무정형 고분자의 기계적 및 광응력적 성질

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Mechanical and Stress Optical Properties of Amorphous Polymers

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Introduction

Mechanical and stress-optical properties over the wide region of temperature and time for amorphous polymer play an important role in many polymer processes.

Read [1] and Osaki *et al.* [2] have attempted to describe the stress-optical behavior of polymer in the range of glass transition by using a modified stress-optical rule. Shimo *et al.*[3] and Isayev *et al.*[4] have obtained master curves of tensile relaxation modulus and strain-optical coefficient for PS and PC from stress relaxation test. However, only a few studies[5, 6] take into account shear relaxation modulus and stress-optical coefficient directly.

In the present study, frequency sweep test was conducted at various temperatures from melt to glassy region. In-house optical setups built in RAS 2 and RSA 3 were used to obtain mechanical and stress-optical behavior of several amorphous polymers used for optical components. Construction of master curves from each data was attempted with the method of reduced variables.

Experiment

Fig. 1 shows the schematic diagram of the experimental set-up for the measurement of shear modulus and stress-optical coefficient using optical trains for polarization-modulation polarimetry, built around a conventional dynamic mechanical system, the Rheometrics Solid Analyser RSA 2. Similar setup was used for RSA 3. The only difference was the Photo-elastic modulator(PEM) instead of Electro-optical modulator(EOM). Optical setup was composed of a Helium-Neon laser, two quarter-wave plates, two polarizers and a optical detector. The lock-in amplifier was used to do FFT.[5]

Under specified oscillatory shear $\gamma(t)=\gamma_0\sin(\omega t)$ if γ_0 is sufficiently small, storage and loss moduli of the material can be described as follows.

$$\sigma_{12}(t) = \gamma_0(G' \sin \omega t + G'' \cos \omega t) \quad (1)$$

Since the strain was set to be sufficiently small that linear viscoelastic behavior holds good over a wide range of frequency. Using the experimental arrangements described above we could measure the refractive index tensor (***n***) in 1-2 plane when a laser beam hit a specimen perpendicularly on 1-2 plane. The components of refractive index tensor with respect to the shear direction can be written as

$$n_{12} = \frac{1}{2} \Delta n_{12} \sin(2\chi) \quad (2)$$

$$n_{11} - n_{22} = \Delta n_{12} \cos(2\chi) \quad (3)$$

Note that extinction angle, χ, is almost $\pi/4$ in our shear experiment.
The behavior of n_{12} during small-amplitude dynamic shear is similar to that of shear stresses.

$$n_{12} = \gamma_0(B' \sin \omega t + B'' \cos \omega t) \quad (4)$$

where B is the strain-optical coefficient.
Then, stress-optical coefficient can be evaluated as follows.

$$C(w) = \Delta n_{12} \sin(2\chi)/(2\sigma_{12}) \quad (5)$$

where δ is phase difference between birefringence n_{12} and shear stress σ_{12}.

$$\Delta n^* / \Delta\sigma^* \equiv C' - iC'' = |C| \cos(\delta) - i|C| \sin(\delta) \quad (6)$$

Results and discussion

Many commercial resins were used in experiments to investigate stress-optical behavior across the glass transition regime. Three sets of data are presented in this manuscript. More data will be shown in the presentation. We have measured complex modulus, stress-optical coefficient and strain-optical coefficient at various temperatures simultaneously. With the results obtained from glassy tool and melt device, construction of master curves have been attempted using the shift factors at each temperature based on a reference temperature.

Polystyrene (DOW Styron 615)

Fig 2 presents the master curves of complex shear modulus and complex stress-optical coefficient of Styron 615. It may be noted that the method of reduced variables based on thermo-rheological simplicity is used to construct one smooth curve of complex modulus in the whole region. Plazek reported that the time-temperature superposition principle sometimes fails in the glass-to-rubber transition region. However, notwithstanding small discrepancies in master curves, we have attempted to construct one single master curve of shear modulus and stress-optical coefficient, respectively.

As shown in Fig. 2(a), the complex shear modulus shows a typical behavior in the whole region from melt to glassy zone. In the high frequency, the storage modulus(G') is almost constant 8.5×10^9 *Pa* and in the low frequency region we can observe the terminal behavior. In contrast, the storage stress-optical coefficient(C') in the low frequency region is negative and very large compared with its magnitude in high frequency region. As frequency increases, storage stress-optical coefficient becomes positive. The stress-optical coefficients in the melt and glassy region are $4.8 \times 10^{-9} Pa^{-1}$ and $8.2 \times 10^{-12} Pa^{-1}$, respectively.

Polycarbonate (GE Lexan 141)

Fig. 3 shows that master curves of complex shear modulus and complex stress-optical coefficient of Lexan 141. As presented in Fig 3(a), mechanical behavior of polycarbonate obtained in experiment shows typical behavior corresponding to glassy, rubbery and glassy-to-rubbery regimes. The obtained shear modulus and stress-optical coefficient in the high frequency region approach a constant values of $6.5 \times 10^{9} Pa$ and $8.0 \times 10^{-11} Pa^{-1}$, respectively. The stress-optical coefficient in the low frequency range is almost constant, $2.3 \times 10^{-9} Pa^{-1}$. It may be noted that the sign of stress-optical coefficient over the whole frequency region is always positive. In particular, it may be mentioned that the magnitude of stress-optical coefficient in the glassy region is one order higher than that of the other polymers.

Zeonex E48R

Figure 4 shows master curves of complex shear modulus and stress-optical coefficient of Zeonex E48R. As shown in Fig. 4(b), the storage stress-optical coefficient in wide frequency range is much smaller than polycarbonate. These phenomena can also be explained by the low polarizability in the composition. The storage stress-optical coefficients in the melt and glassy region are, respectively, $1.0 \times 10^{-9} Pa^{-1}$ and $6.5 \times 10^{-12} Pa^{-1}$, respectively. This is the reason why industry prefers Zeonex E48R in manufacturing precision optical products.

References

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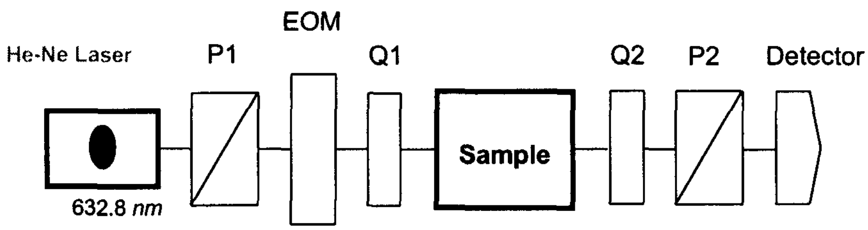


Figure 1. Schematic diagram of the experimental setup for measurement of stress-optical behavior.

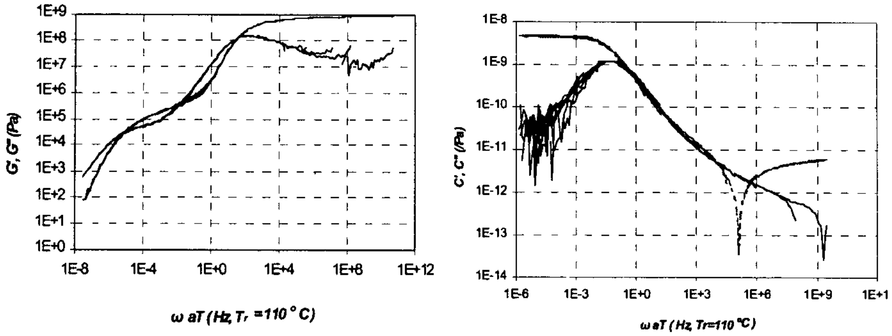
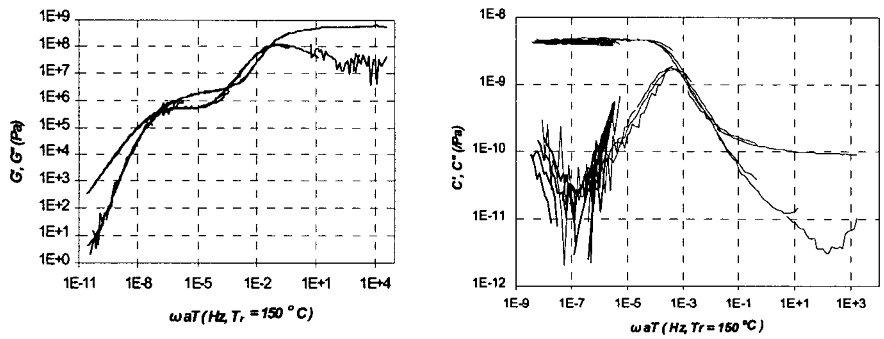
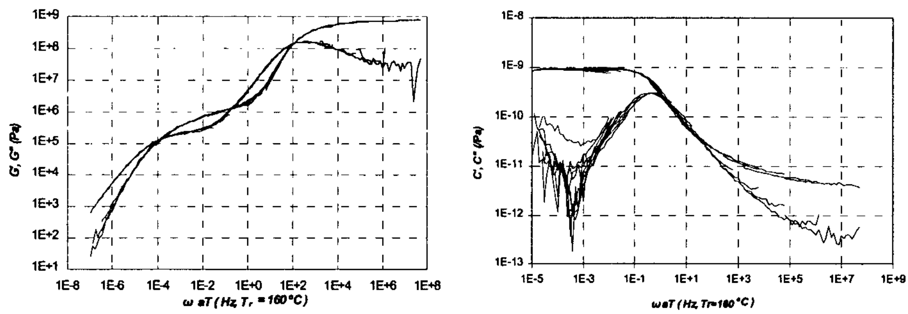


Figure 2. Master curves of (a) complex shear modulus and (b) complex stress-optical coefficient of Styron 615.



(a) (b)

Figure 3. Master curves of (a) complex shear modulus and (b) complex stress-optical coefficient of Lexan141.



(a) (b)

Figure 4. Master curves of (a) complex shear modulus and (b) complex stress-optical coefficient of Zeonex E48R.