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Chemically induced transition phenomena in polyurethanes as seen from generalized mode Grüneisen parameters

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Abstract

Many phenomenological properties of reactive polymers like polyurethanes increase or decrease continuously in the course of the curing process before saturating at the end of the chemical reaction. This holds true for instance for the mass density, the refractive index, the chemical turnover and the hypersonic properties. The reason for this monotone behaviour is that the chemical reaction behaves like a continuous succession of irreversible phase transitions. These transitions are superposed by the sol–gel transition and possibly by the chemically induced glass transition, with the drawback that the latter two highlighted transitions are often hidden by the underlying curing process. In this work we propose generalized mode Grüneisen parameters as an alternative probe for elucidating the polymerization process itself and the closely related transition phenomena. As a model system we use polyurethane composed of a diisocyanate and varying ratios of difunctional and trifunctional alcohols.

1. Introduction

Reactive network-forming polymers like rubbers, adhesives etc have huge technical importance but they are also very important objects for basic research. Of special interest are the genesis of polymer networks and the accompanying changes in physical properties. It is worth noting that technological progress and fundamental research, especially for this material class, are intimately connected. The chemical formation of molecular networks by polymerization is a highly complex process which usually strongly depends on the processing conditions like the curing temperature. As the molecular structure and the molecular interaction potential vary constantly upon curing, the polymerization process can be interpreted as a continuous succession of non-equilibrium phase transitions (NEPTs) at a given temperature.

Studying this sequence, we will focus in addition on two transformations which may take place as a direct consequence of the chemical reactions: the chemically induced sol–gel transition (CSGT) and the chemically induced glass transition (CGT).

Starting with a two-component or multi-component liquid the first stage of the temporal isothermal evolution of the curing process usually leads to a gelled network [1–4] (chemical gel) after a specific curing time t_p . In the course of the NEPTs, having passed the irreversible sol–gel transition during polymerization the polymer is in a ‘soft solid state’ (gel) possessing static shear stiffness. At still larger times or larger degrees of chemical conversion a hard solid state appears. This solid state can show elastic moduli similar to those of crystals. The transition from the soft solid state (gel state) into the rigid solid state is called the CGT [1, 5–7]. Similar to the sol–gel transition case, the nature of the structural glass transition is still a matter of debate [1, 5–8].

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A characterizing feature for the CSGT is the onset of the static shear stiffness $c_{44}^s > 0$ (in Voigt notation) [9]. Other phenomenological properties like the static longitudinal elastic modulus c_{11}^s are also expected to behave anomalously if they couple to the relevant order parameter. Unfortunately, c_{11}^s and especially c_{44}^s for the isotropic liquid or gel state are difficult to measure.

For the whole range of curing times we have escaped from this experimental problem with pure static elastic moduli by measuring the high frequency clamped elastic moduli at hypersonic frequencies using high performance Brillouin spectroscopy (BS) [5, 6, 9]. At Brillouin frequencies f , the elastic moduli of reacting oligomers and polymers become even at moderate viscosities dynamically clamped moduli: $\lim_{2\pi f\tau_i \gg 1} c_{11}(f) = c_{11}^\infty$ and $\lim_{2\pi f\tau_4 \gg 1} c_{44}(f) = c_{44}^\infty$, where τ_i ($i = 1, 4$) are the relevant structural relaxation times for the viscosities η_{11} and η_{44} . In that case the elastic moduli are ‘frequency clamped’ or they behave as ‘quasi-static’ (solid-like) even in the viscous liquid state. Thus they allow for the determination of solid state properties without being renormalized by the relaxational dynamics of the material under consideration. The role of c_{11}^∞ and c_{44}^∞ is for mechanical properties similar to that of the square of the refractive index for dielectric properties as far as quasi-staticity is concerned.

Recently we have shown that so-called ‘mode Grüneisen parameters’ (MGPs) [10], well known in solid state physics as indicators for elastic anharmonicity, are especially sensitive for probing the thermal glass transition at a temperature T_{gs} in structural glasses [5]. It has been demonstrated for different glass-forming materials that the MGPs behave in a jump-like fashion around T_{gs} . In solid state physics the usual thermal expansion is explained by temperature dependent excitation levels within a given anharmonic molecular/atomic interaction potential. A discontinuous temperature behaviour of a MGP is in contrast indicative for a spontaneous change of the intermolecular interaction potential which is usually found at phase transitions.

Taking into account that MGPs are sensitive to phase transitions as well as to glass transitions it seems reasonable to test them as probes for the CSGT and the CGT in order to get a better understanding of these processes.

It is a striking feature of reacting polymers that they permanently change their morphology during curing. This implies that in the course of curing not only the anharmonicity of the molecular interaction potential but also its harmonic part is changed. Since for reacting polymers the change of the phonon frequency f of the selected longitudinal (lower index L) or transverse (lower index T) mode depends not exclusively on the elastic anharmonicity but also on the continuous change of the harmonic part of the potential, the mode Grüneisen parameters change their information content and will therefore be called generalized mode Grüneisen parameters (gMGPs). The gMGPs are defined by

$$\gamma_{L,T}(\vec{q}, u(t)) = \frac{\rho(u(t))}{\omega_{L,T}(\vec{q}, u(t))} \frac{\partial(\omega_{L,T}(\vec{q}, u(t)))}{\partial \rho(u(t))} \quad (1)$$

where the time t is an external and the chemical turnover u is an internal driving parameter for the sound frequencies

$f_{L,T} = \omega_{L,T}/(2\pi)$ at given phonon wavevector \vec{q} , ρ is the mass density.

Recent BS investigations of the polymerization of epoxies using gMGPs were insensitive to the CSGT but yield an unexpected behaviour at the CGT [5]. Taking three reactive polyurethanes (PUs [11]) as model systems we will generalize the observations made on epoxies. Furthermore, we will elucidate the physical background of the gMGP for reacting polymers and especially for the CGT. In other words, the studies of the curing behaviour of polyurethanes should help to deepen the understanding of the transition phenomena accompanying the curing process in reactive polymers.

2. Sample preparation, experimental background and first results

2.1. Sample preparation

The polyurethane adhesives investigated in this paper (well described in [12]) are obtained by room temperature polymerization (RT = 297 K) of the hardener’s isocyanate (NCO) groups with the resin’s alcohol (OH) groups. A stoichiometric ratio between these relevant reactive groups is chosen so that a chemical turnover of 100% is possible, at least in principle.

The hardener Desmodur CD™ from Bayer™ (average molar mass: 300.52 g mol⁻¹) is used for all three polyurethane systems. It consists of 88.9 mol% of diisocyanates and 11.1 mol% of triisocyanates (uretonimine).

Three resins, all of them being mixtures of Desmophen 1380BT™ (average molar mass: 444 g mol⁻¹; three OH groups per molecule) and Desmophen 2060BD™ (average molar mass: 2000 g mol⁻¹; two OH groups per molecule) from Bayer™ are chosen. The following mixing ratios of the Desmophen 1380BT™ and the Desmophen 2060BD™ are used as PU resins: 100:0, 95:5 and 80:20 (molar ratios).

As the hardener and the resin contain molecules with three reactive groups, both contribute during the curing process, by forming network knots, to the molecular network formation. Mechanical tests and specific heat capacity measurements have shown that PU 100:0 and PU 95:5 vitrify during the RT curing, whereas PU 80:20 stays in the viscoelastic state.

The following sample preparation method is used for the polyurethanes: after adding the hardener to the resin in a stoichiometric ratio the mixture is agitated for 15 min by a magnetic stirrer. All samples are prepared in a glove box filled with dry air in order to avoid PU foam formation due to the presence of moisture. As samples containing air bubbles with sizes in the upper nanometre and micrometre ranges are unacceptable for BS, the samples are degassed for 10 min before use. Finally the samples are filled into glass containers sealed against moisture.

2.2. Experimental background: Brillouin spectroscopy, infrared spectroscopy and Abbé refractometry

Since in this work we restrict our interest predominantly to quasi-static properties of amorphous materials, a simplified kinematic approach to Brillouin spectroscopy is

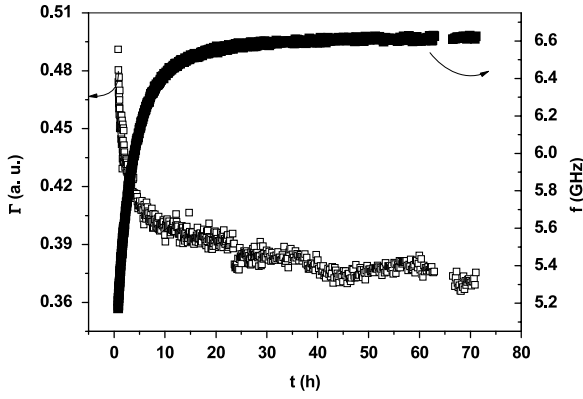


Figure 1. Temporal evolution of the hypersonic frequency f (closed symbols) and the hypersonic attenuation Γ (open symbols) of the longitudinally polarized sound modes of PU 100:0 during RT polymerization.

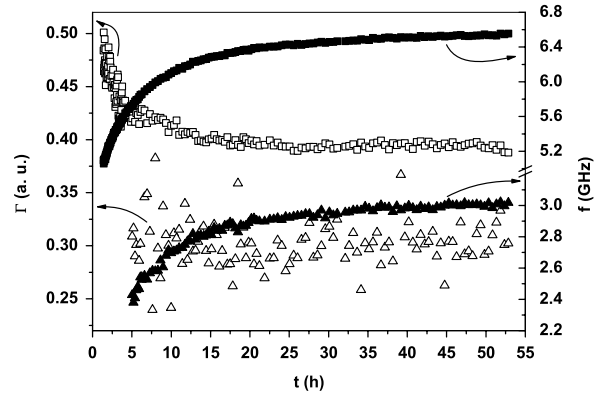


Figure 2. Temporal evolution of the hypersonic frequencies f (closed symbols) and the hypersonic attenuations Γ (open symbols) of the longitudinally (squares) and transversely (triangles) polarized sound modes of PU 95:5 during RT polymerization.

sufficient [5, 6, 9]. In this approach one starts from energy (equation (2)) and momentum conservation (equation (3))

$$\hbar\omega_s = \hbar\omega_i \pm \hbar\Omega \quad (2)$$

$$\hbar\vec{k}_s = \hbar\vec{k}_i \pm \hbar\vec{q} \quad (3)$$

where \vec{k}_i and \vec{k}_s are the optical wavevectors of the incident and the scattered light, ω_i and ω_s are the frequencies of the incoming and scattered light. \vec{q} and Ω are the phonon wavevector and the phonon frequency. For amorphous materials of isotropic symmetry there exist for every phonon wavevector two eigenfrequencies and two eigenvectors. The eigenvectors represent the longitudinal (L) and transverse polarization (T). The transverse mode is doubly degenerate.

From the energy and momentum conservation one obtains immediately a relation for the sound velocity

$$v_{L,T}(\vec{q}) = f_{L,T} \frac{\lambda_{\text{LASER}}}{2n \sin\left[\frac{\Theta_i}{2}\right]}. \quad (4)$$

In equation (4) n is the refractive index of the sample, Θ_i is the scattering angle within the sample, and λ_{LASER} is the vacuum wavelength of the laser. For the so-called 90 A scattering geometry [6] the dependence on the refractive index disappears:

$$v_{L,T}(\vec{q}^{90\text{ A}}) = f_{L,T}(\vec{q}^{90\text{ A}}) \Lambda^{90\text{ A}} = f_{L,T}(\vec{q}^{90\text{ A}}) \frac{\lambda_{\text{LASER}}}{2 \sin[\pi/4]}. \quad (5)$$

A shortcoming of BS might be small Pockels coefficients (acousto-optical coupling coefficients) which complicate or even hinder the detection of shear elastic modes. In this work Brillouin measurements are performed with a modified Tandem BS of the Sandercock type [6].

Knowing the mass density ρ and the hypersonic velocities v_L and v_T of a sample, its hypersonic longitudinal and shear moduli, c_{11} and c_{44} , can be calculated:

$$c_{11,44} = \rho v_{L,T}^2. \quad (6)$$

The chemical turnover measurements (maximal error on absolute values: 5%) are performed in the mid-infrared with

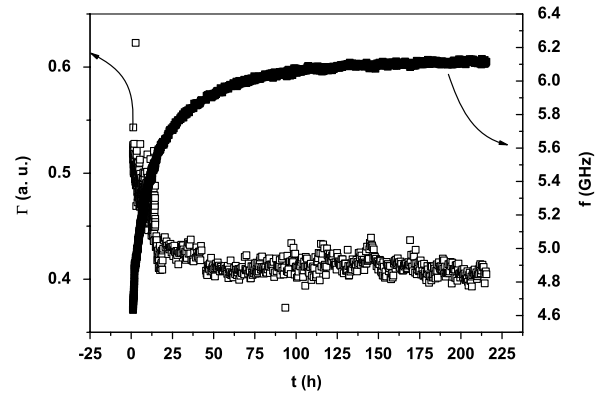


Figure 3. Temporal evolution of the hypersonic frequency f (closed symbols) and the hypersonic attenuation Γ (open symbols) of the longitudinally polarized sound modes of PU 80:20 during RT polymerization.

a Fourier transform infrared spectrometer from Bruker Optics. The quantity u is determined by the temporal decrease of the band of the isocyanate groups (NCO) at 2271 cm^{-1} as it is the relevant reactive group. To avoid external influences (temperature, air composition fluctuations, etc) on the measurement, the height of this NCO band is normalized with that of a reaction independent CH stretch vibration localized at 2975 cm^{-1} .

The refractive index data are measured with a high precision refractometer (Abbemat from Anton Paar OptoTec GmbH, Seelze, Germany) for the optical wavelength 589.3 nm . This refractometer has a high absolute accuracy of 10^{-5} and a relative accuracy of 10^{-6} .

2.3. First results

Figures 1–3 show typical measurements of the longitudinal hypersonic frequencies f_L , the shear hypersonic frequency f_T and the related hypersonic attenuations in the course of room temperature (RT) curing of the three model polyurethane systems. All PU samples qualitatively show the same behaviour. The temporal evolution of both sound mode data

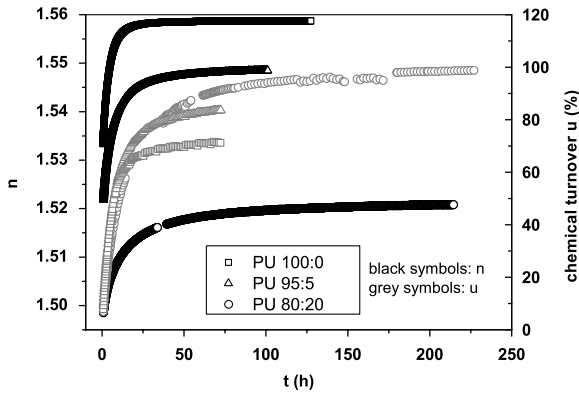


Figure 4. Temporal evolution of the refractive index n (black symbols) and the chemical turnover u (grey symbols) of the PUs investigated, during RT curing.

sets gives no clear hint as to the CSGT or the CGT. It is worth noting that the static shear frequency f_1^s should show a step-like anomaly at the sol–gel transition (CSGT) as well as at the CGT [1, 3–5]. Clearly these anomalies of the static shear frequency are lost at high frequencies.

According to a simple calculation based on the theory of Flory and Stockmayer [3], the sol–gel transition should take place for the PUs studied at around 65–70% of chemical turnover (i.e. after a curing time $t \sim 15$ –25 h; see figure 4). Since the measurements on the transverse phonons are made while they are in the dynamically frozen liquid state, they are already detected at hypersonic frequencies before this transition.

Clearly Γ_L shows a strong decrease in the first hours of the chemical reactions for the PU systems studied. In this region there are structural relaxations present but the relaxation times τ_α shift to bigger values with curing so that after about 10 h the slow motion regime ($f_L \tau_\alpha \gg 1$) is reached where dynamic effects can be neglected.

As no indication of the CSGT or the CGT is found by analysing the hypersonic frequency data, more sensitive probes, such as the gMGP, are needed.

For the evaluation of the gMGPs, knowledge of the mass density $\rho(t)$ and the expansion coefficient $\alpha(t)$ as a function of the curing time is necessary. Using the Lorentz–Lorenz equation [13, 14] (equation (7)) those quantities can be derived from the temporal evolution of the refractive index $n(t)$ while curing at RT:

$$\rho = \frac{1}{r} \frac{n^2 - 1}{n^2 + 2} \quad (7)$$

where r is the specific refractivity. This relation has been experimentally verified to be applicable for many polymers [6]. It was shown for epoxies and polyurethanes that the specific refractivity is even during RT polymerization almost a universal parameter for a given chemical system [5]. In fact, comparing for PU 80:20 the mass density and the refractive index at the beginning and at the end of the curing process leads to the same specific refractivity $r = 0.277 \pm 0.001 \text{ cm}^3 \text{ g}^{-1}$.

Assuming that equation (7) can be used as a suitable relation between $\rho(t)$ and $n(t)$, the temporal expansion

coefficient $\alpha(t)$ is independent of the specific refractivity:

$$\alpha(t) = \frac{1}{\rho} \frac{\partial \rho}{\partial t} = \frac{6n(t)}{n^4(t) + n^2(t) - 2} \frac{\partial n}{\partial t}. \quad (8)$$

Figure 4 shows the temporal evolution of the refractive index n and the chemical turnover u during RT polymerization.

Like for the hypersonic frequency and attenuation data, neither the temporal evolution of the refractive index nor of the chemical turnover show a clear hint of the CSGT or the CGT. Preliminary investigations at the thermal sol–gel transition of a physical gel have shown that the effect of the sol–gel transition on the refractive index is at the limit of resolution even for the high resolution Abbemat refractometer [15]. Assuming a similar small or non-existent coupling in case of the CSGT, no hint of this transition can be found just on the basis of refractive index data. As far as the chemical turnover is concerned it turns out that none of these transitions changes the evolution in a manner leading to a distinct anomaly.

For the evaluation of MGPs it is necessary to have frequency and mass density data at exactly the same points in time or conversions. Smooth curves of the derivatives of these quantities are a further prerequisite. So a suitable parametrization by fitting of the frequency and refractive index data cannot be circumvented. As it turns out, the best fit result is obtained by using a sum of two stretched exponential functions, e.g.,

$$n(t) = n_{e1} - (n_{e1} - n_{s1})e^{-(\frac{t}{\tau_1})^{\beta_1}} + n_{e2} - n_{e2}e^{-(\frac{t}{\tau_2})^{\beta_2}}. \quad (9)$$

The relaxation strength is described by the three n -parameters where the index e denotes the end of the fit and index s the start of the fit. The temporal evolution is parametrized by the time constants τ_1 and τ_2 and the exponents β_1 and β_2 . The fit is only done for the data regions not contaminated by dynamic effects.

3. Theoretical background of mode Grüneisen parameters

As mentioned in section 1, mode Grüneisen parameters (MGPs) are a tool of solid state physics containing general information about the anharmonicity of the elastic interaction potential in crystals [10, 16]. In particular, they give access to the temperature dependence of elastic moduli if the driving parameter for the phonon frequency is the temperature. According to Born and Huang [17] the so-called mode Grüneisen parameters for cubic crystals are defined as follows:

$$\gamma(\vec{p}, \vec{q}) = \frac{\rho}{f(\vec{p}, \vec{q})} \frac{\partial f(\vec{p}, \vec{q})}{\partial \rho} \quad (10)$$

where \vec{p} is the vector of acoustic polarization, \vec{q} is the acoustic wavevector, $f(\vec{p}, \vec{q})$ are the phonon frequencies related to the wavevector \vec{q} and ρ is the mass density. In the context of the thermal glass transition of polymers and other viscous liquids, equation (10) has been adapted to amorphous materials including the dynamically frozen liquid state [5]. The possible temperature (T) dependence of the MGP for the longitudinally

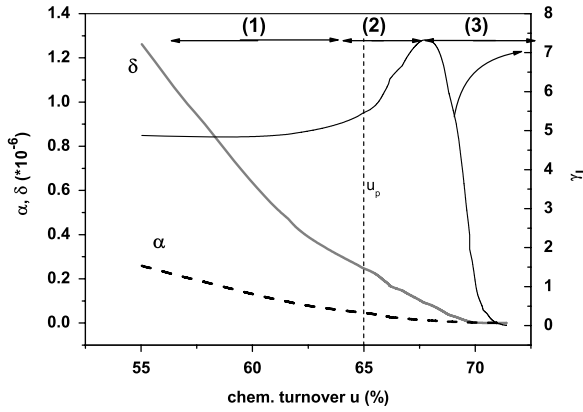


Figure 5. The generalized mode Grüneisen parameter and the parameters δ and α of PU 100:0 as a function of the chemical turnover during polymerization at ambient temperature. Vertical line at u_p : rough estimation of the sol-gel transition of the three PUs (Flory–Stockmayer theory [3]).

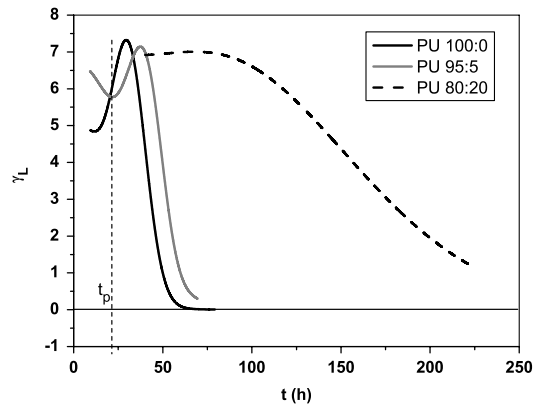


Figure 6. Temporal dependence of the mode Grüneisen parameters of the three polyurethanes investigated, during RT polymerization. The evaluation of the gMGP is limited to the damping-free regions of f_L . Vertical line at t_p : rough estimation of the sol-gel transition of the three PUs (Flory–Stockmayer theory [3]).

(lower index L) and transversely (lower index T) polarized sound modes has been included as follows:

$$\gamma_{L,T}(\vec{q}, T) = \frac{\frac{1}{f_{L,T}(\vec{q}, T)} \frac{\partial f_{L,T}(\vec{q}, T)}{\partial T}}{\frac{1}{\rho(T)} \frac{\partial \rho(T)}{\partial T}} = \frac{\delta_{L,T}(\vec{q}, T)}{\alpha(T)}. \quad (11)$$

Of course equation (11) does not apply to an isothermal curing process. The temperature has to be replaced by the time or a more suitable variable like the chemical turnover u . The same holds for the thermal expansion coefficient which transforms into a temporal or ‘ u dependent’ expansion coefficient $\alpha(t)$ or $\alpha(u)$. As mentioned in the introduction, these generalized mode Grüneisen parameters (gMGPs)

$$\gamma_{L,T}(\vec{q}, t) = \frac{\delta_{L,T}(\vec{q}, t)}{\alpha(t)} \quad (12)$$

or

$$\gamma_{L,T}(\vec{q}, u) = \frac{\delta_{L,T}(\vec{q}, u)}{\alpha(u)} \quad (13)$$

have a different meaning to the classical MGP from solid state physics. In general, the harmonic part, like the anharmonic part, of the elastic interaction potential varies in the course of curing. Whether the gMGP is a suitable probe for isostructural transitions like the CGT and the CSGT will be discussed below. It should be stressed already that gMGPs become meaningless and non-determinable in the limit of long curing times when all original data like the acoustic frequency and the refractive index become time independent. In that case $\delta_{L,T}(\vec{q}, t)$ and $\alpha(t)$ become zero and $\gamma_{L,T}(\vec{q}, t)$ becomes indefinite. In other words, reliable information about the gMGP can be obtained only in a time regime in which both $\delta_{L,T}(\vec{q}, t)$ and $\alpha(t)$ are in internal equilibrium, non-zero and free of dynamic influences. Accordingly the curing rate has to be sufficiently slow for $\delta_{L,T}(\vec{q}, t)$ and $\alpha(t)$ to reach internal equilibrium and thus to develop in a quasi-static way.

4. Discussion

For the following discussion of the gMGPs we stick mainly to the longitudinal gMGP $\gamma_L(\vec{q}, u)$, but give also an example for a shear gMGP $\gamma_T(\vec{q}, u)$. As a consequence of small optomechanical coupling coefficients (Pockels coefficients) the accuracies of the phonon frequencies of shear modes are much smaller in comparison to those of the longitudinal sound modes. As a reminder: in order to discuss $\gamma_L(\vec{q}, u)$ we use from figures 1 and 4 only the parts which are not contaminated by structural relaxation effects. On the basis of these curves, the genesis of the longitudinal acoustic gMGP $\gamma_L(\vec{q}, u)$ for polyurethane 100:0 is shown in figure 5. It should be mentioned that a maximal absolute error of 10% can be attached to all temporal gMGP curves, whereas an absolute error of maximal 20% is accorded to those depending on the chemical turnover.

The measured gMGP curve for PU 100:0 can be divided into three parts (figure 5). It is remarkable that in the turnover regime (1) the $\gamma_L(u)$ curve is rather flat although this regime corresponds to the steepest increase of the sound frequency and refractive index curves (figures 1 and 4). Intuitively, the sol-gel transition would be expected to appear in this regime. A simple estimation based on the statistics of Flory and Stockmayer [3] suggests the percolation threshold for PU 100:0 at $u = 65\%$. Noticing that the small bump at $u \sim 66\%$ in figure 5 is due to errors on the u data, and that the gMGP curve of PU 95:5 (figure 6) does not show any anomaly in this turnover interval, the gMGP does not contain any measurable experimental indication of the CSGT.

Due to the presence of significant hypersonic attenuation in a long time interval at the beginning of the reaction (see also figure 3), the gMGP for PU 80:20 has not been evaluated for turnover values lower than $u = 81\%$.

As the sol-gel transition is not observable in the $\gamma_L(u)$ curves, the question arises of the origin of the maxima found in the $\gamma_L(u)$ curves for PU 100:0 and PU 95:5, which is not found for PU 80:20 (figures 6 and 7).

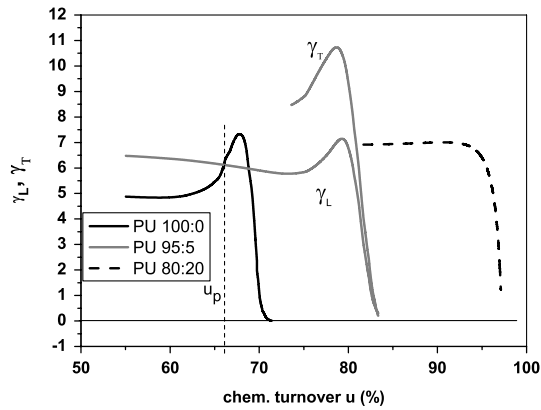


Figure 7. Dependence of the mode Grüneisen parameters of the three polyurethanes investigated on the chemical turnover, during RT polymerization. The evaluation of the gMGP is limited to the damping-free regions of f_L . Vertical line at u_p : rough estimation of the sol-gel transition of the three PUs (Flory-Stockmayer theory [3]).

At first sight it may seem astonishing that two monotonically increasing and saturating curves like $f_L(t)$ and $n(t)$ can lead to a maximum in the related $\gamma(t)$ curve (figure 6), but from a mathematical point of view it is quite obvious. Approximating the original data curves for $f_L(t)$ and $n(t)$ by the sum of two stretched exponentials with parameters compatible with our data yields the observed result. The maximum appears independently of the fit function and the statistical methods (spline interpolation, moving average, moving fit window, etc). Hence the observed γ_L maxima are not artefacts of the data treatment.

In the same context it is useful to recall the turnover dependence of the gMGPs for different compositions of epoxies [5]. For these reactive polymers, sharp maxima are observed which can unambiguously be attributed to the chemical freezing process. Although the peaks found for PU 100:0 and PU 95:5 are smaller and broader than those for the epoxies, the $\gamma_L(u)$ peaks can be attributed tentatively to the CGT of these materials, too.

Figure 5 reflects a polyurethane system whose thermal glass transition temperature lies far above ambient temperature (about 350 K after post-curing). For this PU the curing reaction performed at RT slows down as the molecular network undergoes a chemically induced glass transition usually interpreted as a change of the curing kinetics from the chemically to the diffusion controlled regime [18]. This transition takes place long before all possible reactive groups are consumed ($u = 70\%$). As is seen from figure 7, the same holds true for PU 95:5 ($T_g \sim 310$ K after post-curing). The blocking of the RT curing process at 70% and 83%, for the respective systems, of chemical turnover favours the interpretation of the $\gamma_L(\vec{q}, u)$ peaks as chemically induced glass transitions. In contrast, PU 80:20 (figure 7), which remains viscoelastic at ambient temperature, shows no $\gamma_L(u)$ peak and it cures within the margin of error until $u = 100\%$.

The interpretation as regards the physical origin of the $\gamma_L(u)$ peak given in an earlier publication has to be revised [5]. As already mentioned above, the classical interpretation of

MGPs as sensitive probes for the anharmonicity of the molecular interaction potential is not sufficient in the case of curing processes. Changes of gMGP do not exclusively reflect the variations of the anharmonic part, but also show the continuously varying harmonic part of the interaction potential during polymerization.

As the longitudinal sound frequency f_L (figure 1) and the refractive index n (figure 4) both increases with the tendency of levelling at large curing times, the evolution of their derivatives $\delta(u)$ and $\alpha(u)$ decreases smoothly for PU 100:0 (figure 5). The related $\gamma_L(\vec{q}, u)$ function can show only a maximum when the derivative with respect to the chemical turnover u of the function $\delta(\vec{q}, u)/\alpha(u)$ shows a zero. This condition is obviously equivalent to $\frac{1}{\delta(\vec{q}, u)} \frac{\partial \delta(\vec{q}, u)}{\partial u} = \frac{1}{\alpha(u)} \frac{\partial \alpha(u)}{\partial u}$. This indicates that the maximum of the gMGP strongly depends on the ratio of the relative variations of $\delta(u)$ and $\alpha(u)$.

As discussed above, below the gelation threshold, the $\gamma_L(u)$ curve for PU 100:0 is almost flat (regime (1) in figure 5). Clearly, curing has the same influence on the relative variations of $\delta(u)$ and $\alpha(u)$.

In regime (2), the decrease of $\frac{1}{\delta(\vec{q}, u)} \frac{\partial \delta(\vec{q}, u)}{\partial u}$ is less important than that of $\frac{1}{\alpha(u)} \frac{\partial \alpha(u)}{\partial u}$. In other words, the relative increase of the stiffening is stronger than the relative increase of density. Clearly the formation of new chemical bonds has the greatest influence on the stiffening of the polymer network; that is why we call this regime the ‘stiffening regime’. A different view: the network seems to be already quite rigid, so new bonds change the volume of the sample less than in the regime (1). This stiffening regime is considered as indicative for the chemical glass transition. The exact location of the CGT is in contrast not as obvious. It is not even clear whether the CGT is a sharp transition or a smeared out transition due to chemical heterogeneities in the network formation. Tentatively, the chemical turnover u_g of the CGT is assigned to the maximum position of $\gamma_L(\vec{q}, u)$ as here the most drastic change is observed.

In regime (3), the decrease of the gMGP is based on the interchange of the roles of $\delta(u)$ and the expansion coefficient $\alpha(u)$. This means that the relative increase of density is more important than that of the stiffening in this ‘compacting regime’. Beyond the chemical glass transition, chemical reactions can still take place in the glassy state, just more slowly because of the constraint of the glassy network. The remaining oligomers have swollen the glassy polymer network. Chemical reactions linking these oligomers to the polymer network have the biggest effect on the density as the matrix is already glassy.

For PU 95:5, the same argumentation holds true for the stiffening and compacting regime. It is not certain whether the slight gMGP decrease of regime (1) is physically significant (figure 7). The occurrence of the $\gamma_L(\vec{q}, u)$ maximum at higher degrees of chemical turnover is in accordance with a greater mobility of the network due to the replacements of trifunctional resin molecules by longer bifunctional ones.

Assuming that the harmonic part of the intermolecular interaction potential varies rather continuously during polymerization, the $\gamma_L(u)$ peaks of the glass-forming PUs could

(like the thermal glass transition) be attributed mainly to variations of the anharmonic part of the interaction potential during polymerization. The position of the maximum of the $\gamma_T(u)$ curve for the PU 95:5 sample (figure 7) is roughly in agreement with that of the $\gamma_L(u)$ curve, which favours the argument that the two gMGPs reflect the same freezing process. Moreover, the greater peak height of the $\gamma_T(u)$ curve in comparison to $\gamma_L(u)$ agrees with theoretical considerations [5]. For a final judgment of the agreements between the messages given by the $\gamma_L(u)$ and $\gamma_T(u)$ curves it should be kept in mind that the statistical accuracy of the $\gamma_T(u)$ curve is reduced by a factor of about 3 in comparison to the accuracy of the $\gamma_L(u)$ curve.

A further argument in favour of the interpretation of the gMGP maxima as relating to CGTs stems from the absence of any maximum for the gMGP of the sample PU 80:20 (figures 6 and 7) remaining viscoelastic during polymerization at RT. In the reliable turnover regime for this sample (no excessive hypersonic attenuation) the $\gamma_L(u)$ curve remains completely flat, although the temporal evolutions of the longitudinal sound frequency and the refractive index show qualitatively the similar saturation behaviour as the curves of the vitrifying PUs. The sudden decrease of the $\gamma_L(u)$ curve for PU 80:20 at 97% of chemical turnover is not completely understood but shows that the relative increase of the density is more important than that of the stiffening. Perhaps oligomers which have swollen the polymer network and which are built at the end of the polymerization into the network are again responsible for the essential effect of the density increase. The almost horizontal progression of the $\gamma_L(u)$ curve prior to the sudden decrease could be indicative of the lack of change of anharmonicity in the liquid or viscoelastic state.

Finally, the position or the absence of the $\gamma_L(u)$ peaks with the composition of the resin is in agreement with preliminary TMDSC investigations. For the glass-forming PU 100:0, the chemical turnover value corresponding to the maximum of the gMGP is associated with the end of the step in the specific heat capacity, which should be identified with the static glass transition.

5. Conclusion

High performance Brillouin spectroscopic investigations combined with high performance Abbé refractometry on reactive polyurethane lead to essential information about their polymerization behaviour, even if the nonlinear temporal evolution of the phonon frequencies and the refractive indices does not give any hint either of the chemical sol–gel transition or of the chemical glass transition.

The experiments show that the chemical sol–gel transition of the model polyurethanes does not couple at all, or couple so weakly to the probes used that it cannot be studied by means of the generalized mode Grüneisen parameters. In future, the sensitivity of further methods, already successful in the case of physical gels, will be applied to the chemical sol–gel transition.

The temporal evolution of the generalized mode Grüneisen parameters allows for elucidating the curing process and for differentiating three different polymerization regimes for glass-forming polymers. In particular, the chemically induced glass transition can be tentatively identified by the occurrence of a gMGP maximum. It should be stressed that in the case of reacting polymers the generalized mode Grüneisen parameters display the changes of molecular structure involved during the curing process in addition to the changes of acoustic anharmonicity.

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