Time–Temperature Superposition in the Enthalpy Relaxation Study of Polystyrene

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Enthalpy recovery measurement was used to study the physical aging behavior of a polystyrene. The aging experiments at temperatures (T_A) near T_g were conducted with aging times (t_A) ranging from several minutes to several days. The recovered enthalpy, ΔH(t_A, T_g), increased with t_A, and then a plateau value of ΔH_{plate} appeared in the long time aging experiment. The master curve was successfully constructed concerning the normalized relaxation isotherm of the WLF (Williams–Landel–Ferry) equation to determine the coefficients for the superposition of terms of the WLF equation with polynomial days, which was discussed in terms of temperature dependence near the glass transition temperature (T_g) of the polystyrene. The recovered enthalpy, ΔH_{plate}, which is the value beyond which the recovered enthalpy no longer increases and can be determined by taking long enough t_A, was obtained from the enthalpy relaxation data of ΔH(t_A, T_g) measured by the DSC technique (differential scanning calorimetry); t_A and T_g are time and temperature, respectively, in the aging experiments. Because enthalpy relaxation is usually observed in the aging experiments below T_g, the shift factor is obtained as a result of the relaxation curve superimposed in the region below T_g, which might be inconsistent with the WLF regime. In fact, a few experimental data obtained below T_g are discussed on the basis of the WLF equation [15–17], and we also examined the relationship between the horizontal shift of the relaxation curve and the WLF equation in the enthalpy decay.

Previously, we tried to show that the data of the relaxation function (ϕ) decays in accordance with the time–temperature superposition principle [18], in which the extrapolation of the enthalpy–temperature (H–T) relation was used to derive the ϕ value. The result was not successful in constructing the master curve, which is supposed to come from the derivation of the ϕ value (see Eq. 1) and the overestimation of ΔH(∞, T_A), the amount of enthalpy decay when the sample reached equilibrium at T_A:

\[ ϕ = \frac{ΔH(∞, T_A)−ΔH(t_A, T_g)}{ΔH(∞, T_A)} \]  

The normalized relaxation isotherm of Eq. 1 was considered at first for various properties to describe the structural relaxation, and it was widely used for the enthalpy relaxation of glassy materials [19]. However, it might be unsuitable to determine ΔH(∞, T_A) by extrapolating the H–T relation from the liquid to the glassy state in deriving the ϕ value.

We attempted in this work to calculate ϕ by utilizing the plateau value of the recovered enthalpy, ΔH_{plate}, instead of ΔH(∞, T_A). ΔH_{plate} is the value beyond which the recovered enthalpy no longer increases and can be determined by taking long enough t_A. Although there are no theoretical grounds for these two quantities to be interchangeable, we attempted to use ΔH_{plate} with the expectation that it is more suitable than the value of extrapolation. The process of isothermal aging was improved to obtain stable enthalpy data by avoiding some difficulties of the long time experiment.

EXPERIMENTAL

A polystyrene pellet of G120K (Lot.IF1606) was kindly supplied by Nippon Polystyrene. DSC scans up to 350°C showed...
no peaks resulting from the crystallization and melting, which suggests that the G120K sample does not show any property of a crystalline state. The powdered sample was prepared from a G120K pellet via precipitation with methanol from solution in THF. $T_g = 94^\circ$C was determined by the onset definition in the $T_g$ shoulder [20]. The DSC examinations were conducted with a Seiko DSC 200 instrument using aluminum open sample pans of 5g. The temperature programs employed for the aging experiment are as follows: starting from a temperature of 160°C, well above $T_g$ (the former history is erased), sample polystyrene was cooled to a specified aging temperature at a rate of $-12^\circ$C/min, and then the DSC pan was taken out of the DSC module and placed into the aging cell immersed in an oil bath of $T_A$. After a given aging time, the pan was taken out of the cell and placed into DSC module maintained at $T_A$. The DSC pan was cooled once again to 30°C at a rate of $-12^\circ$C/min. The heating scan was carried out at a rate of 5°C/min between 30°C and 160°C in order to measure the amount of enthalpy relaxed during isothermal aging, and thus that recovered during the scan. The experiment of $t_A = 0$, i.e., that without the isothermal step of an oil bath before the scan, was conducted for the reference scan, the result of which was also used to calculate the heat capacity curve, $c_p(T)$, with reference to the heat capacity data of Indium of 200, 250, 298, 400, and 500K [21, 22]. Furthermore, the $H-T$ relation given for discussion was calculated from the $c_p(T)$ data of $t_A = 0$. The stretched exponential form of Eq. 2 was used as the decay function to analyze the relaxation:

$$\phi = \exp \left[-\left(\frac{t}{\tau}\right)^\beta\right],$$

where $\tau$ and $\beta$ are the relaxation time and shape parameter, respectively. Other details are described in previous works [22, 23].

**RESULTS AND DISCUSSION**

**Recovered Enthalpy**

The heating DSC curve for the polystyrene sample is shown in Fig. 1 for $T_A = 86^\circ$C. It is important to estimate the uncertainties of the DSC curves because most of the data discussed in this paper are directly derived from the curves. In order to ensure data accuracy, the series of aging experiments were repeated three times. In consequence, the heat flow curves of repeated scans were in good agreement within the temperature ranges of 70–90°C and above 120°C, showing that the baselines below and above the $T_g$ shoulder did not shift. The area bounded by two curves of the reference scan and that of the given $t_A$ was calculable, and the $\Delta H(t_A, T_A)$ values were determined.

Figure 2 shows the relation between $\Delta H(t_A, T_A)$ and $t_A$ measured from $T_A = 78^\circ$C to 86°C. As expected, $\Delta H(t_A, T_A)$ increased with $t_A$ after aging, the plateau value appeared. Estimations were made for two time domains where $\Delta H(t_A, T_A)$ increased and the plateau appeared, and then solid lines and dashed lines, respectively, were drawn. $t_{plate}$ was defined as the cross point of solid and dashed lines. The determined $t_{plate}$ value was logarithmically plotted against the inverse absolute temperature in Fig. 3. The linear relation between $\log(t_{plate})$ and $T_A^{-1}$ indicates that the time domain where $\Delta H(t_A, T_A)$ increases gets shorter as the increase in temperature with Arrhenius-type dependence. This result is consistent with the basic concept that the enthalpy decay can be attributed to the dynamics of the polymer chain [24, 25].

Several arguments can be seen over $\Delta H(\infty, T_A)$ in the literature. In some of the earlier literature, it was calculated with empirical procedures based on the area of the $c_p - T$ curve or a linear relationship between the asymptote value and temperature difference of $(T_g - T_A)$ [14, 26–28]. Cowie et al. have repeatedly referred to the asymptote value of the recovered enthalpy for several polymer samples in the curve fitting method of experimental and calculation data for $\Delta H(t_A, T_A)$, in which the calculation data were obtained using Eq. 1 up to long $t_A$ [29–32]. Looking over these references, it follows that the recovered enthalpy really appeared at long $t_A$ is different from the mere extrapolation below $T_g$ from the liquid state in the $H-T$ plot [33], which was evidenced for the G120K sample in

**FIG. 1.** Heating DSC curves of polystyrene (G120K) with the aging of $T_A = 86^\circ$C and without the aging (thick dashed line). The aging times were $t_A = 20, 80, 300, 900, 1800$, and 6000 min in order of decreasing intensity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**FIG. 2.** Recovered enthalpy, $\Delta H(t_A, T_A)$, plotted as a function of logarithmic aging time, $t_A$, for polystyrene (G120K). The solid and dashed lines were applied to determine the time to reach the plateau.
Fig. 4. The solid line of relative enthalpy was calculated from $c_p(T)$ data using the following equation:

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} c_p(T) dT.$$ (3)

$T_1 = 40^\circC$ was chosen [i.e., $T_1 < (T_g - 50)$], being substantially lower than $T_g$ so as to avoid the effect of the $T_g$ shoulder of the $c_p(T)$ curve. The dashed straight line was drawn with the approximation in the range from 100$^\circC$ to 120$^\circC$ to intend the line of the equilibrium value, and the plot indicates the value corresponding with $\Delta H_{\text{plate}}$ determined in Fig. 2. It was experimentally verified that $\Delta H_{\text{plate}}$ is lower than the $\Delta H(\infty, T_\lambda)$ of the extrapolation value.

**Master Curve for Enthalpy Relaxation**

The data of the recovered enthalpy were converted to the relaxation functions (see Fig. 5), in which $\Delta H_{\text{plate}}$ was substituted for $\Delta H(\infty, T_\lambda)$ in Eq. 1 to acquire normalized relaxation isotherms. The accelerated aging experiments in higher $T_\lambda$ are well illustrated in the $\phi$-$t_\lambda$ plot, which clearly shows that the relaxation function of higher $T_\lambda$ reaches a plateau of $\phi = 0$ at shorter $t_\lambda$. It is noteworthy that the rate of isothermal aging is defined as the experimental time scale to reach the plateau region in the relaxation function [34] rather than being defined as the slope of the $\phi$-$t_\lambda$ plot. This is consistent with the usual results that the enthalpy decays at a higher rate in higher temperatures.

Figure 6 shows the result of the superposition of the relaxation functions with the reference temperature of $T_0 = 93^\circC$, in which the shift factor is denoted by $\alpha_T$. Interestingly, a similar temperature dependence could be found between the $\alpha_T$ obtained in Fig. 6 and the $\tau$ value, which was determined by following Eq. 2 [27], through the slope and intercept of the plot of $-\ln \phi$ vs. $t_\lambda$ displayed in Fig. 7. It should be noted that the $\phi$ data included in the plateau region was removed in Fig. 7 to meet with Eq. 2. The similar temperature dependence between $\alpha_T$ and $\tau$ (see the plots of Fig. 8, shown below) means that the same master curve as that of Fig. 6 can be obtained by constructing the superposition for the $\phi$-$t_\lambda$ plots of Fig. 5 using $\tau$ as the reduction factor. This result implies that the same dynamics mode is found for the molecular motion of the respective temperature in the $\phi$ decay at $t_\lambda < t_{\text{plate}}.\alpha_T$ obtained in constructing

**Fig. 3.** The characteristic time of $t_{\text{plate}}$ plotted against 1000/$T_\lambda$ of the absolute temperature for the aging experiments of polystyrene (G120k).

**Fig. 4.** The relation of enthalpy and temperature (solid line) obtained with $c_p(T)$ of the heating scan of $t_\lambda = 0$. The dashed line was drawn to extrapolate $\Delta H(\infty, T_\lambda)$. The enthalpy corresponding to $\Delta H_{\text{plate}}$ determined in Fig. 2 was plotted by circle.

**Fig. 5.** Enthalpy relaxation function $\phi$ for various aging temperatures of $T_\lambda$ from 78$^\circC$ to 86$^\circC$. DOI 10.1002/pen
the master curve was interpreted in terms of the WLF equation written below:

\[
\log(a_T) = -\frac{c_1(T - T_0)}{c_2 + (T - T_0)}
\] (4)

The \(c_1\) and \(c_2\) values were determined from the slope and intercept of the plot of \(-\log(a_T)\) vs \((T - T_0)\), and then \(c_1 = 0.57\) and \(c_2 = 22.4\) were obtained. Our results are lower than those of \(c_1 = 13.6\) and \(c_2 = 27.1\), which were previously reported as the coefficients of polystyrene obtained by means of creep data [14]. In particular, the \(c_1\) obtained in this work was very small in comparison with those presented in the literature [35-38].

What the small value of \(c_1\) means is mentioned here in relation to the temperature range used for \(T_A\). In the fractional expression of Eq. 4, the equation gives a plot of a downward curve; \(c_1\) and \(c_2\) correspond with the curvature and the asymptote line of temperature, respectively. The small value of \(c_1\) appearing in Fig. 8 indicates the sharp bend of the plot. In general, the enthalpy decay is decelerated as the \(T_A\) is lowered, which is accompanied by a larger \(a_T\) factor in the horizontal shift of the \(\phi-t_A\) plot. The increase in the \(a_T\) factor happened in a relatively narrow \(T_A\) range used in this work and gave rise to the sharp bend, which means that the effect of deceleration in the enthalpy relaxation as the temperature decreased is more significant than that seen in the relaxation of creep data in the literature. A reduced \(c_2\) value was found, which means that the distance between the asymptote line and the reference temperature becomes short. It also means a significant increase in \(a_T\) with the decrease in temperature.

Although the experimental condition is fairly different between the research data in the literature and that shown in this work, the usual WLF behavior could be observed for the temperature dependence of the \(a_T\) factor in Fig. 8. The classical free volume theory can be applied for the relationship between the aging temperature and the enthalpy decay. It was assumed that the free volume fraction \(f_g\) of the G120K sample at \(T_g\) is not very different from that of \(f_g = 0.03\) determined from viscoelastic data [35]. Because we have the relationship between \(c_1\) and \(f_g\) as

\[
c_1 = \frac{B}{(2.303f_g)}
\] (5)

from the viewpoint of the \(a_T\) factor of enthalpy decay, \(B\) (the constant of relative free space term [39]) should be quite small, presumably of the order of \(10^{-2}\). Although the idea of \(B\approx1\) has been widely applied in determining the free volume fraction and the thermal expansion coefficient, this idea must be modified in interpreting \(a_T\) measured by the enthalpy relaxation data.
CONCLUDING REMARKS

The recovered enthalpy, $\Delta H(t_A, T_A)$, increased with $t_A$ in the aging experiments, and then the plateau appeared. The plateau value was used to obtain the relaxation function of $\phi$, which enables us to construct the master curve successfully for the $\phi$–$t_A$ relation. The shift factor obtained was interpreted in terms of the WLF equation. The coefficients determined were very low in comparison with those reported in the literature for polystyrene samples by the methods of dynamic viscoelasticity, shear compliance, and creep compliance. The lower value of $c_1$ implies that the deceleration in the rate of enthalpy decay is more significant as the temperature is lowered than that observed in the above-mentioned methods. This conclusion was derived by taking into account the fact that the smaller $c_1$ value is, the sharper the bend is in the plot of $\alpha_f$ and temperature.

REFERENCES

1. See references listed below and ref. 7 for the theory and the examples of how it works in practice concerning WLF equation of Eq. 4: (a) M. Rubinstein and R. H. Colby, Polymer Physics, Oxford University Press, New York (2003); (b) R.T. Bailey, A.M. North, and R.A. Pethrick, Molecular Motion in High Polyamers, Oxford University Press, New York (1981); (c) J.D. Ferry, Viscoelastic Properties of Polymers, Wiley, New York (1961)


