

Information for users of METTLER  
TOLEDO thermal analysis systems

## Dear Customer

The STAR<sup>®</sup> system has once again found very many new users in 2002. The range of applications has now been greatly expanded thanks to the introduction of the exciting new DMA/SDTA861<sup>°</sup> Dynamic Mechanical Analyzer and, more recently, the high pressure DSC827<sup>°</sup> module. The STAR<sup>®</sup> System is extremely versatile and is nowadays used in practically all industries for both quality assurance and research purposes.

In UserCom we often publish articles from somewhat less well-known application areas. We hope that these applications will encourage you to try out one or the other in your field of work.

## Interpreting DMA curves, Part 2

*Dr. Jürgen Schawe*

### Introduction

Part 1 of this series of articles (UserCom15) covers non-isothermal DMA measurements and the dependence of the mechanical modulus on temperature. This second article deals with the frequency dependence of the mechanical properties and quantities of stable samples. Because of the enormous scope of this field, only the basic principles and general rules that explain the behavior of materials are discussed.

In practice, materials are subjected to stresses at many different frequencies. It is therefore extremely important to have a detailed understanding of the effect of frequency on mechanical properties. In addition, it means that materials need to have different properties under different conditions. For example, an adhesive should behave elastically without breaking when it suffers a blow (high frequencies), but should at the same time be able to "accommodate" stress arising from temperature fluctuations (low frequencies) like a liquid.

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## Complex modulus and compliance

### An ideal elastic solid

In shear mode, DMA measures the shear modulus,  $G^*$ , and the shear compliance,  $J^*$ . An ideal elastic material stores the entire mechanical energy responsible for the deformation. When the shear stress is removed, this energy is liberated. The modulus is independent of frequency; stress and deformation (strain) are in phase. In this situation,  $G^* = G'$ , whereby  $G'$  is known as the storage modulus. An example that illustrates this behavior is that of a spring (Fig. 1a).

### An ideal viscous liquid

In an ideal liquid, the applied stress and the strain are phase-shifted by  $90^\circ$ . Because the molecules are free to move, no mechanical energy is stored in the material - the energy is completely converted to heat. The corresponding model is the damping device shown (Fig. 1b). Typically, a liquid is described with the frequency-independent viscosity  $\eta_0$ . In the case of the shear modulus,  $G^*(\omega) = iG''(\omega)$ . The imaginary number,  $i = \sqrt{-1}$ , is a mathematical expression that represents the fact that the mechanical energy is dissipated, i.e. converted to heat.  $G''$  is the loss modulus, where  $G'' = \omega\eta_0$ . In a liquid, the loss modulus therefore increases linearly with the frequency,  $f$ , where  $f = \omega/2\pi$ .

### Viscoelastic materials

In real materials, the reaction to an external stress is accompanied by molecular rearrangements that take place over a wide frequency range. Examples of this are lat-

tice vibrations in solids at about  $10^{14}$  Hz and cooperative rearrangements at the glass transition at about  $10^2$  Hz. Molecular rearrangements are the reason for the different relaxation processes. At higher temperatures, the frequency of the molecular rearrangements increases. The resulting temperature dependence of the relaxation process is discussed in another article in this publication (UserCom16, page 10). The properties of real materials lie between those of an ideal liquid and an ideal solid. Due to the fact that they have both elastic and viscous properties, the materials are said to be viscoelastic. Their behavior is described mathematically by the complex, frequency-dependent modulus

$$G^*(\omega) = G'(\omega) + iG''(\omega) \quad (1)$$

where  $G'$  is the elastic part of the modulus and  $G''$  the energy dissipation part (viscous component). Technical models that illustrate viscoelastic behavior are combinations of springs and damping devices (Fig. 1c).

### The complex compliance

The  $G^*$  modulus describes the relaxation of the mechanical stress for a given strain. In everyday language, a material with a larger storage modulus is said to be "harder".

The DMA experiment can also be performed in such a way that the stress is given and the resulting strain is measured. One then talks of strain retardation. The retardation time is a measure of the time delay in the strain after imposition of the stress. In this case, the compliance,  $J^*$ , is determined. This is also complex and fre-

quency dependent and is given by

$$J^*(\omega) = J'(\omega) - iJ''(\omega) \quad (2)$$

where  $J'$  and  $J''$  are the storage and loss compliances. In simple terms, one can say that a "softer" material has a greater (storage) compliance.

The relationship between modulus and compliance is given by the equation

$$J^*(\omega) = 1/G^*(\omega) \quad (3)$$

This allows the following equations to be derived:

$$J' = G'/(G'^2 + G''^2) \text{ and } J'' = G''/(G'^2 + G''^2).$$

The relationship between the modulus, compliance and loss factor ( $\tan \delta$ ) for a relaxation process is illustrated in Figure 2.

The mechanical behavior of a material can be expressed equally well using the modulus or the compliance. In practice, the quantity used depends on what you are accustomed to, or to practical considerations. For example, the modulus is often used when discussing mechanical behavior in the rubbery plateau, whereas the compliance is used to separate different processes.

## The frequency dependence of modulus and compliance

### An overview of frequency dependence

Figure 3 displays schematic curves of the moduli and compliances for an amorphous polymer. The curves are displayed in log-log presentation. At low frequencies one can see the flow region, in which  $G'$

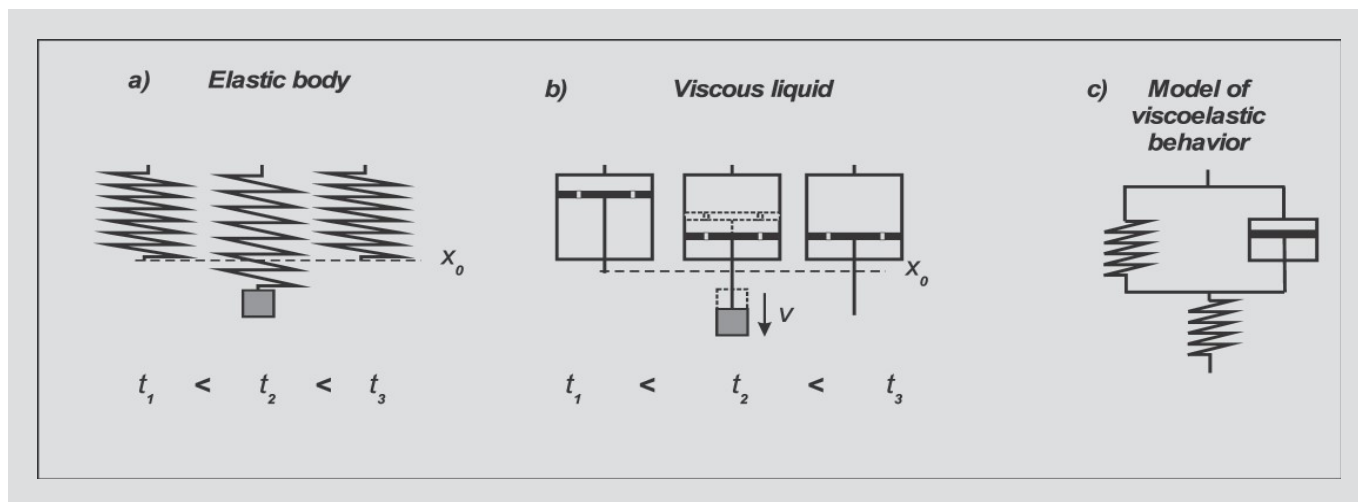


Fig. 1. Models illustrating the mechanical behavior of materials.  $t_1$ ,  $t_2$  and  $t_3$  are the times before, during and after the load was applied,  $x_0$  is the initial length and  $v$  is a constant rate.

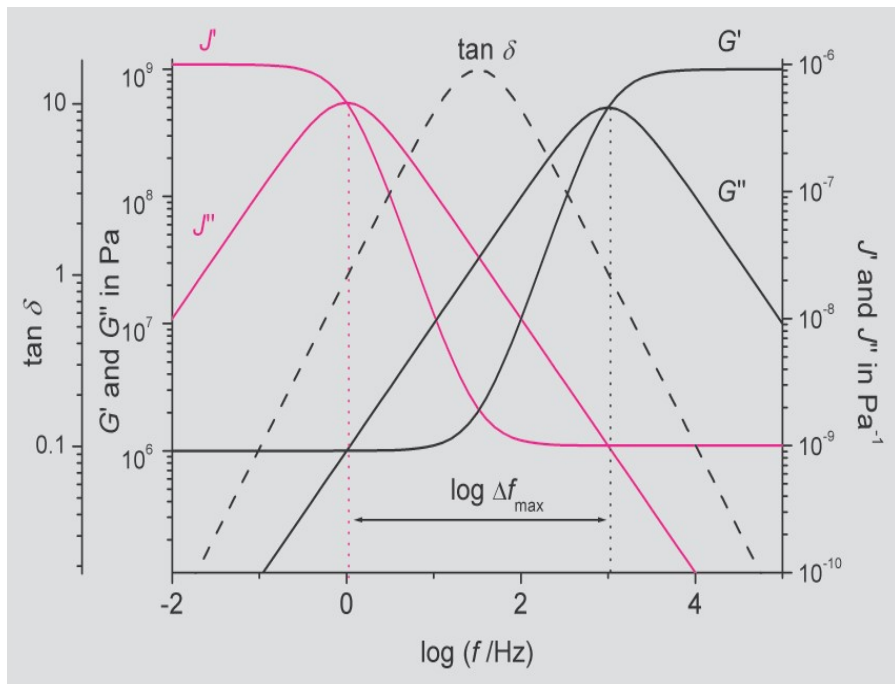


Fig. 2. Basic curve shapes of moduli, compliances and  $\tan \delta$  as a function of frequency.

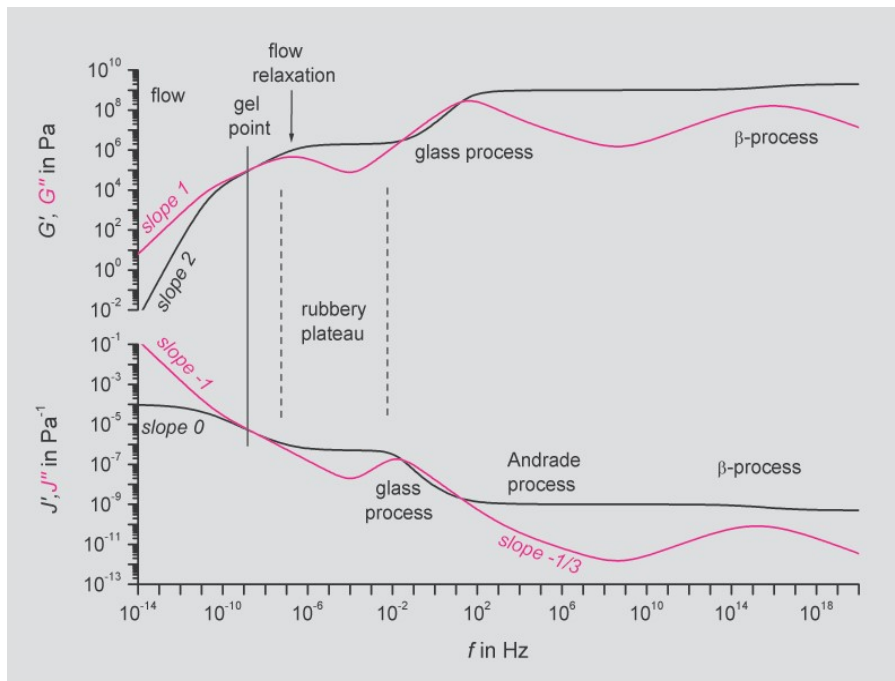


Fig. 3. Schematic curves of moduli and compliances for a viscoelastic material.

and  $G''$  increase with frequency and  $J'$  and  $J''$  decrease. There then follows the region of flow relaxation and the rubbery plateau in which  $G'$  and  $J'$  are almost constant. A large step in the storage part is characteristic for the main relaxation region. In the transition region, the loss components exhibit peaks. At higher frequencies, secondary relaxation ( $\beta$ -relaxation) occurs. The resulting steps in  $G'$  and  $J'$  and peaks in  $G''$  and  $J''$  are then relatively broad. A number of different relaxation processes occur over

the entire frequency range. The frequency corresponds to the characteristic length of the molecular rearrangement considered. The greater the frequency, the smaller is the characteristic length. With secondary relaxation, the characteristic length is about 0.5 nm, whereas at the main relaxation (maximum of  $G''$ ) it is about 2.5 nm and at the corresponding maximum of  $J''$  about 5 nm. The  $\beta$ -relaxation observed in polymers is often attributed to the side chains. With

polymers that do not have movable side chains, it is interpreted as a conformational variation or fluctuation. The nature of these relaxation effects cannot however be reduced to polymer specific processes because it is also observed in low molecular weight glass formers.

Figure 4 displays the modulus of unvulcanized styrene-butadiene rubber (SBR) at  $-10^\circ\text{C}$ . The individual effects are discussed in the following sections.

### Behavior in the glassy state

We begin the discussion of the mechanical behavior at high frequencies. In Figure 4, the storage modulus,  $G'$ , is almost constant above  $10^5$  Hz and the loss modulus is orders of magnitude (decades) less than  $G'$ . The frequency of the mechanical stress fluctuation is much greater than the characteristic frequency of the liquid-specific cooperative rearrangements. This means that these molecular processes, which are the origin of the liquid properties, are not activated. The material behaves just like an elastic solid. As shown in Figure 3, secondary or  $\beta$ -relaxation occurs. With SBR, this process lies outside the actual range measured. At frequencies below the  $\beta$ -relaxation, the Andrade process is often observed. Here the frequency dependence of  $J''$  is described by an exponential law, namely  $J'' \propto \omega^{-1/3}$ . The loss compliance has a slope of  $-1/3$  in the log-log presentation. With SBR, this region can be seen between  $10^5$  and  $10^8$  Hz (see Fig. 5).

### The glass process

The relaxation region in which the storage modulus changes by several orders of magnitude is the glass transition (the main relaxation or  $\alpha$ -relaxation). This relaxation process is measured when the measuring frequency lies in the frequency range of the cooperative rearrangements. If the frequency is lowered still further, the material loses its solid-state properties. With SBR (Fig. 4),  $G'$  changes from about  $10^9$  Pa to  $10^6$  Pa with decreasing frequency. The maximum of the corresponding  $G''$  peak is at a frequency of  $3 \cdot 10^2$  Hz at  $-10^\circ\text{C}$ . The compliance shows analogous behavior except that  $J'$  increases with decreasing frequency (Fig. 5). The maximum of the  $J''$  peak is at  $10^{-1}$  Hz (Fig. 5). Characteristic



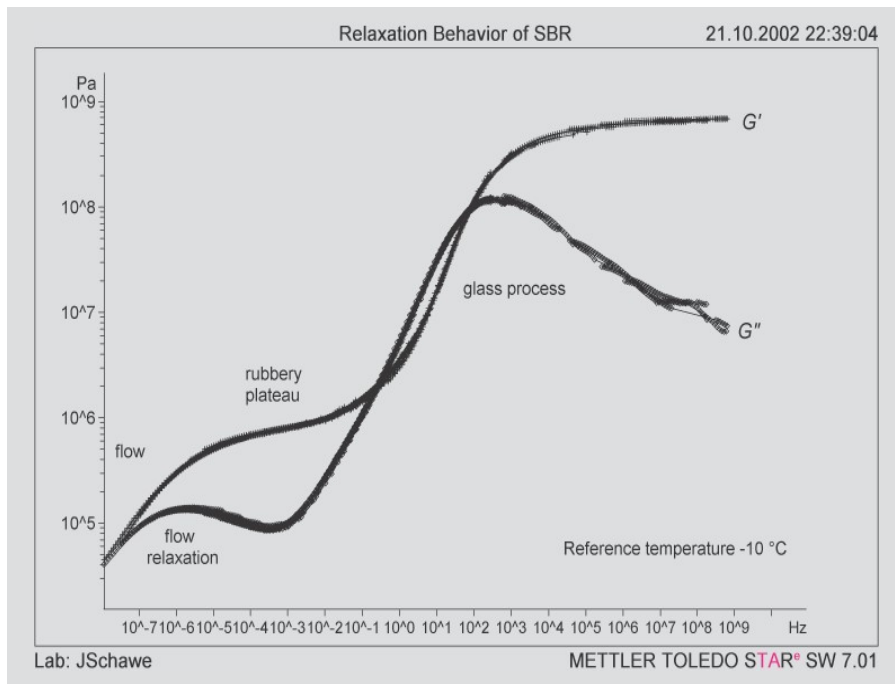


Fig. 4. Storage and loss modulus of SBR at -10 °C.

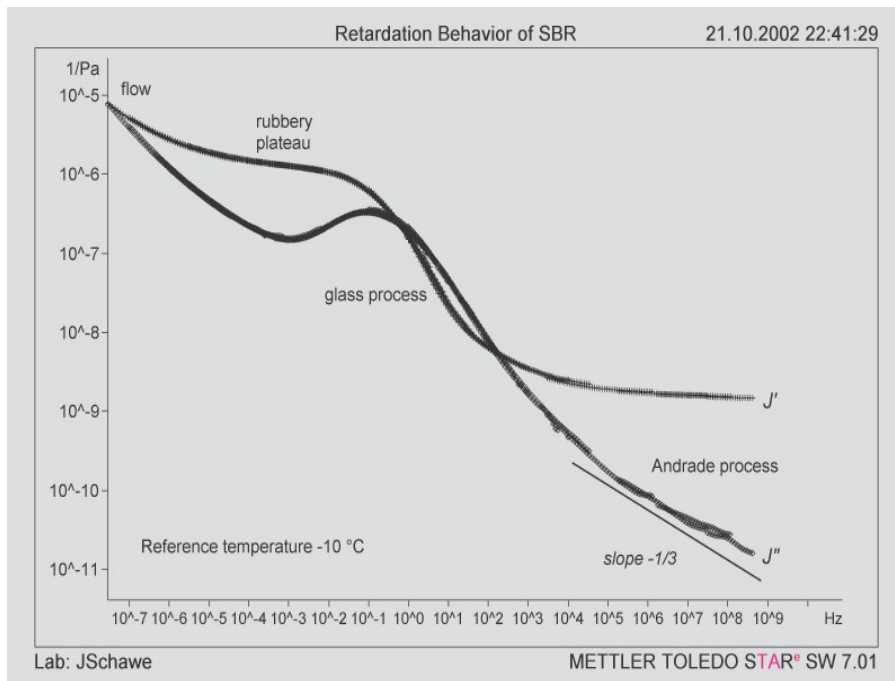


Fig. 5. Storage and loss compliance of SBR at -10 °C.

quantities of the cooperative rearrangements are the relaxation time,  $\tau_G$ , and the retardation time,  $\tau_j$ . At the maximum of the loss peak  $\omega\tau \approx 1$ . The retardation time of SBR at -10 °C is therefore given by the equation  $\tau_j = 1/(2\pi \cdot 10^{-1})$  s, i.e. 1.6 s. Since the relaxation region is measured at higher frequencies in the modulus, the relaxation time,  $\tau_G$ , is  $5.3 \cdot 10^{-4}$  s.

If one considers the simplest possible process for retardation, namely the Debye process (which describes a retardation process with just one single retardation time), then the following equation applies

$$J^*(\omega) = J_0 + \frac{J_\infty - J_0}{1 + i\omega\tau_j} \quad (4)$$

Here  $J_0$  and  $J_\infty$  are the limiting values of

the compliance at low and high frequencies. The relationship between the retardation and relaxation time is then given by the equations  $\tau_G = \tau_j (\log J_0 - \log J_\infty)$  and  $\tau_j = \tau_G (\log G_\infty - \log G_0)$ . The logarithmic distance,  $\log \Delta f$ , between the maxima of the  $J''$  and  $G''$  peaks can then be estimated to be 3.0 (see Fig. 2). The experimental result (3.5) shows that this simple estimate is also approximately valid for real processes. The relatively large distance between the  $J''$  and  $G''$  peaks therefore results from the large change in  $G'$  and  $J'$  at the glass transition.

The shape of the transition provides further information on the relaxation behavior. The curve shape of an isolated process is shown in Figure 6 using  $J''$  as an example. In the log-log presentation, the Debye process has two linear limiting tangents with slopes of 1 and -1. The width at half height of the peak is 1.14 frequency decades. Real processes show appreciably broader peaks - due to molecular interaction there is not just one retardation time but a wide spectrum of times. This results in a broader  $J''$  peak with the slopes of  $\alpha$  and  $-\alpha\gamma$ , where  $0 < \alpha \leq 1$  and  $0 < \alpha\gamma \leq 1$ . The quantities  $\alpha$  and  $\gamma$  are known as Havriliak-Negami (HN) parameters and describe the width of the relaxation transition.

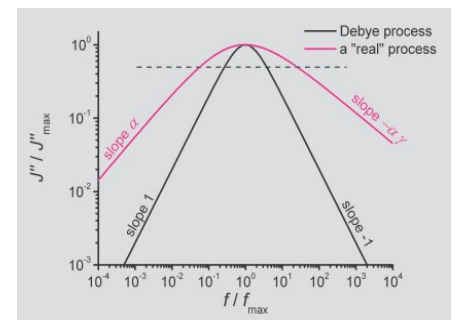


Fig. 6. Curve shape of the loss compliance in the retardation region in log-log presentation. The dashed line marks half the peak height.

The location and width of the relaxation transitions are very sensitive to changes in physical and chemical structure (e.g. to crystallization and changes in the polymer chain), and to fillers, plasticizers and composition in the case of polymer blends or copolymers. Some examples are illustrated in Figure 7.

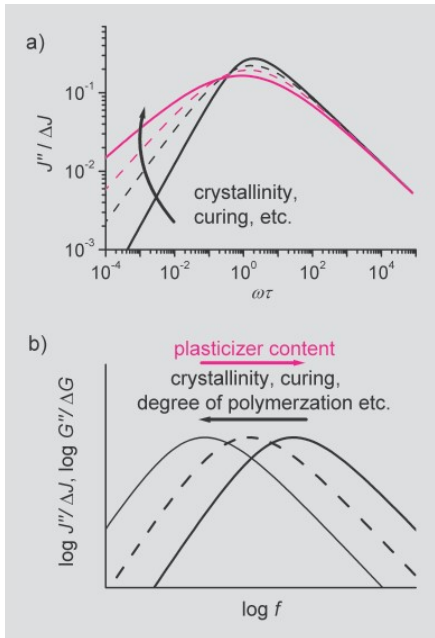


Fig. 7. Schematic curves of different factors that influence the glass process: a) influence of curve shape; b) shift of the frequency position (the arrow indicates the direction of increase of the corresponding quantity).

### The rubbery plateau

Low molecular weight substances begin to flow on decreasing the frequency immediately after the glass transition. Polymers have a characteristic modulus,  $G_0$ , of about 1 Mpa in the rubbery plateau. The plateau is due to the entanglement of macromolecules to form a physical network. The

width of the plateau,  $\log \Delta f$ , depends on the molecular weight,  $M$ , where  $\log \Delta f \propto M^{3.4}$  (Fig. 8). In the plateau,  $G''$  is less than  $G'$ . In the middle of the plateau,  $G''$  has a minimum (Fig. 4). At the end of the plateau, flow relaxation can be seen on the  $G''$  peak (with SBR in Fig. 4 at  $10^{-6}$  Hz). This process cannot usually be seen directly in the compliance curve because it is overlaid by flow.

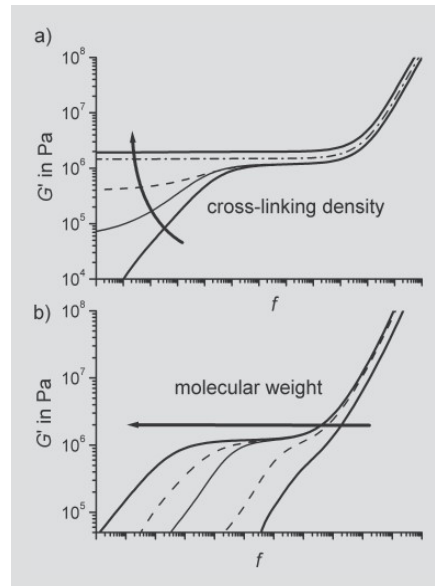


Fig. 8. Schematic curves showing the influence of the degree of cross-linking (a), and molecular weight (b) on the rubbery plateau (the arrow indicates the direction of increase of the corresponding quantity).

With cross-linked materials such as vulcanized elastomers, the plateau modulus,  $G_0$ , is proportional to the mean cross-linking density,  $\kappa$ , where  $\kappa \approx G_0/(2RT)$ . Flow relaxation can only be observed with very lightly cross-linked materials (Fig. 8).

### Viscous flow

At very low frequencies, uncross-linked polymers flow. In the ideal case, the power laws  $G' \propto \omega^2$  and  $G'' \propto \omega$  apply. Here the slopes of the modulus curves in log-log presentation are 2 for  $G'$  and 1 for  $G''$ . At the gel point, the  $G'$  and  $G''$  curves cross over one another.

### Conclusions

Knowledge of the frequency dependence of mechanical behavior is of great value for the practical application of materials and for material optimization. Information is obtained for material optimization because the frequencies at which the different processes occur correlate with the characteristic volumes of the corresponding molecular regions. At higher frequencies, smaller molecular regions are observed.

In comparison to temperature-dependent measurements, frequency-dependent measurements provide additional information about material properties in general and on molecular processes in particular.