Effects of Orientation on the Transport of *d*-Limonene in Polypropylene

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SYNOPSIS

Kinetics and equilibria of sorption and desorption of *d*-limonene in three polypropylene films (unoriented polypropylene [UN], uniaxially oriented polypropylene [UA], and biaxially oriented polypropylene [BA]) were studied at 30°C and various penetrant activities. The weight percent uptake of a saturated vapor of limonene in UN, BA, and UA films ranged from 12.5 to 19.0%. The kinetics of sorption of a saturated vapor of limonene in these polymers exhibits an increasing tendency toward Fickian transport as the degree of orientation increases, with the highly oriented BA approaching a Fickian response. As the penetrant activity is lowered, sorption kinetics tends to show a Fickian response more closely even for the UN and the UA films. Desorption of limonene from the three samples appears to be Fickian and considerably faster than sorption in the initial stages; however, the process decelerates after roughly half of the penetrant has desorbed. Subsequent exposure of the three oriented films to a saturated vapor of limonene resulted in identical sorption kinetics, suggesting the absence of crazing or other irreversible damage often associated with anomalous sorption in glassy polymers. These results illustrate that the concentration-dependent anomalies in kinetics of sorption of a large penetrant such as limonene in the unoriented polypropylene film may be influenced by orientation to yield Fickian transport even at the highest external surface concentration. Thus, the orientation processes appear to affect large-scale swelling-induced relaxations to a larger degree than it does the diffusional processes which are dependent on smaller-scale segmental motions.

INTRODUCTION

Interaction of the flavor compound *d*-limonene with barrier polymers used for packaging applications has been the subject of several investigations.[1-4] The interest in such studies is due to the loss of flavor accompanied by the sorption of *d*-limonene in the polyolefins often used as the inner liner of the food package. A better understanding of the diffusion of such compounds in polymers helps guide material selection and processing consideration to minimize the sorption level in potential barrier polymers. In this work, the kinetics and equilibria of sorption and desorption of *d*-limonene in three polypropylene films with various degrees of orientation were investigated at 30°C and various penetrant activities. The effects of orientation on the mechanism of transport were of primary interest.

Sorption processes in which the transport of the penetrant through the polymer is entirely controlled by the rate of diffusion of the penetrant are referred to as Fickian or Case I transport. In Fickian or Case I diffusion, the rates of relaxation of dilationally induced stresses in the matrix are either very rapid or effectively unmeasurably slow on the time scale of the sorption experiment. Sorption data for much of the uptake process in Fickian systems, which are characterized by a continuous concentration profile, can be expressed by the following relationship:

$$M_t = Kt^n \tag{1}$$

where M_t is the mass of penetrant sorbed at time t, and K and n are system parameters. For Fickian

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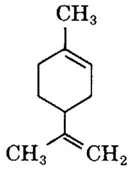
Table I Polymers and Penetrant Used in This Study and Some of Their Salient Physical Properties

Polymer	Nominal Thickness	Additives	Optical Birefringence	% Crystallinity[a]
Unoriented polypropylene (UN)	Original sample ≈ 20 mil; samples were pressed to ≤ 9.25 mil	0.09–0.12% antiblock hindered phenolic antioxidant, Ca stearate	(Pressed UN film) 3.15×10^{-4}	(Pressed UN film) 51.0%
Uniaxially oriented polypropylene (UA)	≈ 2.0 mils	0.017% hindered phenolic anitioxidants	5.18×10^{-3}	63.0%
Biaxially oriented polypropylene (BA)	≈ 0.8 mils	0.017% hindered phenolic antioxidants	7.27×10^{-3}	66.0%

Penetrant	MW	d (g/mL)	bp (°C)	Structure
d-Limonene $C_{10}H_{16}$	136.23	0.8402 @ 20 ± 5°C	175.5–176.5	

[a] From DSC measurements.

transport, K is related to the diffusion coefficient according to eq. (2) and n is 0.5 (Ref. 5):

$$K = 4\left(\frac{D}{\pi l^2}\right)^{0.5} \tag{2}$$

The amount of penetrant sorbed at short times is proportional to the square root of time. Even when the diffusion coefficient is strongly dependent upon local concentration, the square root of time dependency is maintained if Fickian kinetics control. In general, polymers in their rubbery state adjust very rapidly to the presence of a penetrant; as a result, diffusion in these polymers typically follows Fick's law.[6]

Polymer segments in their glassy state, however, are relatively immobile and do not respond rapidly to changes in their condition. Glassy polymers often exhibit anomalous or non-Fickian transport, especially when the sorption uptake is high, say above 5–10% by weight.[7] When the anomalies are caused because the diffusion rate is extremely slow compared to the rate of polymer relaxation, the non-Fickian behavior is referred to as Case II transport. Case II sorption is characterized by a discontinuous boundary between the outer layers of the polymer that are at sorption equilibrium with the penetrant and the inner layers which are unrelaxed and unswollen. In this process, a swelling front moves through the material at a constant velocity governed by the polymer relaxation rate at the front position. Sorption data for Case II transport can also be represented by eq. (1); however, in this case, n is 1.0 and K is proportional to the velocity of the discontinuous moving sorption boundary.[6] Indeed, the parameter that characterizes Case II diffusion is the velocity of the advancing penetrant front. Essentially, unswollen polymer lies ahead of the front, while equilibrium swollen material exists in the region behind the front position.

In the course of our research, we noticed significant deviations from Fickian diffusion at high penetrant concentrations, although polypropylene is in its rubbery state at 30°C ($T_g \simeq -17°C$).[8] This surprising result for a nonglassy material caused us to look more closely at the process of uptake of swelling agents in rubbery semicrystalline polymers, a complex topic with both scientific and practical importance.

EXPERIMENTAL

Materials

The unoriented (UN), uniaxially oriented (UA), and the biaxially oriented (BA) polypropylene films used in this study were kindly provided by the Exxon Chemical Co. Table I describes the polymers and some of their salient physical properties. With the exception of the UN film, all experiments were performed on the as-received films. The UN films were 20 mil thick and therefore required a long time to reach sorption equilibrium. To shorten the equilibrium time for sorption, the thickness of UN films were reduced to 5–10 mil by compression molding. The compression-molded samples were pressed at 150°C and then allowed to cool slowly to room temperature (using water as the coolant) under pressure over a 7 min period. It was anticipated that this would produce an unoriented sample for comparison to the uniaxially oriented and biaxially oriented films. The compression-molded samples were tested between crossed polarized planes to ensure that no orientation had been induced in their structures during the compression-molding process.

The BA films were produced on a chill roll and subsequently oriented in a tenter oven[9] in the machine direction (M) and the transverse direction (T). By the nature of the process used, the BA film is somewhat more oriented in the transverse direction than in the machine direction.

The degree of crystallinity of the three polypropylene films was estimated from DSC measurements using a heat of fusion of 35 cal/g for isotactic polypropylene crystals.[10] As reported in Table I, the three polymers are highly crystalline and their degree of crystallinity increases with the degree of orientation. A Gaertner Scientific Corp. refractometer was used to measure the optical birefringence of the polymers; then, by comparison to the tabulated results of de Vries,[11] the *nominal* draw ratio of the UA and BA films were estimated. The estimated draw ratio for the UA film is 1.5 × 1.0 (M × T), and for the BA film, in the region of (4 × 7) and (5 × 6). Clearly, the biaxially oriented film is more oriented than is the uniaxially oriented film in both directions.

d-Limonene, the penetrant used in this study, was purchased from Aldrich Chemical Co. and was used as received. The molecular structure of limonene and some of its physical properties are also shown in Table I. The vapor pressure of limonene at 30°C was estimated using the Clausius–Clapeyron equation[12] and the vapor-pressure data reported for limonene in *Perry's Chemical Engineer's Handbook.*[13]

Equipment and Procedure

Equilibrium Sorption Studies via Analytical Balance

Kimax™ weighing bottles and a Mettler AE 163 balance were used for *equilibrium* sorption studies. Limonene was placed in Kimax™ weighing bottles. These bottles have ground glass stoppers. Glass hooks were blown on the stoppers so a polymer film could be suspended from the hook. Polymer films were either immersed in the liquid or were hung in the vapor phase. All measurements were performed at 30°C in a constant temperature air bath. After the films were in the saturated environment for approximately 24 h, they were removed and weighed using the balance which was kept inside the air bath. To take the readings, an empty weighing bottle was tared on the Mettler balance. Then, the polymer film was quickly removed from the liquid and its surface was dried using a Kimwipe™ tissue. After drying the liquid from the polymer surface, the polymer film was placed in the tared bottle and weighed. Samples that were suspended in the vapor phase were weighed in a similar manner. The surface of these polymers was usually dry and did not require wiping. Following this procedure, long-term equilibrium sorption studies were performed for the UN film.

To test the accuracy of the measurements for the polymers that were immersed in limonene, Corning cover glasses were used. Three cover glasses were immersed in limonene in three weighing bottles. The same procedure applied to the polypropylene films was applied to these samples. It was assumed that limonene does not sorb into the cover glass; hence, any weight percent uptake recorded at equilibrium was an indication of the percent error in the procedure used on the polymer film. A ±0.5% experimental error associated with the experimental procedure was determined from the measurements with the Corning glass slides.

Kinetics and Equilibrium Studies via McBain Balance

The McBain gravimetric sorption cell used in this study enables one to perform measurements over the whole range of activity. However, the particularly low vapor pressure of limonene at 30°C (2.7 mmHg) makes the measurements more challenging even at unit activity. The sorption cell is double-walled and maintained at a constant temperature by flowing water through the outside layer using a Lauda circulator. The polymer film is suspended from a quartz spring and the film and spring assembly is placed in the cell. Changes in the length of the spring are detected by a cathetometer. The penetrant is stored in the supply ampule (see Fig. 1) and introduced to the cell by opening a valve. A high-temperature MKS Baratron Type 510 A pressure transducer indicates the pressure of the cell. Heating tapes and fiberglass insulating tapes are used to maintain the temperature of the supply ampule and the rest of the system at the desired temperature. After the quartz spring and film are placed

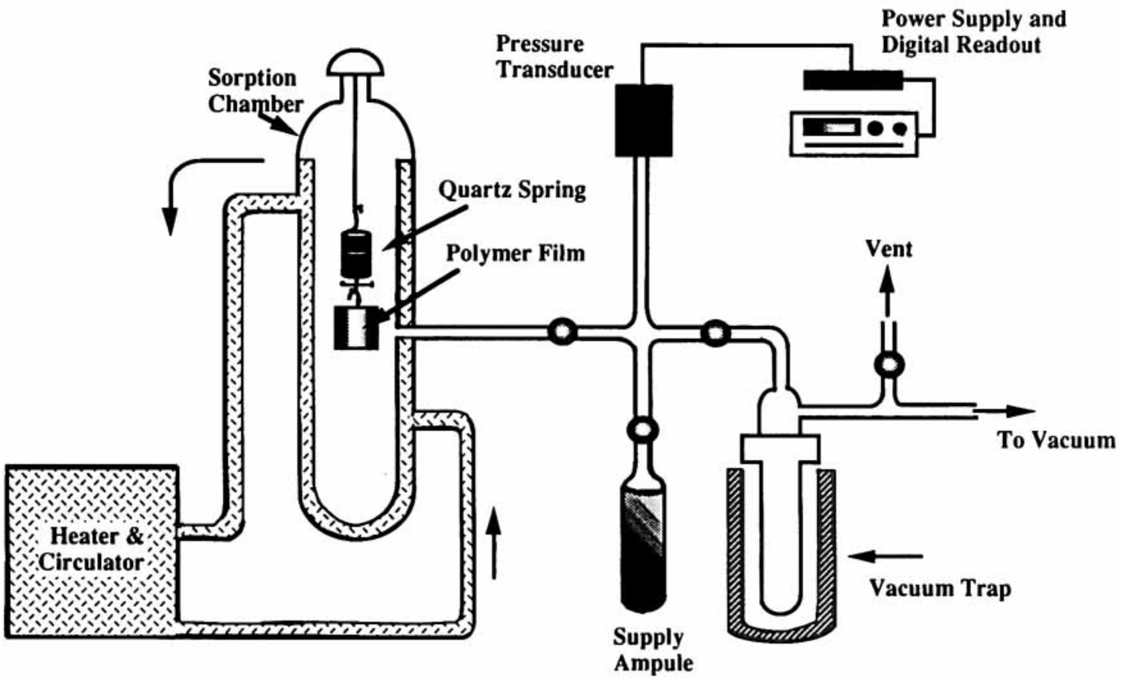


Figure 1 Gravimetric sorption cell and the supporting equipment for sorption equilibria and kinetics studies. The size of the quartz spring and the polymer film is exaggerated. Movement of the spring is detected by a cathetometer.

in the cell, measurements can be performed by first pulling a vacuum on the system and then introducing the vapor. Once sorption equilibrium is reached, the concentration of limonene in the cell is reduced to zero by pulling a vacuum on the cell. Measurements at unit activity can be performed in air by placing limonene in the bottom of the cell.

RESULTS AND DISCUSSION

Equilibrium Sorption Uptake in Unoriented Polypropylene

In the first set of experiments, the sorption level of limonene in unoriented polypropylene was compared for the case where the polymer was directly immersed in *liquid* limonene and for the case where the UN film was placed in contact with the saturated limonene *vapor*.

The compression-molded Exxon polypropylene films were placed in contact with the penetrant in the form of vapor (four bottles) or liquid (three bottles) and the films were weighed in intervals of approximately 24 h for 7 days. Essentially, the apparent changes in weight ceased to occur after the first 24 h. The last set of data in these series was taken after 16 days and it was initially presumed that true equilibrium had been reached. Subsequent tests for longer runs (up to $\approx$ 60 days) showed this not to be the case. The results for equilibrium weight percent uptake for these samples are listed in Table II.

Results for samples that were immersed in limonene as well as the results for films that were placed in limonene vapor are fairly consistent and reproducible. However, on average, equilibrium weight percent uptake for samples that were in the vapor phase is about 10.3% lower than those for the samples that were in the liquid phase.

Two more experiments were performed to further test the above results and determine whether the higher sorption level for films that were immersed in limonene was indeed due to higher sorption or caused by the difference in the procedures used. The sorption cell described previously was used to simulate a weighing bottle for the case where an UN film is in contact with the limonene vapor. The difference between the two systems was in the use of a quartz spring continuously maintained in the presence of limonene (not a balance) to obtain the equilibrium weight percent uptake for the UN film in the vapor. Limonene was placed in the bottom of the cell. The UN film/quartz spring assembly was brought as close to the surface of limonene as possible and changes in the length of spring were observed by a cathetometer.

Table II Equilibrium Weight Percent Uptake of *d*-Limonene in the UN film from Measurements with an Analytical Balance

Sample No.	Film Thickness (mil)	No. Measurements	Film Placed In	Avg Equilibrium Wt % Uptake[a]
1	7.01	6	Liquid	14.3%
2	6.79	7	Liquid	14.2%
3	5.92	6	Liquid	14.3%
4	6.86	6	Vapor	13.3%
5	4.98	7	Vapor	13.0%
6	8.54	7	Vapor	12.3%
7	8.53	7	Vapor	12.5%

[a] Equilibrium wt % uptake = (wt measured − wt of dry film/wt of dry film) × 100.

The equilibrium weight percent uptake calculated for the run done in the cell was 13.9%. This value falls between the values obtained from the Mettler balance for the vapor phase and the liquid phase. It is reasonable to attribute the lower values of uptake for the samples that were in the vapor phase to some amount of desorption from the film during the measurement procedure. Overall, however, all these methods yield rather good results.

An additional important result of the direct liquid immersion sorption equilibrium measurement was obtained from long-term measurement of the equilibrium sorption level in unoriented polypropylene. Sorption uptake in two compressed samples of comparable thickness (6.7 and 6.1 mil) were monitored up to 4 months. After 2 weeks, the uptake level was consistent with the previously reported values of Table II. However, after 1 month, the recorded limonene uptake was, on average, 18.8% and stayed at approximately the same level for the remainder of the study. This increase in the equilibrium sorption uptake may be attributed to sorption of limonene in hard-to-reach amorphous regions of the polypropylene which may not be initially readily accessible to the molecules.

These observations are rather important for food-packaging applications in which the shelf life of the product may be up to 6 months. Clearly, flavor scalping by the polymer becomes a more significant problem for very long term storage, since the polymer–penetrant contact time increases.

Influence of Moisture on the Equilibrium Sorption Level of the UN Film

To determine any second-order effects of moisture on the sorption level of *d*-limonene, three 50/50 (vol %) bottles of limonene and water were prepared. Limonene stays in the top immiscible layer due to its lower density. The contents of the bottles were stirred for 2 days to allow enough time for limonene to become saturated with water. Then, the UN films were placed in limonene with continued stirring throughout the experiment. The change in weight of the samples was measured approximately every 24 h for 4 days. Then, the limonene in the bottles was analyzed for moisture content by Karl–Fischer titrimetry. In a separate experiment, the equilibrium weight percent uptake of pure water in the UN film was determined following the direct immersion procedure used for pure limonene sorption in the unoriented polypropylene film. Results for equilibrium weight percent uptake and for moisture content are given in Table III. The equilibrium weight percent uptake of water-saturated limonene is, on average, 17.0%. Since the equilibrium weight percent uptake for pure water in the unoriented sample is 1.9% and the uptake for pure limonene in the UN film is, on average, 13.8% ± 0.5% (see Table II), sorption of limonene in the UN film in the presence of water is not totally additive. The small amount of increase may be caused by an increase in water sorption in

Table III Equilibrium Weight Percent Uptake of Water-saturated Limonene and Pure Water in Pressed UN Films

Sample No.	Equilibrium Wt % Uptake	Moisture Content of *d*-Limonene Layer (mgH_2O/cc Soln Injected)
1	17.5%	0.20
2	16.7%	0.22
3	17.0%	0.19
4	*For pure water = 1.9%*	

the more dilated polymer matrix due to the presence of limonene. In light of the results for long-term sorption studies, the amount of sorption could be still higher for longer contact times. If the sorption levels of other trace flavor compounds such as linalool, pinene, valencene, and acetaldehyde[14] with a more polar nature are also increased as the result of limonene sorption, an increase in flavor loss should be anticipated. In the case of the unoriented polypropylene film, however, it seems that these effects are not dramatic.

Sorption Kinetics and Equilibria

Analysis of sorption kinetics for a relatively strongly swelling penetrant such as *d*-limonene provides additional insight into the complex morphologies achievable with semicrystalline polymers. Bixler and Sweeting[15] noted that in quenched polymers such as the BA film the high degree of nucleation and rapid growth of crystalline domains tends to increase the probability of incorporation of a given chain into multiple growing lamella. In this case, a high degree of interlamellar linking by amorphous chains exists with extensive complex entanglements in these interlamellar link regions. It is suggested that considerable interchain stress can be maintained when such a polymer is strained or swollen. On the other hand, for a slowly cooled sample, fewer nuclei should result and the lower rates of crystallization should reduce the competition among growing lamellae. This latter factor should reduce the degree of interlamellar linking and reduce interchain stresses during strains. When one superimposes orientation upon quenching history, such as is the case with the BA sample and to a lesser degree the UA sample, an even more complex situation can be envisioned. Deformation and destruction of spherulitic structures may occur and stress-induced recrystallization may actually promote the development of higher levels of crystallization, thereby enhancing the mechanical stability of the film to stresses, including sorption-induced ones.

Semicrystalline rubbery materials, such as the polypropylene films studied here, have properties that are determined by the amorphous and crystalline phase fractions and their detailed morphologies. As noted earlier, interlamellar connectivity and orientation as well as the overall crystalline fraction can alter the response of a semicrystalline rubber to stress induced by external deformation or by exposure to a swelling solvent. Chain immobilization of amorphous segments between crystalline domains can affect both diffusion and relaxation kinetics. Even qualitative predictions of which of these two processes will be influenced the most by a given morphology are totally lacking at the present time. Sorption kinetics and equilibrium studies of these samples have the potential to give insight into this issue.

The values of percent equilibrium uptake of limonene at unit activity in the three polymers listed in Table IV indicate that the UN film has a low equilibrium uptake compared to the UA and BA films. This may be because the interlamellar amorphous regions in the oriented films are more accessible to the penetrant than in the unoriented film due to disruptions of spherulites during the drawing. As reported in Table IV, the percent equilibrium uptake corresponding to hypothetical 100% amorphous polymers (obtained by linear extrapolation) for sorption at unit activity shows the lowest uptake for UN and the highest uptake for the UA film. The normalized value for BA falls between that of UA and UN. If the orientation induced in the UA and BA polymers results in more accessibility of the amorphous regions to the penetrant, the BA film should have the highest uptake for the completely amorphous polymer. The results shown to the contrary here, therefore, are indicative of the presence of additional factors which influence the uptake of limonene. Suppression of swelling due to the presence of effective "physical crosslinking" in the BA film due to the heat-setting processes occurring in the tenter frame process can be cited as the most probable reasons for lower uptake in BA as compared to the UA sample.

The kinetics of sorption of limonene in the three polymers at various limonene activities is shown in Figures 2–4. These plots show the fractional uptake of limonene (defined as the ratio of the amount of

Table IV Sorption Equilibrium Weight Percent Uptake from Quartz Spring Measurements

Polymer	Equilibrium Wt % Uptake	% Uptake for 100% Amporphous Polymer
UN, $a = 0.3$	2.3%	4.7%
UN, $a = 0.6$	9.7%	19.8%
UN, $a = 1.0$	12.5%	25.51%
UA, $a = 0.3$	3.79%	10.24%
UA, $a = 0.4$	8.5%	22.97%
UA, $a = 1.0$	18.7%	50.54%
BA, $a = 0.4$	7.1%	20.9%
BA, $a = 0.65$	7.7%	22.65%
BA, $a = 1.0$	15.0%	44.12%

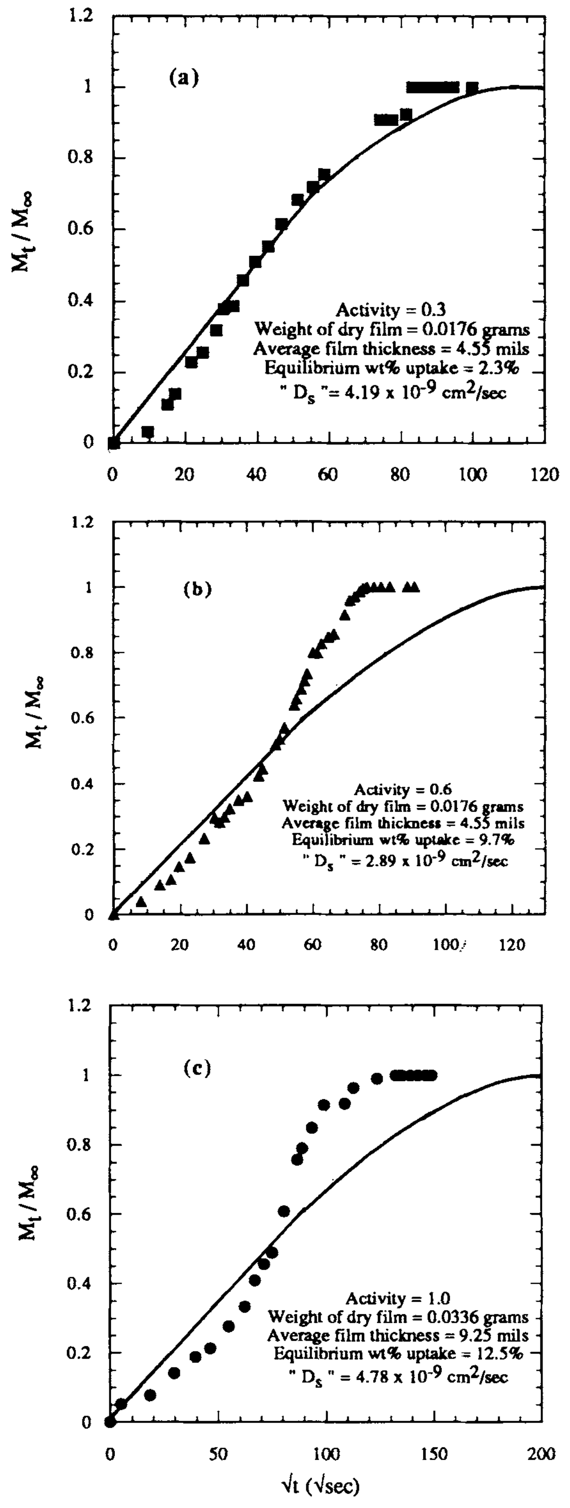


Figure 2 Fickian and experimental sorption curves for sorption of limonene in unoriented polypropylene at 30°C and different limonene activities. The predicted Fickian response is shown with a solid line.

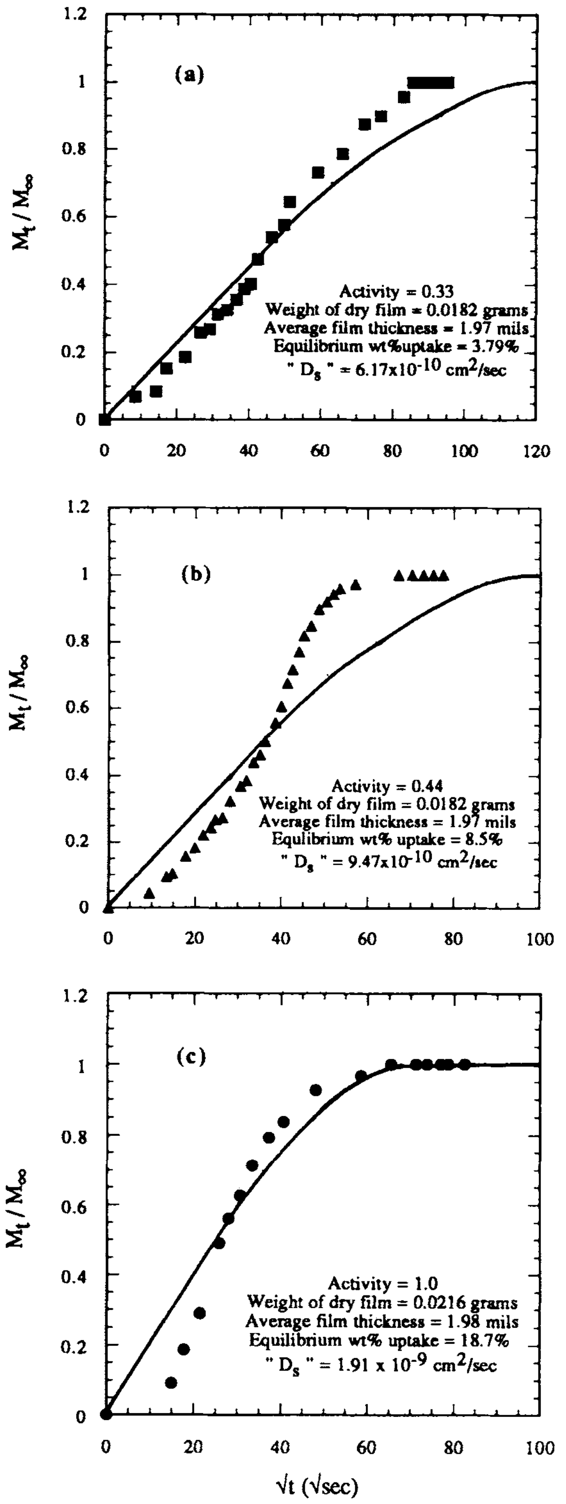


Figure 3 Fickian and experimental sorption curves for sorption of limonene in uniaxially oriented polypropylene at 30°C and different limonene activities. The predicted Fickian response is shown with a solid line.

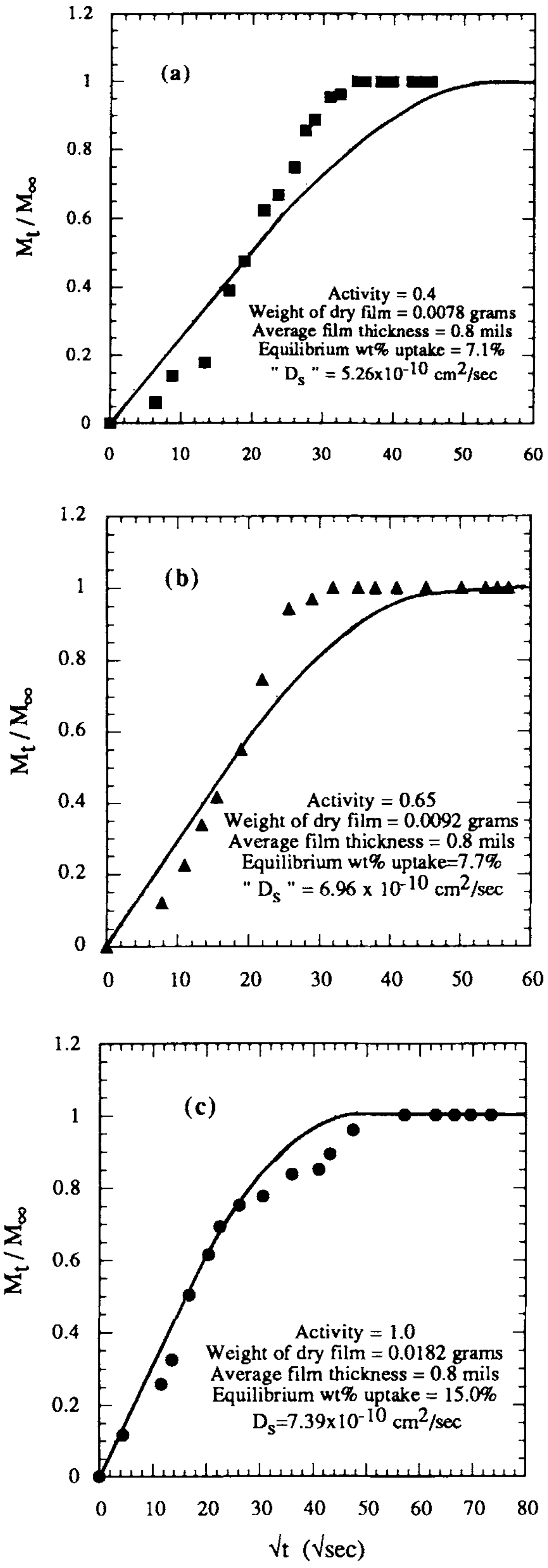


Figure 4 Fickian and experimental sorption curves for sorption of limonene in biaxially oriented polypropylene at 30°C and different limonene activities. The predicted Fickian response is shown with a solid line.

limonene sorbed at any time t, M_t, to the amount sorbed at equilibrium, M_∞) vs. the square root of time. As shown in the plots, the kinetics of sorption in the UN and the UA films shows significant deviations from the linear in the square root of time response typical of Fickian kinetics. To have a better idea of the extent of the anomalies observed, curves corresponding to Fickian transport are also plotted in Figures 2–4. These curves were constructed by estimating a diffusion coefficient from the experimental data based on the *assumption* of Fickian diffusion.

For Fickian kinetics at short times, i.e., $M_t/M_\infty < 0.6$, the diffusion coefficient can be calculated from the relation[5]

$$D = \frac{0.049 l^2}{t_{1/2}} \tag{3}$$

where l is the film thickness and $t_{1/2}$ is the time required for fractional uptake to reach half of its equilibrium value. The half-time is estimated from sorption curves such as the ones shown in Figure 2.

Crank[5] presented the complete theoretical curves of

$$\frac{M_t}{M_\infty} \text{ vs. } \left(\frac{4Dt}{l^2}\right)^{0.5}$$

obtained by solving the differential equations for Fickian transport. Given a value of the diffusion coefficient calculated from eq. (3) by using the experimental value of half-time, it is possible to calculate a theoretical value of the square root of time corresponding to each fractional uptake.

It is clear from the graphs that the kinetics of sorption of limonene at unit activity in the three polymers studied deviates from the expected Fickian diffusion to differing degrees. In cases where the deviation is significant, the "diffusion coefficients" calculated from eq. (3) are not physically meaningful and have been indicated in quotation marks to emphasize this fact. The biaxially oriented film shows only a small deviation at long times; otherwise, it approaches the Fickian curve fairly closely. On the other hand, the UN and the UA samples show *massive* deviations over the full range of the runs. Sorption of limonene in the thinner uniaxially oriented film is accompanied by a mild curling of the film even at lower penetrant activities. The 0.8 mil biaxially oriented film curls up at the initial stages of sorption and uncurls to some extent at later stages, but does not return to its original shape, indicating that some of the stresses exerted on the chains during sorption are not relaxed even when all the penetrant is removed. This behavior for the three polypropylene samples was consistently observed in numerous reproducible runs. At lower activities, a more linear in square root of time response is observed with some deviation from the Fickian response at fractional uptakes beyond 0.6 for the UN and the UA films. A more rapid approach to sorption equilibrium than the one predicted by the Fickian curve is observed for the UN film at all activities.

Sorption data for the three polymers are plotted in terms of the fractional uptake as a function of *time* in Figures 5–7. At unit activity, the responses for the UN and UA samples are reasonably linear on these coordinates, and as expected, the response for the BA film is slightly concave, since it was linear on the square root of time axis. At lower activities where Fickian transport had been observed, the fractional uptake is nonlinear in time.

A clear deviation from Fickian transport is apparent for unit activity sorption of limonene in the unoriented polypropylene sample; however, at lower activities, the kinetics is closer to Fickian characteristics (see Fig. 2). As shown in Figure 5, when plotted vs. time, the unit activity sorption curve in UN falls below the curves for sorption at lower activities. On the other hand, for UA and BA, the higher activity uptake kinetics is more rapid than are that at the lower activities (Figs. 6–7). Given the complexity of the processes involved, we hesitate to speculate on the cause of this rather different response for oriented vs. unoriented sample.

To determine the parameters K and n, the logarithmic form of eq. (1) was used[16]:

$$\text{Log}\, M_t = \text{Log}\, K + n\, \text{Log}\, t \qquad (4)$$

The mechanism of transport in the various films can be distinguished by a comparison of the slope of the plot of Log M_t vs. Log t. Figure 8 shows logarithmic plots of sorption data vs. time for the three polymers studied. The slope of the lines for limonene sorption at different activities in the BA film varies from 0.56 to 0.83 with the unit activity sorption exhibiting the least amount of deviation from Fickian

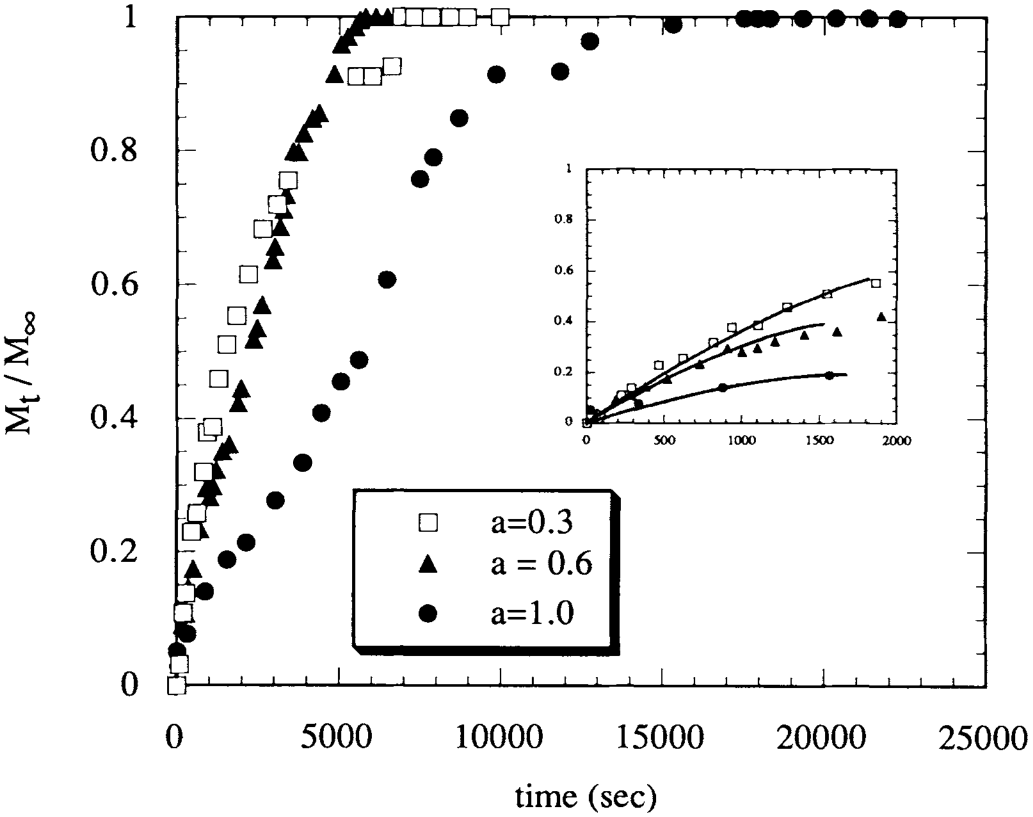


Figure 5 Sorption kinetics for *d*-limonene in unoriented polypropylene film at 30°C and various penetrant activities as a function of time. Expanded scale plot shows the nonlinear response at lower activities.

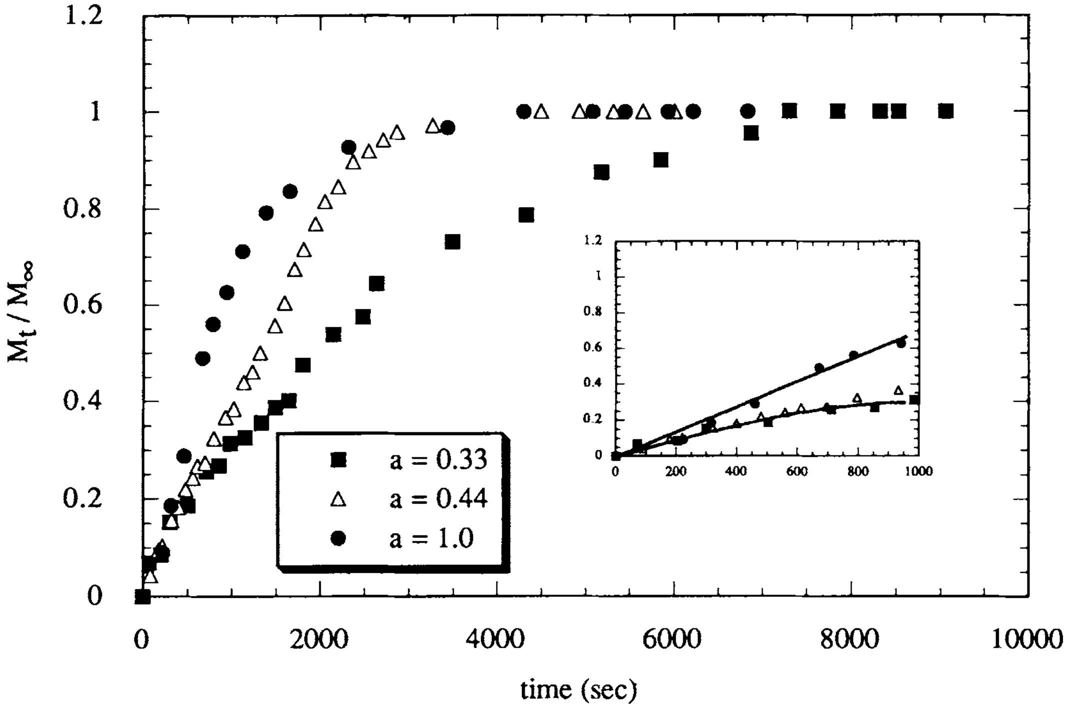


Figure 6 Sorption kinetics for *d*-limonene in uniaxially oriented polypropylene film at 30°C and various penetrant activities as a function of time. Expanded scale plot shows the nonlinear response at lower activities.

transport. For the uniaxially oriented film, the slope of the line approaches one (Case II transport) as limonene activity is increased. For these samples, values of K and n determined from least-square analysis of the data corresponding to the linear portion of the plots are listed in Table V.

Several unit activity sorption runs for the UN film were examined to determine the transport mechanism from the Log–Log plot. Overall, a plot similar to the one shown in Figure 8 was obtained for all the runs studied. The value of n estimated from the slope of the lines is, the average, 0.9, suggesting nearly Case II transport in the UN film at unit activity. As limonene activity is lowered, the transport mechanism shows more tendency toward simple Fickian uptake, with n approaching 0.5.

Thus, it appears that the degree of orientation of the polypropylene samples causes the transport mechanism to move from one extreme to the other. The importance of this observation in packaging applications is best illustrated by the results for unit activity sorption of limonene in the thin (0.8 mil) BA film and the relatively thick (9.25 mil) UN film where the two extremes of orientation are considered. Assuming that the morphology of the 0.8 mil BA film is maintained for a thicker film and the diffusion coefficient as estimated is 7.39×10^{-10} cm^2/s, the half-time for sorption of limonene in a 9.25 mil BA film will be about 10 h and total equilibration would occur in roughly 40 h. The total time to reach sorption equilibrium in the 9.25 mil UN film, which follows Case II behavior, is essentially complete in about 5 h with only the extremely long-term intraspherulitic uptake causing protraction of sorption. Because both samples have approximately the same level of equilibrium sorption uptake, if an approximately similar weight of the two films are used in two different packages, the loss of flavor in the package with the UN film will occur significantly faster than will the flavor loss in the one with the BA film. As a practical matter, however, both will result in almost equivalent scalping within 160 h (for single-sided uptake). Nevertheless, in the UN case, the scalping occurs within a time much shorter than 1 day, whereas the BA could allow storage for 1 week.

Case II behavior of the UN and UA films at unit activity may be further analyzed by estimating the value of front velocity in these samples. Front velocity, V, is related to K by the expression shown in eq. (5):

$$M_t = Kt = 2VC_\infty\rho_{\text{poly}}At \tag{5}$$

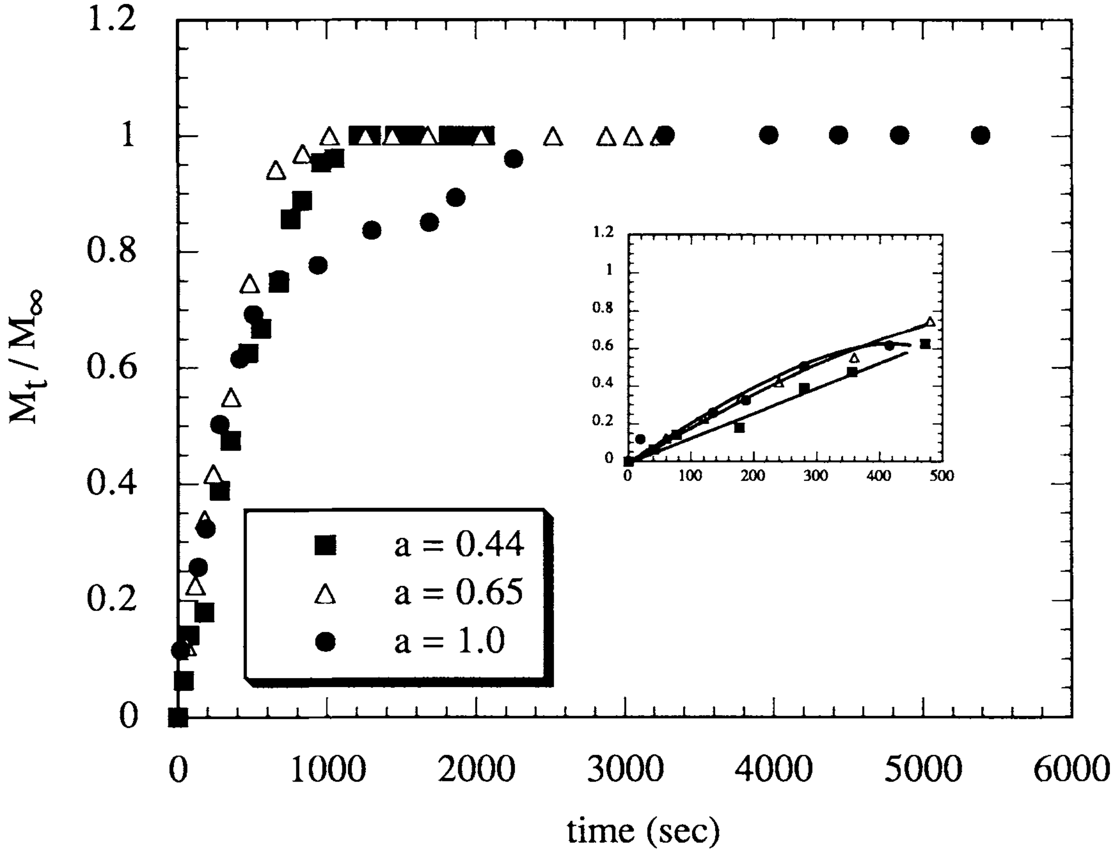


Figure 7 Sorption kinetics for *d*-limonene in biaxially oriented polypropylene film at 30°C and various penetrant activities as a function of time. Expanded scale plot shows the nonlinear response at unit activity.

where C_∞ is the equilibrium sorption uptake, A represents the cross-sectional area, and ρ_{poly}, is the polymer density. Thus, using the appropriate values for K and other parameters in eq. (5), the corresponding V values for the two samples were determined. For the UN film, $V_{\text{UN}} = 8.1 \times 10^{-7}$ cm/s, and for the UA film, $V_{\text{UA}} = 8.7 \times 10^{-7}$ cm/s.

The front velocity in the UA film is of a similar order of magnitude or even larger compared to that in the UN film. These results suggest that the uniaxial orientation process in the polypropylene film studied here was unsuccessful in inhibiting the large-scale molecular relaxations responsible for allowing the moving front to advance perpendicular to the direction of orientation.

Desorption Kinetics and Equilibria

Fickian diffusion equilibrium typically occurs after four sorption half-times. In our experiments, equilibrium was assumed to have occurred after about 10 sorption half-times had passed. Once sorption equilibrium had been reached, the polymer films were allowed to desorb. The kinetics of desorption of limonene from all three polymers at various activities is presented in Figures 9–11. Regardless of the degree of orientation, rapid desorption of limonene from the polymeric films up to $(M_t/M_\infty) \approx 0.6$ are observed at higher activities. For desorption, M_t is the amount of limonene desorbed at time t. Desorption slowed down considerably beyond this point and equilibrium was reached after up to 48 h for the thicker UN films. For comparison, a half-time of 3 min was observed for desorption from a 2 mil-thick UA film, while sorption half-time for the same film was 10 min. At lower activities, initial rapid desorption is observed, but in some cases, the process slows down around fractional desorption of 0.25. All the limonene that was sorbed into the polymers was removed completely during the desorption process. It is likely in such cases that the concentration-dependent nature of the diffusion and relaxation processes at play are of similar orders of magnitude.

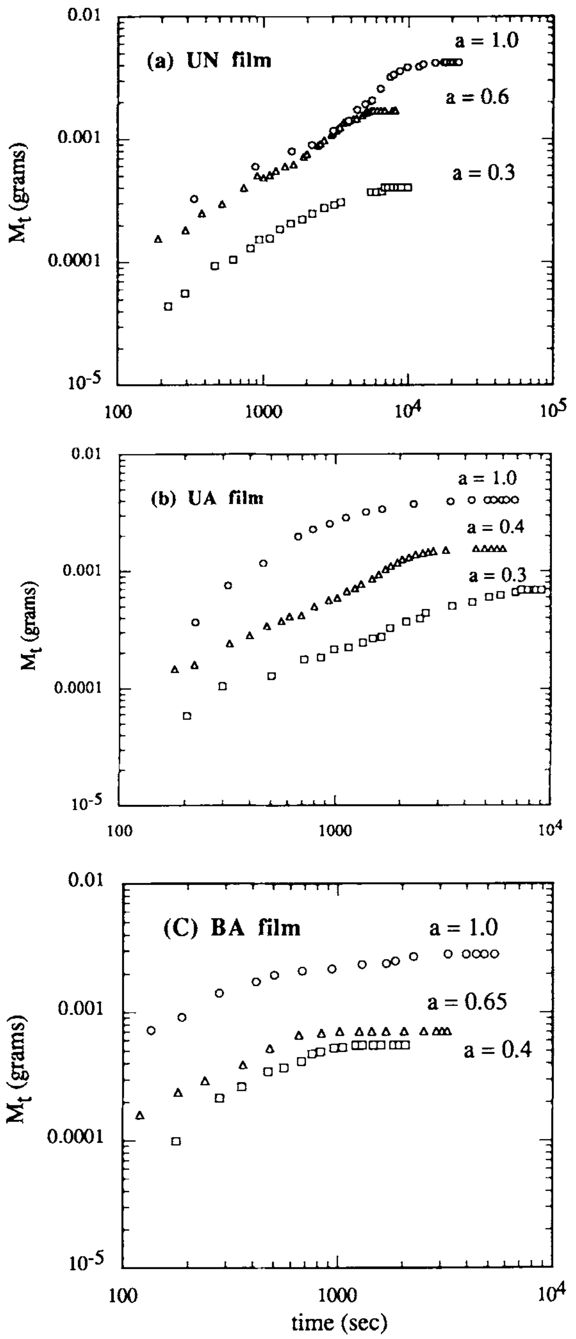


Figure 8 Logarithmic plots for sorption of limonene in (a) unoriented, (b) uniaxially oriented, and (c) biaxially oriented polypropylene films at 30°C and various penetrant activities.

Table V Values of K and n for the Polymers Studied

Polymer	n	$K \times 10^6$ (g/s)[a]
UN, a = 0.3	0.62	2.51
UN, a = 0.6	0.95	5.36
UN, a = 1.0	1.03	0.29
UA, a = 0.3	0.75	1.12
UA, a = 0.4	1.08	0.33
UA, a = 1.0	1.10	1.40
BA, a = 0.4	0.75	3.16
BA, a = 0.65	0.83	3.16
BA, a = 1.0	0.56	—

[a] Values of K in terms of g/s are only meaningful for Case II transport, i.e., $n \approx 1.0$.

Overlay plots of sorption and desorption curves for all films at various activities are shown in Figures 12–14. In the sorption experiments as the concentration of the penetrant inside the polymer increases, a more rapid approach to sorption equilibrium than the predicted Fickian response is observed for all polymers at the three limonene activities (see Figs. 2–4). In the case of desorption, the kinetics decelerates considerably as the limonene concentration inside the film decreases and a slower approach is observed to desorption equilibrium than the one predicted by the Fickian response. This behavior is not consistent with simple Fickian behavior with a concentration-dependent diffusion coefficient that increases with increasing penetrant concentration. For such a system, the sorption curve always lies above the desorption curve. The desorption curve in the present case (see Figs. 12–14) falls well above the sorption curve at higher activities, but the process slows down and the curves cross, as is typical for non-Fickian kinetics.[5,17]

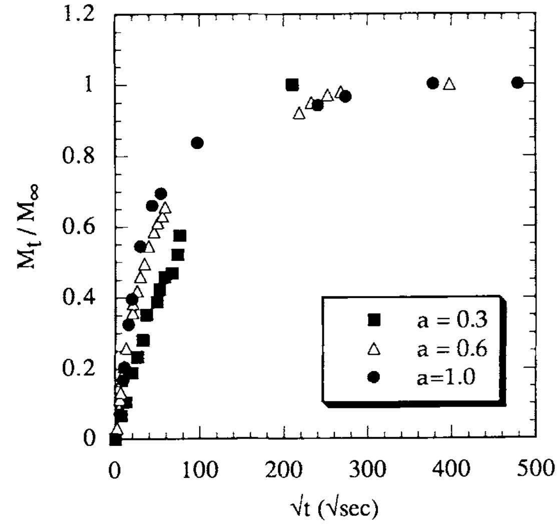


Figure 9 Kinetics of desorption of limonene from unoriented polypropylene at 30°C and various penetrant activities.

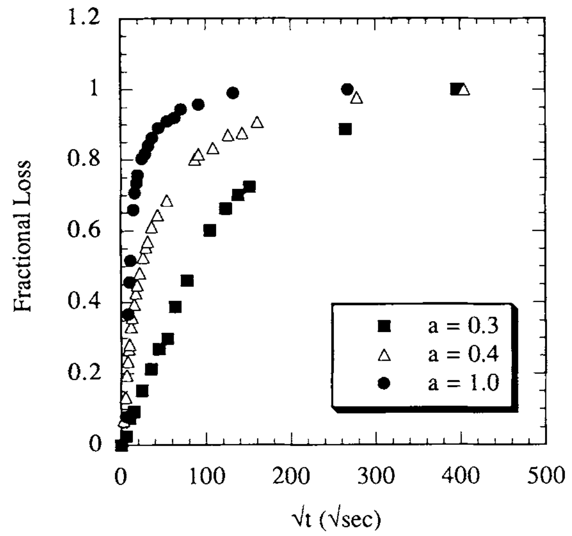


Figure 10 Kinetics of desorption of limonene from uniaxially oriented polypropylene at 30°C and various penetrant activities.

While it is not surprising that the more or less rapid Fickian desorption process from the dilated matrix is faster than is the swelling moderated uptake into the UN and UA samples, the result of the BA sample was surprising. One would expect a strongly increasing diffusion coefficient for *d*-limonene as a function of local concentration due to the strong swelling of the matrix. As noted above, if both the sorption and desorption processes are essentially Fickian for this sample at unit activity, and the *d*-limonene diffusion coefficient increases as a function

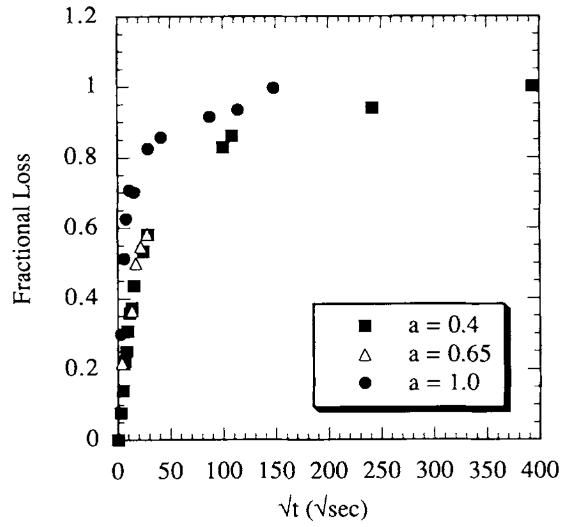


Figure 11 Kinetics of desorption of limonene from biaxially oriented polypropylene at 30°C and various penetrant activities.

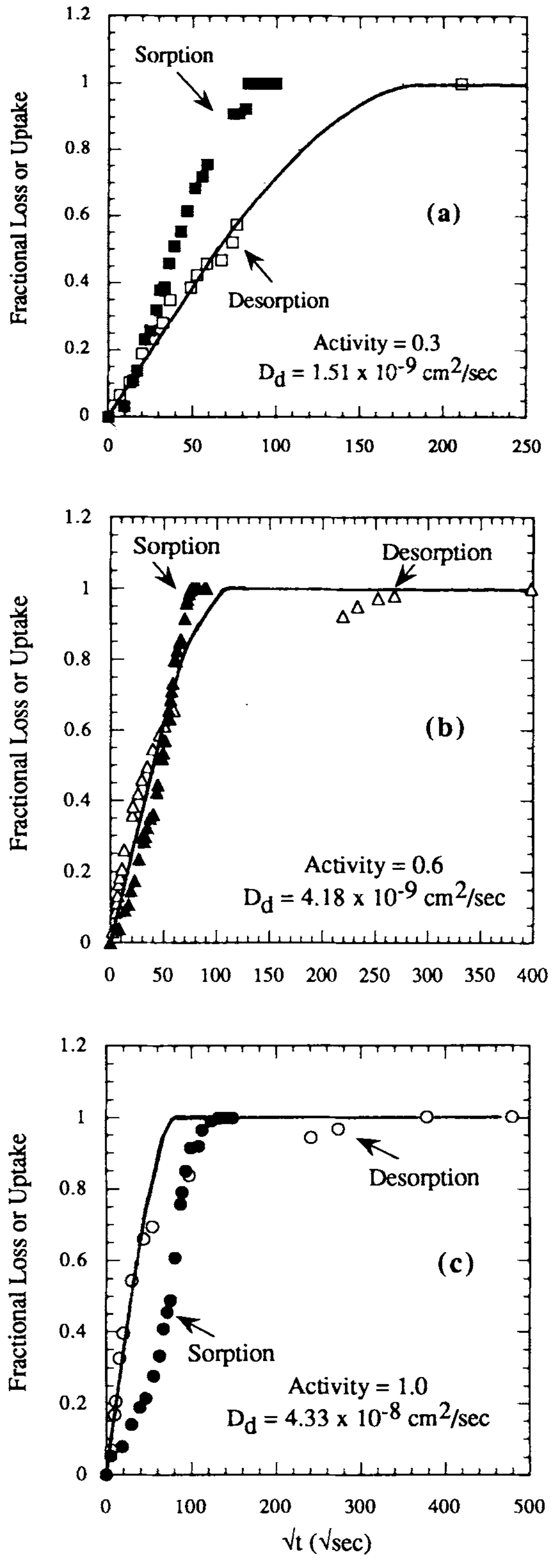


Figure 12 Overlay plot of sorption and desorption curves for unoriented polypropylene at 30°C and various penetrant activities. White symbols represent desorption data. Black points represent sorption data. Solid line shows the predicted Fickian response for desorption.

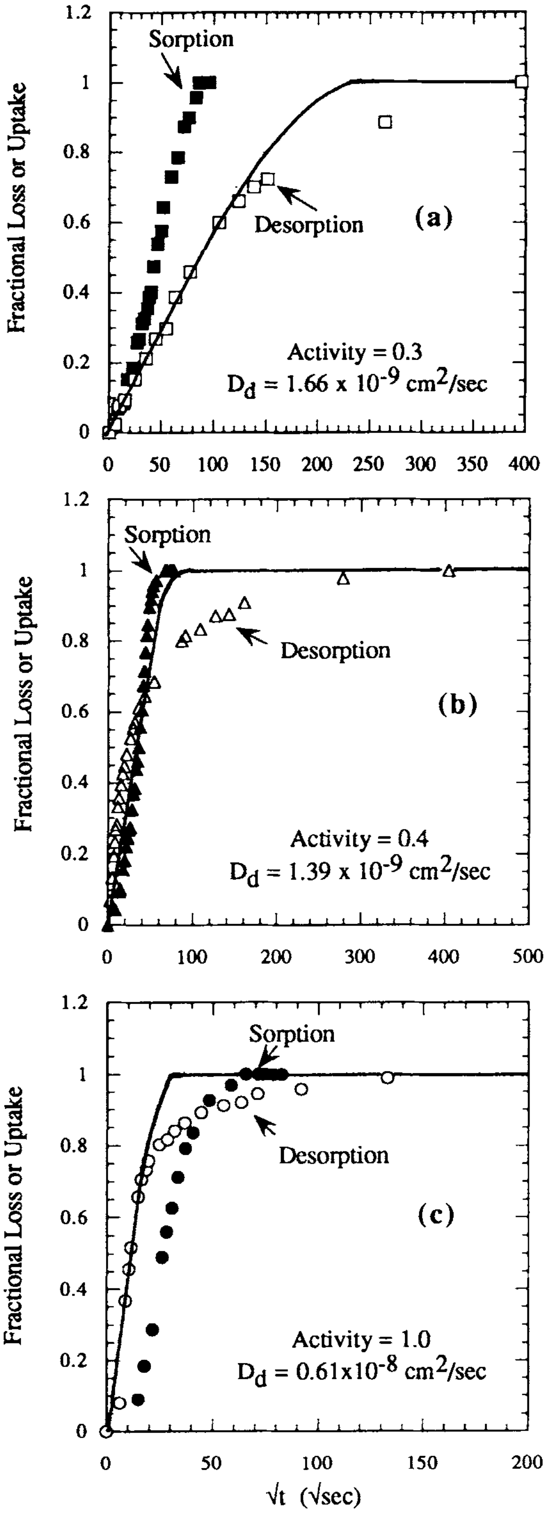


Figure 13 Overlay plot of sorption and desorption curves for uniaxially oriented polypropylene at 30°C and various penetrant activities. White symbols represent desorption data. Black points represent sorption data. Solid line shows the predicted Fickian response for desorption.

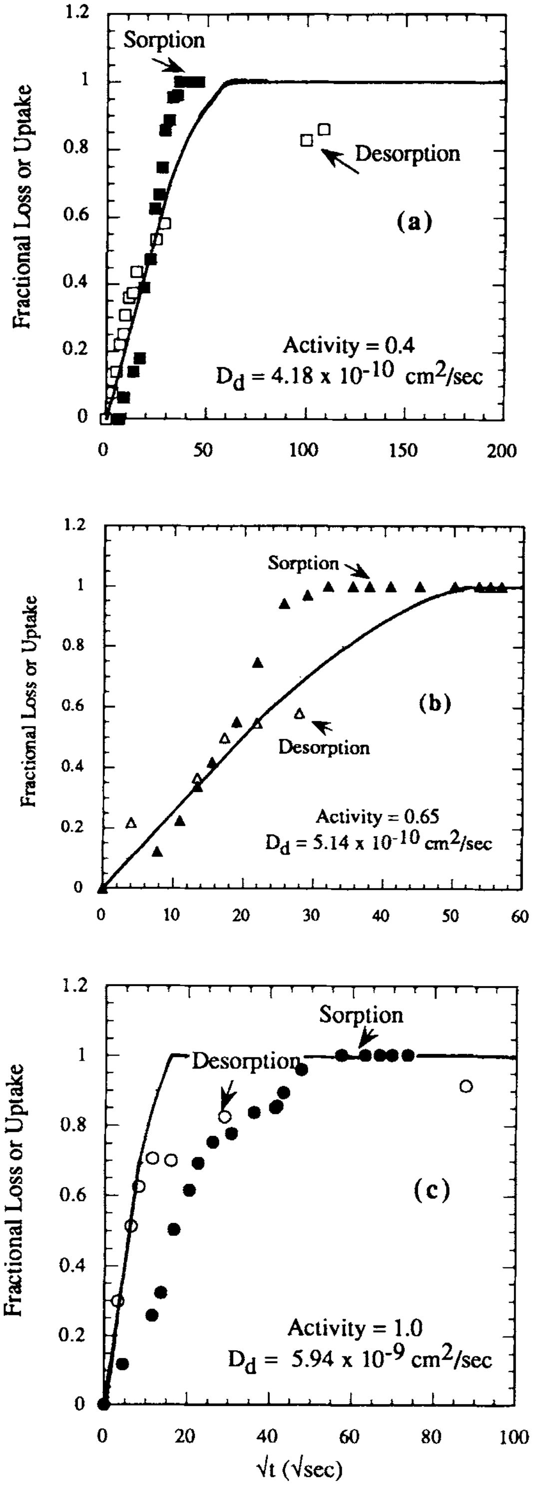


Figure 14 Overlay plot of sorption and desorption curves for biaxially oriented polypropylene at 30°C and various penetrant activities. White symbols represent desorption data. Black points represent sorption data. Solid line shows the predicted Fickian response for desorption.

of local concentration, the sorption response should lie above the desorption response over the full range of the two experiments. The tendency for the desorption response to cross over and eventually lie below the sorption response is a further indication of complex phenomena occurring under the guise of Fickian behavior suggested by the initially linear in square root time replication of M_t/M_∞. A rather simple possible interpretation that one can advance for the data is that, indeed, both processes are Fickian, but that a marked hysteresis in the material properties persists during the initial stages of desorption. Due to the small sample thickness, the desorption process occurs very rapidly and initially "senses" the expanded matrix as a different material with a sufficiently long relaxation time to appear Fickian in nature. It may be that in the later stages of the desorption process the sample is able to relax to a condition more similar to that during an equivalent period during the sorption process. In this case, the concentration-dependent diffusion coefficient would then manifest itself as the more protracted approach to final desorption equilibrium. For a two to four times thicker biaxially oriented sample, one might expect the relaxation to diffusion time scales to change by four to 16 times, since the relaxation time scales should be largely independent of sample thickness while the diffusion time scale varies as l^2. In this case, one would expect the time scale of the desorption process to overlap that of relaxation and a strongly non-Fickian response would occur. Extension to extremely thick (say 9–10 mil) biaxially oriented samples like those in the UN case would change the diffusion time scale by two orders of magnitude and should virtually guarantee observing this behavior. Unfortunately, such samples were not available to us.

For comparison, the three-unit activity desorption responses for UN, UA, and BA are plotted on the normalized time scale $t^{0.5}/l$ in Figure 15. The UN sample has the highest diffusion coefficient for desorption, as expected based on the earlier discussion of the effects of interlamellar connectivity and chain restrictions in the two oriented samples.

Resorption Kinetics at Unit Activity

Polymer films which had once been exposed to a saturated vapor of limonene in a complete sorption/desorption run and were free of any residual limonene from the first exposure were exposed to limonene for a second and third time. These samples had exhibited the largest anomalies at unit activity, and, therefore, their resorption kinetics might be expected to indicate crazing or other irreversible behavior often associated with systems with this type of kinetics. The kinetics of resorption of limonene in the polymers was *identical* to the first sorption. Sorption curves for first, second, and third sorption of limonene in UN film shown in Figure 16 are superimposable; similar results were obtained for the other polymers.

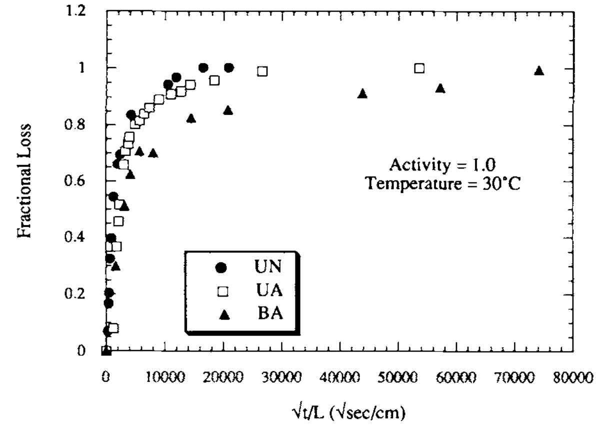


Figure 15 Overlay plot of fractional loss vs. $\sqrt{t}/L$ at unit activity for desorption of limonene from the three polymers studied.

The desorption kinetics was also identical to the kinetics of first desorption for the three polymers studied. These composite results suggest that the relaxations occurring which moderate the uptake and desorption from the various polymer samples are all rather localized in nature and not responsible for permanent morphological changes.

Hypothetical Explanation of Major Qualitative Observations

Clearly, the phenomena at play in the sorption processes for the three different samples are complex; however, we feel that some hypothetical explanations are in order to unify the observations and guide their extension in the future. The amorphous domains of the unoriented samples in inter- and intraspherulitic regions are difficult to reach by a large penetrant such as *d*-limonene (molar volume $\approx$ 162 cm^3/gmol). Diffusion of limonene molecules into the amorphous regions dilates the polymer, thereby promoting rapid sorption of more limonene molecules into the swelled matrix. Once the matrix is dilated, the concentration of limonene in the swelled regions behind the initially advancing molecules reaches the equilibrium concentration very rapidly; hence, the observed Case II kinetics. Contrary to the observations here, Fickian sorption kinetics in

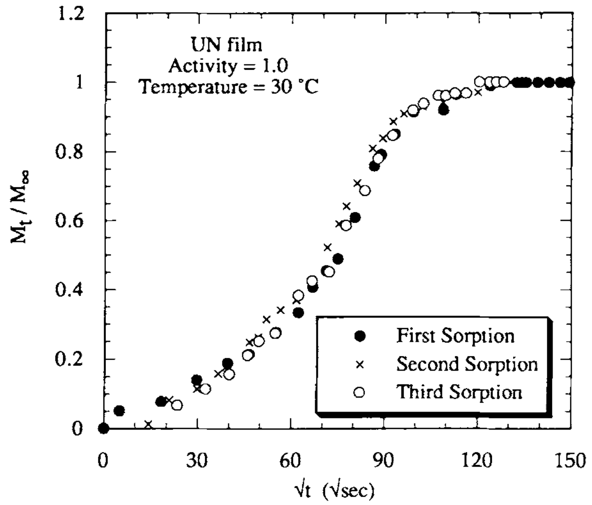


Figure 16 Overlay plot of sorption curves for first, second, and third sorption of limonene in unoriented polypropylene at unit activity and 30°C.

unoriented *polyethylene* films with higher degrees of crystallinity than that of the polypropylene film of this study has been reported.[18] While the same morphological considerations apply to the study of Peterlin et al.,[18] the smaller size of their penetrants (64–110 cm^3/gmol vs. 162 cm^3/gmol for limonene) and lower activities of the sorption measurements may influence the observed kinetics of transport in the two cases. Moreover, the greater flexibility of polyethylene ($T_g \approx -128°C$)[8] vs. polypropylene ($T_g \approx -17°C$) may also promote its tendency to show Fickian behavior even above T_g in the presence of strong swelling stresses. Kinetics of sorption at lower activities in the unoriented polypropylene film of this study also approaches Fickian kinetics more closely than does the response at unit activity.

A higher degree of crystallinity, due to stress-induced crystallization during the orientation process, is present in the uniaxially and biaxially oriented polypropylene films. However, the orientation process also appears to make the amorphous regions more accessible to the penetrant. In the case of the UA film, this effect is not very pronounced based on the kinetic response; however, the equilibrium weight percent uptake at unit activity reveals significant differences between the UA (18.7%) and UN (12.5%) samples. The higher sorption uptake at equilibrium for the UA film is consistent with more accessibility of the amorphous regions in this polymer. This is also supported by the long-term sorption equilibrium results observed for the UN film. After about 1 month, approximately 18.8% equilibrium weight percent uptake was observed in the UN film. The lack of orientation protracts the time required for penetrants to reach some of the hard-to-penetrate amorphous regions, resulting in an initially lower value of uptake. Upon longer contact times, the same equilibrium weight percent uptake is ultimately observed in the two polypropylene samples.

The morphology of the biaxially oriented polypropylene film is harder to envision, since several complicated phenomena occur simultaneously during the orientation process. The amorphous and crystalline regions are drawn by various degrees in two directions. While the crystalline regions are transformed from their original morphology, stress-induced crystallization results in increased crystallinity. The biaxial orientation process also causes the remaining amorphous regions to become more accessible. At unit activity, the transport mechanism for the BA film essentially appears to be Fickian. The equilibrium weight percent uptake for this sample is lower than the values observed for the UN and the UA films, consistent with the lower fraction of amorphous regions present in this polymer. Since the kinetics of sorption at unit activity was nearly Fickian, we expected the transport kinetics at lower activities to follow Fickian or Case I kinetics with a more protracted approach to equilibrium. Clearly, our experimental observations indicate otherwise. These results once again indicate the complexity of the phenomena and emphasize the need for further investigation of the combined effects of crystallinity and orientation in barrier polymers.

SUMMARY

The effects of orientation on the kinetics of sorption and desorption of limonene in polypropylene films with various degrees of orientation were investigated at 30°C and various limonene activities. Case II transport was observed for sorption of *d*-limonene in unoriented polypropylene and uniaxially oriented polypropylene at unit activity, while biaxially oriented polypropylene exhibited nearly Fickian transport. As limonene activity is reduced, the kinetics of sorption in the UN and the UA films approaches Fickian transport. The biaxially oriented sample behaves oppositely, becoming more non-Fickian as vapor activity is reduced. This extremely unusual behavior would presumably disappear at sufficiently lower vapor activities. These activities were not experimentally accessible with the present sorption system.

Desorption kinetics for all polymers appears to be Fickian at the initial stages of desorption but deviate somewhat from the Fickian response at long times. We speculate that the limonene molecules can easily diffuse out of the dilated polymer matrix at the initial stages of the desorption process and the chains relax to their original condition during the final stages of desorption, thereby resulting in longer diffusion times and extending the final approach to desorption equilibrium. The relaxations occurring in the polypropylene films do not result in major morphological changes in the polymer matrix as indicated by the kinetics of resorption which is identical to the kinetics of first sorption for all polymers studied.

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