

## Effects of Annealing and Prior History on Enthalpy Relaxation in Glassy Polymers. 1. Experimental Study on Poly(vinyl chloride)

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**ABSTRACT:** Endothermic peaks below  $T_g$  have been observed by differential scanning calorimetry (DSC) in samples of poly(vinyl chloride) (PVC) which were given a variety of thermal, mechanical, and vapor treatments and subsequently aged for varied times ( $t_e$ ) at several temperatures ( $T_e$ ). The peaks increase in magnitude and shift to higher temperature with increased  $t_e$  and  $T_e$  and appear as the well-known " $T_g$  overshoot" as  $T_e$  approaches  $T_g$ . The magnitude, but not the position, of the peaks is strongly dependent upon the treatment given the sample before aging. The peaks are enhanced by an increased rate of thermal quenching, by tensile or compressive mechanical stressing, and by prior exposure to a swelling vapor (e.g., methyl chloride). Development of the peaks upon aging is suppressed by the presence of a soluble vapor ( $\text{CH}_3\text{Cl}$  or  $\text{CO}_2$ ) during aging. The DSC observations may be qualitatively explained as a consequence of the slow approach toward equilibrium of a system with a broad distribution of relaxation times.

### Introduction

Differential scanning calorimetry (DSC) has revealed enthalpy relaxations occurring near or below  $T_g$  in glassy polymers aged after a wide variety of thermal, mechanical, and solvent or vapor treatments. Illers<sup>1</sup> and Gray and Gilbert<sup>2</sup> observed sub- $T_g$  endothermic peaks in annealed PVC samples which had been rapidly quenched and found that the magnitude and temperature of the peaks increased with increasing annealing time and/or temperature between the quench and the DSC scan. Foltz and McKinney<sup>3</sup> and Petrie<sup>4</sup> demonstrated that the magnitude of the DSC endothermic peak at  $T_g$  (" $T_g$  overshoot") provided a quantitative measure of the enthalpy relaxation which had occurred during prior annealing at temperatures somewhat below  $T_g$ . In a recent study of aging in ABS and SAN, Wysgoski<sup>5</sup> found no endothermic peaks in samples scanned immediately after a rapid quench, whereas aging at room temperature led to a slow development of small, broad endotherms well below  $T_g$ ; with increasing aging temperature, the endotherms became more pronounced and occurred at higher temperatures, appearing as the familiar  $T_g$  overshoot for aging temperatures within about 20 °C of  $T_g$ .

DSC endotherms showing similar dependences upon annealing time and temperature have been observed by Weitz and Wunderlich<sup>6</sup> and others<sup>7-9</sup> in polymers vitrified by cooling through  $T_g$  under high hydrostatic pressure. Application of mechanical stress to polymers in the glassy state, through either compression<sup>10</sup> or tensile drawing,<sup>11</sup>

also results in endothermic maxima below or near  $T_g$ . Matsuoka<sup>12</sup> has suggested that dilation under tensile stress increases the enthalpy of the glass, reducing the relaxation time and therefore increasing the rate of enthalpy relaxation during annealing.

Compared with these studies of enthalpy relaxations induced by thermal and mechanical treatments, reports dealing with vapor or solvent effects on glassy state relaxations are less extensive or explicit but nonetheless suggestive of closely related effects. Chan and Paul<sup>13</sup> found that exposure of annealed polycarbonate to high  $\text{CO}_2$  pressure reduced the magnitude of the DSC endotherm and suggested that sorption of  $\text{CO}_2$  diluted the polymer, increasing its enthalpy relative to the annealed state. Shultz and Young,<sup>14</sup> in studying polystyrene and PMMA samples freeze-dried from naphthalene solutions, observed sub- $T_g$  endothermic maxima which intensified and moved to higher temperature with increasing annealing time or temperature. Their observations were attributed to a broad distribution of relaxation times in the very "open" glass structure produced by the rapid quench and matrix sublimation. Berens and Hopfenberg<sup>15,16</sup> found that prior exposure to a swelling vapor enhances the sorptive capacity of glassy PVC and polystyrene and suggested this effect may be due to an increase of frozen-in free volume; although DSC data were not included in their study, it seemed likely, in view of the other calorimetric findings, that the vapor-swelling process might also produce an enhancement of enthalpy relaxation effects.

The present study was undertaken to confirm the anticipated effects of vapor treatments upon enthalpy relaxations and to directly compare these effects with those of varied thermal and mechanical treatments for a given polymer and similar annealing conditions. The results seem to reveal a common explanation for the effects of the widely diverse treatments. The enthalpy relaxations in all cases closely follow the predictions of a nonlinear, non-exponential relaxation model<sup>20,21</sup> as detailed in part 2.<sup>22</sup>

### Experimental Section

**Materials.** The polymer used in all experiments reported here was a commercial, suspension-polymerized PVC (Geon 103EP, BFGoodrich Chemical Group), obtained as a free-flowing white powder. Optical microscopy and electron microscopy have shown this resin to consist of roughly 2- $\mu\text{m}$  primary particles firmly agglomerated into porous 100–150- $\mu\text{m}$  grains. Molecular weights given by the supplier are  $M_n = 65\,000$  and  $M_w = 205\,000$ . Portions of this polymer were given the following thermal, vapor, and mechanical treatments:

**"Free-Cooled" Samples.** To erase effects of prior history, PVC powder samples were treated 30 min in a circulating-air oven at 120 °C and then allowed to cool to room temperature in the open air. Approximate cooling rates were 100 °C/min from 120 to 100 °C, 60 °C/min from 100 to 80 °C, 40 °C/min from 80 to 60 °C, and 25 °C/min from 60 to 40 °C.

**"DSC-Cooled" Samples.** To provide samples of more closely controlled cooling rate, 15-mg samples in DSC pans were heated 30 min at 120 °C in the DSC instrument, cooled at the maximum nominal cooling rate of 320 °C/min to -150 °C, and allowed to return to room temperature.

**"Liquid-N<sub>2</sub>-Quenched" Samples.** Portions of the PVC powder (~10 g) were heated 30 min at 120 °C and then poured directly into a large excess of liquid nitrogen in a Dewar vessel. Boiling of the liquid N<sub>2</sub> ceased within 2 s, suggesting an average cooling rate of roughly 10<sup>4</sup> K/min; assuming exponential cooling, the rate through the glass transition region may have approached 10<sup>5</sup> K/min.

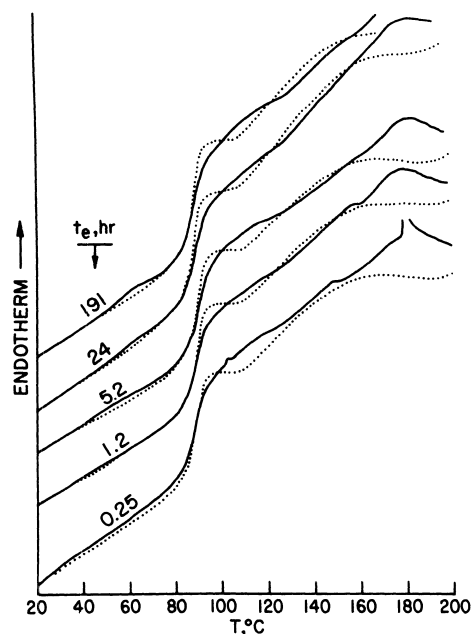
**Methyl Chloride Vapor Treatments.** For study of the effect of vapor swelling on enthalpy relaxations, CH<sub>3</sub>Cl vapor was chosen for its combination of relatively high diffusivity and appreciable solubility in PVC at convenient pressures. Gravimetric sorption measurements by methods previously described<sup>17</sup> showed the diffusivity of CH<sub>3</sub>Cl in PVC at 30 °C to be 1 × 10<sup>-11</sup> cm<sup>2</sup>/s and its equilibrium solubility at 13-kPa (0.13 atm) pressure to be 3.6 mg/g of PVC. For the DSC study, samples of the PVC powder freshly free-cooled from 120 °C were evacuated in a stainless steel pressure vessel and then exposed to CH<sub>3</sub>Cl vapor at selected pressures (200–500 kPa) at 30 °C for up to 17 h. The vessel was then rapidly vented to atmospheric pressure and evacuated for 1 h at 30 °C; the absorbed CH<sub>3</sub>Cl was essentially all removed, since the half-desorption time under these conditions is approximately 30 s.

**Hot-Pressed Sheet.** Fused PVC sheets approximately 0.3 mm thick × 120 mm diameter were prepared by pressing portions of the powder sandwiched in aluminum foil between flat steel plates at 210 °C for 10 s under 133-kN (30000 lb) force. The sheets were cooled by placing the hot steel plates and PVC sheet in a cold press without applying pressure; the cooling rates measured by a thermocouple were approximately 40 °C/min from 210 to 150 °C, 15 °C/min from 150 to 100 °C, and 7 °C/min from 100 to 50 °C. Samples for DSC measurements were punched from the center of the pressed sheets, where flow orientation was minimum.

**Cold-Drawn Sheets.** Strips about 2 × 10 cm were cut from hot-pressed sheets and drawn at 1.3 cm/min in an Instron tensile tester, forming a stable neck with a draw ratio of about 2:1. DSC samples were punched from this drawn region.

**Cold-Pressed Powder.** Small portions of the PVC powder freshly free-cooled from 120 °C were compressed in a 1.1-cm-diameter piston mold under 517-MPa (75000 psi) pressure for 10 min at room temperature, forming opaque, brittle pellets. Fragments of these pellets were used in the DSC measurements.

**Cold-Re-pressed Sheets.** Portions of the hot-pressed sheet described above were cut to ca. 1.1-cm diameter and re-pressed in the piston mold under 517-MPa pressure for 10 min at room



**Figure 1.** DSC scans on PVC cooled through  $T_g$  at 320 °C/min and aged at 20 °C for the indicated times: (—) first scan; (···) second scan.

temperature. DSC samples were cut from these disks.

**Annealing.** After each of the treatments listed above, samples were aged, or annealed, for varying time periods at room temperature (20 ± 2 °C), 40 °C, and 60 °C before DSC scans were run. Two sets of liquid-N<sub>2</sub>-quenched samples were annealed at 40 °C under 100-kPa (1 atm) pressure of CO<sub>2</sub> and CH<sub>3</sub>Cl; all other samples were annealed in air at atmospheric pressure.

**DSC Measurements.** DSC scans were carried out on 15-mg samples with a Perkin-Elmer DSC-2 instrument at a 20 °C/min heating rate from 0 to 200 °C. Samples were then cooled at 320 °C/min back to 0 °C, and a second scan was recorded at 20 °C/min to 200 °C. Figures showing DSC scans were traced directly from the charts recorded at 20-mm/min chart speed and 2-mcal/s full-scale sensitivity; the second scan for each sample, arbitrarily matched to the first at 20 °C, is shown as a reference for estimating magnitudes of endo- and exotherms.

### Results

**"DSC-Cooled" PVC Powder.** Figure 1 shows the full first-heat DSC scans for PVC powders aged at room temperature ( $T_e = 20 \pm 2$  °C) for the indicated times,  $t_e$ , after cooling in the DSC instrument at 320 °C/min. Also shown are second-heat scans after cooling at the same rate from 200 °C. Differences between the two scans above  $T_g$  presumably reflect changes in crystallinity, recrystallization, and melting behavior<sup>1</sup> resulting from the different temperatures (120 and 200 °C) at the start of the preceding 320 °C/min cooling stage. In the region below  $T_g$ , significant differences between first and second scans appear after several hours of aging. Although the changes are small, the first scans show a small sub- $T_g$  endotherm, which grows, narrows, and shifts to higher temperature with increased  $t_e$ .

**"Free-Cooled" PVC Powder.** For these samples, cooled through  $T_g$  at about 60 °C/min, DSC scans were obtained after various aging periods,  $t_e$ , at several temperatures,  $T_e$ . Figure 2 shows the 20–120 °C portions of the curves. For the samples aged at room temperature, a significant sub- $T_g$  endotherm is first apparent after  $t_e = 1$  week. For  $T_e = 40$  °C, the DSC curves closely resemble those obtained on the DSC-cooled samples at  $T_e = 20$  °C. A slight endotherm appears after a few hours of aging and grows and shifts up in temperature with increasing  $t_e$ . The temperature at the endotherm maximum,  $T_{max}$ , appears

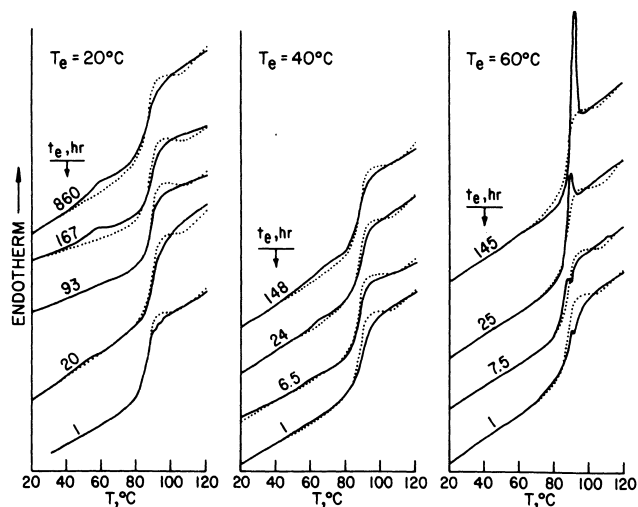


Figure 2. DSC, free-cooled PVC, varied  $T_e$  and  $t_e$ .

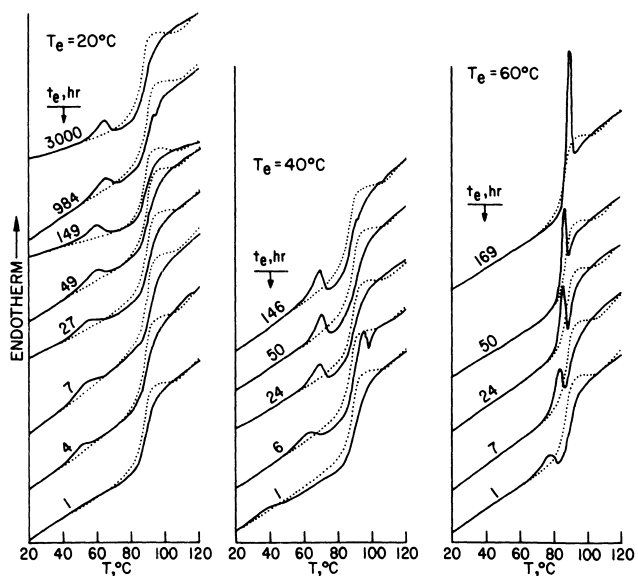


Figure 3. DSC, liquid- $N_2$ -quenched PVC, varied  $T_e$  and  $t_e$ .

somewhat higher for  $T_e = 40^\circ\text{C}$  than for  $T_e = 20^\circ\text{C}$ . When  $T_e$  was increased to  $60^\circ\text{C}$ , a slight endotherm appeared superposed on the  $T_g$  step after the first several hours of aging; for  $t_e \geq 24$  h, the endotherm appears as the " $T_g$  overshoot" widely reported<sup>3,4</sup> in studies of glassy polymers annealed near  $T_g$  and continues to grow with increasing  $t_e$ .

**Quenched PVC Powder.** DSC curves obtained after the indicated aging times and temperatures on PVC samples quenched from  $120^\circ\text{C}$  into liquid nitrogen are shown in Figure 3. In the series at  $T_e = 20^\circ\text{C}$ , a distinct sub- $T_g$  endotherm appears in the first few hours of aging; the growth, narrowing, and shift of this endotherm to higher  $T_{\text{max}}$  with increasing  $t_e$  is now clearly apparent. Between this endothermal peak and  $100^\circ\text{C}$ , the first-heat curves lie below the second scan; it is not clear here whether this reflects an exothermal event or simply an upward shift in  $T_g$  by 2–3  $^\circ\text{C}$  in the first-heat scan as a result of the initial rapid quench. With  $T_e = 40^\circ\text{C}$ , the endothermal peaks are more pronounced and narrower,  $T_{\text{max}}$  is raised, and the "valley" following the peak appears to combine an exothermal process and a shift in  $T_g$  compared with the second scan. The series of curves for  $T_e = 60^\circ\text{C}$  clearly shows the progression of the endotherm, with increasing  $t_e$ , from a separate peak well below  $T_g$  to a spike superposed on the  $T_g$  step.

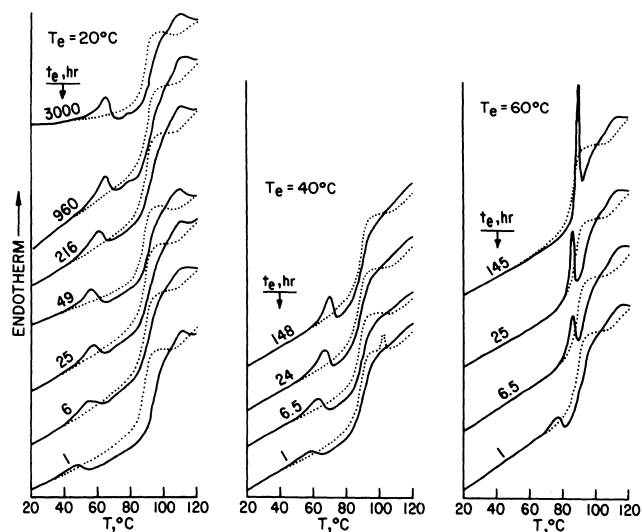


Figure 4. DSC,  $\text{CH}_3\text{Cl}$ -vapor-treated PVC, varied  $T_e$  and  $t_e$ .

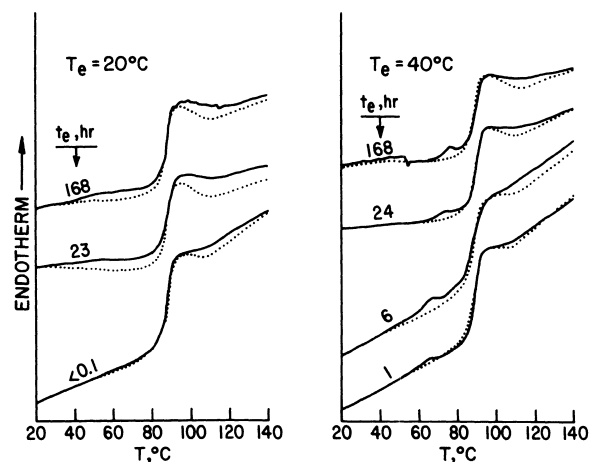


Figure 5. DSC, hot-pressed PVC sheet, varied  $T_e$  and  $t_e$ .

**Vapor-Treated PVC Powder.** Figure 4 shows the DSC curves obtained for free-cooled PVC powders which were subsequently treated overnight with  $\text{CH}_3\text{Cl}$  vapor at  $30^\circ\text{C}$  and 500-kPa pressure, evacuated and finally annealed under the same conditions as the free-cooled and quenched samples. The DSC curves for these vapor-treated samples are remarkably similar to those for the rapidly quenched samples. For equal  $T_e$  and  $t_e$ , the endotherm peak heights and positions, the exothermal valleys, and the  $T_g$  shifts are virtually superposable. The only noticeable difference is the somewhat stronger and narrower endotherms of the vapor-treated samples after annealing at low  $T_e$  and  $t_e$ . Samples treated with  $\text{CH}_3\text{Cl}$  vapor at lower pressure (200 and 300 kPa) show slightly weaker endotherms but otherwise parallel the trends shown in Figure 4. Vapor preswelling and rapid thermal quenching thus seem to have nearly identical effects on the development of enthalpy relaxations during aging of PVC.

In another series of experiments, the duration of the  $\text{CH}_3\text{Cl}$  vapor treatment at  $30^\circ\text{C}$  and 500-kPa pressure was varied from 1 min to 7 h, with annealing conditions fixed at 24 h and  $40^\circ\text{C}$ . The duration of the vapor treatment had virtually no effect on the DSC results; even 1-min exposure to  $\text{CH}_3\text{Cl}$  vapor caused the appearance of the pronounced sub- $T_g$  endotherm shown in Figure 4 ( $T_e = 40^\circ\text{C}$ ).

**Hot-Pressed PVC Sheet.** The 20–140  $^\circ\text{C}$  portions of DSC scans on these samples for varied  $t_e$  at  $T_e = 20$  and  $40^\circ\text{C}$  are shown in Figure 5. Base line slope changes and

