# Effects of Stress and Vapor Exposure Before and During Aging on Enthalpy Relaxation of Poly(vinyl chloride)

A. R. BERENS *and* I. M. HODGE

*BFGoodrich R&D Center*
*Brecksville, Ohio 44141*

Enthalpy relaxations in glassy poly(vinyl chloride) following varied pre-aging treatments and under varied aging conditions have been compared through observations of sub-$T_g$ endothermal DSC (differential scanning calorimetry) aging peaks. The extent of enthalpy relaxation for a fixed time and temperature of aging is progressively enhanced by the imposition and release of increasing mechanical stress before aging. The same effect is produced by sorption and desorption of increasing amounts of $CO_2$ or $CH_3Cl$ vapor before aging. In contrast, the continued application of mechanical stress, or the presence of vapor, during the aging period suppresses enthalpy relaxation. The extent of suppression increases with increasing vapor pressure and solubility or increasing stress. These effects are interpreted as consequences of an increase in the enthalpy of the polymer under mechanical or sorptive stress and an enthalpy relaxation following the release of this stress. In addition to these effects on the DSC endotherm, a pronounced exotherm between the aging peak and $T_g$ is observed for samples which have undergone shear yielding or orientation either before or during aging. This exotherm may be the result of release of stored strain energy during the DSC scan.

## INTRODUCTION

In previous publications (1–4) the authors have discussed the application of differential scanning calorimetry (DSC) to the study of glassy state relaxations, or physical aging, in poly(vinyl chloride) (PVC) and other rigid polymers. These relaxations represent a delayed approach toward equilibrium from the nonequilibrium condition produced in the glass by the thermal and mechanical history it experienced after cooling from above $T_g$. The normal DSC scan traces the absorption of thermal energy as the polymer is reheated and reflects, among other features, the recovery of enthalpy lost by relaxation during aging (5, 6). Enthalpy recovery is manifested as an endothermal aging peak (heat capacity maximum) near or below $T_g$. Our study of PVC showed that DSC curves are strongly dependent upon both the aging conditions and the prior history of the sample. The temperature of the aging peak ($T_{max}$) increases with increasing aging temperature ($T_e$) and aging time ($t_e$), and the peak magnitude ($Cp_{max}$) also increases with increasing $t_e$. For a given $T_e$ and $t_e$, $Cp_{max}$ is enhanced by a variety of treatments before aging, including rapid quenching, mechanical stress, and exposure to a swelling vapor. These treatments presumably produce a higher-enthalpy state at the start of the aging period.

The previous study also provided some evidence that enthalpy relaxation may be affected by the conditions prevailing during aging, as well as by treatments before aging. Specifically, as illustrated in *Fig. 1*, the DSC aging peak was reduced by aging a quenched PVC powder in a $CO_2$ atmosphere, rather than in air, while aging in the more soluble $CH_3Cl$ vapor nearly eliminated the peak.

In the experiments reported here, we further explore the effects of mechanical and vapor-swelling stresses upon enthalpy relaxation. These experiments were done with a single polymer, a commercial PVC resin; thermal history and aging time and temperature were generally kept constant. One of the aims of this work was to provide data for testing the applicability of a mathematical model (2) to nonthermal history effects. Accordingly, systematic variations were made both in transitory mechanical and vapor treatments applied before aging (pre-aging treatments) and in the stress or vapor environment maintained during aging (co-aging treatments).

## EXPERIMENTAL

The design of experiments discussed here was based on results reported previously (1). The DSC aging peak is well developed and yet still distinct from the glass-transition $C_p$ step after a convenient

Reprinted from POLYMER ENGINEERING AND SCIENCE, MID-OCTOBER, 1984, Vol. 24, No. 14

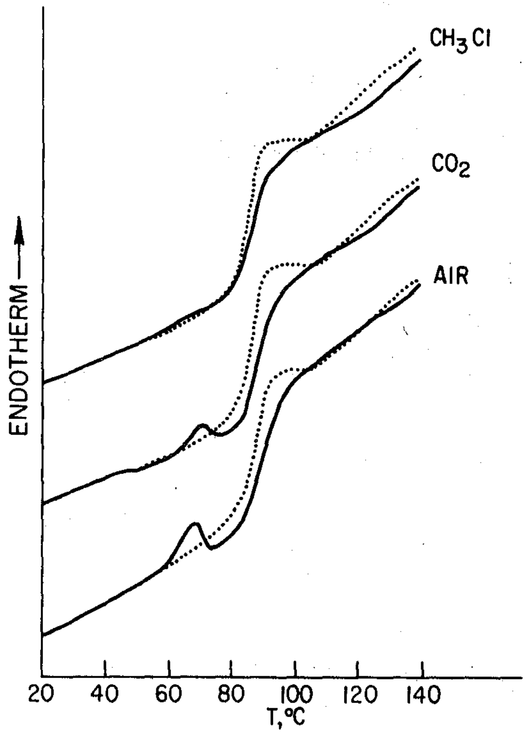

*Fig. 1. DSC curves for quenched PVC powder aged 24 hrs at 40°C under atmospheric pressure of air, CO$_2$, and CH$_3$Cl vapor.*

aging time of 24 hours at about 50° below $T_g$. Accordingly, 24 hours at 40°C ($\cong Tg - 45°$) was chosen as the aging period in most of our further experiments on PVC. The effects of nonthermal pre-aging treatments are most clearly distinguished when the thermal history alone leads to a relatively small aging peak. Hence slow-cooled samples were employed in experiments involving varied pre-aging treatments. Conversely, the effect of stress or vapor exposure during aging is the suppression of the aging peak (see *Fig. 1*), which is most apparent for thermal histories otherwise yielding pronounced peaks, i.e., rapid thermal quenching.

## Material

The PVC used in all experiments reported here was a commercial suspension-type homopolymer, Geon® 103EP (BFGoodrich Chemical Group), which was used either in the powder form as received, or as 0.3–0.5 millimeter (mm) sheets melt-pressed at about 200°C.

## Thermal History

Prior history of both powder and sheet samples was erased by reheating 30 minutes at $Tg + 35°C$ (120°C for PVC). Free-cooled samples were allowed to cool in the open air, with an estimated cooling rate through $Tg$ of about 50°C/min. Quenched-sheet samples were cooled from 120° by plunging into icewater; quenched powder samples were cooled from 120° by pouring into liquid nitrogen.

## Pre-aging Treatments

For comparison of the effects of varied vapor exposures or mechanical stress on subsequent aging, freshly free-cooled PVC samples were given the following treatments at room temperature:

### *Vapor Exposure*

Powder samples were placed in a stainless-steel pressure vessel, evacuated for 15 minutes, exposed to the desired pressure of pure CO$_2$ or CH$_3$Cl vapor for 1 hour, then again evacuated for 15 minutes before opening to the air and transferring to the aging oven.

### *Powder Compaction*

Freshly free-cooled, 1-gram (g) samples of PVC powder were compacted for 10 minutes at room temperature in an 11-mm-diameter piston mold at each of several pressures. The samples were removed from the mold as coherent but friable pellets, which were then aged at atmospheric pressure in air.

### *Uniaxial Compression*

Freshly free-cooled, 6.4 × 0.4 mm discs of PVC sheet were compressed in the 11-mm-piston mold under various pressures for 10 minutes at room temperature. A force of 1000 pounds (lbs) (20,000 psi or 138 MPa pressure on the original disc area) did not cause appreciable cold-flow, but 5000 lbs reduced the sheet thickness by about 30 percent with a corresponding increase in area.

### *Tensile Stress*

Room-temperature Instron-tensile tests at 1-percent-per-minute strain rate showed an average yield stress of 45.8 MPa (~6700 psi) for 6.4 × 100 mm strips cut from freshly free-cooled PVC sheet ~0.4 mm thick. Separate strips were held in the Instron at constant tensions of 75 and 100 percent of the yield stress for 10 minutes; after release of the stress, residual elongations were 2 and 7 percent, respectively. Another strip was cold-drawn to 100 percent elongation at 1 percent per minute. Samples for aging and DSC runs were cut from the stressed portions of these strips and from an unstressed control.

After each of these pre-aging treatments, the PVC samples were immediately transferred to an oven at 40°C for 24 hours aging in air without applied stress. Control samples given the same thermal history, but no further stress or vapor pretreatment, were similarly aged.

## Varied Co-aging Treatments

To determine the effects of nonthermal stresses on enthalpy relaxation, quenched samples of PVC powder and sheet were aged for a fixed time and temperature under the following variations of other conditions:

### *Vapor Atmosphere*

Samples of PVC powder, freshly quenched from 120°C into liquid nitrogen, were placed in a stainless-steel pressure vessel, which was then evacuated for 15 minutes, filled with CO$_2$ or CH$_3$Cl to the desired pressure, and then placed in an oven at 40°C for 24 hours. After this aging period, the vessel was again evacuated and cooled to room temperature, the sample was promptly transferred to aluminum pans, and a DSC scan was obtained.

### *Uniaxial Compression*

Discs of freshly quenched PVC sheet, originally 6.4 × 0.4 mm, were held for 5 hours at 40°C under a constant force of up to 2000 lbs in an 11-mm-diameter piston mold. Appreciable lateral flow and thickness reduction was noted when samples were removed from the mold.

### *Hydrostatic Pressure*

Discs 0.5 inch in diameter were cut from freshly quenched 0.4 mm PVC sheet; these were tight fits in a half-inch piston mold, in which they were held under a constant force of 1000 or 2000 lbs (35 or 70 MPa pressure) during 24 hour aging at 40°C. Lateral constraint minimized shear deformation under these conditions, so the applied pressure was effectively hydrostatic.

### *Tensile Stress*

Strips 6.4 × 100 mm were cut from freshly quenched PVC sheet about 0.4 mm thick. Instron tensile tests on several strips at 40°C, at a strain rate of 1 percent per minute, indicated an average yield stress of 27.6 MPa (~4000 psi). Other strips were held under constant stress, at values from 20 to 75 percent of the yield stress, in the Instron tester during 24 hours aging at 40°C. After releasing the stress and cooling to room temperature, the strips showed residual elongation of up to 8 percent. Samples for DSC measurements were cut from the strips aged under stress and from unstressed strips of identical thermal history.

### DSC Measurements

Immediately after the aging period, DSC scans were run on 15-milligram (mg) samples using a Perkin-Elmer DSC-2 instrument at 20K/min heating rate from 270 to 470K. Samples were then cooled at 320K/min and rescanned as before. Figures showing DSC scans were traced directly from the charts recorded at 40 mm/min chart speed and 2 mcal/sec full-scale sensitivity. Dotted-line curves are for second scans, matched to the first at 290K, and shown as a reference for comparing endotherms and exotherms. More quantitative treatment of the data does not seem justified in the absence of independent instrumental calibration.

## RESULTS

### Pre-aging Treatments

The effects of pre-aging exposure to varied pressures of $CO_2$ and $CH_3Cl$ vapor on the DSC curves of aged PVC powder are shown in *Figs.* 2 and 3. The pressures used were chosen, by reference to independently determined sorption isotherms, to give approximately equal weight percent sorption of the two vapors. Curves B, C, and D in *Figs.* 2 and *3* correspond to about 1, 2, and 4 weight-percent sorption, respectively, of $CO_2$ and $CH_3Cl$; since $CH_3Cl$ is the more soluble vapor, much lower pressures were required to reach equal sorption. With both vapors, there is a progressive increase in the height of the DSC aging peak, and a small shift

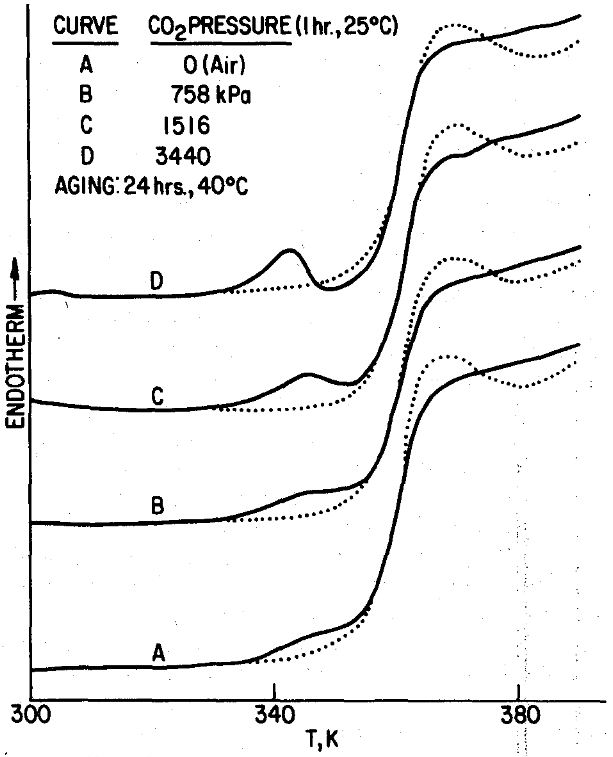

*Fig. 2. Effect of pre-aging exposure to $CO_2$ on DSC of free-cooled PVC powder.*

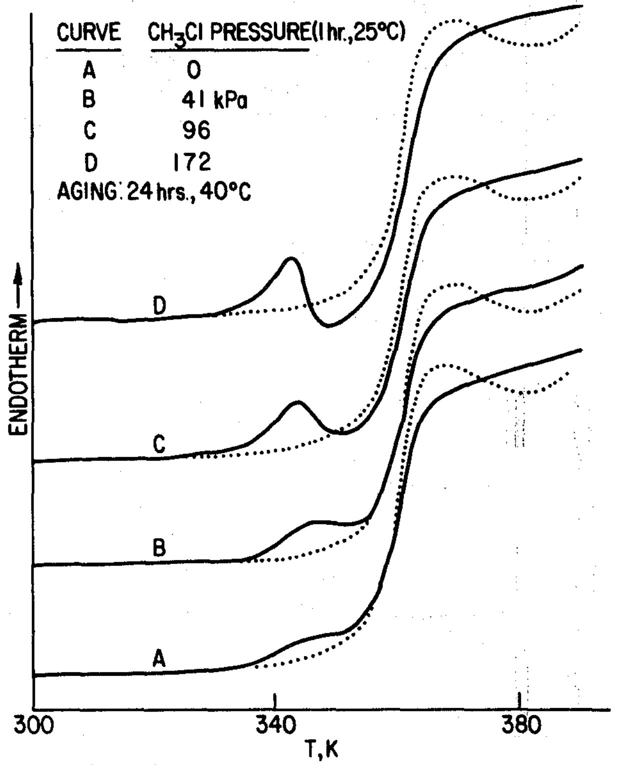

*Fig. 3. Effect of pre-aging exposure to $CH_3Cl$ vapor on DSC of free-cooled PVC powder.*

to lower $T_{max}$, with increasing pressure. The similarity of the two sets of curves clearly suggests that the effect on aging is governed by the extent of sorption or dilation of the polymer, and not by the vapor pressure per se.

The effects of pre-aging application of varied mechanical compressive stress to slow-cooled PVC powder and sheet on DSC curves run after equal subsequent aging cycles are shown in *Figs. 4* and *5*. Again, there is a progressive increase in the DSC aging peak, and a small shift to lower $T_{max}$, with increasing severity of the pre-aging treatment—here, with an increase in the applied compressive stress. In addition, the higher stresses produce a very pronounced exothermal minimum following the aging peak and a significant increase in the apparent $T_g$. These features are much less apparent in vapor-treated samples which show aging peaks of similar magnitude. The results for the compressed sheet samples (*Fig. 5*) suggest that the exotherm and $T_g$-shift may be associated with cold-flow, or shear-yielding, which was very pronounced at 689 MPa stress (Curve C) but not at 138 MPa (Curve B). For the powder samples of *Fig. 4*, the appearance of a marked exotherm after a lower-stress treatment (92 MPa, Curve D) could be explained by stress concentration and subsequent local yielding at points of contact between powder grains.

*Figure 6* illustrates DSC curves for PVC sheet samples aged after application and release of tensile stresses. Pre-aging tensile stress up to 75 percent

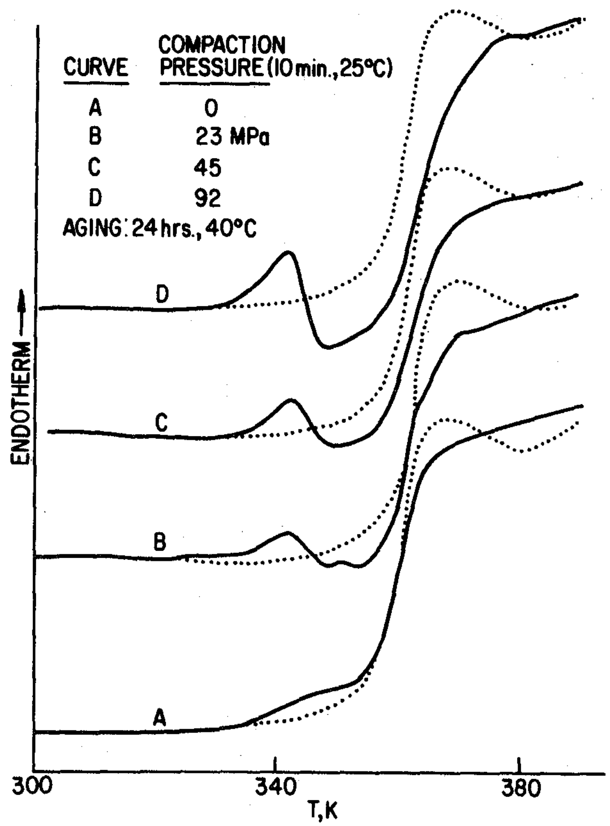

*Fig. 4. Effect of pre-aging compaction on DSC of free-cooled PVC powder.*

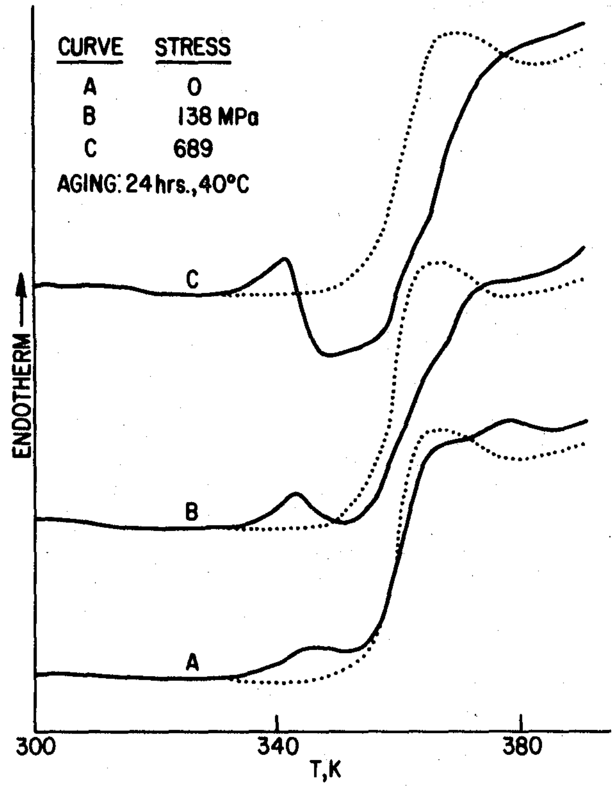

*Fig. 5. Effect of pre-aging uniaxial compression on DSC of free-cooled PVC sheet.*

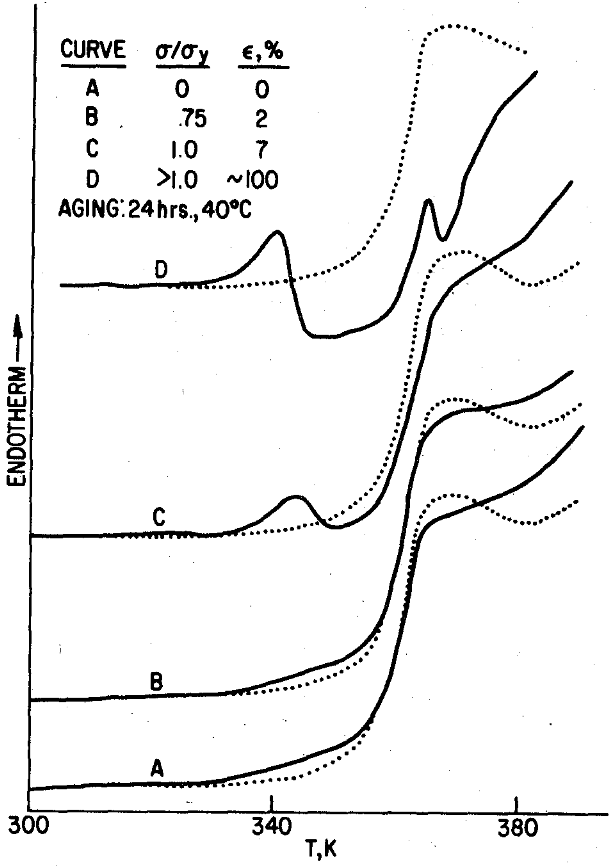

*Fig. 6. Effect of pre-aging tensile stress on DSC of free-cooled PVC sheet.*

of the yield stress produced little effect on the enthalpy relaxation, but stressing just to the yield point caused a pronounced DSC aging peak. Curve D, for a sample cold-drawn 100 percent before aging, again suggests that a strong exotherm and apparent elevation of $T_g$ are related to orientation or yielding.

### Varied Co-aging Treatments

DSC curves obtained on quenched PVC powder samples aged under varied pressures of $CO_2$ and $CH_3Cl$ vapor are shown in *Figures 7* and *8*, respectively. The effect seen here is just the opposite of that produced by vapor exposures before aging: the aging peak is progressively suppressed as the vapor pressure during aging is increased, and the peak position shifts to slightly higher temperature. Once again, however, the effect seems related to the amount of vapor sorbed, rather than the pressure per se, since a much greater pressure of $CO_2$ than of $CH_3Cl$ is needed to produce a similar degree of peak suppression.

The slight peak at about 320K in curves D of both *Figs. 7* and *8* is apparently real and reproducible; it may be an aging peak resulting from release of vapor pressure and the unavoidable few minutes of aging during transfer from the aging vessel to the DSC pan and instrument. Earlier results (1) showed a slight peak at about this temperature for unaged, pre-stressed PVC samples.

An example of the effects produced by aging under uniaxial compressive stress is shown in *Fig. 9*. In comparison to the unstressed control sample, the stress totally suppressed the aging peak, and also produced a broad, deep exotherm and an apparent elevation of *Tg*. The exotherm here, as in the case of pre-aging compressive stress, may be

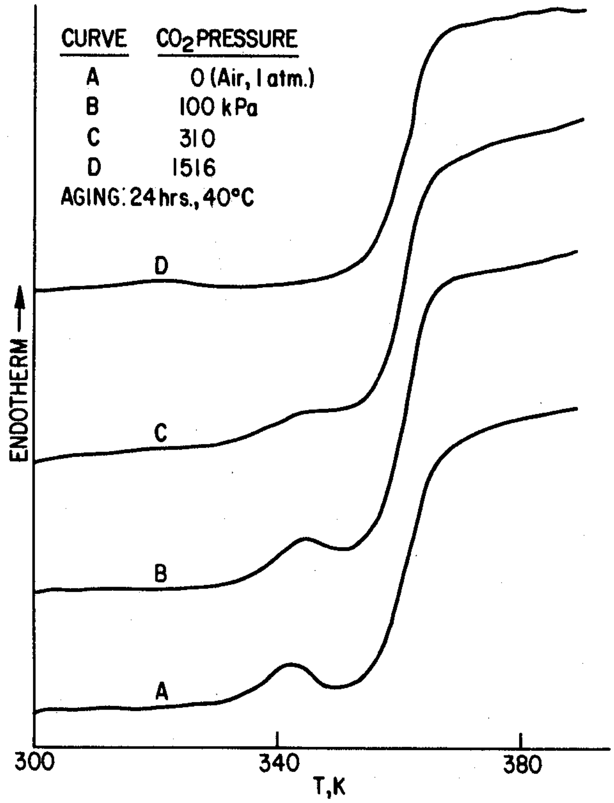

*Fig. 7. Effect of $CO_2$ pressure during aging on DSC of quenched PVC powder.*

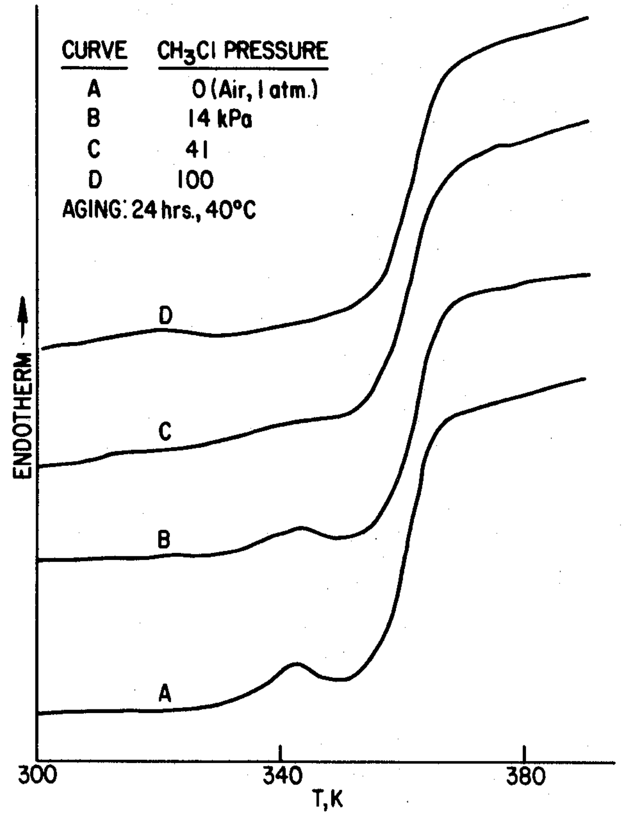

*Fig. 8. Effect of $CH_3Cl$ pressure during aging on DSC of quenched PVC powder.*

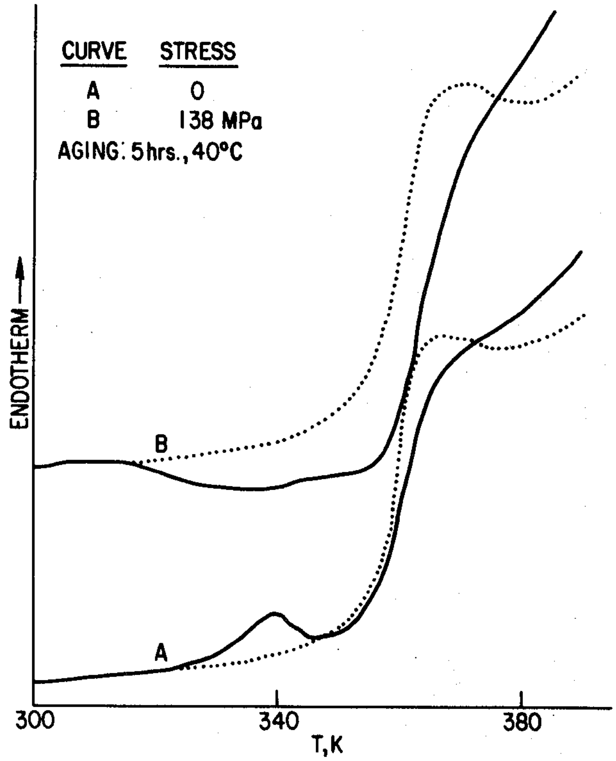

*Fig. 9. Effect of uniaxial compressive stress during aging on DSC of quenched PVC sheet.*

associated with cold-flow, since appreciable deformation was noted after the aging stress was removed.

This interpretation of the exotherm is supported by the results, shown in *Fig. 10*, for samples aged under compressive stress with lateral constraint to prevent cold-flow (thus effectively under hydrostatic pressure). Again, the stress resulted in suppression of the aging peak, but here the exotherm is virtually absent. With increasing hydrostatic pressure, the aging peak shifts to distinctly lower temperature, in contrast to the slight upward shift with increasing vapor sorption. The hydrostatic-pressure effect parallels the effect of decreasing aging temperature or time (1), suggesting that the rate of aging is reduced, or that the average relaxation time is increased.

Finally, the application of tensile stress during aging produced the DSC results shown in *Fig. 11*. To avoid extensive deformation, stress in these experiments was kept below the yield stress. Consequently, the stress effects are not so pronounced as in the compressive cases, nor is there a significant exotherm; but the direction of the effect is still clear, at least for the highest stress (Curve D): Tensile stress during aging tends to suppress the development of the DSC aging peak, just as is the case for compressive stress or for the dilational stress due to the presence of a soluble vapor.

## DISCUSSION

The present results on the effects of pre-aging treatments confirm and extend those reported earlier (1), and support the idea that there is a qualitative equivalence in the effects of thermal, mechanical, and vapor-exposure histories upon subsequent enthalpy relaxation of glassy polymers. Reheating a sample and rapid quenching, application and rapid release of mechanical stress, and sorption and rapid desorption of a vapor all markedly enhance the enthalpy relaxation, and the consequent DSC aging peak, compared to a slowly cooled unstressed polymer sample. The common feature of these treatments, we suggest, is a stress which introduces additional energy into the glass, followed by a release of the stress more rapidly than the added enthalpy can relax out. Consequently, the sample is displaced further from its state of enthalpy equilibrium, and therefore loses enthalpy more rapidly during aging than a slow-cooled sample.

The observed suppression of the DSC aging peak by continued application of mechanical or sorptive stress during the aging period may be explained as a consequence of an applied stress which opposes polymer relaxation. Considering the qualitative parallel between volume and enthalpy relaxations, the swelling stress from a soluble vapor would presumably oppose and tend to suppress both the volume contraction and the enthalpy relaxation. Similarly, relaxation of volume and enthalpy, in a polymer of Poisson ratio <0.5, would be opposed by the dilational effect of mechanical stress having a tensile or shear component. On the other hand, suppression of the aging peak by pure hydrostatic compression during aging may be due to a

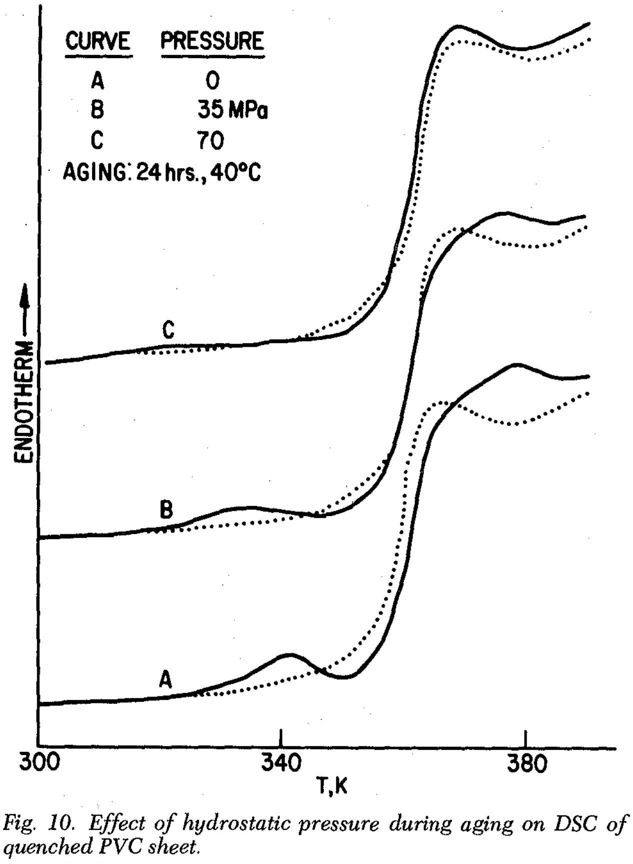

*Fig. 10. Effect of hydrostatic pressure during aging on DSC of quenched PVC sheet.*

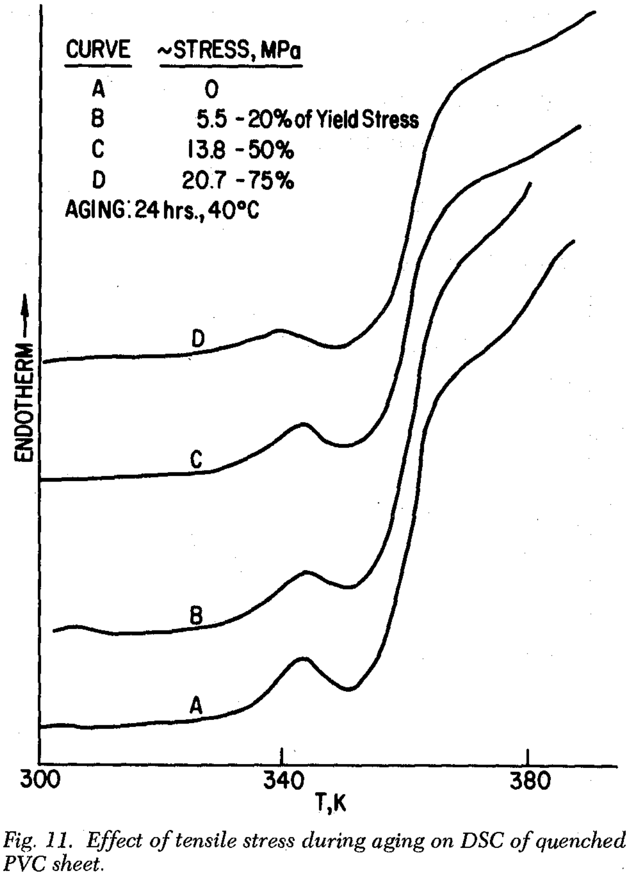

*Fig. 11. Effect of tensile stress during aging on DSC of quenched PVC sheet.*

lengthened average relaxation time resulting from reduced free-volume or configurational entropy.

The behavior of the apparent exotherm between the aging peak and *Tg* seems somewhat different from that of the aging peak itself, in that high uniaxial compressive stress applied either before or during aging cases an enhancement of the exotherm. Similar exotherms have been reported for PVC (8) and polystyrene (9) cooled from the melt under high hydrostatic pressure, and for PVC pelletized by pressing the polymer powder at room temperature (10). These treatments, like our uniaxial-compression experiments, may result in the storage of mechanical strain energy. During the DSC scan, release of this strain may be triggered by the energy absorption of the aging peak to produce the succeeding exotherm. Our results suggest that the storage of strain energy may be enhanced by conditions which produce substantial shear yielding, orientation, or tensile strain.

The adaptation by Hodge and Berens (2) of the glass-transition kinetics treatment by Moynihan, et al. (7), has been very successful in modeling the effects of cooling rate and aging time and temperature upon enthalpy relaxation and recovery. Recently, Hodge and Berens (11) have further shown that this model can reproduce the effects of pre-aging stress and vapor exposure. Efforts to apply the model to aging under stress or vapor are now in progress and will be reported subsequently.

## ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation under the Industry-University Cooperative Research Program through Grant No. CPE-7920740. We thank F. W. Kunig for his experimental assistance and gratefully acknowledge the permission of The BFGoodrich Company to publish this work.

## REFERENCES

1. A. R. Berens and I. M. Hodge, *Macromolecules*, **15**, 756 (1982).
2. I. M. Hodge and A. R. Berens, *Macromolecules*, **15**, 762 (1982).
3. I. M. Hodge and G. S. Huvard, *Macromolecules*, **16**, 371 (1983).
4. I. M. Hodge, *Macromolecules*, **16**, 898 (1983).
5. K. H. Illers, *Makromol. Chem.* **127**, 1 (1969).
6. S. E. B. Petrie, *J. Polym. Sci., Part A-2*, **10**, 1255 (1972).
7. C. T. Moynihan, *et al.*, *Ann. NY Acad. Sci.*, **279**, 15 (1976).
8. W. M. Prest, Jr., J. M. O'Reilly, F. J. Roberts, Jr., and R. A. Mosher, *Polym. Eng. Sci.*, **21**, 1181 (1981).
9. A. Weitz and B. Wunderlich, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 2473 (1974).
10. S. S. Chang, *J. Res. Nat. Bur. Stds.*, **82**, 9 (1977).
11. I. M. Hodge and A. R. Berens, paper presented to High Polymer Physics Division, American Physical Society, Los Angeles, March 21–25, 1983 (to be published).