Second order elasticity at hypersonic frequencies of reactive polyurethanes as seen by

generalized Cauchy relations

Second order elasticity at hypersonic frequencies of reactive polyurethanes as seen by generalized Cauchy relations

M Philipp[1,4]**, C Vergnat**[1]**, U Müller**[1]**, R Sanctuary**[1]**, J Baller**[1]**,
W Possart**[2]**, P Alnot**[3] **and J K Krüger**[1]

[1] Laboratoire de Physique des Matériaux, Université du Luxembourg, 162A,
avenue de la Faïencerie, L-1511 Luxembourg, Luxembourg
[2] Fachbereich Werkstoffwissenschaften, Universität des Saarlandes,
D-66123 Saarbrücken, Germany
[3] LPMI, Université Nancy, France

E-mail: martine.philipp@uni.lu

Abstract
The non-equilibrium process of polymerization of reactive polymers can be accompanied by
transition phenomena like gelation or the chemical glass transition. The sensitivity of the
mechanical properties at hypersonic frequencies—including the generalized Cauchy
relation—to these transition phenomena is studied for three different polyurethanes using
Brillouin spectroscopy. As for epoxies, the generalized Cauchy relation surprisingly holds true
for the non-equilibrium polymerization process and for the temperature dependence of
polyurethanes. Neither the sol–gel transition nor the chemical and thermal glass transitions are
visible in the representation of the generalized Cauchy relation. Taking into account the new
results and combining them with general considerations about the elastic properties of the
isotropic state, an improved physical foundation of the generalized Cauchy relation is proposed.

1. Introduction

The mechanical properties of reactive polymers [1–5] can be varied substantially from those of liquids to those of solids. External parameters like temperature, pressure and chemical conversion cause changes of their mechanical properties via molecular dynamics, anharmonicity and equilibrium and non-equilibrium phase transitions [4–13]. Typical states which may appear are those of liquids, gels, glasses and crystals. At least on a sufficiently large length scale, most of these states show isotropic symmetry [4, 5].

As an example of reactive network-forming polymers polyurethanes (PUs) are used in this work. At the beginning of the chemical reaction these materials behave as liquids when measured at low probe frequencies. At sufficiently high probe frequencies $f = \omega/2\pi$ and small perturbation amplitudes, the same materials behave as dynamically frozen liquids in the linear response regime (Hooke's regime [1–4]). Under the

latter conditions and according to the PUs' isotropic symmetry, the isotropy condition in Voigt notation [1, 2, 4] $c_{12}^\infty = c_{11}^\infty - 2c_{44}^\infty$ ('∞' i.e. $\omega\tau \gg 1$, for all mechanically relevant relaxation times τ) [4, 5] is valid and the elastic tensor contains in principle two independent elastic moduli, the high frequency frozen longitudinal modulus c_{11}^∞ and the high frequency frozen shear modulus c_{44}^∞ [1–5]. The dynamically frozen state is also called the slow motion regime. Decreasing the probe frequency e.g. from the GHz regime to low frequencies the elastic properties undergo in the regime of acoustic excess attenuation a transition from the so-called slow motion regime to the fast motion regime [8, 9]. In the course of polymerization the acoustic excess attenuation regime is shifted to lower frequencies, and as soon as the sol–gel transition [6, 7] is passed, static shear stiffness appears.

Using Brillouin spectroscopy the non-equilibrium chemically induced sol–gel and glass transitions of epoxies and polyurethanes have been investigated recently using the high frequency elastic moduli and pseudo-mode Grüneisen parameters (MGPs) [8, 14]. As a result, the chemically induced glass

[4] Author to whom any correspondence should be addressed.

1

transitions could be identified as an anomaly of the MGPs in the course of polymerization, but the sol–gel transitions did not affect the evolution of the MGPs [14]. For the epoxies the same data were evaluated to analyse the influence of both isostructural transitions on second order elasticity via the generalized Cauchy relation (gCR)

$$c_{11}^{\infty} = 3 \cdot c_{44}^{\infty} + A \qquad (1)$$

with A being a constant for a given material [8, 15]. As a result, neither the chemically induced sol–gel nor the glass transitions were observed in the $c_{11}^{\infty} = c_{11}^{\infty}(c_{44}^{\infty})$ representation.

The finding concerning this non-equilibrium structure formation was a fortiori astonishing because (i) by definition a prominent anomaly of the static shear modulus develops at the sol–gel transition [6, 7] and (ii) by quenching a glass-forming liquid the transition to the forced non-equilibrium state could be evidenced by a violation of the gCR in the glassy state [16].

Based on these controversial findings, the central aim of the present work is twofold: to elucidate the role of non-equilibrium processes like polymerizations for the gCR and in turn to provide a better understanding of the gCR for isotropic (e.g. amorphous) materials. For this purpose we will

 (i) define the physical prerequisites of Cauchy relations for crystalline and amorphous solids and their extension to dynamically frozen liquids,
 (ii) give a new interpretation of the Cauchy parameter A of the gCR,
(iii) display and discuss the measured data for PUs obtained by Brillouin spectroscopy, refractometry and infrared spectroscopy in a more physical way as was done for some of these data, published in [14],
(iv) study the range of validity of the gCR for the selected PUs in order to verify whether the insensitivity of the gCR to the aforementioned non-equilibrium transitions of epoxies was accidental or whether there are more general reasons behind it,
 (v) compare the different physical information provided by the gCRs and MGPs.

2. Sample preparation and experimental techniques

2.1. The polyurethanes

To attain the aforementioned goals the isothermal polymerization of three different stoichiometric polyurethanes (PUs) was investigated. The same products from Bayer™ were used for the three PU compositions: as hardener Desmodur CD™ and as resin different mixtures of Desmophen 1380BT™ and Desmophen 2060BD™. Depending on the resins' mixtures (PU 1380BT:2060BD molar ratios) the PUs are either viscoelastic (PU 80:20) or glassy (PU 95:5 and PU 100:0) after polymerization at room temperature (RT = 297 K) (see [14]).

2.2. Brillouin spectroscopy

Since we are interested in the evolution of elastic moduli at the cross-over from the liquid to the solid amorphous state,

high performance Brillouin spectroscopy (BS) is used to probe the desired elastic properties in the high frequency regime (some GHz). Details of the measurement technique are given elsewhere [8, 9, 14]. Having measured the sound frequencies $f_{L,T}(\vec{q}^{\,90A})$, the longitudinal and transverse sound velocities v_L^{∞} and v_T^{∞} can be calculated (L, longitudinally, T, transversely polarized sound mode):

$$v_{L,T}^{\infty}\left(\vec{q}^{\,90A}\right) = f_{L,T}\left(\vec{q}^{\,90A}\right) \cdot \Lambda^{90A} = f_{L,T}\left(\vec{q}^{\,90A}\right) \cdot \frac{\lambda_{\text{laser}}}{\sqrt{2}} \quad (2)$$

where λ_{laser} is the vacuum laser wavelength, $\Lambda^{90A} = 376$ nm is the acoustic wavelength related to the 90A-scattering geometry and $|\vec{q}^{\,90A}| = 2\pi/\Lambda^{90A}$ is the adjusted phonon wavevector [8, 9, 14]. It should be stressed that in the 90A-scattering geometry the acoustic wavelength Λ^{90A} is strictly independent of the refractive index [8, 9].

In the slow motion regime the longitudinal and transverse sound frequencies f_L and f_T are real quantities. Knowing the mass density ρ of the sample, the longitudinal and shear elastic moduli c_{11}^{∞} and c_{44}^{∞} can be determined according to

$$c_{11,44}^{\infty} = \rho \cdot \left(v_{L,T}^{\infty}\right)^2. \qquad (3)$$

While investigating chemical reactions by Brillouin spectroscopy the accumulation time for the Brillouin spectra has to be short compared to the progress of the chemical reaction (ca 3 min).

2.3. Refractometry

The refractive indices n were measured during the PU polymerizations with a high precision refractometer (Abbemat from Anton Paar OptoTec GmbH) for the optical wavelength 589.3 nm. This refractometer has the high absolute accuracy of 10^{-5} and a relative accuracy of 10^{-6}. Using the measured refractive index data, the mass densities ρ are determined by the Lorentz–Lorenz relation [17, 18]:

$$\rho = \frac{1}{r} \cdot \frac{n^2 - 1}{n^2 + 2} \qquad (4)$$

where $r = 0.277$ cm^3 g^{-1} is the specific refractivity [14]. It was shown for epoxies and polyurethanes that the specific refractivity r is almost a constant during RT polymerization [8].

2.4. Infrared spectroscopy

The degree of polymerization is investigated for the three PUs using a Fourier transform infrared spectrometer from Bruker Optics. The chemical conversion is determined by the temporal decrease of a typical band for the hardener's molecules at 2271 cm^{-1} involved in the reaction process [14]. To avoid external influences on the measurement (temperature, air composition fluctuations, etc) the height of this band is normalized by that of a reaction independent CH-stretch vibration [14].

3. Results and discussion

3.1. Second order elasticity and the generalized Cauchy relation

The structure of the elastic tensor and the number of its independent coefficients is determined by symmetry [1–5]. For single crystals it is well known that under special conditions, which go beyond usual symmetry arguments, the number of independent elastic moduli is reduced [3, 4]. So-called Cauchy relations (CRs) create additional relations between elastic moduli that are usually independent. The necessary conditions derived for the appearance of CRs in crystals are [3, 4] (i) no lattice anharmonicity, (ii) every lattice point is a centre of inversion and (iii) only central forces between lattice sites. For crystals with cubic symmetry the only CR is $c_{12} = c_{44}$, which reduces the number of independent elastic moduli from three to two.

As was already noted in the famous lectures of Sommerfeld [3], a Cauchy relation is not expected for amorphous solids, since none of the prerequisites (i)–(iii) holds. In agreement with this statement, the generalized Cauchy relation deduced by Zwanzig and Mountain [19] for high frequency elastic properties of simple liquids, $c_{11}^{\infty} = 3 \cdot c_{44}^{\infty} + A^{\mathrm{ZM}}(T, p, \ldots)$, does not signify a further reduction of the elastic tensor components for isotropic symmetry. It is rather a different parametrization of Hooke's law for the isotropic state, where $A^{\mathrm{ZM}}(T, p, \ldots)$ is a function depending on the external variables temperature T, pressure p etc. In this relation the prefactor '3' of c_{44}^{∞} is a consequence of the macroscopic elastic isotropy [19].

With this background it is astonishing that recently generalized Cauchy relations (gCRs) according to equation (1) have been reported in the form of linear transformations for the temperature dependent elastic moduli of liquids, glasses including metallic glasses, and ceramics [8, 15, 16, 20–23]. Such generalized Cauchy relations were even noticed during non-equilibrium processes like polymerizations of epoxies [8, 15, 20, 21, 23–25] and annealing of metallic glasses [22, 26]. Most astonishingly, the elastic properties of nanocomposites consisting of different amounts of nanoparticles in a liquid also followed a gCR [20].

Despite the physical relevance of the gCR, the understanding of its physical background was only crude. In an early stage of their work Krüger *et al* combined the CR for cubic crystals with the isotropy relation leading to $c_{11}^{\infty} = 3 \cdot c_{44}^{\infty}$ and added a constant, yielding formally equation (1) [15, 16]. This strategy did not lead to a satisfying interpretation of the Cauchy parameter A. Moreover, the Cauchy parameter A was connected to elastic anharmonicity in the frame of mode Grüneisen parameters [15] (third order elasticity), but this interpretation is probably of limited value if structure formation as observed during polymerizations is considered (see section 3.5).

A step to a better understanding seemed to be made when a gCR was found by the same group for a nanocrystalline ceramic of cerium oxide with a Cauchy parameter A at least ten times larger than those obtained for polymers [20, 21]. Based on these results the magnitudes of the Cauchy parameters A were related to the difference between local and global symmetry.

3.2. The Cauchy parameter A of the gCR

In former publications [20, 21] we have speculated that the Cauchy parameter A is in some way related to the difference between the local asymmetry of the 'elementary units' (EUs) and the global isotropy of the material in question. The EUs are defined as usually in polymer physics (e.g. [5]) with nanoscopic lateral dimensions above the atomic level, thus yielding already continuum properties. These EUs are assumed to have point symmetries differing from isotropy [5]. In the case of a statistical distribution of the EUs, orientation averaging leads to the observed isotropy. The following calculation will show that the physical origin of the Cauchy parameter A can be retraced to the elastic tensor properties of the EUs. Without any important lack of generality we assume in the following that the EUs have cubic symmetry. Hexagonal symmetry leads to the same results; the calculations are just lengthier [27].

Consider the generally valid case of an arbitrary temperature, pressure, etc dependence between the elastic moduli of the EUs, c_{12}^{cub} and c_{44}^{cub}:

$$c_{12}^{\mathrm{cub}} = c_{44}^{\mathrm{cub}} + A (T, p, \ldots) . \tag{5}$$

This relation is reminiscent of that given by Zwanzig and Mountain [19] for high frequency frozen liquids. Making now the crucial restriction that the parameter A does not depend on T, p, etc, equation (5) simplifies to

$$c_{12}^{\mathrm{cub}} = c_{44}^{\mathrm{cub}} + A . \tag{6}$$

The latter relationship implies that both elastic moduli depend on T, p, etc in the same way:

$$\frac{\partial c_{12}^{\mathrm{cub}}}{\partial T} = \frac{\partial c_{44}^{\mathrm{cub}}}{\partial T}, \qquad \frac{\partial c_{12}^{\mathrm{cub}}}{\partial p} = \frac{\partial c_{44}^{\mathrm{cub}}}{\partial p}, \text{ etc.} \tag{7}$$

The elastic moduli of the isotropic material under consideration can now be calculated following an orientation averaging [1, 4] using equation (6):

$$c_{11}^{\mathrm{iso}} = \langle c_{11} \rangle = (3c_{11}^{\mathrm{cub}} + 6c_{44}^{\mathrm{cub}} + 2A)/5 \tag{8}$$

$$c_{44}^{\mathrm{iso}} = \langle c_{44} \rangle = (c_{11}^{\mathrm{cub}} + 2c_{44}^{\mathrm{cub}} - A)/5 . \tag{9}$$

Since the isotropy condition [4, 5]

$$c_{12}^{\mathrm{iso}} = c_{11}^{\mathrm{iso}} - 2c_{44}^{\mathrm{iso}} \tag{10}$$

holds for the isotropic nanostructured material on the typical length scale for BS, the related gCR follows immediately:

$$c_{11}^{\mathrm{iso}} = 3 \cdot c_{44}^{\mathrm{iso}} + A . \tag{11}$$

This is equivalent to

$$c_{12}^{\mathrm{iso}} = c_{44}^{\mathrm{iso}} + A . \tag{12}$$

Equations (6), (7) and (12) show that a gCR is obtained for the isotropic material if the elastic moduli c_{12} and c_{44} of the cubic subunits and the isotropic state depend in the same manner on the external parameters. It has been shown recently [27] that

similar calculations can be performed for EUs of hexagonal symmetry, yielding again the gCR with the slope of 3. This result suggests that identities or proportionalities between the derivatives of the EUs' elastic tensor components with respect to the external parameters are at the physical origin of the Cauchy parameter A. The latter conditions concern those elastic moduli which in principle could be related by classical CRs. It is worth noting that the above discussed procedure nicely shows the significance of the slope of 3 in equation (11) as an indicator for isotropic symmetry!

The Cauchy parameters A occurring in equations (6) and (11) have been successfully compared for a cerium oxide single crystal (cubic symmetry) and a nanocrystalline ceramic made of cerium oxide [21]. If the driving parameter is the temperature in an isotropic solid, this signifies that the anharmonic part of the elastic interaction potential acts in the same way on both elastic moduli c_{12}^{iso} and c_{44}^{iso}.

For the sake of simplicity we ignore in the following the upper index 'iso'. For high frequency frozen liquids and amorphous solids, until now only positive A's have been observed [8, 15, 16, 20–26]. Negative A's, although possible as long as no elastic stability limit is violated, have not been observed yet. From dynamic stability conditions for the high frequency frozen liquid state, it is clear that $c_{11}^{\infty} > 0$ and $c_{44}^{\infty} > 0$ must hold. According to equation (11) this implies that A must be smaller than the minimum of $c_{11}^{\infty}(T, p, u, \ldots)$ (u: chemical conversion). This condition yields the possibility for a rough estimate of the Cauchy parameter A. Elastically soft materials will show small A's, typically of 2–4 GPa [8, 15, 16, 20, 23–25]. On the other hand, for a nanocrystalline ceramic of cerium oxide the Cauchy parameter A is as large as 45 GPa [20, 21] and of the same order of magnitude for metallic glasses [22, 26].

Coming back to the temperature T as the driving parameter for c_{11}^{∞} and c_{44}^{∞} in polymerized samples, the Cauchy parameter A becomes equal to the modulus $c_{11}^{\infty}(\neq c_{11}^{0})$ at the temperature T_{stab} for which $\lim_{T \to T_{stab}} c_{44}^{\infty} \to 0$ holds. To put it differently, at the temperature T_{stab} the Poisson number goes to 0.5. The latter limit can be considered as the ultimate stability limit, for which the material behaves for each frequency as a liquid.

Having read the papers of Fioretto *et al* and their interpretation of the Cauchy parameter A [23, 25] we want to make the following comments.

(i) As shown above, the gCRs are based on the applicability of elasticity theory, otherwise complex elastic tensors would be involved. Any gCR of liquids will break down at sufficiently low frequencies since c_{44} becomes a complex quantity in the excess attenuation regime before going to zero. It should be stressed that the shear mode becomes overdamped for low frequencies, whereas the longitudinal mode does not.

(ii) gCRs may exist even if no frequency dependence of the elastic moduli is present. This seems to be the case for the nanocrystalline ceramic of cerium oxide. In such a case the interpretation of A by Fioretto *et al* in terms of the static adiabatic longitudinal modulus becomes meaningless. If hypersonic dynamics are present, the interpretation of A by Fioretto *et al* is in contradiction to ours given above.

(iii) We agree with Fioretto *et al* that for low excess attenuation a pseudo-gCR can still be approximated, but this will be at the cost of the slope and the Cauchy parameter A. If hypersonic dynamics start to play a role these dynamics usually affect the shear modulus more strongly than the longitudinal one. Thus first of all the slope of the linearized $c_{11}(c_{44})$-relation will decrease.

This influence of hypersonic excess attenuation on the gCR slope might be a reason for slopes smaller than 3 observed in the literature.

Some years ago we calculated a relation between temperature-driven longitudinal and transverse MGPs γ_L and γ_T on one hand and the Cauchy parameter A of the related temperature-driven gCR on the other [15]:

$$A = 2 \cdot c_{11}^{\infty}(T_0) \cdot \frac{\gamma_T(T_0) - \gamma_L(T_0)}{1 + 2\gamma_T(T_0)} \tag{13}$$

where T_0 is the considered reference temperature. This relation will be discussed in section 3.5 in the frame of the third order elasticity's role for gCRs.

3.3. First interpretation of the experimental data

Having established a more physical insight concerning the gCR and particularly the Cauchy parameter A, we will discuss now the experimental data obtained during the room temperature polymerizations of three PUs.

Since the frequency of visible light is about 5×10^{14} Hz, the refractive indices are derived from dynamically frozen dielectric constants. As discussed above, there exists a simple relation between refractive indices n and mass densities ρ (see equation (4)).

Figure 1 shows the calculated data of mass density ρ as a function of chemical conversion. The used conversion data have been measured as a function of time and have been published previously [14]. Beside the fact that this kind of representation is physically more reliable than plots versus the time, it also has a shortcoming: in this parametric plot both coordinate values are affected by errors. Obviously, the density increases with the chemical conversion and decreases with increasing concentration of the resin component Desmophen 2060BD. The bending of these curves is most important at the beginning of the polymerization. In the chemical conversion regime $u > 30\%$, $\rho(u)$ behaves almost linearly.

As a matter of fact, the evolution of the mass density shows no hint of the sol–gel transition or of the chemical freezing process. The slight irregularities of these curves are solely due to the evaluation difficulties of the infrared spectroscopic bands [14]. Consequently, neither the sol–gel transition nor the chemically induced glass transition produce an anomaly within the mass density versus chemical conversion curve. In other words, the onset of static shear stiffness at the sol–gel transition does not affect the mass density of the PU. The same argument holds true for the further onset of shear rigidity at the chemically induced glass transition.
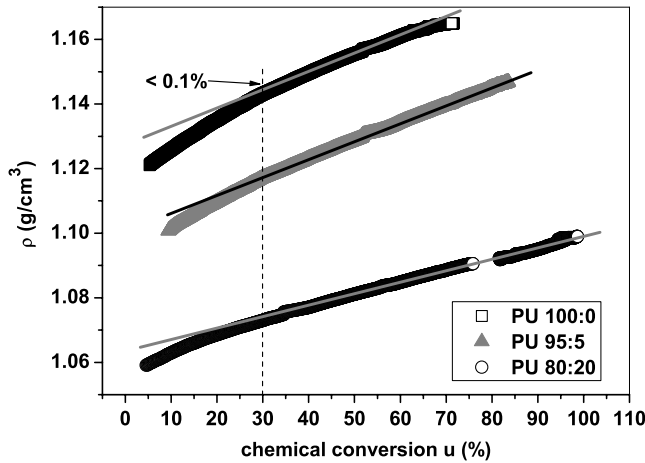
Figure 1. Mass densities ρ versus chemical conversion u for the three polyurethanes during the polymerization at 297 K. As indicated, the deviation from linearity in $\rho(u)$ is smaller than 0.1% between 30 and 70% of chemical conversion for PU 100:0.
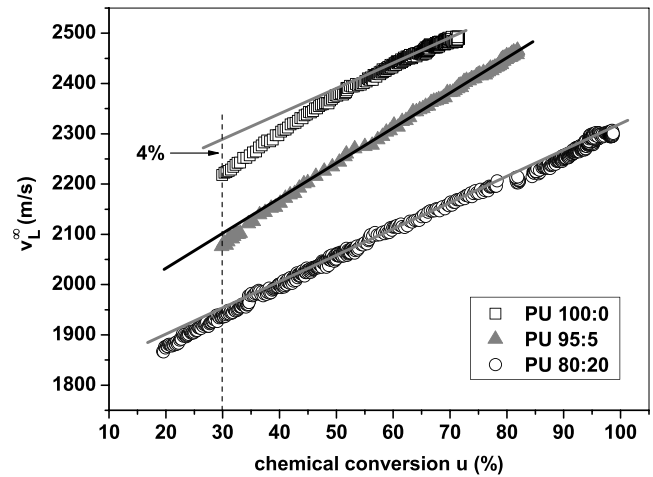

Figure 2. Transverse hypersonic velocities v_T^∞ versus chemical conversion for the three polyurethanes during the polymerization at 297 K. The small black dots shown below 55% (PU 100:0 and 80:20), respectively below 40% (PU 95:5), of chemical conversion are calculated via the gCRs (see section 3.4).

As in the case of the mass density, the transverse and longitudinal hypersonic velocities v_T^∞ and v_L^∞ were measured as a function of time but plotted versus the chemical conversion (figures 2 and 3, respectively). All data shown in figures 2 and 3 are high frequency frozen properties; sound velocity data showing acoustic excess attenuation are omitted for the representation of the gCRs (cf [14]). Because of the extremely small Pockels coefficients for the shear phonons, PU 80:20 was the most difficult to measure, which results in the large data scatter. Only above a chemical conversion of 40% (PU 95:5), respectively 55% (PU 100:0 and 80:20), could shear phonons be resolved from the noise (see figure 2). A first inspection of figures 2 and 3 shows that PU 80:20 reacts to almost 100%. The other polyurethane compositions, which reach smaller final degrees of polymerization, have undergone a chemical glass transition. These glass-forming PUs continue to polymerize only slightly after chemical freezing [14].

Figure 3. Longitudinal hypersonic velocities v_L^∞ versus chemical conversion u for the three polyurethanes during the polymerization at 297 K. As indicated, the deviation from linearity in $v_L^\infty(u)$ is 4% between 30 and 70% of chemical conversion for PU 100:0.
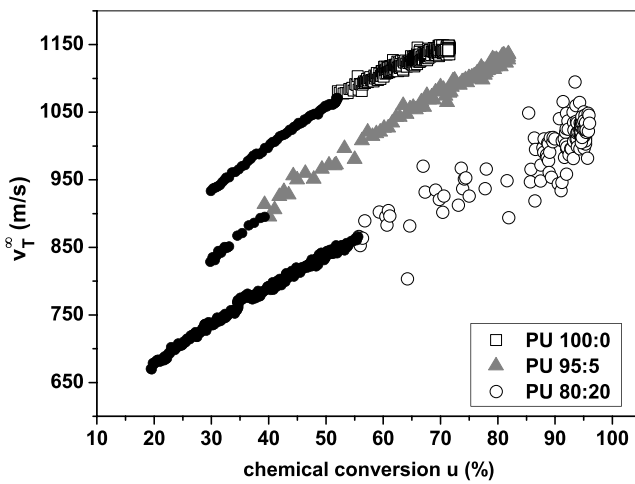
A comparison of figure 1 with figures 2 and 3 reflects a qualitatively similar behaviour of the mass densities and the hypersonic velocities. The PUs stiffen with an increasing degree of chemical crosslinks (related to the chemical conversion) and become softer with an increasing concentration of the resin component Desmophen 2060BD. There is, however, a difference between the evolution of ρ and v_L^∞ as a function of chemical conversion: the v_L^∞-curve is much more bent below 55% of chemical conversion than ρ. Considering high frequency frozen elastic properties, the increase of the longitudinal modulus c_{11}^∞ is essentially not produced by densification. Unfortunately, we have no experimental access to the shear modulus c_{44}^∞ for conversions below 55%. Provided that the gCRs given below are valid below $u = 55\%$ (except for PU 95:5), the lacking shear moduli c_{44}^∞ and velocities v_T^∞ can be calculated (see figure 2 and section 3.4).

According to our previous work [14] the sol–gel transition should take place for all PUs between conversions of 65 and 70%, and the glass transition of PU 100:0 and 95:5 around 70, respectively 80%. Taking again into account the evaluation difficulties of the chemical conversions, there are no hints of chemically induced sol–gel or glass transitions in the hypersonic velocities. This result suggests that the structural changes accompanying the sol–gel and glass transition do not affect either the shear or the longitudinal deformation at hypersonic frequencies. The reason for this is probably the different couplings of the static and the high frequency deformation modes to the order parameters of the chemically induced sol–gel and glass transitions. In line with the results found for epoxies, this result predicts the existence of gCRs for all three PU compositions and for the whole considered range of chemical conversion.

3.4. Experimental verification of the gCRs

Indeed, the gCRs displayed in figure 4 confirm the linear behaviour between c_{11}^∞ and c_{44}^∞ previously found for
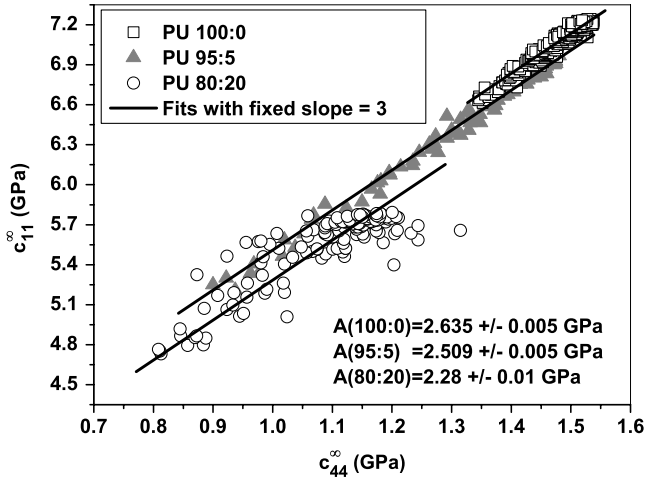
Figure 4. The evolution of the gCRs for the polyurethanes during the polymerization at 297 K with the chemical turnover as a parameter.
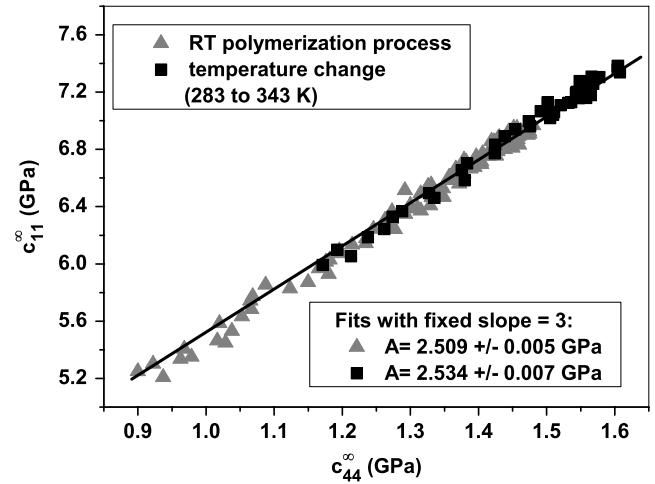

Figure 5. Comparison between PU 95:5's gCRs for the polymerization (triangles) and for a temperature variation of the polymerized sample (squares).

the non-equilibrium process of polymerization in epoxies [8, 15, 20, 23–25]. Although this kind of structure formation has only been studied for two classes of polymers, it seems now to be certain that at least under certain circumstances gCRs are not violated either by isostructural phase transitions or by non-equilibrium. The striking question remains why the moduli c_{11}^{∞} and c_{44}^{∞} do not develop independently during the non-equilibrium polymerization, as was observed during the quenching of a glass-forming liquid [16]. We believe that the slow and smooth development of the properties during the studied polymerizations is probably responsible for this behaviour. In other words, as long as v_{L}^{∞} and v_{T}^{∞} reach their local equilibrium during the collection time of each data point, gCRs are not violated. A similar result was reported for the annealing of metallic glasses [22, 26].

Closer inspection of the data presented in figure 4 shows that the slope of the three different gCRs is consistent with a value of 3 within the margin of error. This value is in line with the assumed macroscopic isotropic symmetry of the PU samples [19]. The three gCRs show a small, but significant, variation of the Cauchy parameter A with the resin composition: the A parameters vary between 2.3 GPa and 2.6 GPa for PU 80:20, respectively PU 100:0. These results are a first hint of a dependence of A on the molecular arrangement, which changes with the resin composition, of course.

Taking into account the completely different chemical compositions of polyurethanes and epoxies, it seems astonishing that for both material classes very similar values for the Cauchy parameter A (close to 2.5 GPa) are discovered [8, 15, 20, 23–25]. On the other hand, as discussed above the condition $A < \min\{c_{11}^{\infty}(u)\}$ should hold, which limits the Cauchy parameter A roughly to the rather similar measured values of c_{11}^{∞} at the beginning of the polymerization process.

Since the sound velocities v_{L}^{∞} were measured in the high frequency frozen regime for all PUs, we could calculate the corresponding v_{T}^{∞}-data for conversions between 30 and 55% using the gCRs. As expected, the v_{T}^{∞}-curves are also bent at low degrees of polymerization (see figure 2).

As published previously [8, 15, 16, 20–23], gCRs can also be determined for temperature dependent measurements. Representative for all compositions, figure 5 shows a comparison of the gCRs obtained from polymerization and from temperature dependent measurements performed on PU 95:5. Within the margin of error both gCRs possess the same Cauchy parameter A. The evaluations of the temperature dependent gCRs for PU 100:0 and PU 80:20 lead to the Cauchy parameters $A = 2.60 \pm 0.01$, respectively $A = 2.41 \pm 0.03$, agreeing well with the values observed for the polymerizations. This implies the interesting result that the Cauchy parameter A measured as a function of temperature around the fixed point at room temperature can be used to predict the polymerization behaviour of $c_{44}^{\infty}(u)$ on the basis of $c_{11}^{\infty}(u)$-data. It should be stressed that this experimental evidence is rather astonishing from the physical viewpoint. The variations of the elastic moduli c_{11}^{∞} and c_{44}^{∞} are expected to be driven by completely different physical processes during the non-equilibrium polymerization on one hand and during the cooling/heating experiment on the other. Network formation modifies the harmonic and the anharmonic part of the elastic part of the thermodynamic potential (called the 'elastic potential'), whereas the temperature variation of the elastic moduli is predominantly driven by the anharmonicity of the elastic potential [8, 14].

3.5. Second order versus third order elasticity

In a previous paper, Krüger *et al* [15] related by a simple calculation the gCR in the case of temperature dependent measurements for amorphous materials to the anharmonicity (third order elasticity) of the elastic potential, using thermal mode Grüneisen parameters (see equation (13)) [1, 4]. This interpretation means that, under conditions where temperature (or pressure) changes modify the elastic moduli, c_{12}^{∞} and c_{44}^{∞} are driven in an identical manner, only by anharmonicity. Under these conditions the Cauchy parameter A could be interpreted in terms of mode Grüneisen parameters.

The situation is surely different in the case of reactive network-forming polymers like epoxies and polyurethanes. These materials significantly change their morphology in the course of polymerization. Thus, due to polymerization, a successive change of the elastic potential is expected, superimposed by changes of these properties due to gelation and chemical freezing [14]. There is *a priori* no reason why under these conditions a linear relation between c_{11}^∞ and c_{44}^∞ should hold true. In contrast to this expectation, the experimentally observed gCRs indicate that the elastic moduli c_{12}^∞ and c_{44}^∞ are driven in an identical manner even in the presence of non-equilibrium processes and isostructural transition phenomena.

Two relevant questions remain. (i) Why do strong morphological changes due to the formation of a molecular network on one hand and temperature changes on the other yield the same Cauchy parameter *A*? (ii) Why does the initial composition of the PUs related to different concentrations of Desmophen 2060BD change the Cauchy parameter *A* whereas morphological changes due to the formation of a molecular network do not?

(i) The high frequency frozen moduli of condensed matter for given external parameters can be derived from the elastic potential. The splitting of this potential into only a quadratic and a cubic part is of course an approximation. Whereas the temperature dependence of the elastic moduli is predominantly determined by the cubic part of the potential, the dependence upon structure formation during polymerization cannot be specifically attributed. Pure mathematical arguments are sufficient to show that the gCR related to polymerization and that related to temperature change are identical as soon as both gCRs have one point in common. This is always true if the temperature measurement is started after polymerization has finished, and this result is independent of the physical mechanism behind both processes.

Table 1 shows the values for the thermal MGPs at the reference temperature $T_0 = 297$ K of isothermal polymerization for PU 100:0 and PU 95:5. Obviously the *A*-values calculated on the basis of temperature-driven MGPs are compatible with those derived from gCRs. However, from the point of view of data analysis the calculated values of *A* are rather uncertain. This calculation leads at least to a rough idea of elastic anharmonicity at the end of polymerization within the glassy state. Considering the behaviour of thermal MGPs at the glass transition, it is expected that the degree of anharmonicity is larger for lower degrees of polymerization. Since the Cauchy parameter *A* is invariant in a given gCR, according to equation (13) the thermal MGPs of the transverse and the longitudinal acoustic mode have to change in such a way that the factor $[\gamma_T(T_0) - \gamma_L(T_0)]/[1 + 2\gamma_T(T_0)]$ remains almost constant. It is worth noting that the thermally induced MGPs and the polymerization induced pseudo-MGPs have nothing in common, since the first remains physically meaningful at the end of polymerization whereas the latter does not [14].

(ii) A unique gCR was observed for nanocomposites consisting of different amounts of silica nanoparticles mixed in the same glass-forming oligomer [20]. Although we did not expect such a nanoparticle-concentration-dependent gCR,

Table 1. Hypersonic frequency and refractive index data and thermal mode Grüneisen parameters γ_L and γ_T as determined during a temperature variation around $T_0 = 297$ K performed on the polymerized 95:5 and 100:0 PUs. The Cauchy parameters *A* were calculated according to equation (13).

	PU 95:5	PU 100:0
f_L (GHz)	6.63 ± 0.01	6.57 ± 0.01
$\mathrm{d}f_L/\mathrm{d}T$ (GHz K^{-1})	$(-63 \pm 2) \times 10^{-4}$	$(-51 \pm 1) \times 10^{-4}$
f_T (GHz)	3.09 ± 0.01	3.03 ± 0.01
$\mathrm{d}f_T/\mathrm{d}T$ (GHz K^{-1})	$(-39 \pm 5) \times 10^{-4}$	$(-29 \pm 6) \times 10^{-4}$
n	1.5473 ± 10^{-4}	1.6118 ± 10^{-4}
$\mathrm{d}n/\mathrm{d}T$ (K^{-1})	$(103 \pm 3) \times 10^{-6}$	$(-180 \pm 1) \times 10^{-6}$
γ_L	6 ± 1	7.0 ± 0.1
γ_T	9 ± 2	8 ± 4
A (GPa)	2 ± 2	1 ± 3

it was proven to exist at least until 20 vol% of silica in the oligomer. That mixtures of reactive network-forming oligomers do not necessary follow a gCR as a function of composition is demonstrated in this work for the modification of our PU by Desmophen 2060BD. Already the introduction of small amounts of Desmophen 2060BD into the liquid reference polyurethane PU 100:0 (leading to PU 95:5 and PU 80:20) results in a nonlinear change between c_{11}^∞ and c_{44}^∞. This behaviour is reflected in the decrease of the Cauchy parameters *A* of the gCRs with the addition of Desmophen 2060BD. Contrariwise and astonishingly, the formation of chemical crosslinks of a given PU composition maintains linearity between both elastic moduli until the end of polymerization.

4. Conclusion

The evolution of the hypersonic longitudinal and shear moduli during the polymerization of polyurethanes yields the surprising result that the generalized Cauchy relations remain valid during the non-equilibrium chemical reactions. Even more, the polymerization-driven gCRs are identical to the related temperature-driven gCRs. This behaviour can be derived using simple mathematical arguments and confirms the results previously found for epoxies. Even the chemical sol–gel transition and the chemically induced glass transition do not violate these relations. A model calculation based on an orientation averaging applied to non-isotropic elementary units shows that the same dependences of certain elastic moduli of these units on the driving parameter (temperature, pressure, chemical conversion, etc) is at the origin of the Cauchy parameter *A*. The Cauchy parameter *A* is interpreted as an ultimate stability limit for the high frequency frozen longitudinal modulus of the isotropic state. In contrast to the behaviour of other multi-component systems, changing the amount of Desmophen 2060BD in PU leads to a nonlinear relation between the transverse and the longitudinal elastic moduli, thus violating gCRs which depend on the concentration of Desmophen 2060BD. The effect of second order and third order elasticity on the generalized Cauchy relation is not quite clear yet, and needs further investigations.

References

[1] Auld B A 1973 *Acoustic Fields and Waves in Solids* vol 1 (New York: Wiley)

[2] Nye J F 1972 *Physical Properties of Crystals* (Oxford: Oxford Press)

[3] Sommerfeld A 1945 *Vorlesungen über Theoretische Physik* Band 2 *Mechanik der Deformierbaren Medien* (Leipzig: Harri Deutsch)

[4] Grimvall G 1986 *Thermophysical Properties of Materials* (Amsterdam: North-Holland, Elsevier)

[5] Ward I M 1971 *Mechanical Properties of Solid Polymers* (London: Wiley)

[6] de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (London: Cornell University Press)

[7] Brinker C J and Scherer G W 1990 *Sol–Gel Science—the Physics and Chemistry of Sol–Gel Processing* (San Diego, CA: Academic)

[8] Krüger J K *et al* 2007 *Ageing and the Glass Transition* (*Springer Lecture Notes in Physics* vol 716) ed M Henkel, M Pleimling and R Sanctuary (Berlin: Springer)

[9] Krüger J K 1989 *Optical Techniques to Characterize Polymer Systems* ed H Bässler (Amsterdam: Elsevier)

[10] Donth E 1992 *Relaxation and Thermodynamics in Polymers, Glass Transition* (Berlin: Akademie)

[11] Venkateshan K and Johari G P 2006 *J. Chem. Phys.* **125** 014907

[12] Corezzi S, Fioretto D and Rolla P 2002 *Nature* **420** 653–6

[13] Parnell S, Min K and Cakmak M 2003 *Polymer* **44** 18 5137–44

[14] Müller U, Philipp M, Bactavatchalou R, Sanctuary R, Baller J, Zielinski B, Possart W, Alnot P and Krüger J K 2008 *J. Phys.: Condens. Matter* **20** 205101

[15] Krüger J K, Baller J, Britz T, le Coutre A, Peter R, Bactavatchalou R and Schreiber J 2002 *Phys. Rev.* B **66** 012206

[16] Krüger J K, Britz T, le Coutre A, Baller J, Possart W, Alnot P and Sanctuary R 2003 *New J. Phys.* **5** 80

[17] Lorentz H A 1880 *Wied. Ann. Phys.* **9** 641

[18] Lorenz L V 1880 *Wied. Ann. Phys.* **11** 70

[19] Zwanzig R and Mountain R D 1965 *J. Chem. Phys.* **43** 4464

[20] Krüger J K *et al* 2005 *J. Physique* IV **129** 45–9

[21] Bactavatchalou R, Alnot P, Baller J, Kolle M, Müller U, Philipp M, Possart W, Rouxel D, Sanctuary R, Tschöpe A, Vergnat C, Wetzel B and Krüger J K 2006 *J. Phys.: Conf. Ser.* **40** 111

[22] Pineda E and Crespo D 2008 *Rev. Adv. Mater. Sci.* **18** 173–6

[23] Fioretto D, Corezzi S, Caponi S, Scarponi F, Monaco G, Fontana A and Palmieri L 2008 *J. Chem. Phys.* **128** 214502

[24] Yamura H, Matsukawa M, Otani T and Ohtori N 1999 *Japan. J. Appl. Phys.* **38** 3175–8

[25] Caponi S, Corezzi S, Fioretto D, Fontana A, Monaco G and Rossi F 2008 arXiv:0806.1486v1 [cond-matt.soft]

[26] Wen P, Johari G P, Wang R J and Wang W H 2006 *Phys. Rev.* B **73** 224203

[27] Müller U 2007 *PhD Thesis* Saarland University, Saarbrücken, Germany