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Determination of the Elastic Moduli of Polymer Films by a New Ultrasonic Reflection Method

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Summary: The development and first applications of a new ultrasonic reflection method for determination of the viscoelastic properties of polymer films are reported. The complex shear modulus G* and the complex longitudinal modulus $L^*=K^*+4/3\,G^*$ of the samples are derived from the measured complex reflection coefficients of an ultrasonic shear and longitudinal wave, respectively. From G and L the Young's modulus E, the compression modulus K and the Poisson ratio ν can be calculated for isotropic materials. A $LiNbO_3$-transducer (10° rotated Y-cut) is used for the simultaneous excitation of longitudinal and transversal ultrasonic waves, which allows to determine different elastic constants by one measurement. A measuring cell with normal incidence of the ultrasonic waves is used. The equipment has been applied to study the time dependence of the moduli during film formation from an aqueous polymer dispersion and the isothermal curing of an epoxy resin. Furthermore, the temperature dependence of the elastic constants of a carbon-black filled rubber and during non-isothermal crystallization of a semi-crystalline polymer has been studied.

Introduction

The relationship between the material properties of polymers and acoustic parameters have been studied for a long time.[1-3] When propagated in a polymeric material, longitudinal and shear acoustic waves are influenced by polymer's structures as well as by molecular relaxation processes.

Until now longitudinal wave and shear wave experiments are performed by different experimental setups. For the characterization of the mechanical properties of an isotropic polymeric material at least two elastic constants have to be measured. Therefore the combination of longitudinal and shear waves experiments in one setup, which yields two moduli simultaneously, is of practical interest for a fast characterization of the mechanical behavior of polymeric systems. Recently[4], we adapted a shear wave reflection technique described by Mason[5] as early as 1949 for measurements of the complex dynamic shear modulus $G^*=G'+iG''$, to the high frequency digital technique. With this equipment we were able to monitor time-dependent isothermal processes (e.g. film formation of paints or isothermal

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crystallization) in polymeric systems[6-10]. Furthermore, we performed temperature dependent studies of melting and crystallization of semi-crystalline polymers[8,9] and of the glass transition behavior of amorphous polymer films[8] using this method.
The aim of this work was to develop an apparatus capable of measuring both the complex shear modulus G^* and the complex longitudinal modulus $L^*=L'+iL''$ in viscoelastic polymer films. In the present work the principle of the method is described. As representative examples the isothermal film formation of a polymer dispersion, the temperature dependence of the moduli in carbon-black filled rubber, non-isothermal crystallization of a semi-crystalline polymer and isothermal epoxy curing are presented.

In any isotropic material the Young's modulus E, the compression modulus K and the Poisson ratio ν can be evaluated from the two measured moduli G' and L'. The moduli are related according to the following expressions.

$$E=\frac{3L-4G}{L/G-1}, \quad K=L-\tfrac{4}{3}G, \quad \nu=\frac{L/2-G}{L-G} \quad . \tag{1}$$

This yields the possibility of a full mechanical characterization of a isotropic material (not limited to polymers) by one combined experiment with simultaneous shear and longitudinal wave excitation.

Experimental technique

Principle and configuration

The experimental arrangement of the ultrasonic reflection method is shown in Fig. 1. A phase stable short needle pulse is generated by a commercial pulse generator plug-in card (SR9000, Matec Inc.) and applied to a $LiNbO_3$-transducer bonded to a glass rod (Schott F7). The typical length of the glass rod was 15 mm with a diameter of 20 mm. The transducer was used for both transmitting and receiving ultrasonic waves. A 10° rotated Y-cut was used for the transducer to generate both longitudinal waves of 8 MHz and shear waves of 5 MHz with only one transducer. To avoid damage to the input amplifier, the pulse generator plug-in card integrates a fast electronic switch which is used to connect the transducer first to the output of the pulse generator and then to the input amplifier also located on this plug-in card. A digitizing plug-in card (SR9010, Matec Inc.) was used for digitalization of the received signal with a sample rate of 100 MHz and the transfer into the PC. The received first longitudinal and first shear wave echoes are time separated due to their different ultrasonic velocities in the glass rod.

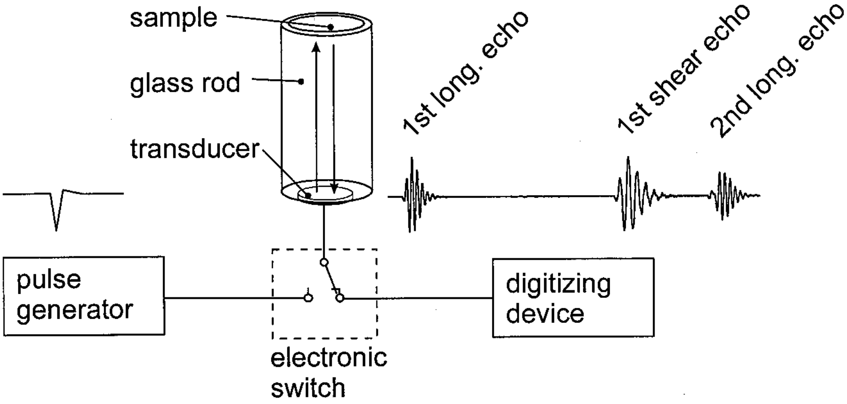

Figure 1. Basic measurement principle.

If the ultrasonic wave (normal incidence) is reflected off the interface between glass rod Q and sample media S, the complex reflection coefficient r^* is given by

$$r^* = r \cdot \exp(i\Delta\varphi) = \frac{Z_S^* - Z_Q}{Z_S^* + Z_Q}, \tag{2}$$

where Z_S^* and Z_Q are the complex acoustic impedances of the sample media and the glass rod. Note that there is no mode conversion between longitudinal and shear wave in the case of normal incidence. The complex reflection coefficient is $r^*=r\exp(i\Delta\varphi)$ with the absolute value $r=|r^*|$ and the phase shift $\Delta\varphi$. Because of the neglectable ultrasonic attenuation in the glass rod the acoustic impedance of the glass is considered to be a real number Z_Q. Under these assumptions one can derive from Eq. 2:

$$Z_S^* = Z_Q \frac{1 - r^2 + i2r\sin\Delta\varphi}{1 + r^2 + 2r\cos\Delta\varphi}. \tag{3}$$

Eq. 3 can be used for both the evaluation of the longitudinal and the shear impedance if the reflection coefficient r and the phase shift $\Delta\varphi$ is determined for both types of waves separately. The complex dynamic shear impedance $Z_{S,s}^*$ of the sample is related to the complex dynamic shear modulus G^* by:

$$Z_{S,s}^{*2} = (R_s + iX_s)^2 = \rho(G' + iG'') \ . \tag{4}$$

For the complex dynamic longitudinal impedance $Z^{*}_{s,l}$ and the complex dynamic longitudinal modulus *L** an analogous equation holds:

$$Z_{S,l}^{*2} = (R_l + iX_l)^2 = \rho(L' + iL'') \ . \tag{5}$$

The real and imaginary parts of the longitudinal and the shear modulus are given by:

$$G' = \frac{R_s^{\,2} - X_s^{\,2}}{\rho}, \quad G'' = \frac{2R_s X_s}{\rho}, \quad L' = \frac{R_l^{\,2} - X_l^{\,2}}{\rho} \quad \text{and} \quad L'' = \frac{2R_l X_l}{\rho} \ . \tag{6}$$

A special measurement program (C++ and assembler) was developed to determine r and $\Delta\varphi$ for the longitudinal and shear wave. From this values the corresponding moduli are calculated and visualized by the software. First, the digitized longitudinal and shear wave echoes in time domain (see Fig.1) are sought and cut-and-paste into separate waveforms. To avoid influences of the reflection on the upper surface of the sample, each echo is cut off after the first oscillation and the remaining part of the waveform is set to zero. Then the Fourier transformation is performed for each of those waveforms. From the real and imaginary part of the Fourier transform the amplitude and phase spectra are calculated. The reflection coefficients are then estimated using the actually measured amplitudes A and phases φ of the loaded cell and the previously stored amplitudes A_0 and phases φ_0 of the unloaded cell for both the longitudinal and shear wave echo:

$$r = \frac{A}{A_0}, \ \Delta\varphi = \varphi - \varphi_0 \ . \tag{7}$$

Using Eqs. 3-6, the corresponding longitudinal and shear modulus can then be calculated. Details of the procedure are described for the shear wave reflection technique in reference[4].

Measurement cell and temperature control

An example for a typical measurement cell is shown in Fig. 2. The glass rod is surrounded by a housing of stainless steel. The high frequency signal is applied to the left connector. The temperature of the cell is measured by a PT100 (right connector) in conjunction with a multimeter (Prema 5017) connected to the serial interface of the PC.

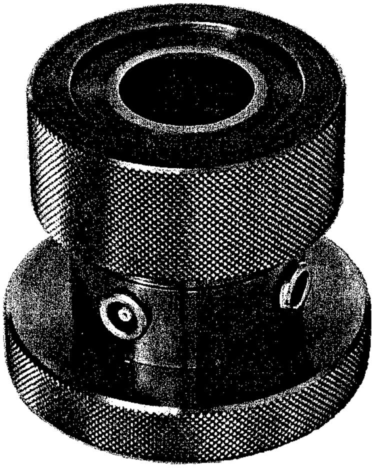

Figure 2. Measurement cell for concurrent longitudinal/shear wave measurements.

The temperature of the cell must be accurately stabilized. Therefore the measurements were performed in an aluminum container chosen large enough ($0.5*0.5*0.5\ m^3$) for evaporation experiments (for details see[4,6,10]). The temperature in the container was controlled in the range from 15 to 85°C with an accuracy of 0.01K using a liquid thermostat (Julabo F33). If necessary, the setpoint of the thermostat can be controlled by the PC using a serial connection.

Results

Isothermal measurement during film formation

The time evolution of the measured L' and G' values during the isothermal film formation of an aqueous acrylic dispersion with 18 w-% TiO_2 at 25°C is shown in Fig 3 together with the calculated values of E' and K'. The measurement was started with the unloaded cell which was already at the measurement temperature. The amplitude and phase values obtained without sample are necessary to calculate the reflection coefficient and the phase shift from Eq. (7).

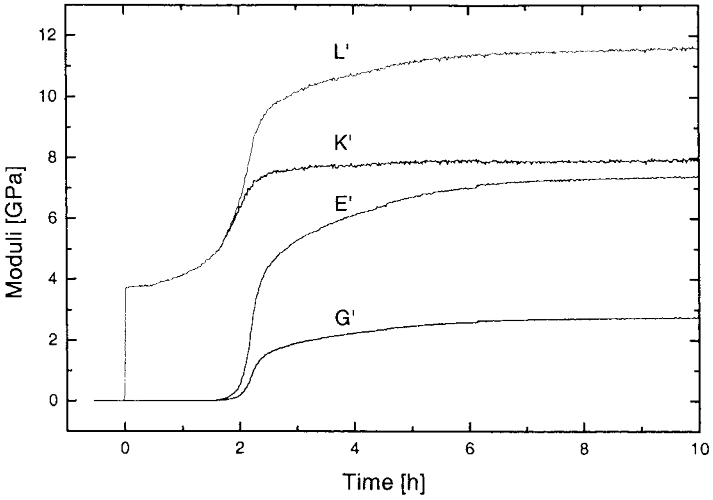

Figure 3. Time evolution of the ultrasonic moduli during the film formation of an acrylic dispersion with 18 w-% TiO_2.

At time t=0 the acrylic dispersion is applied to cell. The shear modulus of the acrylic dispersion is nearly zero because the aqueous polymer dispersion mainly consists of waver and can be considered as a liquid. The longitudinal modulus is therefore basically equal to the compressional modulus of the liquid, which has here a value in-between that of the compressional modulus of the water and that of the polymer. In the first phase of film formation the water evaporates and the compressional modulus increases due to the increasing polymer-to-water ratio in the aqueous dispersion, whereas the shear modulus remains nearly zero. In the second phase the polymer particles merge and form a film. Since the viscoelastic contribution of the polymer becomes dominant, the shear modulus increases considerably. After the film is almost free of water, all moduli remain constant.

Non-isothermal measurements during crystallization

The setup can also be used for non-isothermal measurements of the moduli. Since the delay time of the longitudinal and shear wave echo is strongly temperature dependent, it is necessary to perform a calibration measurement of the unloaded cell (without sample). The temperature dependent amplitudes and phases of the unloaded cell $A_0(T)$

and $\varphi_0(T)$ are recorded before the experiment and used for the calculation of the reflection coefficient r(T) and the phase shift $\Delta\varphi(T)$ with sample.

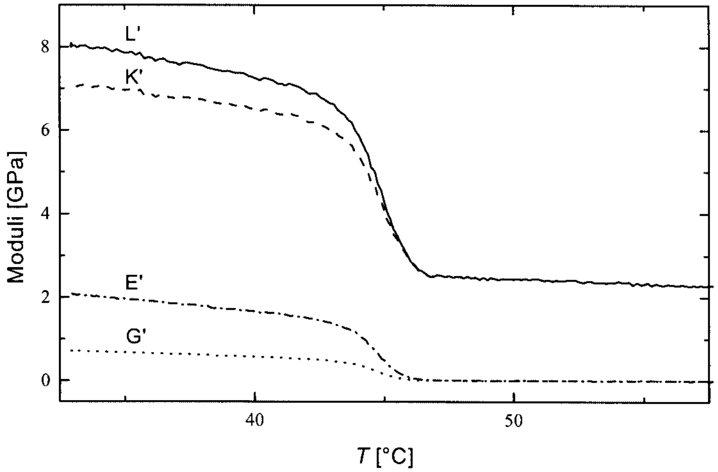

Figure 4. Temperature dependence of the moduli during cooling of polyethylene glycol with a cooling rate of 10 K/h.

Fig. 4 shows the temperature dependence of the moduli during the cooling of polyethylene glycol (PEG2000, Merck). The cooling rate was 10 K/h and the film thickness was 400 µm. The molecular weight of the PEG was M_w=1860 g/mol and M_n=1830 g/mol, measured by MALDI TOF. PEG is a semi-crystalline polymer. The equilibrium melting temperature is T_m^0=51.2°C. As temperature decreases, the PEG forms crystals which arrange to a supermolecular spherolitic structure. Since the stiffness of the crystalline phase exceeds that of the amorphous PEG considerably all moduli increase during the crystallization. The final degree of crystallization is φ=0.87 as determined by WAXS. A more detailed description of the ultrasonic properties during crystallization is given in[8,9]. For non-isothermal crystallization the crystal growth should be described by the Kolmogoroff[11] equation instead of the Avrami equation as described in references[8,9].

Temperature dependent measurements on elastomers

The third example is the temperature dependence of the moduli in a carbon black filled natural rubber material (carbon black content: 46 phr = 31.5 w-% , 18.7 v-%) in the glass transition region as shown in Fig. 5. This experiments are interesting since the polymeric materials with different phases are often not thermo-rheological simple. Therefore the time-temperature superposition principle[2] can not be applied and direct high frequency measurements are necessary to characterize the material (e.g. for testing of the wet-skid behavior of tires). During the measurement, the rubber is pressed to the measurement cell to ensure good acoustic contact. The main glass-to-rubber transition of the rubber matrix is indicated by a maximum in G'' and L'' and by a step in G' and L'. The glass transition temperature measured by DSC is -63°C, whereas the "dynamic" glass transition temperature determined here (maximum of G'' and L'') is about -10°C. This temperature shift is due to the much higher measurement frequency of the ultrasound compared to that of the DSC.

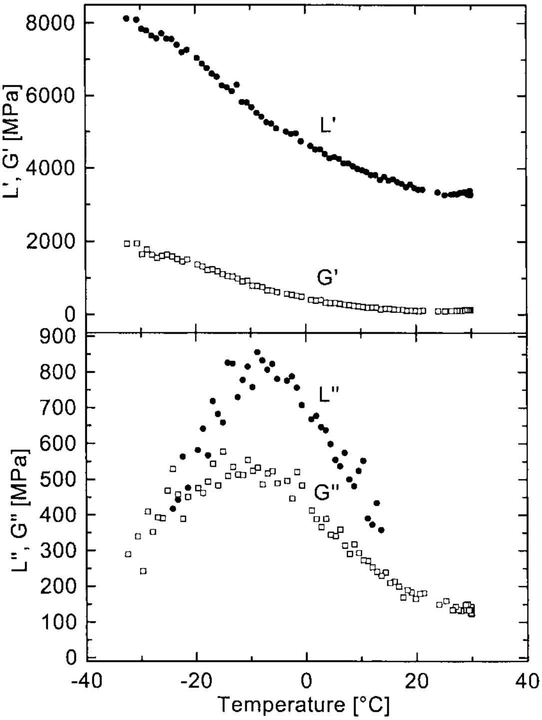

Figure 5. Longitudinal and shear modulus of a carbon black filled rubber sample.

Monitoring of an isothermal reaction

As a fourth example the time evolution of the shear modulus G' and the compressional modulus K' during the curing reaction of an epoxy resin is shown in Fig. 6. The system used was a diglycidyl ether bisphenol A/hexahydrophthalic anhydride/2,4-ethyl methyl imidazole mixture (mass ratio: 120g/100g/2.4g). The isothermal curing temperature was 70°C.

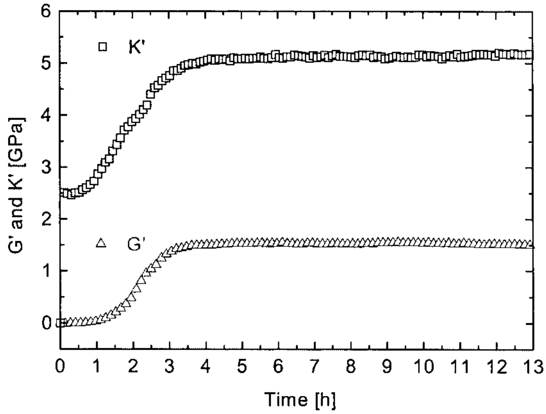

Figure 6. Time evolution of the moduli G' and K' during the curing reaction of an epoxy resin.

At time t=0 the preheated liquid mixture was applied to the cell. The glass transition temperature of the unreacted mixture is about –40°C. Therefore the sample is a liquid and the shear modulus G' is nearly zero. The longitudinal modulus at t=0 represents the compressional modulus of the mixture.

During the reaction, the glass transition temperature increases with conversion and finally reach a value about 15 K above the curing temperature of 70°C. The sample vitrifies during the reaction and the ultrasonic moduli increase accordingly. After 4 hours of reaction, the final values of the moduli are achieved. For a more detailed description of longitudinal wave experiments during isothermal curing see[12].

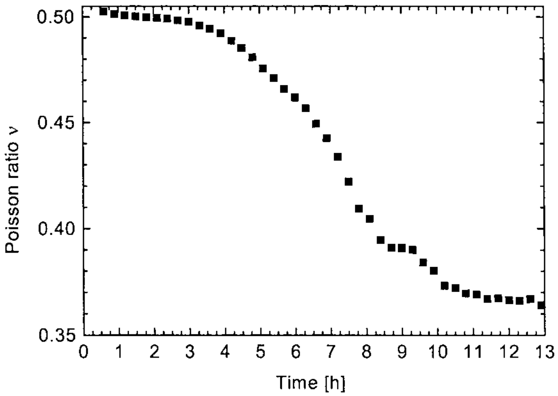

Figure 7. Poisson ratio during the curing reaction of an epoxy resin.

Using Eq. 1 it was possible to calculate the time evolution of the Poisson ratio during the curing reaction (Fig. 7). The Poisson ratio starts from a value of 0.5 (incompressible liquid) and decreases to a final value of 0.37 (cross-linked polymer network).

Conclusion

It has been shown that the newly developed combined longitudinal/shear wave reflection measurement method offers several new possibilities for the characterization of polymeric samples. Typical applications of the method are the measurement of the time evolution of the moduli during film formation from aqueous polymeric dispersions, isothermal polymerization (e.g. curing of epoxy resins), isothermal and non-isothermal crystallization, phase transitions in block-copolymers[13] or hardening of cements[14]. It is also possible to measure the temperature dependence of the moduli for a wide class of materials. Therefore the method may be considered as an "ultrasonic film rheometer".

Acknowledgement

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