

Determination of Formation and Relaxation of Crazes by Permeability Measurements

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Synopsis

Formation and relaxation of crazes on different polymeric films are determined by permeability measurements in a high pressure test cell. Thermal dependence of the films permeability has been studied and interpreted on the basis of segmental movement of the macromolecules.

These permeability measurements also offer a way to determine the glass transition temperature of amorphous films.

INTRODUCTION

Recently a large amount of work has been done on the transport properties of gases and vapors in glassy polymers.¹⁻⁴ Special attention has been concentrated on the effect of organic liquids and vapors in initiating the crazing process in amorphous thermoplastic polymers and on the kinetics of craze growth and vapor sorption in such films.⁵⁻⁹ However, besides this case of solvent attack, crazes in glassy polymers can also result from the application of a stress greater than a certain critical value which may be theoretically described.¹⁰⁻¹² Once these crazes are formed, their growth is a complex function of temperature in the sense that the craze length increases with temperature up to a maximum value, and then decreases.¹³ When the test temperature approaches the glass transition temperature (T_g) of the polymer, a relaxation process sometimes occurs causing the crazes to disappear.¹³⁻¹⁴

The phenomenon of craze relaxation at T_g could then be used to obtain information on the nature of this transition in thermoplastic polymers that are able to craze.

The usual ways to determine the T_g in polymers are by differential thermal analysis (DTA) or by differential scanning calorimetry (DSC), both based upon the variation of rate of heat exchange corresponding to the phase transition; or by dilatometry based upon the change of specific volume as a function of temperature (T_g is the temperature at which there is a discontinuity in the slope of the experimental curve), or finally to a change of the shear modulus with temperature in the transition zone. But the T_g of many polymers is affected by the methods and the conditions by which the measurements are made. In particular, the presence of water or of various organic solvents causes a change in

chain motions and consequently a plasticization of the polymer with a lowering of the elastic modulus and of the temperature at which the glass transition occurs.

Recently a simple method of T_g determination based on craze relaxation has been proposed by Salee.¹⁴ This author has observed that the temperature at which the crazes induced on a polymer sample disappear, is very close to the T_g of the polymer itself. The crazed regions in the polymer are similar to a porous sponge in which the cell walls are constructed of highly oriented chains.¹⁵ When the temperature approaches the T_g and the segmental movement increases, a disorientation of the molecules occurs with a consequent disappearance of the crazes. The use of the crazed polymeric materials as permeable membranes recently proposed (see ref. 16) suggested that the T_g of these polymers may be determined by following the temperature at which the flux through the film decreases dramatically.

EXPERIMENTAL

A high-pressure test cell¹⁷ has been used to investigate the permeability to water of several crazed polymers. Experiments were performed under an applied pressure ΔP of 40 atm which was higher than the threshold values of craze formation for all the polymers studied. Materials studied included commercial poly(vinyl acetate) (PVAc), poly(vinyl chloride) (PVC), polystyrene (PS), and nylon 6 samples. Craze-free films of these materials (circa 0.1 mm thick) were prepared by solvent evaporation. The crazes on the polymeric films were created by a pressure impact effect in the test cell.¹⁶ The fact that the membranes are held in place by a stainless steel porous support causes a sudden application of pressure in the high-pressure permeability cell to localize stress concentration in the polymer with subsequent craze formation. Preliminary experiments were carried out to verify the temperature influence on the phenomenon.

For example, in one approach, the measurements were performed preheating an impermeable membrane in the cell to a temperature higher than the T_g of the material and then applying high pressure. No permeability was observed.

The results clearly showed that in this situation no craze formation was induced in the polymeric film. When the same experiment was repeated after cooling down the membrane to a temperature lower than the T_g , a significant permeability was measured.

T_g measurements were also made by using the Clash-Berg Torsional Stiffness Tester.¹⁸ With this device it is in fact possible to obtain the shear moduli after 10 sec, $G(10)$, at different temperatures. Then from the curve $G(10)$ versus T , the T_g of a given polymer in the desired environments can be calculated.¹⁹ This temperature is related to the more common glass transition temperature determined from dilatometric measurements (T_g') by means of the relationship:

$$T_g = T_g' + 4.4^\circ\text{C}$$

(as found in ref. 20).

Samples for these measurements were made by molding the polymer powders in a 62-m \times 12-mm compression mold under a pressure of 100 kg/cm².

Some of these samples were stored under vacuum for at least two weeks while others were kept under water for the same time period.

RESULTS AND DISCUSSION

In Figure 1 shear modulus after 10 sec, $G(10)$, is plotted versus temperature for PVAc and PVC samples. Tests were made in paraffin oil for the samples kept under vacuum, and in water for those kept under water.

It must be noted that while for PVAc the results obtained in paraffin oil are very different from the ones obtained with the samples immersed in water, for the PVC there is no significant difference between the data obtained in the two environments. For PVAc the T_g measured under water is lower than the one obtained in a dry atmosphere (Table I), the one usually reported in the literature.¹⁴

By preparing thin films of a given polymer it is possible to test them in a conventional reverse osmosis high-pressure cell using a specific liquid; and by measuring the permeability, it is possible to determine the formation and the relaxation of the crazes and eventually the glass transition temperature (T_g'') of the polymer itself.

Results of water permeability data as a function of temperature for PVAc and PVC films, at an applied pressure of 40 atm appear in Figure 2.

The flow rate for the PVAc membranes becomes practically zero at $T = 15^\circ$, while for the PVC film, a strong decrease is observed upon increasing the tem-

TABLE I
Glass Transition Temperature of Various Polymers

Polymer	T_g	T_g'	T_g''
PVAc in air	33	29	—
PVAc in water	16	—	17
PVC in air	82	82	—
PVC in water	82	—	80
PS in air	103	99	—
PS in water	103	—	—

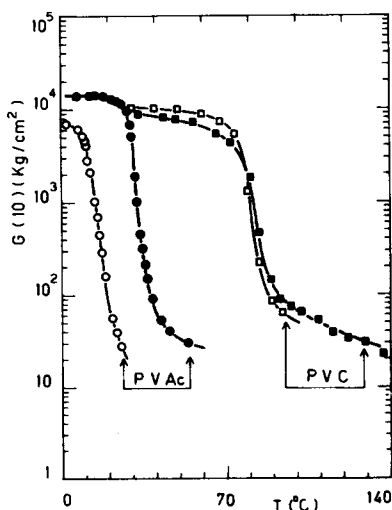


Fig. 1. Shear modulus after 10 sec vs. temperature for PVC (\square) and PVAc (\circ) polymers. Full symbols refer to wet samples, open symbols to the dry ones.

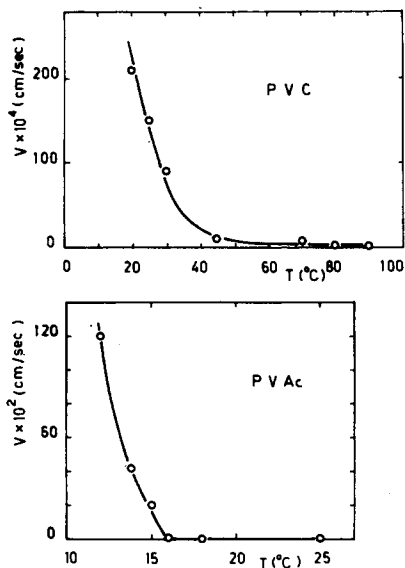


Fig. 2. Permeability data vs. temperature for PVC and PVAc polymers ($\Delta P = 40$ atm).

perature and the permeability reaches an asymptotic very small value at $T = 80^\circ\text{C}$.

The existence of the very low permeability at $T > T_g$ for the PVC films can be correlated with the low crystallinity present in this polymer. In fact, crystalline polymers can be permeable, as reported by Bierembaum et al.²¹ if opportunely stressed. The porosity of the films is connected with the presence of a raw lamellar structure. These lamellae can be "peeled apart" if the film is elongated and they then form a microporous structure.²¹ Obviously the microporosity induced with this effect is not very sensitive to the temperature, at least for temperatures far from the melting zone.

The experiments performed with PS at different temperatures revealed that the permeability is consistently lower at 80°C than at 20°C , but it was not possible to reach the temperature of zero permeability because it was too close to the boiling temperature of the liquid used. Permeability measurements made on nylon 6 samples at increasing temperatures present a maximum at temperatures of about 50°C and then decrease. Although the part of the curve for $T > 50^\circ\text{C}$ can be explained with effects similar to the ones described for the PVC, the increase of permeability with temperature has no clear explanation as yet and must be related to some different craze-relaxation mechanism active in this polymer.

In conclusion, it seems that permeability measurements may offer a way to determine the formation and relaxation of crazes in polymeric films and eventually serve to measure the T_g of amorphous films in the environment in which we would like to know their physical properties. With this technique the heating rate dependence of the T_g has no value as it is measured at constant temperatures.

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