Volume Retardation of Polystyrene

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ABSTRACT: Isothermal volume retardation and shear-creep compliance are measured over a wide temperature range including the glass-transition region, the upper limit T_g^+ to the lower limit T_g^- . The equilibrium volume V_2 at the temperature below T_g^+ is estimated from amount of vertical shift necessary for composing isotherms plotted in V vs. $\log t$ into a master curve (V , volume of the polymer; t , time). In the vicinity of T_g^+ , the temperature dependence of V_2 estimated as above agrees with that in the rubbery state. In the temperature range below T_g^- , however, the dependence differs from it. It is shown that horizontal shift factors of the volume retardation obtained in T_g^+ to T_g^- show a temperature dependence described fairly well by the WLF equation. The equation fits data on shear-creep compliance measured in the rubbery state. It is indicated that the rate of the volume retardation is represented as $\theta(T) \cdot \chi(V - V_2)$ where χ and θ are functions of temperature and $V - V_2$, respectively.

Anomalous isotherms which have a maximum, were studied experimentally. This phenomenon is qualitatively explained by an assumption of a wide distribution of retardation times. A position of the maximum is also interpreted in terms of a retardation time.

KEY WORDS Polystyrene/Volume Retardation/Equilibrium Volume/
Shift Factor/WLF Equation/Anomalous Isotherm/

The volume of a glassy substance undergoes an isothermal contraction or dilation accompanied by a retardation. This characteristic phenomenon, especially for organic polymers, has been studied extensively by numbers of investigators.²⁻⁹ Much progress has been made in explaining the phenomenon. However, there are still problems to be studied; for example, distribution of retardation times, relation of free volume to the distribution of retardation times, and equilibrium volume at a temperature far below glass transition temperature.^{9,14}

In the present paper,¹ we report data on contraction isotherms and shear-creep compliances of polystyrene which were measured as a function of temperature, including the glass transition point of the polymer. The time-temperature relation on the volume retardation was studied and then compared with that on the shear-creep compliance. Temperature dependence of the equilibrium volume of the polymer was also studied in a temperature range below the glass-transition point. It is shown that time-temperature reducibility² may be assumed for the

volume retardation in the temperature range from the glass-transition point to 60 degrees below it. In the glass-transition region, equilibrium volume is still located on the extrapolation from that in the rubbery state. Temperature dependence of horizontal shift factors for superposition of the isotherms is fairly well explained in terms of the WLF equation.¹⁰ The equation was adapted to fit the data on shear-creep compliance measured in the rubbery state. Both temperature dependences of equilibrium volume and horizontal shift factor varied at around a temperature corresponding to the lower limit of the glass-transition region. The basis for our time-temperature reducibility on the volume retardation was clarified experimentally. Furthermore, anomalous isotherms* were studied for which the volume of the polymer goes through a maximum with time toward normal value. We believe that those isotherms may be an indication of some features which are rem-

* Such isotherms have been reported by Kovacs.² Systematic analysis, however, has not been attempted as yet.

inherent of wide distribution of the retardation times.

EXPERIMENTAL DETAILS AND RESULTS

Specimens

Specimens were prepared by heating pelletized polystyrene at 150°C for one hour in vacuum and then molding it into a small rod at about 200°C in vacuum. Mitsubishi Dialex HF-66 was used as the starting material, the molecular weight of which is in the order of 5×10^4 to 10^5 . Thermal expansion of the polymer was measured while temperature was being decreased at a rate of about 1 degree per minute. The glass transition region was determined by this dilatometry¹¹; the upper limit of that T_g^+ is about 97°C and the lower limit T_g^- is about 73°C. These results are presented in Figure 1.

Figure 1. Thermal expansion and equilibrium volume of polystyrene. Open circles present the thermal expansion measured. The upper limit of the glass-transition region T_g^+ ; 97°C. The lower limit of that T_g^- ; 73°C. These are determined from the intersections between lines A, B, and C, as described in reference 11. Equilibrium volumes estimated from amounts of vertical shifts are normalized with respect to the value at 97.5°C.

Retardative Volume Change

A mercury-dilatometer which consists of a bulb capacity of 10 cm³ and capillary diameter of 0.06 cm was used for measurements of volume change. Throughout measurements of the isotherm, the specimen was equilibrated at a temperature T_1 , 115°C, in an oil bath before

Figure 2. Isotherms of volume retardation for polystyrene obtained after quenching from 115°C to various temperatures. The temperatures are shown alongside isotherms.

each quenching. After that the dilatometer was transferred immediately from the bath to another bath maintained at a temperature T_2 . Results are shown in Figure 2. Small scattering of the data in Figure 2 is due mainly to a small fluctuation in temperature caused from switching of the heater and/or change of room temperature.

The contraction isotherms were measured at twelve temperature points ranging from 97.5°C to 38°C. Among these, the isotherms at 97.5 and 95°C alone reached the respective equilibrium values during the observation times.

When the specimen before reaching the equilibrium at T_2 was heated to T_3 , which is lower than T_g^+ , and allowed to make a retardation at T_3 , its volume goes through a maximum toward contraction.² The isotherms obtained under such experimental conditions will be called hereafter "Anomalous isotherms". Three different conditions distinctive in their character were set up: (1) 115°C → 80°C → 88°C where T_2 and T_3 are higher than T_g^- . (2) 115°C → 61°C → 75°C where only T_3 is higher than T_g^- . (3)

Figure 3. Anomalous volume retardation for polystyrene at 88°C. Each of these isotherms is obtained under a quenching condition; the polymer has been maintained at 80°C during time z after being quenched from 115°C to that temperature and then heated up to 88°C. Each z is shown alongside the isotherm.

Figure 4. Anomalous volume retardation for polystyrene at 75°C. Each of these isotherms is obtained under a similar quenching condition to that for the isotherms shown in Figure 3 varied in temperature combination; 115°C → 61°C → 75°C.

Figure 5. Anomalous volume retardation for polystyrene at 61°C. Each of these isotherms is obtained under a similar quenching condition to that for the isotherms shown in Figure 3 varied in temperature combination; 115°C → 42°C → 61°C.

115°C → 42°C → 61°C where both T_2 and T_3 are lower than T_g^- . Under these three conditions, a series of experiments was performed, in which the periods z for the retardation at T_2 were varied. The results are shown in Figures 3, 4, and 5.

Shear-Creep Compliance

Torsional creep tests were made with an arrangement almost similar to that described by Iwayanagi.¹² A differential transformer was used for detecting the torsion angle precisely and change in the angle was automatically recorded. The specimen was immersed in a silicone oil within a bath with electric heaters and a coiled tube for cooling water. Before each measurement at a temperature below 120°C, the specimen was annealed at 120°C. After that the temperature of the specimen was cooled. Throughout all measurements, a rod-shaped specimen 0.6 cm in diameter and 4 cm in effective length was used for the measurements at temperatures below 120°C. In the temperature range above 120°C, torsion force necessary for measurement is so small that it becomes difficult to apply the differential transformer to detect the torsion angle. In order to avoid this

Figure 6. Shear creep compliance (cm^2/dyn) of polystyrene against logarithmic time. Specimen is brought to each temperature after being annealed at 120°C . Cooling rate for passing glass transition region is kept at $2^\circ\text{C}/\text{min}$.

difficulty, a rod-shaped specimen 1.0 cm in diameter and 2 cm in effective length was used for the measurements in this temperature range. It was certified that data obtained from two of the specimens were in agreement with each other at medium temperatures. The results are presented in Figure 6.

DISCUSSION

Superposition of Contraction Isotherms and Equilibrium Volume

According to Kovacs,² when the isotherms represented as $(V - V_2)/T_2$ are taken against $\log t$, the resulting curves found over the temperature range from T_g to about ten degrees below T_g can be superposed as a single master curve by horizontal shifts of these curves, where V is an instantaneous specific volume, V_2 is the equilibrium volume at T_2 , t is observation time and T_g is the glass-transition temperature somewhat lower than T_g^+ . Furthermore Kovacs² has shown that the temperature dependence of the respective amounts of horizontal shift, called horizontal shift factors, would be approximately represented in terms of the WLF equation.¹⁰

The situation mentioned above is applicable to the isotherms presented in Figure 2. If these isotherms are composed into a single curve by horizontal and vertical shifts, the amount of the vertical shift may provide information on the equilibrium volumes of the isotherms. Fol-

Figure 7. Master curve for isotherms of volume retardation in the vicinity of T_g^+ reduced to 85°C .

lowing this procedure, we obtained a master curve resulting in a temperature range of 97.5°C to 85°C , and this master curve is shown in Figure 7. The relative values of V_2 estimated from the vertical shifts are presented in Figure 1, where the values of V_2 are normalized with respect to the value measured at 97.5°C . In Figure 1 another V_2 measured at 95°C is also plotted in comparison with the estimated value. The estimated value agrees with the measured value, and all of the estimated values lie on the line extrapolated from the equilibrium volumes in the rubbery state. This fact reinforces the prediction deduced from the free volume theory of viscoelasticity.^{13,14}

Because the isotherms show almost parallel lines with each other, it is impossible to determine the shift factors as unitary values as to the isotherms obtained at temperatures from about 80°C to about 70°C . However, if an

Figure 8. Master curve for isotherms of volume retardation in glassy state reduced to 38°C .

Figure 9. Relative amounts of vertical shift in glassy state against temperature. Solid lines A and B show the slopes of thermal expansion in the rubbery state and the glassy state taken from the curve in Figure 1.

Figure 10. Superposition of isotherms in glassy state resulting from an assumption that equilibrium volume would be still located on the straight extrapolation from that in the rubbery state.

isotherm below 70°C at small t deviates from a line, a determination of the vertical and the horizontal shift factors become possible. The master curve in the temperature region below 61°C is presented in Figure 8. The relative amounts of the vertical shift are shown in Figure 9, in comparison with the slopes of thermal expansions in the glassy state and the rubbery state taken from Figure 1. The behavior of V_2 at these temperatures is different from that at higher temperatures and the temperature dependence of V_2 is almost equal to that of the glassy-polymer volume. If one assumes that the equilibrium volumes still lie on the extrapolation from the rubbery state even at these low temperatures, the isotherms at these temperatures cannot be composed into a single curve,

as shown in Figure 10.

Time—Temperature Reducibility

As is well known, creep compliances as a function of logarithmic time are composed into a master curve by horizontal and vertical shift.¹⁵ This procedure is applied to the present data, and the resulting master curve is presented in Figure 11. The horizontal shift factors, $\log a_T$, are shown in Figure 12. The solid curve shows the WLF equation presented as a universal formula^{10,16} in the following

$$\log a_T = \frac{-8.86(T - T_s)}{101.6 + (T - T_s)}, \quad (1)$$

Figure 11. Master curve for shear creep compliance (cm^2/dyn) of polystyrene reduced to 100°C.

Figure 12. Temperature dependences of horizontal shift factors used in plotting the master curves shown in Figures 7, 8, and 11. Shift factors of volume retardation at high temperatures are normalized with respect to the value at 97.5°C. Those at low temperatures are normalized with respect to the value at 61°C. Solid curve presents the universal WLF equation^{10,16} with $T_s = 139^\circ\text{C}$, which is adapted to fit the data on shear-creep compliance at temperatures above T_g^+ .

where T_s is 139°C. The value of T_s is determined so that the equation may describe the data of the horizontal shift factors obtained at temperatures above T_g^+ . As is well established by Hideshima,¹⁷ the temperature dependence of the horizontal shift factors is described by the WLF equation at temperatures higher than T_g^+ ; however, the dependence deviates suddenly from the equation below T_g^+ on account of the glass transition. The horizontal shift factors of the volume retardation obtained in the previous section are compared with those of the shear creep compliances, as shown in Figure 12. The temperature dependence of the shift factors of the volume retardation in the vicinity of T_g^+ is described fairly well by the WLF equation which fits the data on the shear compliances obtained at temperatures higher than T_g^+ . Such dependence is very distinct from the behavior at temperatures below T_g^- .

Adam⁴ proposed a theoretical equation manifesting the isothermal volume retardation. His equation can be written as,

$$\frac{dV}{dt} = \theta(T_2) \cdot \chi(V - V_2), \quad (2)$$

where $\theta(T_2)$ is a function of T_2 only, and χ is a function of $(V - V_2)$. Considering that $(dV/d \ln t)$ can be reformed as $(dV/dt)t$, eq 2 satisfies the condition for the time—temperature reducibility. The horizontal shift factor corre-

sponds to $\theta(T_2)/\theta(T_{2r})$ where T_{2r} is a reference temperature. The relative values of dV/dt are graphically determined on the isotherms where the values of $V - V_2$ are constant. In this procedure, the values of V_2 obtained in the previous section are used. The results are presented in Figure 13 and are compared with data from shift factors already shown in Figure 12. Both of these results agree well throughout the temperature range investigated. The time—temperature reducibility on the volume retardation may be understood from the formalism of eq 2.

Anomalous Isotherms

A systematic study of the anomalous isotherms is not formed in literature. It has been suggested that the anomalous isotherm is one of several phenomena which may reveal information on distribution of retardation times.^{1,14} The mechanism of the occurrence of the anomalous isotherms is qualitatively explained on the basis of the assumption for the distribution of the retardation times. Let us assume that an apparent volume retardation of a polymer comprises many retardation elements which are characterized by the retardation times. When the polymer is quenched from T_1 to T_2 and is made to retard at T_2 during period z , the retardation elements having shorter retardation times than z make the transitions from the states at T_1 to those at T_2 while the retardation elements having longer retardation times than z remain in the states at T_1 . In this situation, if the polymer is heated from T_2 to T_3 , the retardation elements which have reached the states at T_2 start to make transitions from the state at T_2 to T_3 so that the shorter the retardation time, the faster the start will be. And, then, the retardation elements remaining in the state at T_1 start to make transitions from the state at T_1 to T_3 . On the basis of this explanation, it is expected that the time $t_{\max}$ at which the anomalous isotherm shows the maximum will closely relate to the time z throughout the anomalous isotherms obtained in each combination of T_1 , T_2 , and T_3 . Figure 14 shows the correlation between $t_{\max}$ and z , obtained from Figures 3, 4, and 5. The apparent activation energies of retardation are obtained from Figure 14, since the ratio of

Figure 13. Temperature dependences of horizontal shift factor and relative value of rate of volume contraction dV/dt determined at a constant value of $V - V_2$.

Figure 14. Relation between $t_{\max}$ and z : $t_{\max}$, time corresponding to maximum position on an anomalous volume retardation; z , time during which polymer having been maintained at a temperature of 80, 61 and 42°C before being heated up to a final temperature.

Figure 15. Apparent activation energies obtained from temperature dependence of shear-creep compliance presented in Figure 12 and that of value $z/t_{\max}$ taken from the results shown in Figure 14.

z to $t_{\max}$ expresses the ratio of the averaged effective retardation time at T_2 to that at T_3 . These values are about 80 kcal/mol above T_g^- and about 50 kcal/mol below T_g^- . These activation energies would reflect the temperature dependence of the effective compliances in the non equilibrium states, and these values may be compared with the apparent activation energies of the shear creep compliances obtainable from data in Figure 12. This comparison is shown in Figure 15. The values of the apparent acti-

vation energies obtained from the volume retardations and that from the shear compliances are in fair agreement with each other for the temperature range studied.

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