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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) The goal of this research was to gain an understanding of the transport/morphology relationships in semi-crystalline polymers. It was hoped that this research would lead to the development of inexpensive high barrier materials with desirable mechanical properties. Briefly we have found that: 1) Uniaxial drawing is an extremely effective way to increase the barrier of semicrystalline films. For HDPE with a 20x draw, barrier improves by a factor of = 500 for Cl_4 ; = 50-100 for O_2 and CO_2 and = 25 for H_2 . 2) The mechanism for this improvement is less clearly understood; however it is not due to major changes in percentage crystallinity or an increase in amorphous density. At this stage it appears to be due to a reduction in amorphous chain mobility. K. U. W. T. D. | | | |
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FINAL TECHNICAL REPORT

By H. Sha and I. R. Harrison
On Project 21364-MS

OUTLINE

- (1) Introduction
- (2) Development of Permeation measurement apparatus
- (3) Sample preparation
- (4) Measurement of transport parameters
- (5) Characterization of the sample morphology
- (6) A brief discussion/summary

(1) Introduction

The goal of this research is to acquire an understanding of the transport-morphology relationships of crystalline polymers. This may lead to the development of inexpensive high barrier materials with certain mechanical properties. The transport property of a crystalline polymer is potentially very useful in probing its amorphous region which is much less accessible to characterization than the crystalline component.

The following areas have been carried out:

- 1) An extensive literature search in this area

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2) Design, set-up and improvement of a computerized permeability measurement apparatus, including the software for system control, data collection and manipulation.

3) Preparation of samples with different morphological features. A typical crystalline polymer, high density polyethylene, was chosen as the sample for this research.

4) Measurement of transport parameters

5) Characterization of sample morphologies

(2) Development of permeation measurement apparatus

There are many possible ways to measure film permeation properties. The one we established was a modified continuous flow-time lag system basically consisting of an isobaric film chamber and a detector. The film to be tested is sealed in the chamber and two continuous gas currents flow through both side of the film. One of the gas flow (upper stream) contains a fixed concentration of permeant while the other flow (lower stream) is pure carrier gas (usually N_2). The permeant gradually diffuses through the film into the lower stream and its concentration is detected by the detector as a function of time. The coefficients of permeability, diffusion and sorption of the film can be obtained with one experiment on this system.

The first detector used was an analytical gas chromatograph (AGC). However, the AGC detector had a limited sensitivity (lower limit approximately 10 ppm). It worked well with isotropic HDPE thin films which had relatively higher permeability, but failed to detect permeation through highly oriented HDPE films which had much higher barrier than the isotropic ones. In order to improve the sensitivity of the system, the AGC was replaced by a quadruple mass spectrometer gas analyzer. This improved the minimum detectable limit to ca. 10^{-4} torr, corresponding to ca. 0.1 ppm, i.e. the sensitivity was increased by a factor of 100. This enabled us to measure the permeability of some relatively large molecules through oriented HDPE films which had high barrier properties. Operation of the system and data collection are controlled by an Apple II computer. Software for this purpose was developed and improved. Now under the control of the computer the system is able to run continuously for a sufficiently long period of time (e.g. a



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week) which is sometimes necessary to measure the diffusion of relatively big molecules such as freon and carbon tetrachloride.

(3) Sample preparation

Efforts have been made to make samples with different morphological characteristics. These include: 1) single crystal mat with lamellae parallel to the surface of the film, 2) melt crystallized films with isotropic spherulitic structure, and 3) uniaxially oriented films with a microfibrillar morphology drawn from isotropic melt-crystallized films.

Single crystal mats were obtained by filtering a suspension of HDPE single crystals grown from dilute solution. The resultant mat was very brittle and weak. Measurement of the permeation property of these mats was not successful because of their lack of mechanical toughness.

Isotropic melt crystallized films were molded on a hot press. The films were pressed in the hot press at c.a. 150°C and then cooled in the air under room temperature.

Isotropic films were then drawn using a wide range of draw temperatures and draw rates. All the films were drawn in one stage, and draw ratios ranging from 3 to 20 were obtained. Two techniques were used in controlling the draw temperature: an environmental chamber (oven) and a pair of "hot nips" which was devised in this lab. The oven heats up the whole sample being drawn and will more or less anneal the sample before, during and after the drawing process. The hot nip technique, on the other hand, supplies heat only to the "necking" region of the deforming film and thus has no annealing effect. Almost all the drawn films were nearly transparent and very tough in the draw direction. Depending on their draw ratio, the film should have morphologies ranging from a composite of spherulitic and fibrillar (low draw ratio) to a completely fibrillar structure (high draw ratio).

(4) Measurement of permeation parameters

Permeability of these films to a variety of gases and organic vapors with different molecular sizes were measured on the apparatus mentioned above. In the measurement process, the concentration of the permeant on the lower stream side of the film is recorded as a function of time. An integration of the C (concentration)-t (time) curve yields a Q-t curve, where Q is the total amount of permeant

diffused through the film during the time period (t). When equilibrium is reached, C will be constant and the corresponding Q-t plot will be a straight line. The permeability coefficient P is obtained from the slope of the straight line; from the intercept of the extrapolated straight line with the time axis, the "time lag" τ is obtained. The diffusion coefficient, D, is calculated as $D = l^2/6\tau$, where l is the thickness of the film. The sorption coefficient, S, is calculated as $S = P/D$.

All measurement were controlled and data collected by an Apple II computer. Software for data manipulation were also developed which enabled us to obtain permeation parameters from the vast volume of original data quickly and accurately.

Measurement of the single crystal mats was not successful due to its lack of mechanical toughness. The results from isotropic and oriented films are briefly presented below.

(1) With increasing draw ratio λ , the permeation of all permeants showed similar behavior (FIG. 1 & FIG. 2): both P (permeability coefficient) and D (diffusion coefficient) drop steadily up to the highest draw ratio attained. This drop of P and D has been observed by Peterlin et.al and Ward et.al and explained as a consequence of the reduced amorphous chain mobility and the formation of impermeable microfibrils or "crystal shutters" in the highly drawn samples. However, the sharp drop of P and D within a very narrow region of λ , which was reported by both of the above authors and attributed to the complete transformation of the polymer morphology from spherulitic into microfibrillar within a given range of λ , was not observed here. In addition, the levelling off of P and D at high λ was also not observed.

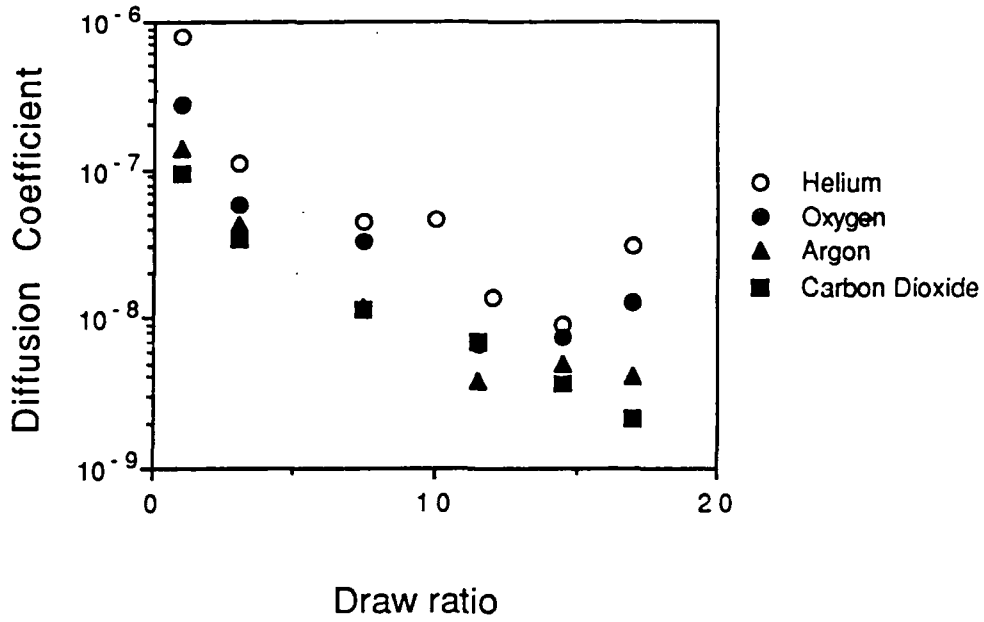


FIG.1 Changes of Diffusion Coefficient with Draw Ratio

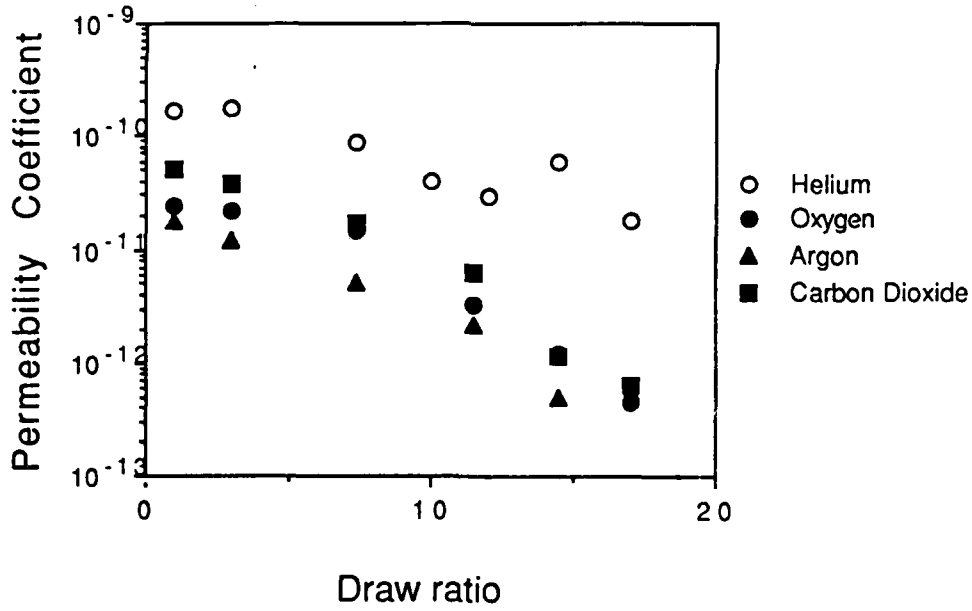


FIG. 2 Changes of Permeability with Draw Ratio

(2) The way in which P changes with λ is somewhat different from that in which D does. The drop in D is relatively fast at low draw ratios and slows down as λ becomes higher, while P drops more rapidly in the high λ region than it does in the low λ range. As a result, S showed a maximum on the S - λ curve (Fig. 3). Peterlin had reported a similar observation with the sorption of ethylene chloride in oriented HDPE but the draw ratio at which S has its maximum was much smaller.

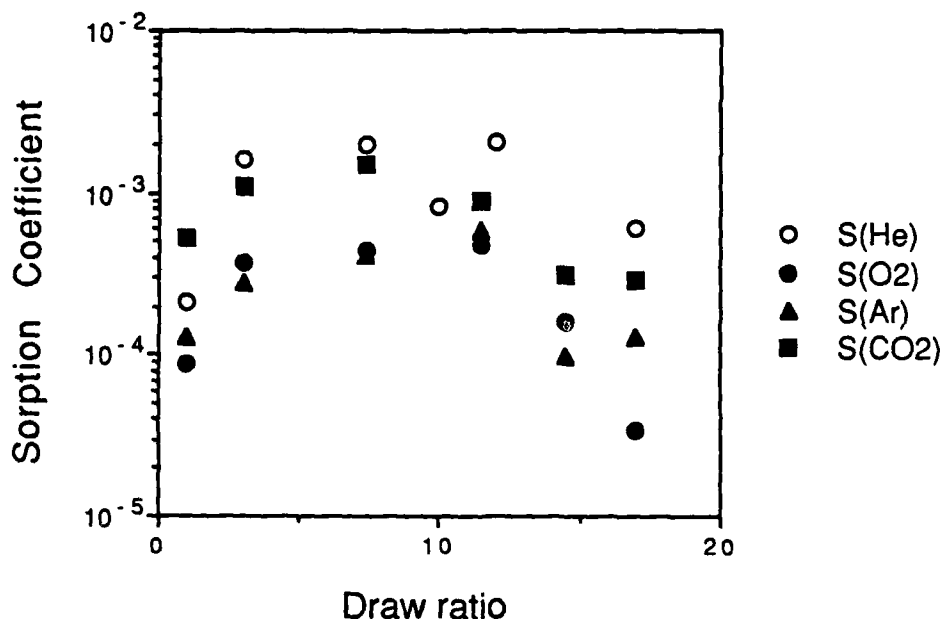


FIG. 3 Change in Sorption Coefficient with Draw Ratio

(3) The diffusivity of a permeant in the films is closely related to its molecular size. As a rule, the smaller the molecule, the higher its P and D values. In addition, the P and D values of larger molecules drop faster with an increasing draw ratio, e.g., as λ varies from 1 to 17, the D value of He drops only about 25 times, while the D of CCl_4 , a much larger molecule, drops more than 400 times. From another point of view, it can be seen that the molecular size dependence of diffusivity is greater in samples with higher draw ratios (FIG. 4).

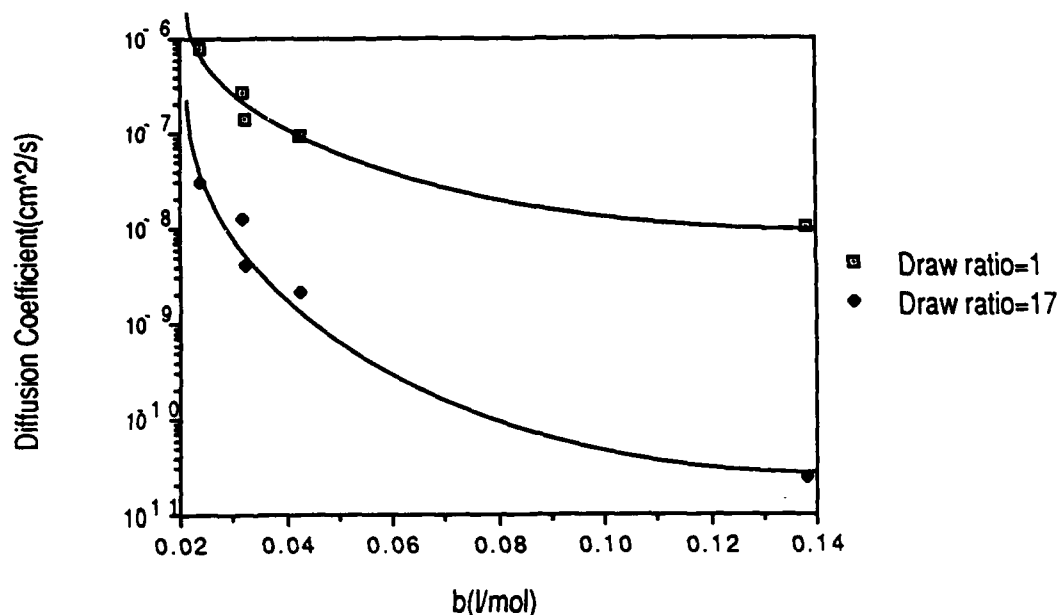


FIG. 4 Dependence of Diffusion Coefficient on The Van de Wall's volume of The Permeants at Different Draw Ratios

Characterization of the films

(1) Thermal analysis

Thermal analysis of the samples revealed that:

(a) the degree of crystallinity of the films increased with draw ratio only slightly, from 78% for the undrawn film to 83% for the sample with a draw ratio of 20. Although permeation takes place only in the amorphous phase of the polymer, it is obvious that the drastic change in the film's permeability upon drawing can not be attributed to variations in their degree of crystallinity.

(b) With increasing draw ratio, the melting peak shifted to higher temperature and the peaks became narrower, indicating a tendency towards increasingly perfect crystalline structure in films with high draw ratios.

(2) Density measurement

The results from density measurement were rather scattered but still showed some trend: e.g. for films drawn at a fixed draw rate, the ones drawn at higher temperature usually has a higher density; samples drawn at lower draw rate generally show higher density;

and samples drawn with the hot nip technique usually have densities lower than those drawn in the oven.

Based on a two phase model and the combination of results from thermal analysis and density measurements, amorphous density has been calculated as a function of draw ratio. Again the results were somewhat scattered but still revealed some general features. The apparent amorphous density showed a decrease with increasing draw ratio, implying that the drop in the film's permeability was not due to reduced free volume upon drawing, as had been proposed by some authors. In addition, this reduction in amorphous density with draw ratio might be used to elucidate the previously observed maximum on the sorption coefficient v.s. draw ratio curve of the films. Further investigation in this aspect is desired.

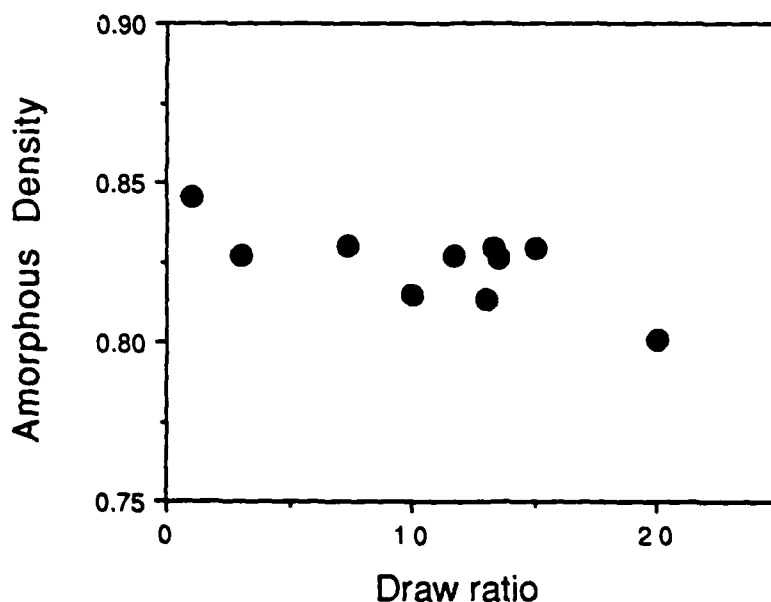


Fig. 5 Variation of amorphous density with draw ratio

(3) Dynamic mechanical thermal analysis (DMTA)

Significant differences were observed between the DMTA results of isotropic and oriented films (measurements were made in a direction parallel to the draw direction). We will only be concerned with changes in the γ transition which is generally believed to be associated with the amorphous region and therefore is more relevant to the transport properties of the polymer: (a) orientation (drawing)

reduced the intensity of the γ transition, (b) the activation energy of the γ transition for an oriented ($\lambda=15$) film is approximately 50% higher than that for an isotropic sample, and (c) the transition seemed to shift to lower temperature (about 5°C at 3HZ). Both (a) and (b) are indications of more restriction on amorphous chains in the oriented polymer and provide evidences that reduced amorphous chain mobility is among the main factors that lead to the transport property changes upon drawing. However, the mechanism for (c) is not yet clear. It is believed that the γ transition for HDPE is composed of three secondary transitions. One possibility is that drawing suppresses the component at higher temperatures end and causes the apparent γ transition as a whole to shift downward. Further investigation is needed to clarify this point.

(6) A brief discussion/summary

- 1) Uniaxial drawing is an extremely effective way to increase the barrier property of crystalline polymers.
- 2) For HDPE, the drastic reduction with increasing draw ratio in permeability is not caused by a decrease in its amorphous content, nor by reduced fractional free volume.
- 3) Drawing reduces chain mobility in the amorphous phase of the polymer, as is shown by DMTA results, and leads to the decrease in its permeability.
- 5) The maximum in the sorption-draw ratio is probably associated with the decrease of amorphous density upon drawing.
- 6) Uniaxial drawing has greater effect on the permeability of gases/vapors with larger molecules. In the future it is possible to use permeants with different molecular sizes to probe the morphological details in crystalline polymers.