Viscoelasticity and birefringence of bisphenol A polycarbonate

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The dynamic Young's modulus, E^*, and birefringence of bisphenol A polycarbonate were measured over the glassy to rubbery plateau zone. Measurements were performed over the frequency range of 1 to 130 Hz at various temperatures between 148 and 170°C. A modified stress-optical rule was applied in characteristic analysis of the glassy and glass transition regions. It was earlier proposed to replace the stress-optical rule which, generally, was valid only at relatively low frequencies corresponding to rubbery plateau and rubbery flow regions. E^* could be separated into two component functions, E_R^* and E_G^*. The stress-optical coefficients,C_R and C_G, associated with the respective components were 5.0×10^{-9} and 3.5×10^{-11} Pa^{-1}. In constructing master curves of E_R^* and E_G^* with the method of reduced variables, an unlike temperature dependence was found. This result could account for the breakdown of the time–temperature superposition principle for E^* reported by several investigators.

(Keywords: bisphenol A polycarbonate; stress-optical rule; birefringence; dynamic mechanical properties; glass transition)

INTRODUCTION

When one applies stress to polymeric materials, the phenomenon of optical birefringence can be observed. Birefringence measurements have been used to study the viscoelasticity of polymers[1–4]. In the viscoelastic region ranging from the low modulus end of the glass transition to the completion of the flow zone, a linear relation between applied stress and observed birefringence was revealed for amorphous polymers[4]. The phenomenon is also the case for concentrated solutions[4]. As a consequence, a general rule was evolved between applied stress and resulting birefringence. This is the so-called stress-optical rule:

$$\boldsymbol{n}(t) = C\boldsymbol{\sigma}(t) \tag{1}$$

where $\boldsymbol{\sigma}(t)$ is the deviatoric Cauchy stress tensor and $\boldsymbol{n}(t)$ is the deviatoric refractive index tensor. The coefficient C is the stress-optical coefficient, believed to be a characteristic material constant of each polymer. Therefore stress measurement can be replaced by birefringence measurement when the former is difficult as for some polymer melts.

There have been many reports on dynamic birefringence measurements since the birefringence technique was applied to the dynamic deformation of polyethylene in 1961[5]. But in the glass transition zone the stress-optical rule was not valid and it could not be used in a simple way[6]. Modifications of the stress-optical rule in the transition region were made by Read[7], Priss *et al.*[8] and the present authors[9].

In these modified rules the modulus is assumed to be composed of two components representing rubbery and glassy states. The stress-optical rule is supposed to work separately for the stress derived from each component, resulting in the following equations:

$$E(t) = E_R(t) + E_G(t) \tag{2}$$

$$O(t) = C_R E_R(t) + C_G E_G(t) \tag{3}$$

where $E(t)$ is the Young's relaxation modulus, $O(t)$ is the strain-optical coefficient, and $E_R(t)$ and $E_G(t)$ are component modulus functions. C_R and C_G are the associated stress-optical coefficients. The modification proposed by the present authors[9] differs from earlier ones[7,8] in the definition of the coefficients: the stress-optical coefficient for polymer melts is assigned to C_R; the ratio $O''(\omega)/E''(\omega)$ of the dynamic measurement at high frequencies is assigned to C_G (see discussion following equations (6)–(9)). The coefficient was confirmed to be independent of ω at high frequencies for polystyrene. The merit of this modification over the earlier ones was discussed elsewhere[9–11].

In previous studies[9–11], we applied the modified stress-optical rule to polystyrene to investigate the details of the relaxation mechanism in the glass-to-rubber transition region. We have been able to relate C_R and C_G of various polymers to their molecular structures and to determine quantitatively their contribution to the mechanical response of the polymer in that region.

In this study, we measured the dynamic birefringence and Young's modulus of bisphenol A polycarbonate in the region over the rubbery plateau to the glassy state using the modified stress-optical rule. Consequently, the behaviour at temperatures above and below the glass transition is discussed.

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EXPERIMENTAL

Sample

A bisphenol A polycarbonate, poly(oxycarbonyloxy-1-phenylene isopropylidene-1,4-phenylene), was investigated. It was supplied by Idemitsu Petrochemical Co., Ltd. The molecular weights determined with light scattering and gel permeation chromatography are $M_w = 1.6 \times 10^5$ and $M_n = 8.0 \times 10^4$. The pellet was dissolved in dichloromethane with desired concentration of about 5%. Subsequently, the film was cast through evaporation of the solvent over a hot plate. The film was dried for a few days in a vacuum oven at 120°C prior to measurements.

Measurements

The mechanical and birefringence measurements were performed simultaneously with an oscillatory rheometer (Rheospectoler DVE 3, Rheology Co., Ltd, Kyoto, Japan) and an optical system attached to the rheometer. The optical system was simply composed of a helium–neon gas laser, two polarizing films, a compensator and an optical detector. The response signal from the optical detector was analysed with a lock-in amplifier. Details of the optical apparatus and data acquisition system for dynamic birefringence measurements have been reported previously[9–11].

The measurement was performed with dynamic tension mode at isothermal conditions for 10 temperatures from 170°C down to 148°C. The frequency was scanned over the range from 1 to 130 Hz at each temperature. The measured stress and birefringence were represented by the complex Young's modulus

$$E^*(\omega) = E'(\omega) + iE''(\omega) \qquad (4)$$

and the complex strain-optical coefficient

$$O^*(\omega) = O'(\omega) + iO''(\omega) \qquad (5)$$

These are complex ratios of the stress to the strain and of the birefringence to the strain, respectively. In equation (5), O' is the in-phase strain-optical coefficient and O'' is the out-of-phase strain-optical coefficient.

RESULTS AND DISCUSSION

Young's modulus and strain-optical coefficient

The complex Young's moduli of polycarbonate, measured at temperatures from 170°C down to 148°C near the glass transition temperature, are presented in *Figures 1* and *2*. As seen in *Figure 1*, the dynamic Young's modulus E' shows extensive change with frequency in the middle of the temperature range investigated but at the lower temperature bound of 148°C (or 150°C) and the upper bound of 170°C shows gradual variation with frequency, resulting in little frequency dependence. At 148 and 150°C, E' is of the order of 10^9 Pa, corresponding to the value of modulus in the glassy state of many polymers. At 170°C, the highest temperature investigated, E' is of the order of 10^7 Pa over the frequencies. Compared with the E'' values at the same temperatures in *Figure 2*, E' is larger by a factor of about five. These features in the range of 148 to 170°C are typical characteristics of the glass-to-rubber transition of amorphous polymers[12].

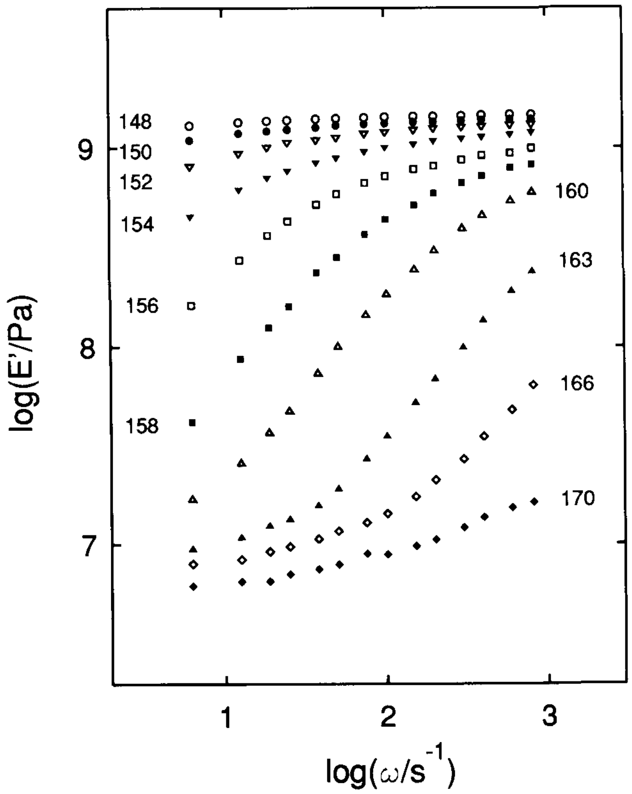

Figure 1 Frequency dependence of storage Young's modulus at 10 temperatures (numbers in figure are temperatures in °C)

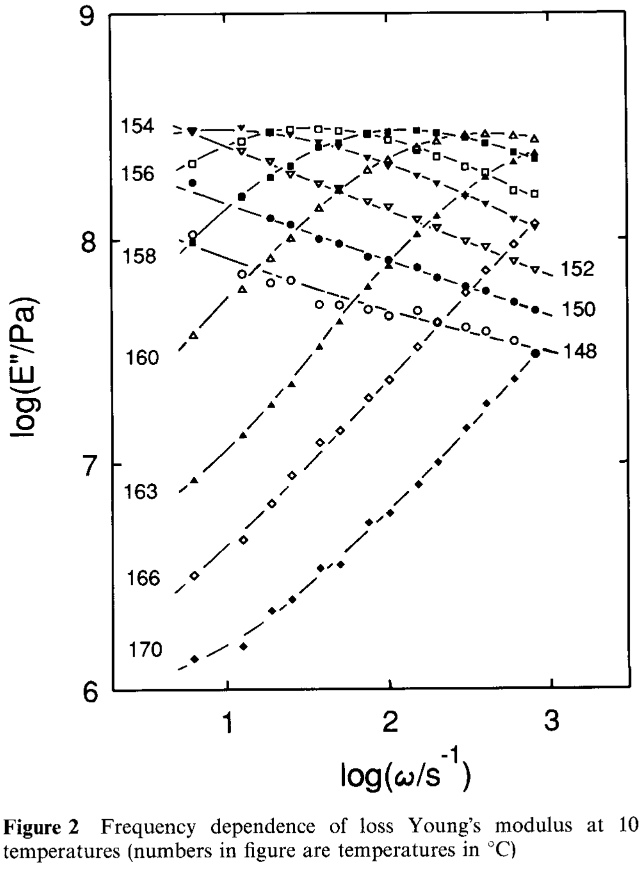

Figure 2 Frequency dependence of loss Young's modulus at 10 temperatures (numbers in figure are temperatures in °C)

In *Figure 2*, E'' increases with increasing frequency at high temperatures and decreases with increasing frequency at low temperatures. At intermediate temperatures of 158 and 156°C, maxima are detected. The features of E' and E'' at 170°C may be a sign of the onset of the rubbery plateau.

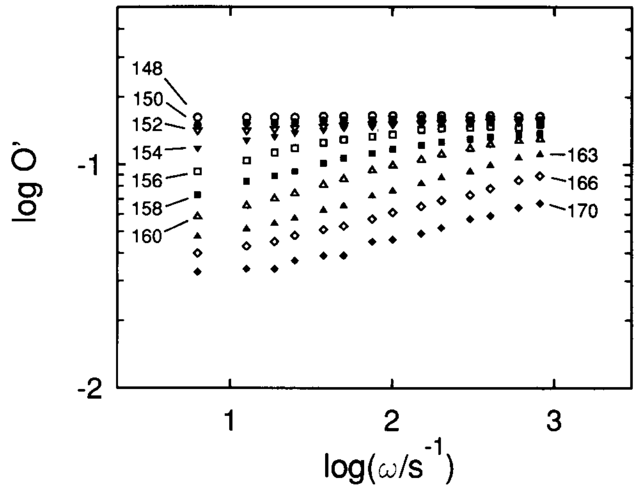

Figure 3 Frequency dependence of in-phase strain-optical coefficient at 10 temperatures (numbers in figure are temperatures in °C)

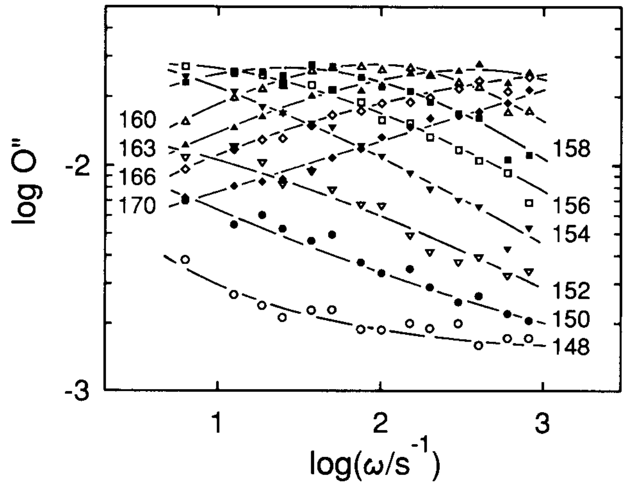

Figure 4 Frequency dependence of out-of-phase strain-optical coefficient at 10 temperatures (numbers in figure are temperatures in °C)

The real and the imaginary parts, O' and O'', of the strain-optical coefficients are shown in *Figures 3* and *4*, respectively. The shapes of the O' curves in *Figure 3* are similar to those of the E' curves in *Figure 2*. O' increases monotonically with increasing frequency or with decreasing temperature, the frequency dependence becoming more gradual with decreasing temperature. At temperatures below 152°C, the flat features of E' in *Figure 1* and O' in *Figure 3* are almost the same at each temperature.

Master curves of E* *and* O*

In order to characterize the dynamic behaviour of polymers, the modulus measured in a limited frequency or temperature range is usually extended over a wide reduced frequency range with the time–temperature superposition principle[12]. There are, however, many reports stating that careful attention is needed to apply the time–temperature superposition principle in the transition zone owing to the existence of different relaxation mechanisms[12–14]. Also the strain-optical coefficient may not be amenable to time–temperature superposition near the glass-to-rubber transition because of the complex properties of birefringence[4]. Despite these problems, which will be revealed later to be not insignificant for polycarbonate, we have constructed master curves with time–temperature superposition to allow us to speculate on the behaviour at various temperatures.

Master plots of E^* and O^* are presented in *Figures 5* and *6*, respectively. Constructions were made by the horizontal scaling of log–log plots from the experimental data to give visually coherent continuity. The reference temperature used for both plots was 160°C. The reduced frequency was extended over around nine decades in the reduced scale. In both cases of E^* and O^* the superposition principle can be applied as a fair approximation. Only for E^* in the lowest frequency range in *Figure 5* and for O^* in the highest frequency range in *Figure 6* do scattering of the data appear due to the lower accuracy of the measurements. For the case of dynamic E', the curve varies sigmoidally, with an increase of about 10^2 around the glass transition zone. Compared with the associated E^*, O^* changes in a simpler manner. Variations in properties are obtuse and only of the order of 10 over the whole range of reduced frequency. Therefore, O^* seems to be less sensitive to stimulation or deformation for this polymer than does the complex

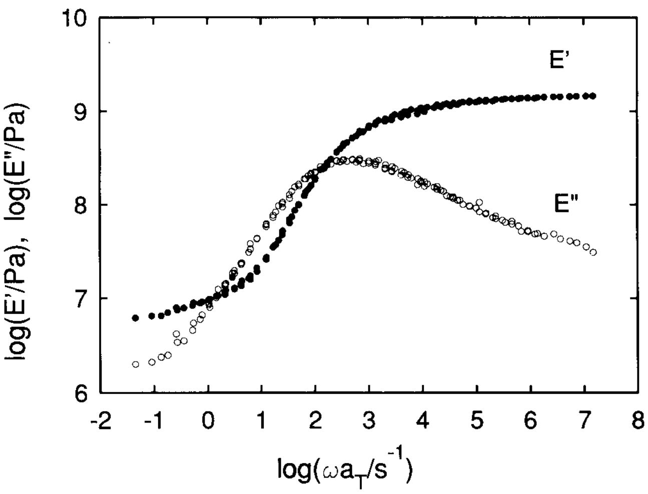

Figure 5 Master curves of complex Young's modulus built with time–temperature superposition principle, $T_r = 160°C$

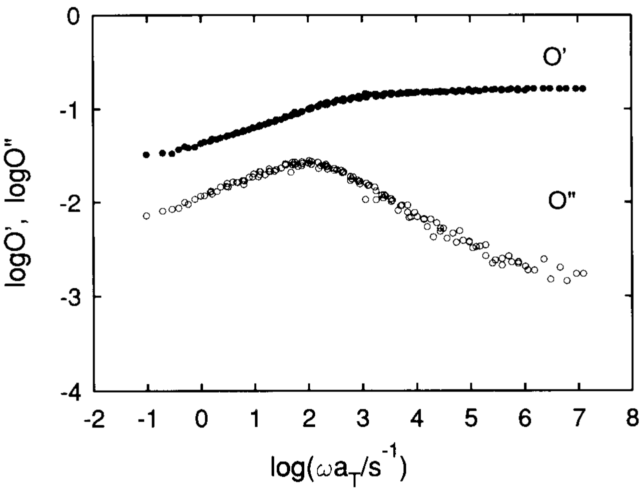

Figure 6 Master curves of complex strain-optical coefficient built with time–temperature superposition principle, $T_r = 160°C$

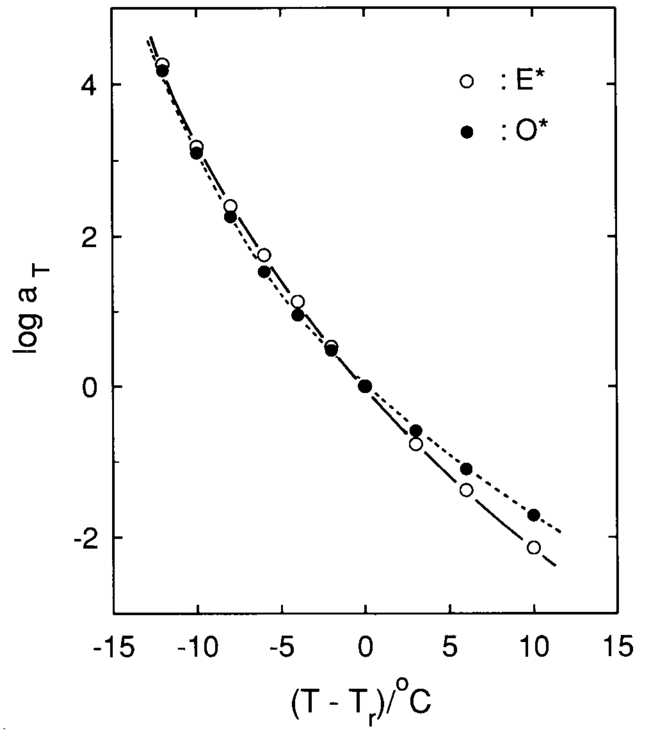

Figure 7 Temperature dependence of shift factors of complex Young's modulus and complex strain-optical coefficient, $T_r = 160°C$

Young's modulus E^*. In contrast with the shapes of the E' and O' curves, the variations of E'' and O'' are convex to the abscissa and involve maxima. The maximum in E'' is at a higher frequency than that in O''. At higher frequencies, both E'' and O'' have a tendency to decrease with the same slope.

Values of the shift factors, obtained in constructing the master curves shown in *Figures 5* and *6*, are plotted *versus* temperature in *Figure 7*. The temperature dependence of a_T for O^* is slightly different from that of E^*, the latter showing a somewhat larger variation than the former. This propensity is in fact similar to that previously reported for polystyrene[9] and may imply the failure of the time–temperature superposition of E^* or O^* in a rigorous sense.

Modification of stress-optical rule

In order to describe the behaviour of modulus and birefringence in the glass and in the glass-to-rubber transition zones, we have proposed the modified stress-optical rule, equations (2) and (3). The equations for dynamic quantities can be written as follows:

$$E' = E'_R + E'_G \qquad (6)$$

$$O' = C_R E'_R + C_G E'_G \qquad (7)$$

$$E'' = E''_R + E''_G \qquad (8)$$

$$O'' = C_R E''_R + C_G E''_G \qquad (9)$$

where E'_R and E'_G are the real parts of the complex modulus functions E_R^* and E_G^*, respectively, and E''_R and E''_G are the imaginary parts. The subscript G represents the glassy state and R denotes the rubbery state; the notations imply that the dispersion of the R component occurs at lower frequencies than that of the G component, C_R and C_G, assumed to be independent of frequency and temperature, are the associated stress-optical coefficients in the rubbery and glassy states, respectively.

From the definition, we may initially assume that the role of $E_R^*(=E'_R+iE''_R)$ is relatively small compared with that of $E_G^*(=E'_G+iE''_G)$ at high frequencies. The transposable notion may be possible at low frequencies. Noting that the real part of the complex modulus is an increasing function of frequency and the imaginary part is a function vanishing at both ends of high and low frequencies, we conjecture that the strain-optical coefficient O'' should be approximated by $C_G E''_G$ in the glassy region and O' by $C_R E'_R$ in the rubbery plateau region.

As seen earlier, the feature of E^* at 170°C, which accords with the end of the lower frequency region in *Figure 5*, was considered as the onset of the rubbery plateau. Accordingly, by comparing E^* with O^* at the end of the lower frequency region in *Figures 5* and *6*, one can ascertain that O' and O'' are proportional to E' and E'' with the same constant of proportionality. We can obtain that constant, the stress-optical coefficient C_R, by consideration of E^* and O^* at 170 and 166°C. The approximate value of C_R for the investigated polycarbonate is $5.0 \times 10^9\ \mathrm{Pa}^{-1}$, which is in fair agreement with the stress-optical coefficient for the melt quoted in the literature[15]. Comparing the glassy region in *Figures 5* and *6*, we obtain $C_G = 3.5 \times 10^{-11}\ \mathrm{Pa}^{-1}$ from comparison of E'' and O''.

With C_R and C_G determined, the component functions E'_R, E''_R, E'_G and E''_G can be obtained by solving the equations of the modified stress-optical rule as a set of linear simultaneous equations. In order to confirm the procedure of evaluating the coefficients, O^* is compared with $C_R E^*$ at a high temperature (*Figure 8*) and with $C_G E^*$ at low temperatures (*Figure 9*). Evidently, $O' \approx C_R E'$ at 170°C and $O'' \approx C_G E''$ at low temperatures.

Master curves of E_R^* *and* E_G^*

The modified stress-optical rule was applied to the set of data obtained at each temperature. The method of reduced variables was again used to draw master curves of complex functions, E_R^* and E_G^*, taking 160°C as the reference temperature. However, this operation could not be made for E_R^* at low temperatures (148, 150 and 152°C) because of the negligible E''_R (≈ 0).

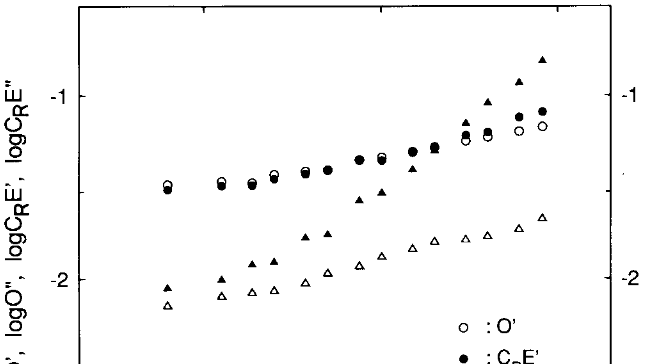

Figure 8 Comparison of strain-optical coefficients and main terms of the equation for modified stress-optical rule, $C_R E^*$, at 170°C, corresponding to onset of rubbery plateau zone

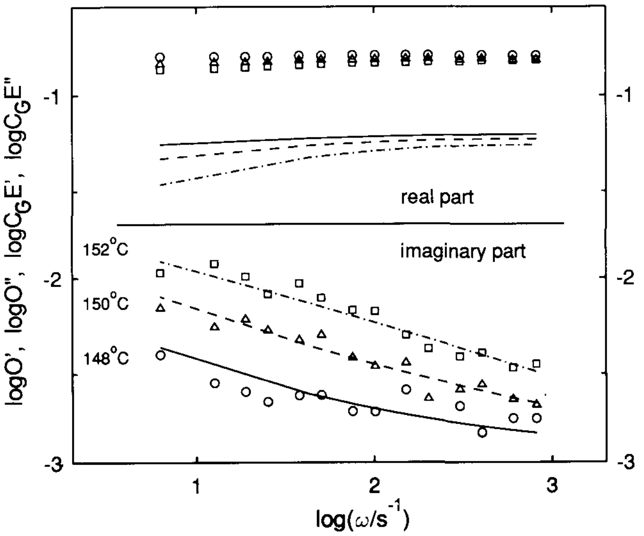

Figure 9 Comparison of strain-optical coefficients and main terms of the equation for modified stress-optical rule, $C_G E^*$, at 148, 150 and 152°C, corresponding to glassy zone

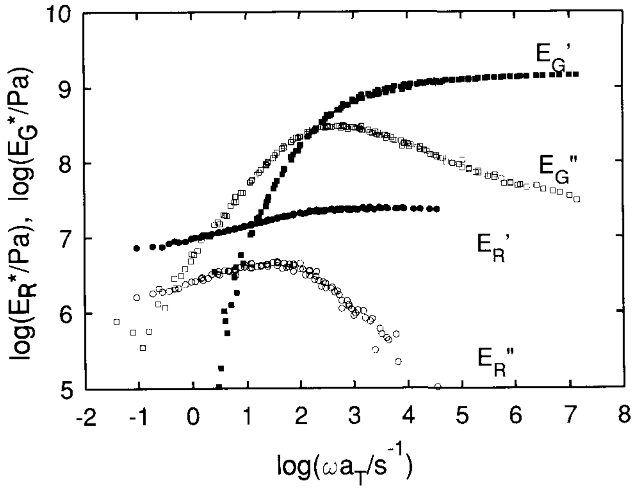

Figure 10 Master curves of separated constituent modulus functions, E_R^* and E_G^*. Time–temperature superposition principle was applied; $T_r = 160$°C

As shown in *Figure 10*, the time–temperature superposition principle works well for the two separated functions. The real parts, E'_R and E'_G, increase with increasing frequency and level off. The imaginary parts, E''_R and E''_G, increase with frequency, pass through maxima and fall. The frequency corresponding to the maximum of E''_R is lower than that of E''_G by a factor of about eight. The characteristic values of these functions are shown in *Table 1*. In the table, $E'_{R\infty}$ and $E'_{G\infty}$ are the dynamic moduli at the higher end of the reduced frequency in *Figure 10*.

From the curves displayed in *Figure 10*, the contributions of the glassy and rubbery components to the mechanical properties are phenomenologically obvious. In the low frequency region, corresponding to the rubbery plateau, glassy functions increase markedly with increasing frequency and decreasing temperature. In contrast, variations of the rubbery functions are piecemeal. That is, the contribution of glassy components to the mechanical properties rises notably over the whole range of the glass transition zone.

With translation to the high frequency region, the two real parts of the functions level off and the temperature and frequency dependence become insignificant. Ultimately, we can discern that the contribution of the rubbery component to the glassy modulus is about 1.6%. Although there are insufficient data for definite conclusions about the rubbery plateau, it can be recognized that the contribution of the glassy mode to physical properties can be discounted in the low frequency region. Hence we can conclude that E_R^* is the dominant component in the region from the lower end of the glass-to-rubber transition to the rubbery plateau, assigned to long time relaxations. Conversely, with decreasing temperatures, the function E_G^* comes to mainly control the physical properties.

We have observed that E_G^* can be reduced to a function independent of polymer species if the frequency scale is suitably chosen[16]: only E_R^* exhibits slight variation with polymer species[16]. We have also seen that the complex Young's modulus E^*, resulting from addition of E_R^* and E_G^*, shows almost the same behaviour, scarcely dependent on polymer species. In contrast, the variation of birefringence with frequency in this study is dissimilar to that found for polystyrene[9]. This indicates that the main factor causing the variation of birefringence is the different values of C_R and C_G.

For the purpose of determining the temperature dependence of the separated composite functions E_R^* and E_G^*, the shift factors a_{TR} and a_{TG} respectively are plotted against temperature in *Figure 11*. The difference in

Table 1 Characteristic values of E_R^* and E_G^*

$E'_{R\infty}$(Pa)	$E'_{G\infty}$(Pa)	$E''_{R\max}$(Pa)	$E''_{G\max}$(Pa)	$E'_{R\infty}/E'_{G\infty}$
2.3×10^7	1.4×10^9	4.3×10^6	3.0×10^8	0.0164

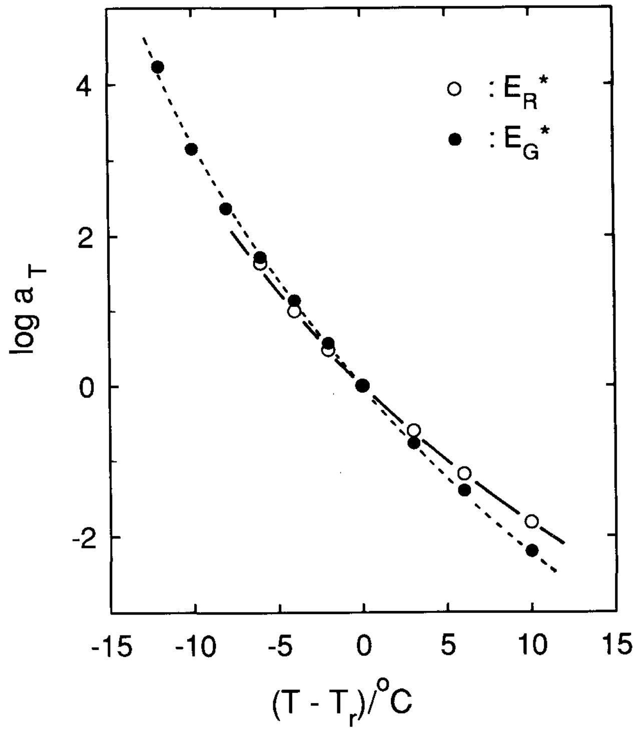

Figure 11 Temperature dependence of shift factors of separated constituent modulus functions, E_R^* and E_G^*; $T_r = 160$°C

temperature dependence is obvious, that of a_{TG} being larger than that of a_{TR}. It is worth noting that the shift factor a_T for O^* in *Figure 7* agrees with a_{TR} at high temperatures and with a_{TG} at low temperatures. Many reports of the breakdown of the time–temperature superposition principle in the transition region have been made[12–14]. The results of the present study confirm the fact that the operation of the time–temperature superposition principle in the transition region is unattainable because of the overriding effect of different relaxation mechanisms.

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