Annealing of Plasticized PVC.   Dilatometric and DSC Observations

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Synopsis

Isothermal dilatometric measurements on quenched, plasticized PVC have been made at a series of temperatures, and a mathematical expression has been obtained to describe the specific volume as a function of time. The results of these measurements, along with those obtained using differential scanning colorimetry (DSC) for the change in enthalpy accompanying annealing, clearly show a change in the character of the annealing process with rising temperature; but the underlying molecular kinetic mechanism apparently remains unchanged.

INTRODUCTION

The annealing of PVC compositions and the accompanying effects on physical properties have long been a subject of interest.[1-4] The present study was undertaken to characterize the dimensional changes during annealing of certain compositions, so it utilized a dilatometric technique, which is inherently more sensitive to annealing effects than are other methods that have been used elsewhere.[1,3,4,5] Although there is a previously reported[2] dilatometric investigation on PVC, it concerned itself with unmodified resin, and the results at high temperature contain effects of thermal degradation. To avoid this difficulty and to make the results of more practical interest, we have used compositions containing plasticizer.

The features of note we wish to report are the distinct appearance of two annealing processes when the logarithmic time rate of change of specific volume is considered as a function of temperature and the suggestion of a common molecular kinetic mechanism behind each process.

EXPERIMENTAL

The subject compositions of this report consisted of Escambia (Air Products) 2200 resin, dry-blended with 2 phr Thermolite 31 (M. and T. Chemicals) stabilizer, and either 20 or 40 phr di-2-ethylhexyl phthalate. The blending technique involved dropwise addition of the premixed liquids to 1 kg of the resin powder which was stirring in a Henschel mixer. Subsequent analysis of the dry blends by Soxhlet extraction with petroleum ether confirmed their expected compositions and indicated uniformity of mixing. Consolidation of the dry blends to form the samples for dilatometric and DSC measurement was done by fusing them in open glass tubes at 210°C followed by quenching to 0°C. Sample resi-

dence time in the 210°C medium was 3 to 5 min. Little discoloration was noted in the final product.

Dilatometric measurements were done in a thermostat-equipped water bath which maintained its set temperature within ±0.02°C. The dilatometers were of Pyrex glass construction with precision-bore capillaries of 1-mm I.D., supplied by Kontes Glass Company. Uniformity of the bore was checked by means of a method reported by Bekkedahl[6] and found to be within the manufacturer's specification of ±0.01 mm. Procedures for preparing the dilatometers for use were also essentially those described by Bekkedahl.[6] A typical experiment consisted of heating a specimen (about 2 g) in its dilatometer for a length of time at some temperature T_1 followed by a quench to a lower temperature T_2 at which the annealing proceeded. The accompanying volume change was monitored by observing the meniscus position of the confining fluid (mercury) in the capillary through a telescope attached to a vertical vernier scale. Error analysis, as well as practice, indicated a precision of about ±0.03 mm³/g in the measurement of specific volume change over a period of 100 hr following quenching.

DSC measurements were conducted in air on a du Pont 990 thermal analyzer. Specimens weighed about 15 mg and, as with the dilatometer specimens, were used only once. Those specimens with which measurements were made of endotherm position as a function of time (see below) received their thermal history in a mercury-filled glass bulb of the size and shape of our dilatometer specimen chambers. Other specimens received their treatments in small, stoppered test tubes.

RESULTS AND DISCUSSION

Dilatometry

Dilatometric measurements were carried out on the compositions cited above by quenching from $T_1 = 100.0°C$ to temperatures in the range of $-10.0°C < T_2 < 60.0°C$. Glass transitions for the two materials were determined by DSC measurement at 20°C/min to be 20° to 50°C (20 phr) and −20° to +30°C (40 phr), so that with the compositions and range of temperatures used, annealing has been observed below, within, and above the glass transition.

Analysis of the data indicated that a single general relationship could describe the time dependence of the specific volume regardless of the value of T_2:

$$\overline{V}(t) - \overline{V}(0.05 \text{ hr}) = A + B \log_{10}(t - t_0). \tag{1}$$

The origin of time here is at the onset of quenching, whereas the origin of the volume change is taken at 0.05 hr (3 min) after quenching begins. This has allowed the start of an experiment to be associated with a clearly defined, and therefore reproducible, event, namely, the removal of the dilatometer from its heating bath. It also eliminates thermal contraction from the analysis since thermal equilibration required about 3 min or less. The left side of the above equation, then, is the difference between the specific volume at time t and that at 0.05 hr, while the quantities A, B, and t_0 have been fixed for each experiment by nonlinear regression analysis. An excellent fit of the data to eq. (1) was indicated in all cases, as the square of the correlation coefficient was always greater than 0.98.

Other workers,[1,4] using different techniques and compositions to study annealing in PVC, have also found a linear dependence of properties on the logarithm of time. The present work has established the validity of this logarithmic behavior down to the very earliest stages of annealing. Of course, eq. (1) cannot be valid at very long annealing times since it predicts that, in the limit, $V(\infty) = -\infty$. Therefore, it is only an approximation, but one which works very well for the time span of our experiments ($10^{-1}-10^2$ hr).

Since the quantity t_0 is small ($t_0 \simeq 0.02$ hr), for most of the duration of annealing the parameter of interest when one is considering annealing rate is B. Figures 1 and 2 show the observed values of B and the dependence on T_2 over the specified range. Vertical lines about each datum point represent a calculated relative uncertainty of ±5% based on the reproducibility of the dilatometer experiments. The curve through the data points in each case has been fitted by eye. Note that B itself is negative, and we have given here the quantity $-B$ in units of mm^3/g.

Two things may be cited regarding these data. First, from a practical standpoint, annealing as conducted here would be a small contributor to dimensional instability. Since the specific volumes of our materials were in the range of 700 to 800 mm^3/g at these temperatures, the change in specific volume is between 0.2 and 0.4 parts per thousand for every unit change of the logarithm of time in hours. Second, it appears from the figures that the rate of annealing must pass through at least two maxima. Although because of equipment limitations no data were collected on the 40 phr material at temperatures below $-10°C$, one can be certain that the coefficient $-B$ must become smaller there as molecular motions are frozen out.

TABLE I
Endotherm Area as Affected by DSC Rate of Heating

Material	T_2, °C	DSC heating rate, °C/min	ΔH, cal/g
20 phr	20	10	0.52 ± 0.02
	20	20	0.60 ± 0.02
	20	50	0.74 ± 0.03
	50	10	0.30 ± 0.02
	50	20	0.31 ± 0.02
	50	50	0.26 ± 0.04
40 phr	−10	20	1.49 ± 0.02
	−10	50	1.57 ± 0.02
	20	10	0.81 ± 0.02
	20	20	0.81 ± 0.02
	20	50	0.74 ± 0.08

Differential Scanning Calorimetry

DSC measurements were carried out to further examine the dependence of $-B$ on T_2, and they show the value as well as the necessity of sometimes using more than one technique in a study in order to characterize a phenomenon. Specimens of each material were quenched from 100°C and annealed at one of two temperatures, these being on either side of the value of T_2 corresponding

to the minimum in the magnitude of $-B$. After a given time, DSC thermograms were recorded at heating rates of 10°, 20°, and 50°C/min. Thermograms of samples annealed at the lower temperatures all showed a large endotherm superimposed on the glass transition. Each of those for the higher temperature annealings also indicated an endotherm; however, this was located at temperatures above the glass transition and moved progressively higher with longer duration of annealing. Endotherm areas were measured using the thermogram of a freshly quenched sample as a baseline and converted to changes in enthalpy using a factor determined from the melting endotherm of indium metal and its known heat of fusion. Table I lists the results of these measurements. The uncertainties given are due to the precision of area measurement, which was ±0.1 cm^2 except for two cases (50°C/min measurement on 20 phr material annealed at 50°C and 50°C/min measurement on 40 phr material annealed at 20°C), where there was some ambiguity in baseline placement.
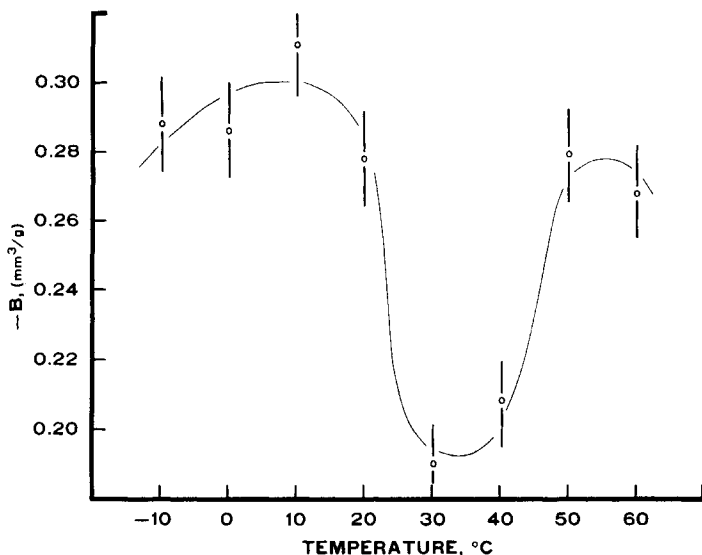

Fig. 1. Temperature dependence of dilatometric rate coefficient (20 phr DOP, $T_1 = 100$°C).

The item of note here is that, for both materials, within the given uncertainty the apparent enthalpy change due to annealing rises with increasing heating rate for the lower value of T_2, but is unaffected by the heating rate at the higher value of T_2. These results seem to signal a change with temperature in the character of the annealing process, and, indeed, the behavior observed here has also been noted in unplasticized PVC by Illers.[4] According to Illers, there are two annealing processes that occur in PVC. The one at lower temperatures is a relaxation effect due to glass formation, whereas the other, at higher temperatures, is a thermodynamically definable process. More specifically, this latter process is thought to involve some change in crystallinity of the polymer.[4]

DISCUSSION

The behavior of the dilatometric coefficient shown in Figures 1 and 2, then, can be interpreted as reflecting a change in the annealing from simply being an effect of the glass transition to being an ordering phenomenon. Not only is the

change with temperature in the character of the annealing seen clearly in the dilatometric coefficient; but also the fact that the two annealing processes obey the same function of time, eq. (1), suggests that the same molecular kinetic mechanism controls them both. In the case of the relaxation process, retarded changes in the conformation of the macromolecular backbone are thought to constitute the relevant mechanism.[7] Therefore, the notion that this also controls the high-temperature annealing was explored a little further.
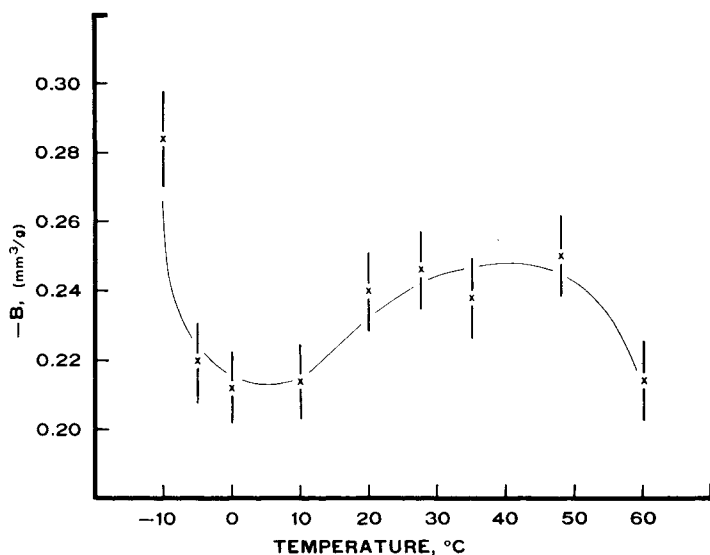

Fig. 2. Temperature dependence of dilatometric rate coefficient (40 phr DOP, $T_1 = 100°C$).

It was noted above that during annealings at the higher temperatures, the endotherm on the DSC thermogram would shift upward on the temperature scale. Figure 3, then, shows the endotherm position T_m for the 40 phr material plotted as a function of the logarithm of the annealing time at various temperatures. A least-squares treatment yielded the straight lines drawn through the data points. Although statistical analysis indicates an apparent small, but real, change in slope with temperature, the isotherms are very nearly parallel. This prompted the assumption that time/temperature superposition is operative. Shift factors a_T were calculated so as to superimpose the isotherms, and an Arrhenius relationship was assumed to represent the dependence of a_T on temperature. The included activation energy was found to be 106 kcal/mole, which is of the order of magnitude of the value found by Kovacs[8] for the relaxation process in polystyrene. This, then, provides some support for the idea that the two annealing processes in PVC are both controlled kinetically by the same type of molecular events—movements of the polymer backbone.

As a final point, it may be mentioned that the dilatometer experiments suggest something about the nature of the supposed crystallization process of annealing. The kinetics of this process are represented by eq. (1) even in its earliest stages. In contrast, dilatometric measurements with highly crystallizable polymers (e.g., polycaprolactone) quenched from the melt show the effects of crystallite formation and subsequent annealing of those crystallites to be distinct.[9] In fact, annealing here has been called secondary crystallization,[9] and its effects are linear in the logarithm of time. Couple this with the results of Figure 3 showing an-

nealing-endotherm movement to higher temperature, and it can be suggested that the crystallization process of annealing is one in which no new ordered regions are being formed; instead, some of those already present when quenching is complete change in such a way as to increase their melting temperatures. Two possibilities for this to occur are by an increase either in size or in the degree of internal perfection. The methods used in this investigation did not seem capable of further resolving this point.
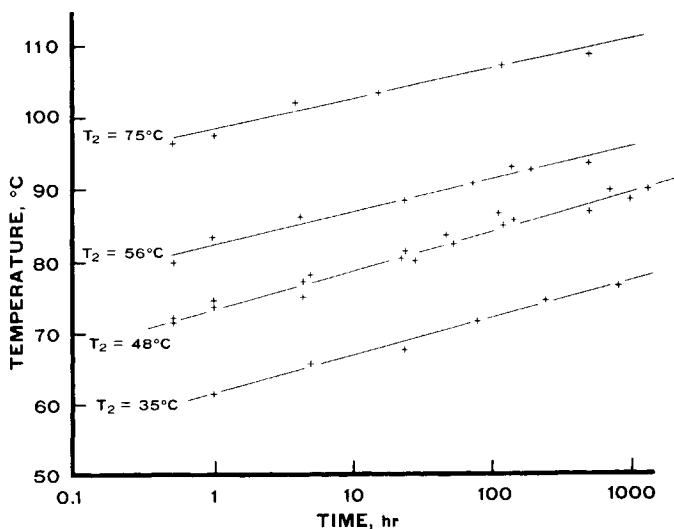

Fig. 3. DSC endotherm position as a function of annealing time (40 phr DOP).

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