

Orientation in Uniaxially Drawn Polystyrene Plasticized by CO₂ Sorption

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SYNOPSIS

Uniaxial drawing experiments of the polystyrene films plasticized by a sorption of compressed CO₂ gas at pressures up to about 18 MPa were carried out with strain rates ϵ of 0.0290 and 0.0079 s⁻¹. The drawing was performed successfully with draw ratio λ up to 4 at the temperatures of 308.15, 318.15, 328.15, and 338.15 K. The Hermans orientation function f of the drawn samples was determined from the dichroic ratio measured by an infrared spectrophotometer. While f value increases with increasing ϵ or λ , it decreases with increasing CO₂ pressure or temperature. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that the physical properties of polymeric materials are much influenced by molecular orientation.^{1,2} Since thermoplastic polymers become ductile above their glass transition temperatures, T_g , a drawing at temperatures higher than T_g induces the orientation in polymers. Several semicrystalline thermoplastics such as polyethylene and polypropylene with T_g below ambient temperature are oriented by a cold drawing. Most amorphous polymers, however, have their T_g fairly higher than ambient temperature: The T_g 's of polystyrene (PS) and poly(methyl methacrylate) (PMMA) are around 380 K. To reduce the T_g of polymers, it is necessary to add adequate organic solvents into the polymers. However, it is difficult to remove the additives completely from polymers after drawing in such cases.

Recent studies have shown that the T_g of amorphous polymers is significantly depressed by sorption of compressed gases: The T_g 's of PS³⁻⁵ and of PMMA^{4,5} in compressed CO₂ gas decrease below the experimental temperatures at moderate CO₂ pressures. Furthermore, CO₂ gas has been widely used in polymer processing such as extraction of low molecular weight compounds,^{6,7} impregnation with additives,^{8,9} produc-

tion of microcellular foams,¹⁰⁻¹² and conditioning of membranes.¹³⁻¹⁵ The plasticizing effect of CO₂ plays a very important role in most of those applications.

The use of compressed CO₂ gas as a plasticizer for polymer drawing is advantageous because its complete removal from the polymer is accomplished simply by decreasing the CO₂ pressure. The rapid release of the pressure brings about the cooling of the drawn polymer instantaneously by an adiabatic expansion of the gas. Consequently, both the orientational and swelling structures of the polymer can be frozen. Hence, it is expected that physical properties of the polymers drawn in CO₂ differ from those of the hot-drawn polymers. Nevertheless, there has been so far no attempt to produce oriented polymers by making use of compressed CO₂ gas as a plasticizer in the drawing process. This is due mainly to the technical difficulty in drawing polymer films under compressed CO₂.

This paper describes the uniaxial drawing of PS films plasticized by CO₂ sorption and presents the effects of pressure, temperature, strain rate, and draw ratio on the Hermans orientation function of the films.

EXPERIMENTAL

Materials

A PS ($M_w = 3.60 \times 10^5$, $M_n = 1.58 \times 10^5$, and $T_g = 381$ K) film (0.1 mm thick) was prepared by conventional extrusion through a linear slit die on a

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Table I Minimum Drawable Pressure, P_m , of PS at Different Strain Rates and Temperatures When the Draw Ratio λ is 4

T (K)	P_m (MPa)	
	$\epsilon = 0.0079$ (s^{-1})	$\epsilon = 0.0290$ (s^{-1})
308.15	10.0	— ^a
318.15	7.4	7.7
328.15	6.2	6.6
338.15	— ^b	5.5

^a At this temperature, there is no P_m .^b Not measured.

chill roll and then annealed at 423 K for 5 h. No orientation in the polymer was confirmed from an infrared dichroism measurement. The film was cut into the strip samples (15 mm width \times 50 mm length). EG grade CO₂ (99.999% purity) purchased from Showa Tansan Co. was used without further purification.

Methods

An *in situ* uniaxial drawing apparatus developed in our laboratory was used. The apparatus and the operation methods have been described in detail elsewhere.¹⁶ Uniaxial-drawing experiments in CO₂ were carried out at pressures up to about 18 MPa and at the temperatures of 308.15, 318.15, 328.15, and 338.15 K. Two strain rates ϵ were adopted (0.0290 and 0.0079 s⁻¹). The draw ratio λ , which is defined as the final sample length divided by the original sample length, was used up to 4. The drawing experiments were performed after the PS films were allowed to stand in CO₂ for at least 3 h at desired conditions. Since the holding time is about 20 times longer than the equilibration time estimated from the diffusivity data reported by Berens and Huvar,¹⁷ the sorption equilibrium is considered to be completely reached. CO₂ gas was rapidly released immediately after drawing and pressure was reduced to an atmospheric one within a few seconds.

Infrared Dichroism

The polarized spectra were taken on a Shimadzu 8500 Fourier transform infrared spectrophotometer at a resolution of 4 cm⁻¹ with a total of 20 scans. A Shimadzu GPR-8000 aluminum wire-grid polarizer was used. To obtain the two perpendicular polarization measurements, PS films in place of the po-

larizer were rotated 90°. The dichroic ratio R at the 906 cm⁻¹ band is calculated as $R = A_{||}/A_{\perp}$, where $A_{||}$ and A_{\perp} are, respectively, the absorbances parallel and perpendicular to the drawing direction. Six R values for each sample were measured at intervals of 5 mm moving along the drawing direction and averaged R values were used to calculate the Hermans orientation function.

RESULTS AND DISCUSSION

Uniaxial drawing of PS films with $\epsilon = 0.0079$ s⁻¹ and $\lambda = 4$ in CO₂ at 308.15 K was successfully carried out at pressures above 10 MPa. When the strain rate was increased from 0.0079 to 0.0290 s⁻¹ with the constant draw ratio, it was impossible to draw PS films at 308.15 K under any CO₂ pressure up to 18 MPa used in this work. The results for the strain rate of 0.0079 s⁻¹ show that PS is ductile under that condition. Since it was confirmed from hot-drawing experiments with $\epsilon = 0.0079$ s⁻¹ at atmospheric pressure that PS is not ductile at temperatures below the T_g , the results in CO₂ suggest that the T_g of PS in CO₂ at pressures above 10 MPa is lower than 308.15 K. On the contrary, Wang et al.³ reported that the T_g behavior of PS as a function of CO₂ pressure showed a T_g minimum and that the T_g of PS in CO₂ at 307.15 K did not decrease to a temperature below the experimental one. Their data imply that PS in CO₂ cannot be ductile under any pressure at 308.15 K. The contradiction between our results and theirs may be attributed to different T_g 's of PS used in each study; T_g 's of PS used by Wang et al. and in our work are 373 and 381 K, respectively.

There is a minimum drawable pressure, P_m , of PS films at a given temperature. Values of P_m at different temperatures are summarized in Table I. At any temperature, P_m values at a lower strain rate are smaller than those at a higher strain one. The glass transition pressure, P_g , at a given temperature may be estimated from the extrapolation of P_m vs. ϵ to the intercept at $\epsilon = 0$ s⁻¹.

The nominal draw ratio was equal to the actual one in any drawn PS films. No change in appearance except for the dimensions was found and no microbubble was detected by the scanning electron microscope. The latter result suggests that the rapid release of CO₂ gas just after the drawing process brings about an instantaneous freezing of the drawn PS films to the glassy state and prevents the liberation as bubbles of CO₂ dissolved in the polymer matrix.

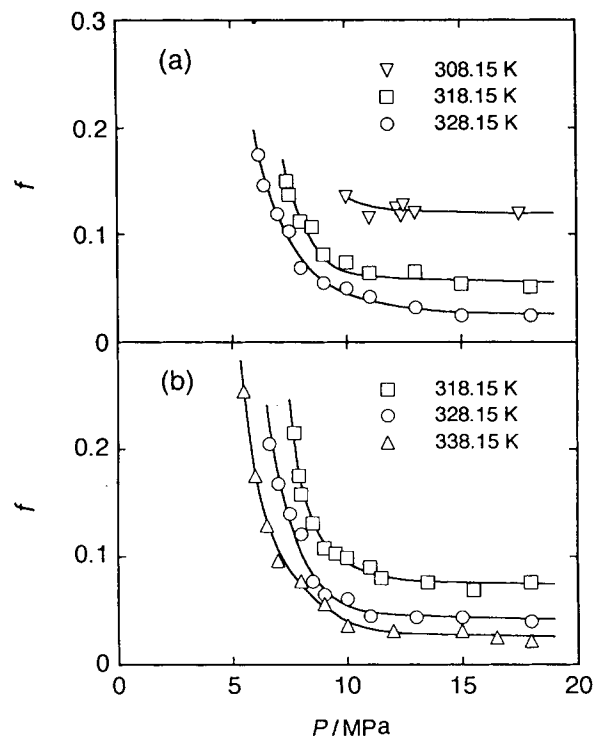


Figure 1 The Hermans orientation function f for uniaxially drawn PS films with $\lambda = 4$ as a function of CO_2 pressure P at different temperatures: (a) $\epsilon = 0.0079 \text{ s}^{-1}$; (b) $\epsilon = 0.0290 \text{ s}^{-1}$.

The Hermans orientation function f is calculated from the dichroic ratio R by use of the following relation:

$$f = \frac{R - 1}{R + 2} \cdot \frac{R_0 + 2}{R_0 - 1} \quad (1)$$

where $R_0 = 2 \cot^2 \alpha$, α being the angle between the dipole moment vector of the considered vibration and the chain axis. The 906 cm^{-1} band due to a vibration out-of-plane mode of the benzene ring was used. The α value for the vibration was reported to be 35° .¹⁸

Figure 1(a) shows the CO_2 pressure dependence of f for PS films with $\epsilon = 0.0079 \text{ s}^{-1}$ and $\lambda = 4$ at the temperatures of 308.15, 318.15, and 328.15 K. A similar plot for the results with $\epsilon = 0.0290 \text{ s}^{-1}$ at the temperatures 318.15, 328.15, and 338.15 K is shown in Figure 1(b). Since the temperatures are higher than is the critical temperature of CO_2 (304.2 K), the drawing experiments were carried out with no phase transition of CO_2 . It is found that, at any temperature, f values show a steep decrease from P_m and approach a constant value with increasing CO_2 pressure. At a given CO_2 pressure, f values be-

come smaller with increasing temperature. From the results at the same temperature and pressure, it is clear that high molecular orientation in PS films is obtained at a higher strain rate when the draw ratio λ is 4. Among the experiments with $\lambda = 4$, the largest value of f , 0.254, is obtained when ϵ is 0.0290 s^{-1} at 318.15 K and 5.5 MPa.

To obtain more information on the effect of the strain rate on the f value, the draw ratio λ was varied in the range of 1–4 at 318.15 K and 10 MPa. Figure 2 shows the draw ratio λ dependence of f for two strain rates. An approximately linear relationship between f and λ holds for two different strain rates. A high orientation is obtained by increasing ϵ for a given draw ratio. Thus, it is considered that a relaxation of orientation occurs almost steadily and that its relaxation time does not change during the strain process. The molecular arrangement by drawing is accompanied by no expulsion of CO_2 and no change in the molecular mobility of PS.

From the influence of experimental conditions of drawing on the Hermans molecular orientation function, the following conditions are suggested: To get high molecular orientation in PS films, drawing should be carried out with a high strain rate and a high draw ratio at the pressure near the P_m and at the relatively low temperature.

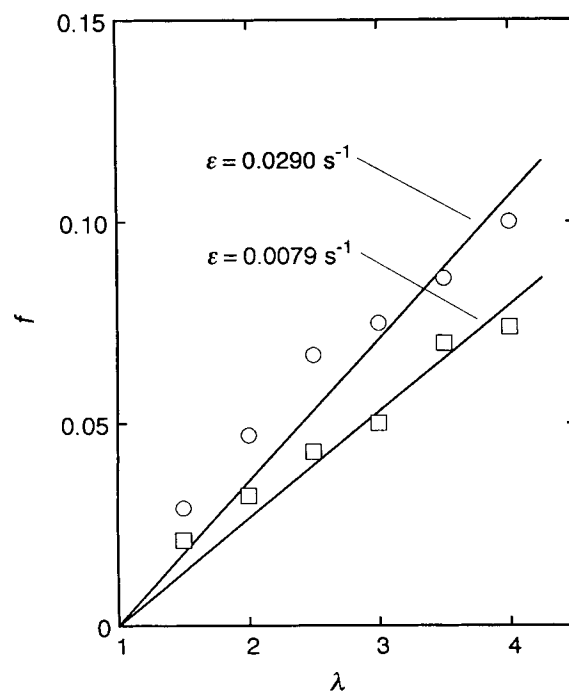


Figure 2 The Hermans orientation function f as a function of draw ratio λ for PS films drawn uniaxially in CO_2 at 318.15 K and 10 MPa for two strain rates.

The basic information obtained in this work is very useful to promote research and development in this polymer drawing process. A study is now in progress to elucidate various physical properties of the oriented polymers. Preliminary experimental results obviously show that gas permeability of the polymers oriented by this drawing method is higher than that of the hot-drawn one.

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