Density distribution in quenched polymers

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This paper reports theoretical and experimental results on the density distribution in thermally quenched polystyrene. The thermal quenching process is a thermodynamically non-equilibrium process, so that the physical properties of the quenched polymer are not homogeneous. From non-equilibrium thermodynamics and the concept of change of free volume a theoretical analysis of the density change due to quenching is presented. A computer simulation of the theory is compared with experimental results. It is found that through incorporating heat transfer and differential thermal expansion calculations with analysis of the effects of mean pressure and cooling rate on density, the dependency of quenching on density can be quite accurately predicted.

(Keywords: density distribution; free volume; polystyrene; glass transition temperature; heat transfer)

INTRODUCTION

Significant changes in mechanical properties of polymers after heat treatment have been previously reported[1–4]. It has been noted that the heat quenching process can dramatically improve impact strength, fatigue life and other mechanical properties. It has also been reported that the density of the polymer changes during quenching[1]. This paper presents a theoretical model for prediction of the density changes and compares these results with experimental results for polystyrene quenched in ice water and liquid nitrogen.

The process of quenching a polymer from a temperature, T, above the glass transition temperature, T_g, of the material to a lower temperature is a complex phenomenon. During the process the temperature and its gradient vary rapidly with both sample position and time. It is also accompanied by a secondary phase change. At every point in the polymer, as the temperature changes from the temperature above T_g to a temperature below T_g, the polymer changes from a liquid-like state to a solid-like state. At the same time thermal contraction differences with position may result in the development of thermal stresses.

The samples used in this study were fabricated from commercial unplasticized polystyrene sheet cut into $0.635 \times 1.27 \times 10.16\,\mathrm{cm}^3$ ($0.25'' \times 0.5'' \times 4''$) strips. After cutting and carefully surface polishing, the polystyrene was heated in an oven above its glass transition temperature (100°C). It was maintained at this temperature for approximately 2.5 h to allow it to come to thermal equilibrium. It was then rapidly quenched in either ice water or liquid nitrogen. The ice water was stirred to enhance heat transfer.

After the quenching process, a segment of the sample near the centre of the length was removed by microsawing. This section was then sliced into even smaller pieces. The location where each piece was taken from the original sample was noted and then the piece was placed in a gradient density column to measure its density. Experimentally it was observed that the quenched material exhibited relatively high density near the centre that decreased towards the surface, except that at the layers very close to the surface the density rapidly increased. Typical results from this experiment are shown in *Figures 1* and *2*.

Hutchinson and Kovacs[5] have used the concept of free volume to explain the volume changes resulting from cooling. They report that the greater the cooling rate the larger the free volume and hence the lower the final density of the polymer. The higher density at the surface, where cooling is most rapid, appears at first glance to be in contradiction to this concept. There must, therefore, be factors in addition to rate of cooling that affect density. Williams, Ferry and Kovacs[6,7] have investigated the effect of the pressure during cooling on density. They report that increasing the pressure during cooling results in an increase in sample density. It is suggested that the high surface density observed in this study, in this rapidly cooled surface region, can be attributed to the compressive stresses induced at this point by differential thermal contractions during the quenching process. Below this surface layer the density rather rapidly decreases and then increases with further depth. The following is a description of a theoretical and experimental investigation of the density changes occurring during the quenching process.

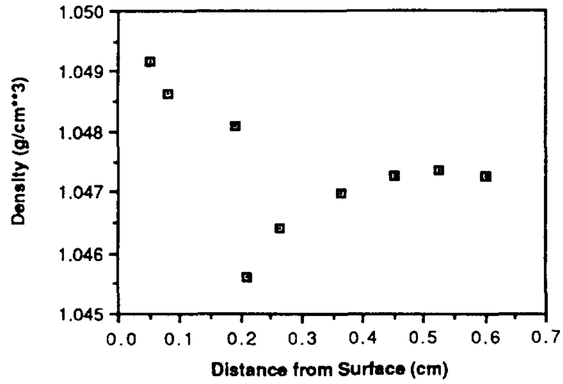

Figure 1 Density of pieces removed from liquid nitrogen quenched polystyrene as a function of distance from the quench surface

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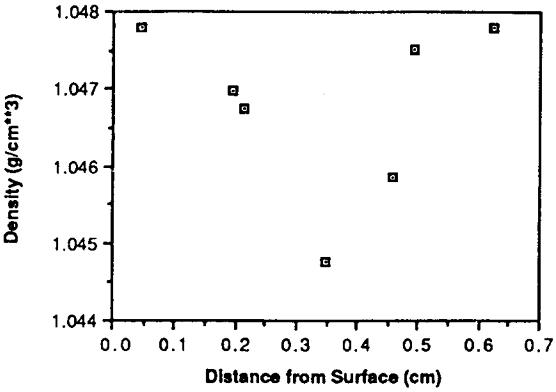

Figure 2 Density of pieces removed from ice water quenched polystyrene as a function of distance

THEORETICAL

We consider the geometry shown in *Figure 3*. Suppose the system to be closed, i.e. there is no mass transfer in the system, with thermal stresses $\sigma_1, \sigma_2, \sigma_3$. A system property ϕ can, in general, be described as a function of the state variables:

$$\begin{aligned} \mathrm{d}\phi = {} & (\partial\phi/\partial T)_{P,Z,\sigma_1,\sigma_2,\sigma_3}\,\mathrm{d}T + (\partial\phi/\partial P)_{T,Z,\sigma_1,\sigma_2,\sigma_3}\,\mathrm{d}P \\ & + (\partial\phi/\partial Z)_{P,T,\sigma_1,\sigma_2,\sigma_3}\,\mathrm{d}Z + (\partial\phi/\partial\sigma_1)_{T,Z,P,\sigma_2,\sigma_3}\,\mathrm{d}\sigma_1 \\ & + (\partial\phi/\partial\sigma_2)_{T,Z,P,\sigma_1,\sigma_3}\,\mathrm{d}\sigma_2 + (\partial\phi/\partial\sigma_3)_{T,Z,P,\sigma_1,\sigma_2}\,\mathrm{d}\sigma_3 \end{aligned} \tag{1}$$

where Z is the parameter introduced by Hutchinson and Kovacs[5] describing the non-equilibrium state of the system.

Letting $\phi = v$ and considering one dimensional quenching, (heat transfer in direction 1 only), and assuming that $\sigma_1 = 0$; $\sigma_2 = \sigma_3 = \sigma$ with no atmospheric pressure change, this equation can be written as:

$$\begin{aligned} \mathrm{d}v = {} & (\partial v/\partial T)_{Z,\sigma_2,\sigma_3}\,\mathrm{d}T + (\partial v/\partial Z)_{T,\sigma_2,\sigma_3}\,\mathrm{d}Z \\ & + (\partial v/\partial\sigma_2)_{T,Z,\sigma_3}\,\mathrm{d}\sigma_2 + (\partial v/\partial\sigma_3)_{T,Z,\sigma_2}\,\mathrm{d}\sigma_3 \end{aligned} \tag{2}$$

Here the free volume is considered to be a function of cooling rate, temperature T, the stresses σ_1, σ_2 and σ_3, and the parameter Z. Suppose a hypothetical pressure π produces the same change of volume as $\sigma_1, \sigma_2, \sigma_3$. As a first approximation it is reasonable to take π as the mean or hydrostatic component of the stress, i.e. assume $\pi = (\sigma_1 + \sigma_2 + \sigma_3)/3 = 2\sigma/3$. The thermodynamics of the system may then be written as:

$$\mathrm{d}v = (\partial v/\partial T)_{Z,\pi}\,\mathrm{d}T + (\partial v/\partial Z)_{T,\pi}\,\mathrm{d}Z + (\partial v/\partial\pi)_{T,Z}\,\mathrm{d}\pi \tag{3}$$

We assume that the equilibrium volume of the system v_∞ can be expressed as $v_\infty = v_g\{1 + \alpha_l(T - T_g)\}$ and express the relative departure of the specific volume as $\delta = (v - v_\infty)/v_\infty$. Here T_g is the reference temperature where $v_\infty = v_g$ at equilibrium. The left side of equation (3) can then be written as:

$$\begin{aligned} \mathrm{d}v & = \mathrm{d}\{(1+\delta)v_\infty\} \\ & = v_\infty\,\mathrm{d}\delta + (1+\delta)\,\mathrm{d}v_\infty \\ & = v_\infty\,\mathrm{d}\delta + (1+\delta)\{(\partial v_\infty/\partial\pi)_{T,Z}\,\mathrm{d}\pi + (\partial v_\infty/\partial T)_{\pi,Z}\,\mathrm{d}T \\ & \qquad + (\partial v_\infty/\partial Z)_{T,\pi}\,\mathrm{d}Z\} \end{aligned}$$

β_l and α_l are defined as:

$$(\partial v_\infty/\partial\pi)_{T,Z} = -\beta_l v_\infty \qquad (\partial v_\infty/\partial T)_{\pi,Z} = \alpha_l v_\infty$$

where α_l is the thermal expansion coefficient of liquid polystyrene, while β_l is the liquid compressibility. Noting that $(\partial v_\infty/\partial Z)_{T,\pi} = 0$, and assuming $\delta \ll 1$, it is found that:

$$\mathrm{d}(1+\delta)v_\infty = v_\infty\,\mathrm{d}\delta + (\partial v_\infty/\partial\pi)_{T,Z}\,\mathrm{d}\pi + (\partial V_\infty/\partial T)_{\pi,Z}\,\mathrm{d}T \tag{4}$$

Rearranging this equation yields:

$$\begin{aligned} v_\infty\,\mathrm{d}\delta & = \{(\partial v/\partial\pi)_{T,Z} - (\partial v_\infty/\partial\pi)_{T,Z}\}\,\mathrm{d}\pi \\ & \quad + \{(\partial v/\partial T)_{\pi,Z} - (\partial v_\infty/\partial T)_{\pi,Z}\}\,\mathrm{d}T + (\partial v/\partial Z)_{T,\pi}\,\mathrm{d}Z \\ & = \{\partial(v - v_\infty)/\partial\pi\}_{T,Z}\,\mathrm{d}\pi \\ & \quad + \{\partial(v - v_\infty)/\partial T\}_{\pi,Z}\,\mathrm{d}T - (\partial v/\partial Z)_{T,\pi}\,\mathrm{d}Z \end{aligned} \tag{5}$$

Equation (5) may be approximated by:

$$v_\infty\,\mathrm{d}\delta = -\beta'_f v_\infty\,\mathrm{d}\pi + \alpha'_f v_\infty\,\mathrm{d}T + (\partial v/\partial Z)_{T,\pi}\,\mathrm{d}Z \tag{6}$$

where β'_f and α'_f are constant. Using the definition of δ

$$v_\infty(\partial\delta/\partial Z)_{T,\pi} = (\partial v/\partial Z)_{T,\pi}$$

and supposing that[8]:

$$(\partial\delta/\partial Z)_{T,\pi}(\mathrm{d}Z/\mathrm{d}t) = -(\delta/\tau)$$

where τ is the retardation time, we obtain:

$$\mathrm{d}\delta/\mathrm{d}t = -\beta'_f\frac{\mathrm{d}\pi}{\mathrm{d}t} + \alpha'_f\frac{\mathrm{d}T}{\mathrm{d}t} - (\delta/\tau) \tag{7}$$

Doolittle[8], assuming that the retardation time depends only on the free volume of the polymer, expressed τ in the following form

$$\tau = \tau_0\exp\{(b/f) - (b/f_0)\} \tag{8}$$

where b is a constant of the order of unity, and f is the fractional free volume defined by:

$$f = (v - v_0)/v_\infty = (v_\infty - v_0)/v_\infty + (v - v_\infty)/v_\infty = f_\mathrm{T} + \delta \tag{9}$$

where $f_\mathrm{T} = (v_\infty - v_0)/v_\infty$ and as defined previously $\delta = (v - v_\infty)/v_\infty$, i.e., the relative excess volume with respect to the occupied volume v_0. Ferry has assumed that[7]:

$$f_\mathrm{T} = f_0 + \alpha_f(T - T_g) - \beta_f(P - P_0) \tag{10}$$

α_f is the thermal expansion coefficient for the free volume, and β_f is the free volume compressibility of the polymer. In the case considered here

$$f = f_0 + \alpha_f(T - T_g) - \beta_f\pi + \delta \tag{11}$$

The volume change can, therefore, be written as a function of the free volume change, temperature and pressure as:

$$\frac{\mathrm{d}\delta}{\mathrm{d}t} = -\beta'_f\frac{\mathrm{d}\pi}{\mathrm{d}t} + \alpha'_f\frac{\mathrm{d}T}{\mathrm{d}t} - \left(\frac{\delta}{\tau_0}\right)\exp\left(\frac{b}{f_0} - \frac{b}{f}\right) \tag{12}$$

From the above we conclude that, to calculate the free volume, it is necessary to know the thermal stress

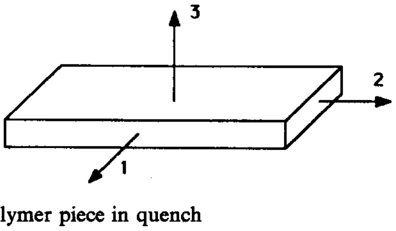

Figure 3 Polymer piece in quench

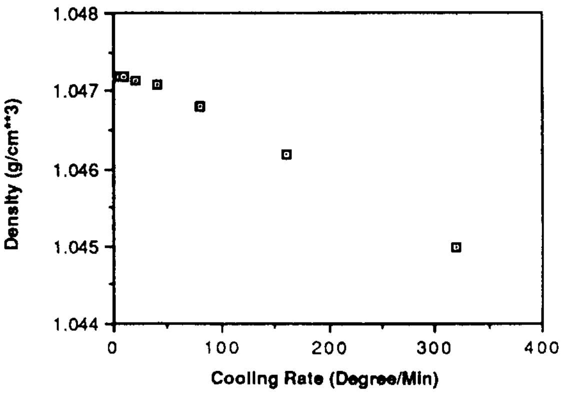

Figure 4 Density change associated with different cooling rates

distribution, and the cooling rate within the sample during the quenching period.

Generally, for one dimensional quenching the residual stresses are very large in the 2, 3 directions and the stress in the 1 direction can be neglected. The net forces in the 2 and 3 directions are zero hence:

$$\int_{-L/2}^{L/2} \sigma(x_1, t)\, dx_1 = 0$$

where $\sigma = \sigma_2 = \sigma_3$. x_1 stands for dimension in direction 1. By assuming rheological behaviour in which E is zero above some critical temperature and a relatively large constant below this temperature (i.e., the material either has no memory at all or complete memory), Wust[15] has shown that a general theory may be reduced to the simpler theory of Aggarwala and Saibel[9]:

$$\sigma(x1, t) = \int_{t(z)}^{t} 6\beta \left\{ \frac{i}{b - z(t)} \int_{z(t)}^{L/2} \frac{\partial}{\partial t'} [\alpha T(x_1', t')]\, dx_1' - \frac{\partial}{\partial t'} [\alpha T(x_1, t')] \right\} dt' \qquad (13)$$

where $t(z)$ is the time at which the position, z, passes through T_g, $z(t)$ is the position of the solidification line at any time t, and α is the thermal coefficient of expansion. In this study the β was taken as 0.11×10^8(Pa) in order to agree with earlier experimental results in this laboratory[18].

In the following, Fourier heat transfer is assumed. For a second order thermodynamic phase change the latent heat is zero. Heat conduction can, therefore, be approximated as:

$$\frac{\partial T}{\partial t} = \left(\frac{k}{\rho c}\right) \frac{\partial^2 T}{\partial x^2} \qquad (14)$$

Two boundary conditions and one initial condition are needed to fully pose the problem. Initially the material is all at a uniform temperature. Symmetry allows us to model the system by half of the total width, L, yielding an adiabatic condition at the centre plane. The face in contact with the quenching fluid is undergoing convective cooling. However, examination of Heissler charts[13] indicates that the temperature response for a planar system, when the Biot number is infinite, can be closely approximated by systems where the Biot number is as small as 10. For the system considered here, a Biot number of 10 requires the heat transfer coefficient to be greater than about 50 W/m°C. Heat transfer coefficients at least this high are formed in natural convection systems in water. With forced or agitated convection on the outside, as in the system considered here, the Biot number will certainly be large enough to assume the surface temperature will be the same as the final temperature, i.e. the water temperature. That is, the thermal resistance to heat flow in the solid can be taken as being much greater than the interfacial thermal resistance[13]. For this set of conditions the surface temperature is very nearly the ambient water temperature. This greatly simplifies the analysis.

The boundary conditions used in the computer simulation were:

(1) At $t = 0$, $T = T_i$, (T_i is the initial temperature);
(2) At the sample centre ($x = L/2$), $\partial T/\partial x = 0$, due to symmetry ($L$ is the width of the sample);
(3) At the surface $x = 0$, $T = T_\infty$ for all times greater than 0, (T_∞ is the temperature of ice water).

In the numerical simulation of equation (12) the term dT/dt is represented by an average value. This average value is taken as the average cooling rate from time $t = 0$ to the time when the temperature is the mid temperature between T_i and T_∞.

ONE DIMENSIONAL NUMERICAL SOLUTION AND EXPERIMENTAL RESULTS

Quasi-equilibrium density changes of polystyrene were measured after cooling from above T_g to room temperature at different cooling rates under atmospheric pressure. Before the heating and cooling, the samples were cut into small pieces with the aid of a diamond saw. A Perkin-Elmer DSC-2 was used to control the cooling rate. The results of these tests are shown in *Figure 4*.

To explore the effect of pressure on density, experiments were conducted in which samples in a high pressure cylinder were held under different pressures during the cooling. To maintain the cooling rates at a nearly constant low value, the cylinder holding small samples was placed in an oven at 110°C, two hours later the oven was shut down and with the cylinder and samples in place allowed to cool to room temperature over 24 h. *Figure 5* shows the density change of polystyrene as a function of the pressure applied during this cooling cycle.

The procedure for calculating the density distribution is summarized as follows: first the calculation of the temperature distribution $T = T(x, t)$ in the polymer was

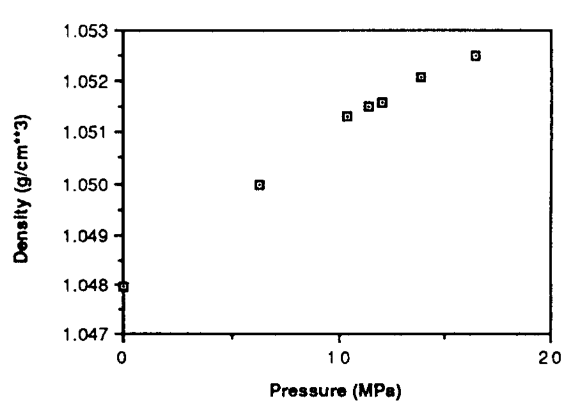

Figure 5 Density change associated with different sample pressures

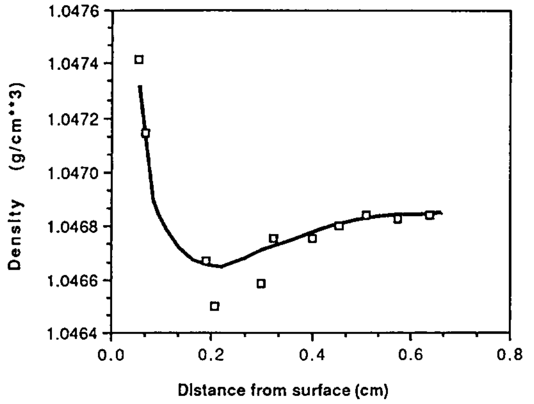

Figure 6 Comparison of experimental (□) and computer calculated (—) density distribution in ice quenched polystyrene

performed; then the thermal stresses in the polymer were estimated. Finally the calculation of the free volume and sample specific volume, v was made. The density change can be determined from $\rho = 1/v$.

It should be pointed out that the discussion above is not limited to one dimensional heat transfer. If the temperature change $T(x, y, z, t)$ and resulting stresses can be calculated, then the density distribution within a three-dimensional quenched polymer can be found by the same general approach.

Experiments were conducted with both one-dimensional and three-dimensional quenching, but the computer simulation was performed only for the one dimensional quenching process. The sample preparation and density measurement were as previously described. To perform the one-dimensional quenching tests, samples were sandwiched between relatively large amounts of material such that heat transfer was effectively restricted to be normal to the 0.25″ face in the 0.5″ dimension. The results for change in density due to three-dimensional quenching are shown on *Figures 1* and *2*. *Figure 6* shows a comparison of the results of the computation of density using equation (12) (solid line) with measurement of the density (circle data points) for one dimensional ice water quenched polystyrene. All the parameters used in this computation are from Brandrup and Immergut[14], Ferry[7], Flory and Fox[16,17], Doolittle[8] and Kovacs[5] and are listed below.

Glass transition temperature, $T_g = 100.0$°C
Thermal conductivity, $k = 0.0306$ cal/s °C cm
Specific heat, $C_p = 0.439$ cal/°C
$\alpha_f = 4.8 \times 10^{-4} (°\mathrm{C})^{-1}$
$\alpha_l = 6.0 \times 10^{-4} (°\mathrm{C})^{-1}$
$\alpha_g = 2.0 \times 10^{-4} (°\mathrm{C})^{-1}$
$b_0 = 1.0$
$\beta_f = 1.0 \times 10^{-10} (\mathrm{Pa})^{-1}$
$\beta_l = 2.2 \times 10^{-10} (\mathrm{Pa})^{-1}$
$\rho_0 = 1.0284$ g/cm^3
$f_0 = 0.025$
$\tau_0 = 100$

Here ρ_0 is the initial equilibrium density of polystyrene for a temperature of 110°C. Initial temperature $T_0 = 110$°C and β'_f is chosen as $1.0 \times 10^{-10} (\mathrm{Pa})^{-1}$. The numerical calculation was accomplished in a VAX computer. *Figure 6* shows a comparison of the calculated densities with the experimental determined values.

CONCLUSIONS

The distribution in density as a function of position in quenched polystyrene has been investigated both experimentally and theoretically. The free volume (and hence density) is governed by two effects, the rate of change of temperature and the hydrostatic component of the thermal stresses.

At the points near the surface, in the quenched polystyrene, the cooling rate is high and thermally induced compressive stresses are quite large. Previous work in this laboratory, using various techniques[2] indicates that quenching in ice water and allowing the samples to achieve thermal equilibrium at room temperature, results in surface residual stresses of approximately 15 MPa. At the surface these stresses are apparently large enough to dominate because the calculated and experimentally determined density at the surface is larger than that inside the sample.

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