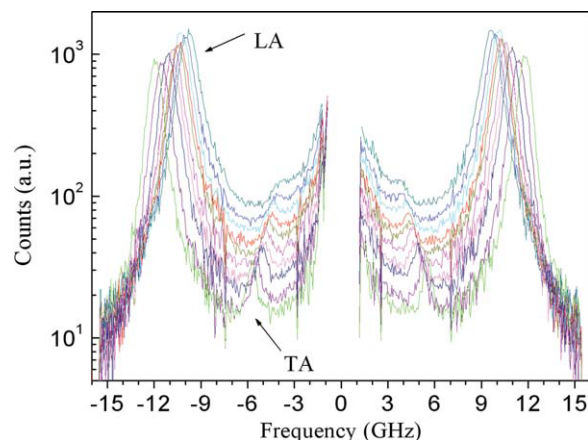


Figure 3 Brillouin light-scattering spectra of 5 : 2 DGEBA–DETA during the isothermal polymerization at $T = 2^\circ\text{C}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

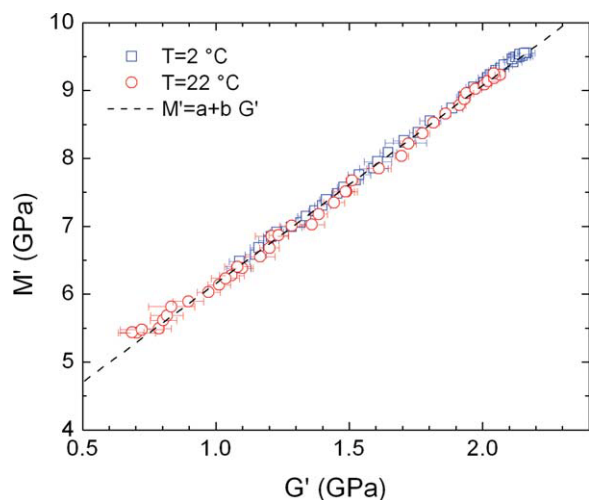


Figure 4 M' versus G' of 5 : 2 DGEBA-DETA at $T = 2$ and 22°C . The dashed line is the best linear fit: $M' = (3.12 \pm 0.08) + (3.00 \pm 0.02)G'$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

experiment. In general in isotropic systems, the longitudinal modulus (M) and the shear modulus (G) are mutually independent elastic constants. Only if the atoms interact through a central potential does the Cauchy relation, $M = 3G$, hold. Molecular liquids, in particular, the reactive mixtures and the so-obtained chemical glasses, are usually far from showing a central potential, and the Cauchy relation does not apply in its original version.

A generalized Cauchy relation for isotropic liquids was introduced.²¹ It is expected to be valid not only for solids but also for viscoelastic liquids at frequencies high enough to probe the elastic response of the system. In recent years, several authors have reported a Cauchy-like relation close to the glass transition for different liquids, including curing systems.²²⁻²⁴

$$M' = A + BG'$$

where B has been found to be close to 3 and A comes out to be a system-dependent constant, which at ambient pressure, does not appreciably depend on temperature.

The evolution of M' versus G' is reported in Figure 4 for the investigated reactions. From this representation, we recognize a Cauchy-like relation, $M' = A + BG'$, connecting M' and G' .²² Surprisingly, the experimental data obtained from the mixture reacted at different temperatures collapsed well onto a single line, with $A = 3.00 \pm 0.02$ and $B = 3.12 \pm 0.08$ GPa. These findings support the general validity of a Cauchy-like relationship and confirm that it is possible to extend the range of physical conditions for its applicability. In fact, our data suggest that it holds as well for the apparent M and G in the

presence of the structural relaxation processes. The general validity of the Cauchy-like relationship is the necessary result to obtain, in the following, the evolution of the Debye level in terahertz.

The characterization of the vibrational density of state in the terahertz frequency region can be obtained by the study of the Raman spectra, once the relaxational contribution is removed. To study the BP evolution and, in particular, to correctly assess the BP changes occurring during the polymerization reaction, it is important to take the changes of the Debye level into account.⁹ In fact, the BP is, by definition, the excess of states over the Debye level, which changes during the reaction because of the density and the sound velocity increases. It has been shown that the shift and intensity variation of the BP during an isothermal polymerization can be fully explained by the modification of the elastic properties of the reactive mixture, and a master curve can be drawn accordingly for each reaction.⁹

The Debye frequency [ω_{DB}] can be obtained as

$$\omega_{\text{DB}} = \frac{6\pi^2 \rho N_A N_F \langle v \rangle^3}{M} \quad (4)$$

where ρ is the density, N_A is Avogadro's number, N_F is the number of atoms per molecule, M is the molar weight, and $\langle v \rangle$ is the mean sound velocity and is defined as

$$\langle v \rangle^{-3} = (\langle v_L \rangle^{-3} + 2\langle v_T \rangle^{-3})/3$$

where the longitudinal sound velocity (v_L) and transverse sound velocity (v_T) are the elastic, solidlike velocities for which the Debye model has been formulated. The number of atoms in the mixture does not change during the reaction (no molecule is expelled as byproduct). We calculated N_F and M in eq. (4) by averaging the corresponding values for the two components (DGEBA and DETA), weighted by their molar fraction.

To correctly calculate the values of $\langle v \rangle$ during the polymerization we considered the inelastic x-ray scattering (IXS) measurements at $T = 2^\circ\text{C}$, reported in ref. 9 to be performed in the terahertz frequency range, that probed the LA excitations exactly in this elastic limit. To estimate v_T , which was not accessible in the IXS experiment, we exploited the Cauchy-like relation in the elastic limit. To obtain the same information for $T = 22^\circ\text{C}$, we considered the same v_L evolution as a function of chemical conversion measured at $T = 2^\circ\text{C}$, and we normalized the data on the elastic limit of v_L measured at $T = 22^\circ\text{C}$ (i.e., around 2% lower than that measured at $T = 2^\circ\text{C}$).

Here, we compared the BP evolution for a given mixture, that is, 5 : 2 DGEBA : DETA, undergoing

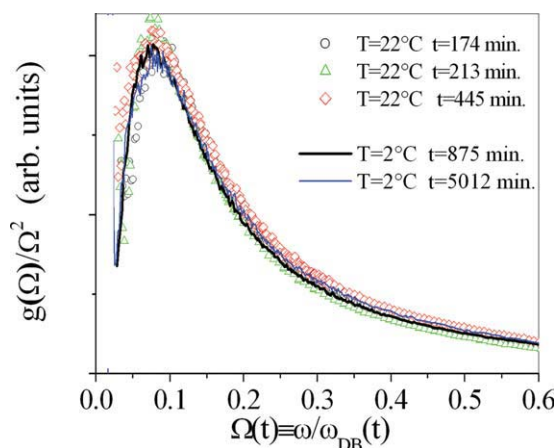


Figure 5 Reduced density of states $g(\Omega)/\Omega^2$ rescaled using as scaling parameter $\Omega(t) = \omega/\omega_{DB}(t)$ where t is the reaction time. The data are obtained for the mixture 5 : 2 DGEBA–DETA at $T = 2^\circ\text{C}$ (lines) and $T = 22^\circ\text{C}$ (open symbols). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

isothermal polymerization at different temperatures, that is, $T = 2$ and 22°C . The frequency axis of the Raman spectra was rescaled as $\Omega = \omega/\omega_{DB}$, where the invariance of the total number of vibrational modes imposed that the intensity of the spectra must be also rescaled according to⁹

$$\frac{g(\Omega)}{\Omega^2} = \frac{g(\omega)}{\omega^2} \omega_{DB}^3 = \frac{I_{BP}(\omega)}{\omega} \omega_{DB}^3 \quad (5)$$

The rescaled spectra for the reaction at $T = 2^\circ\text{C}$ are reported in Figure 5, with solids lines. In the same figure, the rescaled spectra for the reaction at $T = 22^\circ\text{C}$ are also shown, with symbols, to assess the effect of temperature on the spectral shape of the BP. Interestingly, within the experimental uncertainty, they collapsed on the same master curve. As already found,^{9,25,26} the results confirm that the BP variation followed the Debye level modification during the reaction time. Moreover, in the explored temperature range, the data clearly indicated that for a given concentration of reagents, the temperature evolution of the Boson Peak frequency (ω_{BP}) also evolved according to the relative modification of the Debye level.

CONCLUSIONS

In conclusion, we studied the variations of the vibrational spectra induced by covalent bond formation during the process of chemical vitrification of a reactive mixture polymerizing at different temperatures. We found that (1) a generalized Cauchy relation was valid in the viscoelastic regime also in the presence of the structural relaxation processes and (2) a master curve for BP could be obtained as the poly-

mer structure developed at the two investigated temperatures; that is, the shape of the BP remained unchanged despite the differences in the molecular actions involved both in the cooling and the chemical vitrification process.

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