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DYNAMIC VISCOELASTIC PROPERTIES AND ENTANGLEMENT SPACING OF A NEWLY DEVELOPED AMORPHOUS POLYOLEFIN

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ABSTRACT

Dynamic viscoelastic properties of a newly developed amorphous polyolefin which contains five-membered rings in the main chain were measured by means of a plate-plate-type rheometer. The frequency dependence curves of the storage modulus G' and of the loss modulus G'' at various temperatures can be superposed onto master curves by a horizontal shift along the frequency axis. The shift factor follows the WLF equation. The average molecular weight between entanglement loci of this amorphous polyolefin can be roughly estimated at 5100 from the minimum value in $\tan \delta$ and the pseudoequilibrium modulus of the entanglement network.

INTRODUCTION

Polycarbonates (PC) and polymethyl methacrylate (PMMA) are currently used for optical and electronic devices. However, these polymers have some faults such as insufficient heat resistance and relatively high water absorbability. An amorphous polyolefin, Zeonex, has been newly developed for use in these devices, eliminating the above faults of PC and PMMA. The characteristics of this amorphous polyolefin are noncrystallinity, high transparency and low birefringence. The glass transition temperature of the amorphous polyolefin is $\sim 140^\circ\text{C}$, which is almost congruent with that of PC but is significantly higher than that of PMMA [1–3].

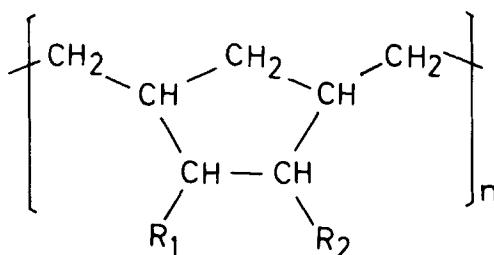


FIG. 1. Chemical formulae of the amorphous polyolefin. R1 and R2 are hydrocarbon substituents.

The chemical formula of the amorphous polyolefin has not been reported in detail. Figure 1 shows the chemical structure of the main chain of the amorphous polyolefin as reported by the developer [3]. The amorphous polyolefin contains five-membered rings in the main chain and does not contain any polar groups. It is expected that the amorphous polyolefin can be applied not only to optical and electronic devices but also to other high technological uses. In order to achieve this, it is important to determine the processability or workability of the polymer, and it is expected that the molecular structure and the basic rheological properties will then be clarified in detail.

In the present paper, I discuss the dynamic viscoelastic properties and the entanglement spacing of the amorphous polyolefin.

EXPERIMENTAL

Polymer samples Z430 and Z250 were purchased from Nihon Zeon Co. Ltd. The specific refractive index increment, dn/dc , in toluene was measured by means of a differential refractometer ($\lambda = 633$ nm, Chromatix KMX16). The weight-average molecular weight was measured with a low-angle laser light-scattering photometer (LLALS, $\lambda = 633$ nm, Chromatix KMX6). The scattering angle was $\sim 5^\circ$. Figure 2(a) shows the relationship between $\Delta n (= n - n_0)$ and the polymer concentration c , where n and n_0 are the refractive indices of the polymer solution and the solvent. The value of dn/dc can be obtained as the slope of the straight line as $0.0454 \text{ mL} \cdot \text{g}^{-1}$ at 25°C . Thus, the small value of dn/dc is likely to be ascribed to the similarity of the chemical components between the polymer and the solvent. In Fig. 2(b), Kc/R_θ is plotted against the polymer concentration for samples Z430 and Z250. Here, K is the optical constant, and R_θ is the excess Rayleigh ratio given by $R_{\theta s} - R_{\theta 0}$, where $R_{\theta s}$ and $R_{\theta 0}$ are, respectively, the Rayleigh ratios of the polymer solution and the solvent. The weight-average molecular weight, M_w , obtained as a reciprocal value of the intercept of the ordinate, is shown with the number-average molecular weight, M_n , in Table 1.

The rheological properties were measured in the temperature range $160\text{--}225^\circ\text{C}$ by using a plate-plate-type rheometer (Rheometrics mechanical spectrometer, Model

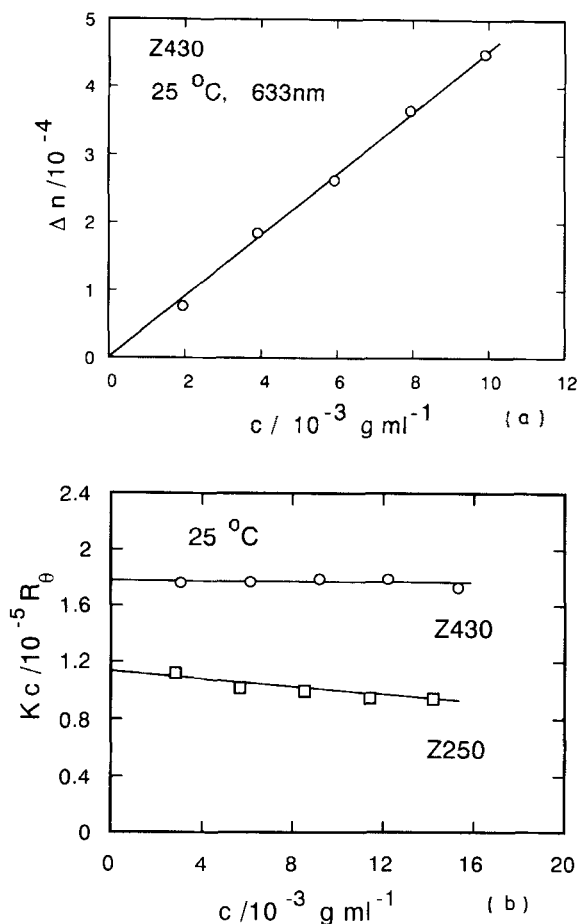


FIG. 2. (a) Difference in the refractive indices Δn plotted against polymer concentration c . (b) Kc/R_{θ} plotted against c .

605) with a plate diameter of 2.5 cm. The angular frequency ranged from 0.01 to 100 sec^{-1} , and the strain amplitude was less than 0.1, at which all the systems showed linear viscoelasticity. By returning to the measurement at 160°C after the measurement at 225°C, it was confirmed that the polymer samples were thermally stable during the rheological measurements.

RESULTS AND DISCUSSION

Dynamic Viscoelasticity

Figure 3 shows the storage modulus G' and loss modulus G'' plotted against angular frequency ω for Z250 at various temperatures from 160 to 225°C. The

TABLE 1. Characteristics of the Sample Polymers

Sample	$M_n \times 10^4$	$M_w \times 10^4$	M_w/M_n^a	$dn/dc, \text{mL} \cdot \text{g}^{-1}$
Z430	2.45	5.56	2.27	0.0454
Z250	4.17	9.71	2.33	—

^aData from GPC-LLALS.

system shows a transition from a glassy state to a rubbery state at 160°C and shows a flow region at 225°C. This is typical behavior of amorphous polymers with a relatively high molecular weight. The frequency dependence curves of G' and G'' at various temperatures can be superposed onto master curves by a horizontal shift along the frequency axis. That is, the time-temperature superposition principle can be applied [4]. Figure 4 shows the master curves of G' and G'' for Z250 and Z430 at the reference temperature of 160°C. G' and G'' can be superposed by a common shift factor a_s . The master curves represent the frequency dependence at a constant temperature, which can cover a relatively wide frequency range. In a low frequency region, G' and G'' decrease sharply with decreasing frequency. That is, the systems are almost in the flow region. In the intermediate frequency region, G' and G'' show the rubbery plateau region where they become relatively flat. In the higher frequency region, we can observe the beginning of the glass transition region, where G' and G'' are approximately proportional to $\omega^{1/2}$. In this region the frequency dependence of G' and G'' seems to be independent of the molecular weight, as shown in other amorphous polymers such as polystyrene and polymethyl methacrylate [5, 6]. This is quite reasonable in the glassy state, because the main chain

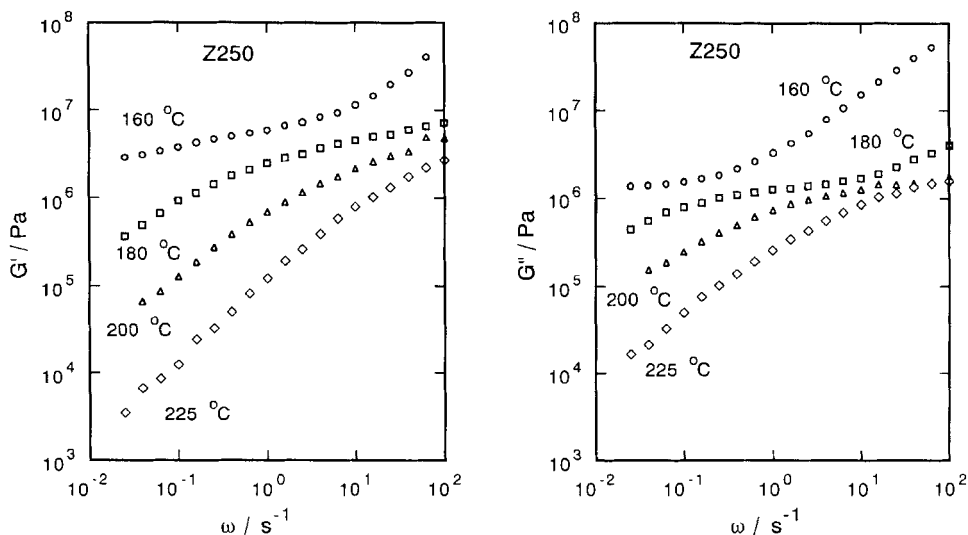


FIG. 3. Storage modulus G' and loss modulus G'' plotted against angular frequency ω for Z250 at various temperatures.

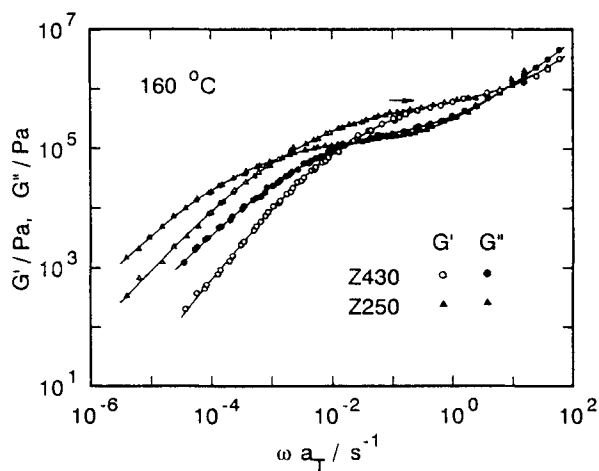


FIG. 4. Master curves of G' and G'' for Z250 and Z430 at the reference temperature 160°C .

backbone is almost immobilized and only the local motion of the side chain is allowed.

The shift factor a_T employed for the time-temperature superposition follows the WLF equation [4]

$$\log a_T = \frac{-c_1(T - T_0)}{c_2 + (T - T_0)} \quad (1)$$

where c_1 and c_2 are constants, and T_0 is a reference temperature. As shown in Fig. 5, the plot of $-(T - T_0)/\log a_T$ vs $(T - T_0)$ can be represented by straight lines

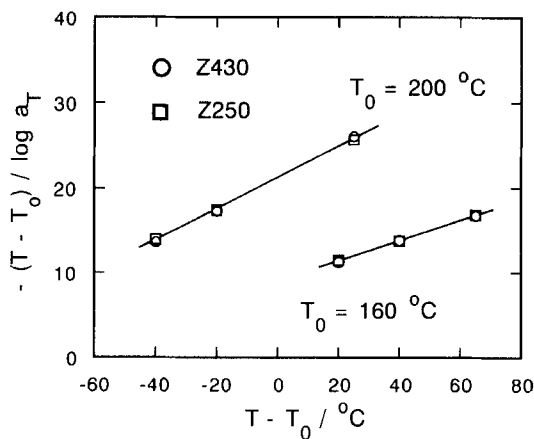


FIG. 5. $-(T - T_0)/\log a_T$ plotted against $(T - T_0)$ for $T_0 = 160$ and 200°C .

for the two choice of $T_0 = 160$ and 200°C . The values of c_1 and c_2 can be calculated from the slope s and the intercept i as $c_1 = 1/s$ and $c_2 = i/s$. The resultant values are $c_1 = 8.33$, $c_2 = 75.0$ for $T_0 = 160^\circ\text{C}$ and $c_1 = 5.36$, $c_2 = 113.6$ for $T_0 = 200^\circ\text{C}$ for both systems Z250 and Z430. The Vogel temperature T_V , given by $T_0 - c_2$, is obtained as 85.0°C for $T_0 = 160^\circ\text{C}$ and 86.4°C for $T_0 = 200^\circ\text{C}$. The Vogel temperature is usually $\sim 50^\circ\text{C}$ below the glass transition temperature T_g , i.e., T_g is calculated as $\sim 136^\circ\text{C}$, which is approximately equal to the value measured by means of DSC, 140°C [2, 3].

Entanglement Spacing

There are several methods of estimating the average molecular weight between entanglement loci, M_e [3]. However, it is difficult to obtain the precise value of M_e for polymers with a broad distribution of molecular weight. According to the Marvin-Oser theory [7, 8] and Graessley [9], the minimum in $\tan \delta$ ($= G''/G'$) is closely related to M_e by

$$\tan \delta_{\min} = 1.04 \left(\frac{M}{\alpha M_e} \right)^{-0.80} \quad (2)$$

Here α is given by M_c/M_e , where M_c is the critical molecular weight at which zero-shear viscosity sharply increases by entanglement coupling (e.g., with the 3.4 power of the molecular weight). Although the relation between M_c and M_e is not simple, they are approximately related as $M_c = 2M_e$ [4]. Usually, M in Eq. (2) can be approximately replaced by M_n [3, 9]. Figure 6 shows $\tan \delta$ plotted against $\log \omega$ for Z250 and Z430. The minimum values of $\tan \delta$ are 0.352 and 0.500 for Z250

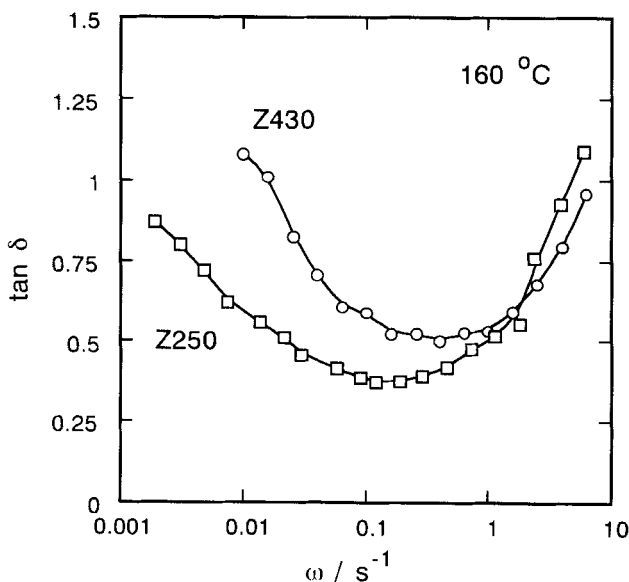


FIG. 6. Loss tangent $\tan \delta$ plotted against $\log \omega$ for Z250 and Z430 at 160°C .

and Z430, respectively. Using $\alpha = 2$, the average value of M_e for both systems as calculated from Eq. (2) is ~ 5100 .

The value of M_e can also be estimated from the pseudoequilibrium modulus G_N of the entanglement network according to the equation

$$G_N = \rho RT/M_e \quad (3)$$

Here ρ is the density of the system and R is the gas constant. However, it is difficult to accurately determine the value of G_N for polymers having a broad distribution of molecular weight, in which G' decreases progressively in the rubbery plateau region. From the frequency dependence curve of G' for Z250 in Fig. 4, the value of G_N can be roughly estimated at $6.2\text{--}6.5 \times 10^5$ Pa, which is near an inflection point of the curve of $\log G'$ vs $\log \omega$ as shown by an arrow. Using $\rho = 1.01$ and Eq. (3) [3], M_e can be calculated as 5200–5500, which is close to the value estimated from $\tan \delta_{\min}$.

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