

Novel Rolltruded Membranes. III. The Effect of Processing Temperature on the Gas Transport Properties of Isotactic Polypropylene

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SYNOPSIS

The solubility and diffusivity of CO₂, N₂, and CH₄ in isotactic polypropylene [iPP] thin films produced via rolltrusion solid-state processing have been studied. Processing temperatures between 50 and 125°C and draw ratios between 1 and ca. 10 are reported. Variations in the transport coefficients and the activation energies, in conjunction with the molecular theory of diffusion of Pace and Datyner,^{22,23} were used to assess changes in the micromorphology of the polymer due to this unique processing mode. Specifically, it has been found that the formation and destruction of microvoid volume were necessary to account for the large increases in solubility and decreases in the heats of solution. Additionally, changes in the tortuosity of the diffusive pathways—due in part to crystallite orientation and to the formation of impermeable amorphous regions in the microfibrillar morphology—were found to influence the diffusivity significantly. The tortuosity actually decreased in contrast to the behavior obtained for uniaxially drawn films. Based upon these observations, it is suggested that triaxial stresses induced in rolltruded polymer films are responsible for this morphology and its function in polymer membranes. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Rolltrusion solid-state processing has been introduced as a technique for the production of polymeric thin films from commercially available and even for solvent-intractable engineering polymers.^{1,2} These films may be suitable for membrane applications in high-temperature and/or harsh chemical environments. This process is unique in that it combines the high compressive force of rolling with the high stress of drawing to produce a *triaxially* ordered morphology, as verified by X-ray (SAXS and WAXS) and electron microscopy. Materials so processed display improved mechanical properties in three dimensions.^{3–10}

Recently, we have reported on the transport of several gases in isotactic polypropylene [iPP] films rolltruded at 150°C.² Membranes produced under

these conditions do not show the dramatic decline in flux that is often encountered in uniaxially drawn films, especially at high draw ratios.^{11–20} From a morphological perspective, three factors are believed to influence the transport properties:

1. microvoid formation and elimination,
2. tortuosity changes due to crystallite orientation and thermal treatment of the film, and
3. variations in amorphous chain stiffness.

Consequently, the amorphous matrix is judged to be comprised of three regions, namely,

1. relatively impermeable, highly strained, amorphous tie molecules embedded in the microfibrils (as suggested by Peterlin et al.¹⁴),
2. highly permeable microvoids of low density, and
3. permeable but less strained amorphous chains of the microfibrils that constitute the continuous phase.

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It is the relative distribution of amorphous material between these regions that determines the transport characteristics of the processed films.

In highly uniaxially drawn polymers, the amorphous material in the microfibrils is highly strained and hence relatively impermeable, so that dramatic declines in the diffusivity (and solubility) of various penetrants is typically observed.¹¹⁻²⁰ In comparison, rolltruded films tend to be more permeable, because the simultaneous compression and elongation of the polymer in the roller nip improves the permeability of the amorphous regions of the microfibrils without sacrificing the mechanical integrity of the processed film.³⁻¹⁰

In this paper, we consider some results of processing temperatures below 150°C. The morphological changes mentioned above and in the previous paper² are consistent with variations in transport properties at these lower processing temperatures. The distribution of amorphous material alters the transport properties. For comparison purposes, we also include transport data for a crazed rolltruded film produced at 75°C.

THEORY

In semicrystalline polymers the crystallites are considered to be impermeable, effectively reducing the solubility and diffusivity of a penetrant.²¹ To a first approximation, the solubility of a penetrant is proportional to the volume fraction of amorphous material so that

$$S_o = \alpha_a S_a \quad (1)$$

where s_o and s_a are the observed and amorphous solubilities, respectively, and α_a is the amorphous volume fraction. The available volume for diffusion is similarly reduced. However, two additional empirical factors must be considered, specifically: the role of the crystallites in lengthening the diffusive pathways, and their ability to constrain the amorphous tie molecules. These factors can be highlighted using

$$D_o = \frac{\alpha_a D_a}{\tau \beta} \quad (2)$$

where τ is the tortuosity, β is the chain immobilization constant, and D_o and D_a are the observed and amorphous diffusivities. As noted already,² only the amorphous solubility and diffusivity are considered.

The heat of solution (ΔH_s) and the diffusive activation energy (E_d) are also important parameters

used to assess the morphological origins of the changes in the transport properties of rolltruded polymers. We have previously used the molecular theory of Pace and Datyner^{22,23} as a semiquantitative guide to establish the molecular scale variations responsible for the observed changes in ΔH_s and E_d as well as in s_a and D_a . For small changes in the amorphous phase density, the theory predicts that

$$\Delta H_s \approx -k_1 CED_p r_e^2 - k_2 \left(\frac{\epsilon}{k} \right)_g + k_3 \frac{B^{1/4} CED_p^{3/4} d^a}{r_e^{4.1}} \quad (3)$$

and

$$E_d \propto \frac{B^{1/4} CED_p^{3/4} d^a}{r_e^{1.4}} \quad (4)$$

where CED_p [J cm^{-3}] is the cohesive energy density of the polymer, r_e [nm] is the equilibrium or average chain separation of the amorphous polymer chains, B [J nm mole^{-1}] is the "chain bending modulus" of the amorphous chains (which we assume is related to chain stiffness, β), d is the penetrant diameter, and $(\epsilon/k)_g$ [K^{-1}] is the Lennard-Jones potential of the penetrant. Since the solutioning process can be viewed as a two-step "hole" formation and "hole" filling process, the first two terms on the right-hand side of eq. (3) represent the hole-filling energy and the third is the hole-formation energy. Only the changes in B and r_e are considered to be appreciably affected by rolltrusion processing. In contrast, the CED_p is not expected to be influenced by processing, since this would imply that the solubility of the polymer in a given solvent could be altered by solid-state processing. This is an unlikely event, although the rate of solutioning may be changed.

Since the amorphous volume fraction can be experimentally determined and changes in the chain immobilization constant can be estimated from the E_d , eq. (2) is used to estimate the relative changes in the tortuosity, τ , induced by rolltrusion processing using

$$\frac{\tau_{\text{rolltruded}}}{\tau_{\text{original}}} = \frac{D_{a,\text{original}}}{D_{a,\text{rolltruded}}} \left[\frac{(\alpha_{a,\text{rolltruded}})^{-0.61}}{(\alpha_{a,\text{original}})^{-0.61}} \right] \times \exp \left[\frac{(E_{d,\text{rolltruded}} - E_{d,\text{original}})}{RT} \right] \quad (5)$$

The functional dependence of the tortuosity on the α_a in iPP has been determined empirically by Vieth

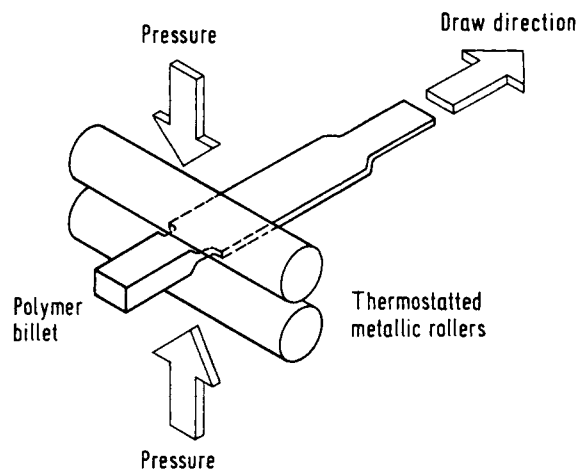


Figure 1 Schematic⁶ of the rolltrusion apparatus and coordinate system used.

and Weurth employing the two-phase concept,²⁴ which is a limitation.

EXPERIMENTAL

Sample Preparation

The rolltrusion technique is illustrated in Figure 1 and is detailed elsewhere.^{1,3-10} Processing conditions, final film thicknesses, and crystalline volume fractions of the unprocessed and rolltruded films are given in Table I. Values for α_c were estimated from density data determined using a density gradient column.¹

Electron Microscopy

The fracture surface morphology of the crazed film was examined at 5 kV with a Hitachi S-800 field emission microscope (FEM) used in the scanning mode.

Permeation Measurements

Experimental permeation tests were conducted with CO₂, N₂, and CH₄ at an upstream driving pressure of 75 psia and permeation temperatures (T_d) ranging from 30 to 70°C. At all times, the permeate pressure was kept below 10 torr and was therefore considered negligible compared with the upstream pressure. The permeation apparatus, which is based on the time-lag method, is described elsewhere.¹

Table I Pertinent Characteristics of the Rolltruded Films Shown as a Function of Processing Draw Ratio and Temperature

| Processing Temperature [°C] | Draw Ratio | α_c |
|-----------------------------|------------|-----------------|
| As-Received | 1.0 | 0.53 |
| 150 | 6.8 | 0.72 |
| 150 | 10.2 | 0.66 |
| 150 | 14.0 | 0.66 |
| 150 | 19.8 | 0.69 |
| 125 | 4.7 | 0.65 |
| 125 | 9.1 | 0.63 |
| 100 | 3.9 | 0.59 |
| 100 | 4.9 | 0.56 |
| 100 | 7.4 | 0.55 |
| 75 | 4.9 | 0.53 |
| 75 (Crazed) | 8.7 | NA ^a |
| 50 | 4.9 | 0.42 |

^a Not available.

RESULTS

The "X-fold," or multiple increase or decrease, in the "amorphous" permeability of N₂, CO₂, and CH₄

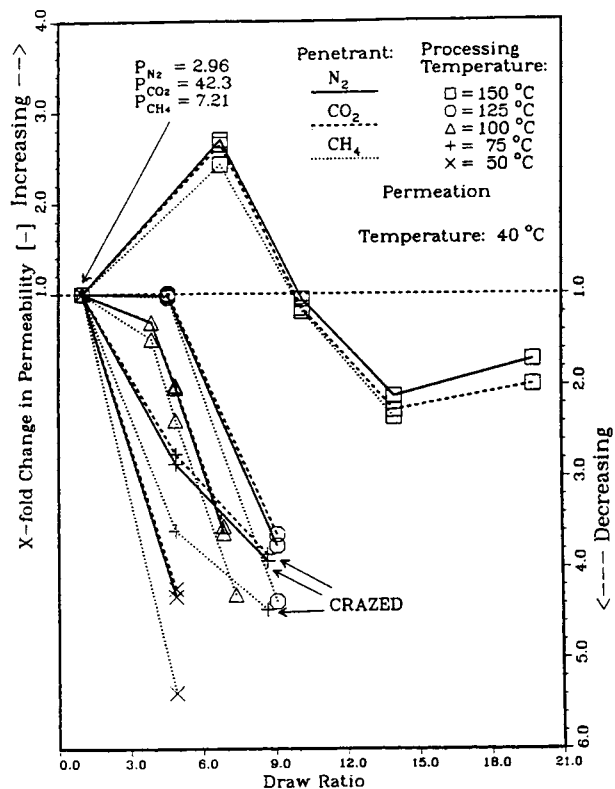
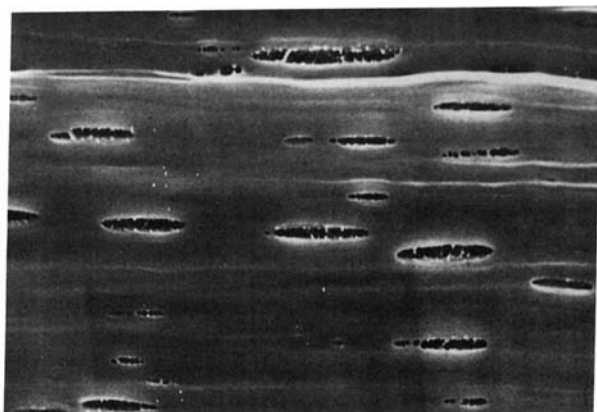
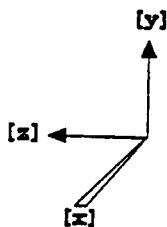


Figure 2 Dependence of P_a on the rolltrusion draw ratio and temperature. P_a s for each gas in unprocessed IPP are listed (units: 10^{10} cm³[STP] cm cm⁻² sec⁻¹ cmHg⁻¹).

for the variously rolltruded iPP films relative to the unprocessed film is shown in Figure 2. The results at $T_p = 150^\circ\text{C}$ have been analyzed in another paper,² but are included here for comparison.

All of the films considered in this study were transparent except the one produced at $T_p = 75^\circ\text{C}$ and draw ratio (DR) ~ 8.7 , which was uniformly stress-whitened and is marked CRAZED in the figures throughout this paper. It was used as a reference film and represents the opposite end of the deformation spectrum when compared with the unprocessed film. Craze rolltruded films have also been obtained at processing temperatures up to 150°C , but these are not considered here. The FEM photomicrograph in Figure 3 shows that this film has a number of large macrovoids which make the determination of α_a difficult. Consequently, the α_a value of the uncrazed film processed at the same temperature (75°C) but to a lower DR (ca. 4.9) is appropriate and useful for the normalization of the transport coefficients.



3 μm

Figure 3 Field emission microscopy photomicrographs for the crazed film of iPP rolltruded at $T_p = 75^\circ\text{C}$ to $DR \sim 8.7$.

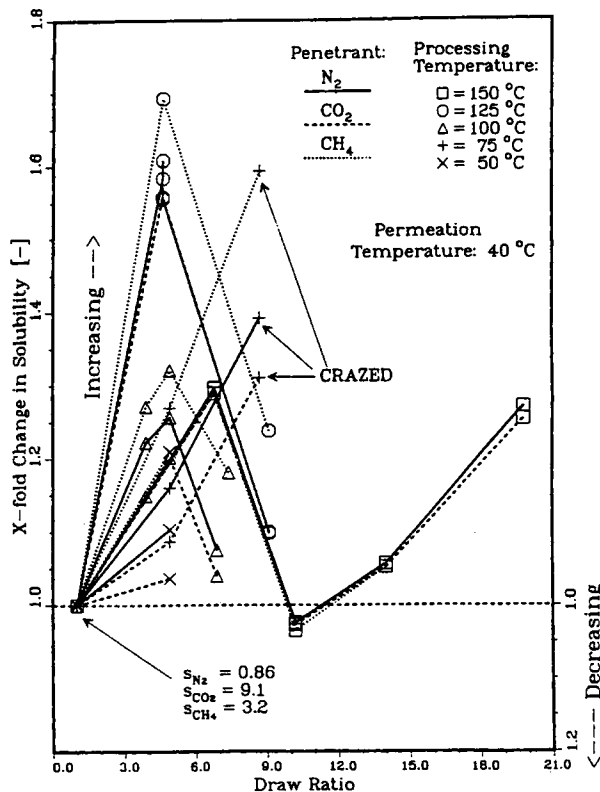


Figure 4 Dependence of s_a on the rolltrusion draw ratio and temperature. S_a s in unprocessed iPP are listed (unit: $10^3 \text{ cm}^3[\text{STP}] \text{ cm}^{-3} \text{ cmHg}^{-1}$).

Figures 4 and 5 show the X-fold changes in amorphous solubility and diffusivity for different processing conditions for each penetrant. From this data, ΔH_s and E_d values were calculated and plotted in Figures 6 and 7, respectively, as functions of the processing conditions.

DISCUSSION

Figures 4 through 7 show that the gas transport properties of rolltruded iPP can vary substantially with processing temperature and draw ratio. These changes in the transport coefficients and activation energies may be attributed to variations in the amorphous chain stiffness, diffusive pathway tortuosity, and crystallite orientation, as well as to the formation of relatively impermeable amorphous regions and microvoids. The influence of the processing conditions on the transport properties and morphology of iPP is now considered.

Figure 7 shows that the diffusive activation energy, E_d , generally increases as a result of rolltrusion processing at processing temperatures $< 150^\circ\text{C}$. Ac-

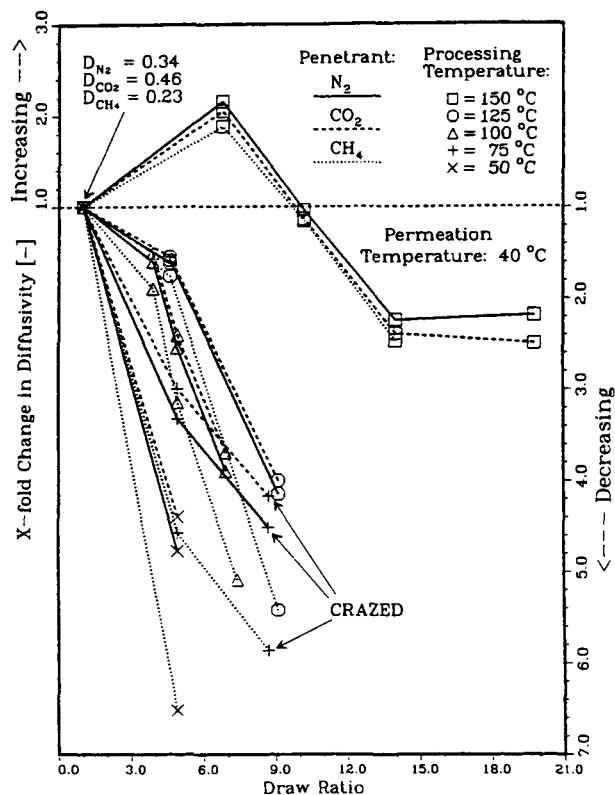


Figure 5 Dependence of D_e on the rolltrusion draw ratio and temperature. D_e s for unprocessed iPP are listed (units: $10^6 \text{ cm}^2 \text{ sec}^{-1}$).

According to eq. (4), an increase in E_d can result from an improvement in B (or β) or from a contraction in the average amorphous chain separation, r_e . The average improvement in the E_d for processing temperatures below 150°C is typically $> 4 \text{ kJ/mole}$; this corresponds to a 5% reduction in r_e . This situation is unrealistic, since it would yield an amorphous density above that of the crystalline phase. In comparison, an increase in B of ca. 35% is more feasible and would yield a similar enhancement in E_d . Hence, it appears that variations in the E_d most likely (but not exclusively) result from changes in the amorphous chain stiffness.

The variations in the E_d illustrated in Figure 7 indicate that the amorphous chain stiffness displays maxima (i) as the processing temperature is lowered at $DR \sim 5$, and (ii) as the draw ratio is increased at processing temperatures of 75 and 100°C . These maxima in the chain stiffness, predicted from the E_d , appear initially to be inconsistent with the dependence of the mechanical properties of iPP on rolltrusion processing conditions. Specifically, it is reported that the tensile strength and modulus of rolltruded iPP increase monotonically with draw

ratio and decreasing processing temperature.^{3,4} Intuitively, one would expect a related trend in the chain stiffness that is associated with the transport properties.

The difference between the dependence of the E_d and the mechanical properties on the processing conditions may be due to the formation of localized, highly strained, relatively impermeable amorphous regions that have been created during rolltrusion. This morphology has been predicted to account for large decreases in the transport coefficients of several penetrants in uniaxially processed films¹¹⁻²⁰ which cannot be explained on the basis of the changes in the crystallinity, E_d , and/or ΔH_s . These amorphous regions represent high-energy permeation pathways that are simply avoided or circumvented by the penetrant and therefore do not contribute significantly to the measured E_d values. (For instance, only a ca. 10 kJ/mol increase in the activation energies is necessary to produce a 50-fold decline in the transport coefficients!) Conversely, these highly strained amorphous regions are expected to contribute significantly to an improvement in the mechanical properties⁷ of the polymer. Accordingly, since the E_d and the mechanical properties are af-

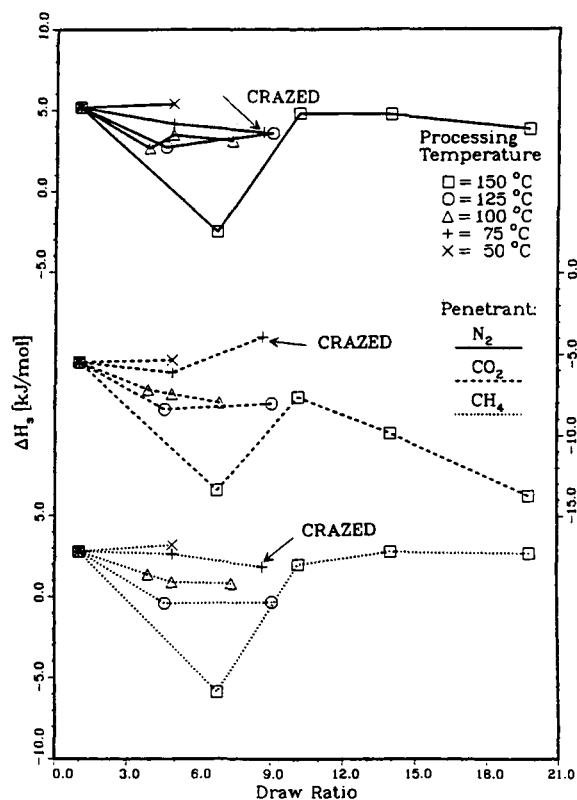


Figure 6 Heats of solution plotted as a function of rolltrusion processing draw ratio and temperature.

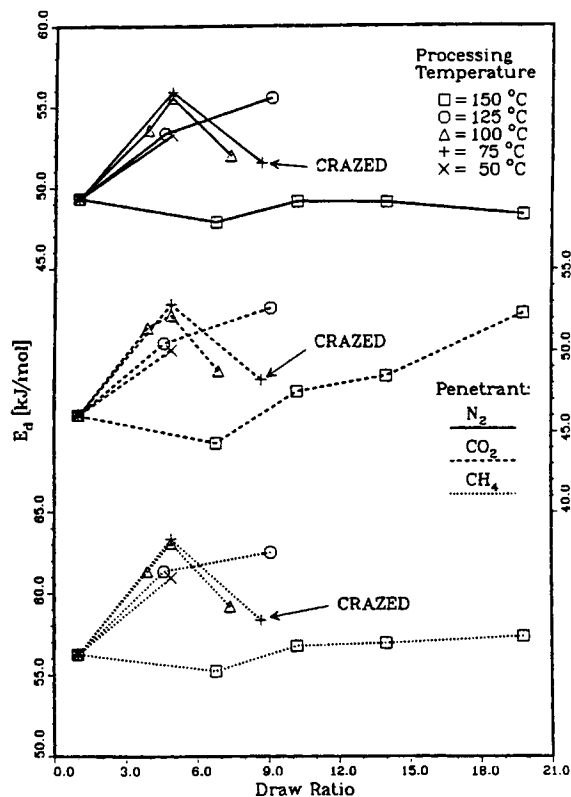


Figure 7 Diffusive activation energies plotted as a function of rolltrusion processing draw ratio and temperature.

ected differently by changes in the morphology, it follows that two different trends for the processing temperature dependence of the amorphous chain stiffness may emerge.

Measured E_d values, however, give little indication of the extent to which the processing conditions influence the formation of these impermeable amorphous regions. Instead, since these regions behave essentially as diffusion "blockers," like the crystallites, changes in the diffusive pathway tortuosity (τ) and the amorphous diffusivity (D_a) are considered more appropriate for use.

The film processed at 125°C to DR \sim 4.7 exhibits a 4.1 kJ/mol increase in E_d for N_2 (see Fig. 7) and a 23% increase in α_c (see Table I). From eq. (5), these changes are estimated to yield a ca. 5.2-fold reduction in the D_a of the rolltruded film compared with the unprocessed film. This value is about 3.5-fold greater than the measured 1.5-fold reduction in the D_a of the rolltruded film shown in Figure 5. A fraction of the difference between the calculated and measured decline in the D_a may be ascribed to an increase in microvoid content induced in the polymer during processing (as discussed later). However,

to account for the 3.5-fold discrepancy, microvoids levels corresponding to at least 60% of the amorphous volume of the polymer would be required. Since this is untenable, the difference between the predicted and measured diffusivities indicates that a reduction in tortuosity is responsible. The X-fold changes in the τ for all of the rolltruded films considered in this paper as estimated from eq. (5) are presented in Figure 8. Since eq. (5) accounts for variations in the degree of crystallinity, α_c ($= 1 - \alpha_a$), the trends observed in Figure 8 can be attributed to changes in the crystallite orientation and/or alternatively to the fraction of relatively impermeable amorphous material that is induced through processing.

Perhaps changes in crystallite orientation associated with rolltrusion processing are responsible for a reduction in the τ as discussed in the previous paper.² The "barrier" area of the crystallite surfaces parallel to the chain (c) direction is often significantly smaller than is normal for this direction. In a randomly oriented polymer there is no preferential orientation of any of these surfaces. During rolltrusion processing however, the lateral surfaces of the crystallites are preferentially oriented parallel to the

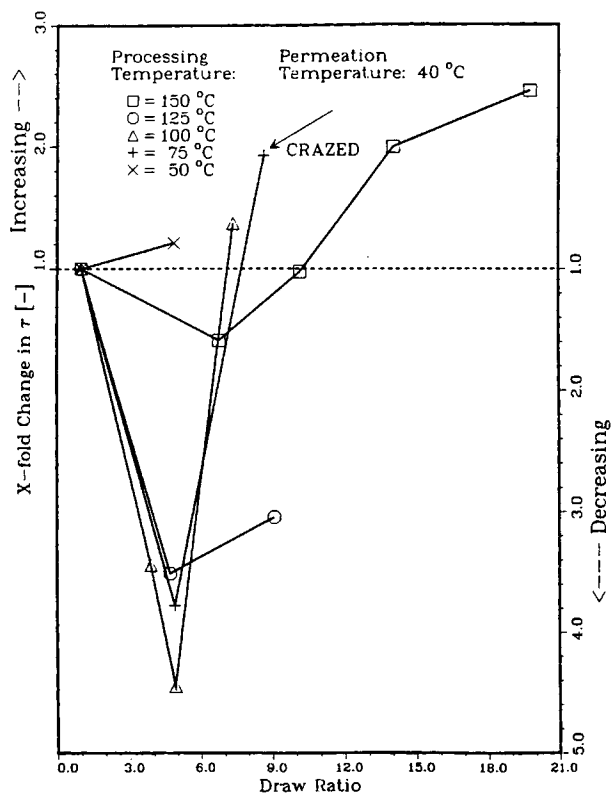


Figure 8 Dependence of the tortuosity on the rolltrusion processing draw ratio and temperature.

draw direction (and hence normal to the diffusive flux in this study). This orientation reduces the length-to-width (L/W) ratio of the "diffusive blockers" (crystallites), as defined by Nielsen²⁵; hence this causes a reduction in the tortuosity.

Crystallite orientation, as measured by the crystalline orientation function, f_c , increases rapidly with increasing DR but then levels off above DR ~ 8 for rolltruded iPP.⁶ Hence, it follows that the initial drop in the tortuosity shown in Figure 8, for draw ratios below about 5 and processing temperatures above 50°C, seems to be attributable mostly to crystallite orientation.

In Figure 8, τ (1) varies dramatically as the processing temperature is lowered, and (2) increases with $DR > ca. 5$. This behavior is not predicted by the trend in the f_c , for two possible reasons:

First, although crystallite orientation measured by f_c is relatively insensitive to processing temperature, the L/W ratio (anisotropy) of the crystallites may be altered. Sun³ has shown that the lamellar thickness increases rapidly with processing temperature for $T_p \geq 100^\circ\text{C}$ when compared to the unprocessed sample. An increase in the c-axis dimension will raise the L/W ratio of the crystallites (diffusive blockers) and therefore also the τ . Additionally, shearing of the crystallites due to processing may also raise the L/W ratio and hence the τ . Both processes will occur without an obvious change in the f_c but with a dramatic effect on the τ values.

Second, an increase in the fraction of impermeable amorphous material also accounts for an increase in the τ . In fact, this change is likely to be responsible for the large increases in τ at $T_p = 50^\circ\text{C}$ and $DR \sim 5$ compared with the behavior noted at higher processing temperatures (i.e., 75, 100, and 125°C).

Several authors¹¹⁻¹⁸ have attributed the formation of impermeable amorphous regions in uniaxially processed films to densification of highly strained amorphous tie molecules that arise from improved amorphous chain packing in microfibrils. Although a similar trend in the amorphous regions may arise from rolltrusion, several important features exist that distinguish the transport properties and hence morphology of rolltruded versus uniaxially drawn films.

First, significant reductions in the D_a of gases and vapors, on the order of 10- to 400-fold, have been reported for uniaxially drawn film morphology.¹¹⁻¹⁸ By way of comparison, the maximum decline in the D_a is approximately 6.8-fold for CH_4 in iPP rolltruded at 50°C, as indicated in Figure 5. Second, in

rolltruded films, a significant fraction of the decrease in the D_a results from a general enhancement of the E_d . In contrast, the E_d of various penetrants does not change appreciably in uniaxially drawn films, so increases in the fraction of impermeable amorphous material must account for the dramatic declines that take place in the D_a . Hence, it appears that the amorphous morphology in rolltruded materials is more "open" than it is in uniaxially drawn films. This behavior is consistent with the triaxial orientation of the polymer induced by rolltrusion.³⁻¹⁰ Although triaxial orientation of the crystallites has been verified by X-ray and birefringence studies of rolltruded iPP, the transport results in this paper indicate that the level and type of orientation are also influenced dramatically by the morphology of the amorphous regions.

The more "open" morphology is also supported by the solution results in Figure 4, which show that the s_a increases for most of the rolltruded films. In contrast, the solubility generally falls below the unprocessed film value for uniaxially drawn films, especially at high draw ratios.¹¹⁻¹⁸ It is unlikely that the improvement in the s_a of N_2 , CO_2 , and CH_4 in rolltruded iPP results from a *uniform* expansion of the amorphous chain separation, r_e . Indeed, if it is assumed that (1) the solubility is proportional to free volume in the polymer, (2) the volume expansion is well distributed throughout the amorphous phase, and (3) the expansion occurs in the two dimensions perpendicular to the chain axis (i.e., neglecting expansion along the chain axis), then at least a 3% increase in the equilibrium chain separation is required to accommodate a 1.1-fold increase in sorption capacity. More dramatically, a 10% increase in the r_e is necessary to account for the > 1.3 -fold improvements in the s_a at processing temperatures $\geq 100^\circ\text{C}$. Expansions in the r_e of this size seem high, considering that only a 5% expansion²³ in the amorphous chain separation occurs whenever iPP is heated from room temperature to just below its melting point.

A more plausible explanation for the relatively large increase in the s_a depends upon the presence of microscopic voids in rolltruded iPP films; microvoids being localized regions of low polymer density. For iPP films drawn uniaxially at processing temperatures near room temperature,²⁶ microscopic crazing tends to produce microvoids with typical dimensions on the order of 100 to 500 Å by 20 to 60 Å. Defects of these dimensions are expected in rolltruded polymers, although their size, number, and distribution may vary with processing conditions.

The presence of microvoids in the film rolltruded at draw ratios less than about 6 also accounts for the decline in ΔH_s (see Fig. 6) obtained for each penetrant at processing temperatures above 50°C. From eq. (3) it can be deduced that the ca. 8 kJ/mole decline in the ΔH_s of N_2 rolltruded at 150°C to a DR ~ 6.8 (see Fig. 6) would require a uniform expansion of 13% in r_e , thus yielding an amorphous density below that of the molten polymer. However, microvoid formation could produce a decline in ΔH_s by reducing the hole formation energy, and still not violate the condition that the average chain separation in the permeable *nonporous amorphous phase*²⁷ ought to be smaller than that of the molten polymer! Furthermore, because of the large dependence of ΔH_s on the r_e , it is unnecessary (although it is possible) for the average chain separation in the microvoids to be larger than the penetrants in order to produce a large decline in ΔH_s . This situation is unlikely to arise, since the decline in ΔH_s is generally small for processing temperatures below 150°C.

Microvoid formation also explains the divergence of the trends in the ΔH_s and the E_d . A uniform expansion in r_e is expected to lower the E_d , according to eq. (4), which is opposite to the general trend shown in Figure 7. However, the formation of isolated microvoids should not contribute to the experimentally determined E_d s in Figure 7 (although they do contribute to an improvement in the diffusivity), since isolated microvoids do not represent the rate-limiting step in the diffusion process. In contrast, sorption in rolltruded polymers occurs preferentially in the more energetically favorable sites, namely the microvoids, because of the reduction in hole formation energy. Hence, microvoid formation appears to be the only morphology consistent with an increase in E_d and s_a and a reduction in the ΔH_s .

Whatever the draw ratio, the overall microvoid content is expected to increase as the processing temperature is reduced. This would be consistent with the observation that crazing (a unique form of void formation) is enhanced as the T_p is lowered in many polymers.²⁶ Figure 9 is a plot of the s_a of N_2 , CO_2 , and CH_4 versus processing temperature in rolltruded iPP formed to draw ratios of about 5. The initial increase in the s_a as the T_p is lowered is consistent with the predicted increase in microvoid content. However, lowering T_p to 100°C and below results in a decrease in s_a , in contrast to the expected increase in the microvoid content. At least two factors may account for this reduction in the s_a . First, the fraction of impermeable amorphous material in-

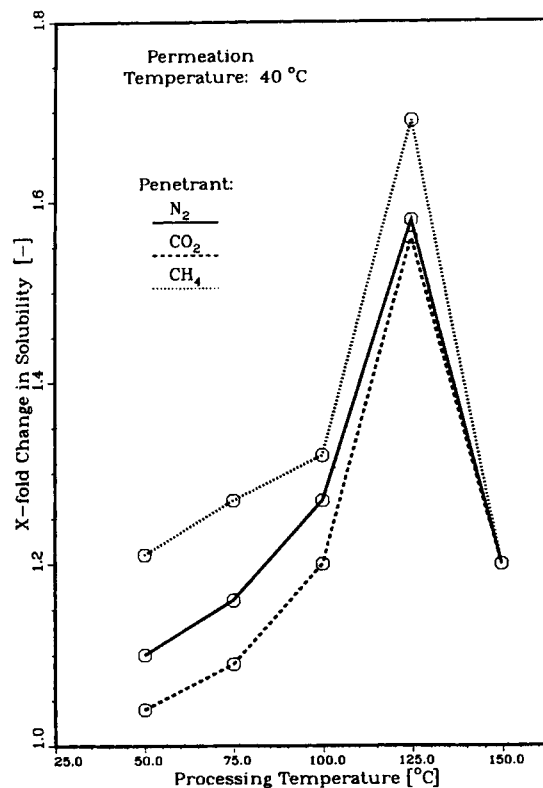


Figure 9 Processing temperature dependence of s_a for a constant draw ratio of ~ 5 .

creases dramatically at the lowest processing temperature, as deduced from the changes in τ . Second, the ΔH_s appears to increase generally as T_p is lowered at this draw ratio (ca. 5).

At moderate draw ratios (6 to 10), the ΔH_s changes little with draw ratio for processing temperatures below 150°C, as illustrated in Figure 6. This result is consistent with a small change in the "sorption morphology" and therefore also in the microvoid content. The general decline in the s_a at moderate draw ratios with respect to values at DR ~ 5 (see Fig. 4) probably derives from an increase in the fraction of impermeable amorphous regions, as deduced from the large increases in τ at these DRs.

Only at a processing temperature of 150°C are DRs greater than 10 obtainable. Since the solubility also increases at these draw ratios (as shown in Fig. 4), microvoid content must be enhanced—especially in view of the continued increase in the fraction of impermeable amorphous material. An increase in s_a at these higher draw ratios contrasts markedly with the dramatic decline that has been reported for uniaxially drawn polymers (LDPE,^{11,12} HDPE,¹⁵⁻¹⁷ iPP^{18,19}) for a wide variety of penetrants (O_2 , CO_2 , $MeCl_2$, toluene, and others). Several of these authors

have postulated that the number of sorption sites decreases dramatically in uniaxially drawn polymers due to transverse contraction and densification of the polymer to form impermeable amorphous regions. Apparently, the triaxial stresses induced during rolltrusion may hinder the formation of these regions in order to account for the improvement in the s_a per se.

Crazed Film

When the DR is increased to approximately 8.7 at $T_p = 75^\circ\text{C}$, iPP becomes uniformly opaque due to significant crazing. Under these conditions Figure 3 shows that *macrovoids* are formed throughout the polymer with dimensions on the order of $3.0\ \mu\text{m}$ in length (draw direction) and $0.3\ \mu\text{m}$ in width. Since the gas separation results²⁸ indicate that the actual separation factors for a CO_2/N_2 mixture in this film are slightly higher than in the unprocessed film, it may be concluded that the *macrovoids* are isolated regions embedded in the film. Therefore, they must be similar to, but much larger than the microvoids considered previously.

For all three penetrants used in this investigation, s_a is about 60% higher in the crazed film than it is in the uncrazed film processed at the same temperature (75°C), but to a lower draw ratio 4.9 (see Fig. 4). An increase in s_a is consistent with *macrovoid* formation, in agreement with the increases in s_a due to microvoid formation, considered previously.

Although D_a does not increase, the rate of decline in D_a with draw ratio is reduced dramatically, as illustrated in Figure 5, because of *macrovoid* formation (crazing). The limited improvement in D_a , compared to s_a , is due to the dramatic increase in τ (see Fig. 8). Evidently, the fraction of impermeable amorphous material is enhanced in this crazed film.

Overall, the results obtained with the crazed film of iPP suggest that D_a and s_a will be enhanced at all processing temperatures above the craze draw ratio. Therefore, rolltrusion induced-crazing points to a novel route to biphasic and possibly asymmetric polymeric film formation by using a continuous solid-state processing technique. In the extreme case (i.e., where *macrovoids* form the continuous phase), microporous membranes may also be produced from engineering polymers (to be reported later) using the rolltrusion processing technique.

CONCLUSION

Changes in the gas transport coefficients of rolltruded iPP result from subtle variations in the poly-

meric morphology that may be used as a paradigm for other systems.

1. Based upon changes in the E_d , the amorphous chain stiffness displays maxima with draw ratio and processing temperature in rolltruded iPP.
2. Microvoids are formed during rolltrusion. The film microvoid content tends to increase with increasing draw ratio and decreasing processing temperature.
3. Relatively impermeable amorphous material is formed in rolltruded polymers, the fraction of which is enhanced with increasing draw ratio and decreasing processing temperature. Triaxial orientation of the polymer induced by rolltrusion produces a more "open" morphology than is obtained in uniaxially drawn polymers of comparable DR values. This is evidenced by the higher D_a and s_a values.
4. Variations in diffusive pathway tortuosity are attributed to changes in crystallinity, crystallite orientation, and to the formation of localized, relatively impermeable amorphous regions in the microfibrils. The influence of each of these factors is dependent upon the processing conditions.
5. Rolltruded films are comprised of isolated (a) highly permeable microvoids and (b) relatively impermeable amorphous material embedded in (c) permeable amorphous material. The distribution of amorphous material between these regions is determined by the processing conditions.
6. Crazing improves the film transport coefficients without sacrificing film selectivity and therefore may be useful for generating biphasic and possibly asymmetric films that display both high flux and good selectivity.

The authors thank Dr. Kojima of the Materials Science and Engineering Department at the University of Pittsburgh for the field emission micrographs. They are also grateful to Aristech Chemical Corporation, Pittsburgh, PA, for providing the polypropylene used in this work.

NOMENCLATURE

| | |
|---------|---|
| B | chain bending modulus [J nm/mole] |
| CEd_p | cohesive energy density of the polymer [J/cm ³] |
| d | penetrant diameter [nm] |
| D_a | amorphous diffusivity [cm ² /sec] |

| | |
|------------------|---|
| DR | draw ratio |
| E_d | diffusive activation energy [kJ/mole] |
| ΔH_s | heat of solution [kJ/mole] |
| P_a | amorphous permeability [$\text{cm}^3\{\text{STP}\} \text{cm}/\text{cm}^2/\text{sec}/\text{cmHg}$] |
| r_e | equilibrium chain separation [nm] |
| s_a | amorphous solubility [$\text{cm}^3\{\text{STP}\}/\text{cm}^3/\text{cmHg}$] |
| T_p | processing temperature [$^{\circ}\text{C}$] |
| T_d | permeation temperature [$^{\circ}\text{C}$] |
| α_a | amorphous volume fraction |
| α_c | crystalline volume fraction |
| $(\epsilon/k)_g$ | Lennard-Jones potential of the penetrant [K^{-1}] |
| β | chain immobilization factor |
| τ | tortuosity |

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Received October 24, 1994

Accepted March 7, 1995