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Desorption of Erucamide Vapor in Vacuum from Erucamide/Isotactic Polypropylene Films[1]

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ABSTRACT: Desorption rates of erucamide from erucamide/isotactic polypropylene (i-PP) blends were measured microgravimetrically under vacuum. Experimental data were used for testing our theoretical description of diffusion processes in the erucamide/i-PP system, a partially inhomogeneous binary and incompatible system, and for the calculation of the diffusion parameters. For films containing 4.6% and 8.0% erucamide, the kinetic curves show good agreement with the Fickian law. However, for films containing 24.0% and 44.0% erucamide, the experimental results were explained by assuming two terms for the overall transport process, a diffusional term which describes in the amorphous regions of spherulites, and a term describing the release from the globules to the amorphous region of spherulites. An equation was derived to describe our experimental data for these high erucamide content blends (24.0% and 44.0%).

Introduction

The fundamental cause of the migration of slipping and antiblocking additives (erucamide, oleamide, palmitamide, etc., and in general fatty acid amide derivatives) to the surface of polyolefins is derived from the fact that, at temperatures above their melting points, typically above 130−160 °C, the additive is very soluble in the polyolefins, but at ordinary ambient temperatures the solubility is very much reduced.[1] Thus such additives dissolve readily in the polyolefins during mixing and remain in solution at high temperatures; on cooling below their melting point, their solubility decreases abruptly and they become incompatible. Some segregation of the additive now occurs at the surface of the polyolefin. Thus, in a system such as that formed by erucamide/isotactic polypropylene (i-PP), after cooling the erucamide segregates in globules and a small part remains located as microcrystalline domains in the amorphous parts of i-PP spherulites.[2] This migration to the surface produces a concentration gradient and the additive (erucamide) diffuses to the surface of the polyolefin, imparting the slipping and antiblock properties. Probably the migration from globules to the polyolefin surface takes place through the surrounding and amorphous parts of i-PP spherulites.

The desorption process of additives from polymers has so far received little attention, particularly for the case of the desorption of small molecules that have very weak thermodynamic and hydrodynamic interactions with a polymer. When the diffusant molecules are large, and/or have strong specific interaction with a polymer, the desorption process may become much more complex. Also, when the present system is studied under static conditions, it shows a characteristic dual Fickian mechanism of migration.[3] A number of experimental techniques have been devised to measure the diffusion coefficient (*D*) of a solute by monitoring either the release from, uptake into, or permeation through a polymer layer.[4] However, due to the possible changes of the morphology and location of additive molecules in the spherulites, different diffusion coefficients were obtained by these methods. The last of these three procedures has been used by some of the present authors[3] to measure the diffusion coefficient of erucamide in i-PP. Diffusion coefficients of gases and vapors in polymers may be conveniently measured using gravimetric methods which utilize a microbalance or quartz spring apparatus.[4,5]

Before going into theoretical considerations needed for the interpretation of our experimental data, we must settle up some points which may be important in the consideration of some apparent peculiarities of our experimental results. In the three types of diffusion experiments which can be carried out for estimating diffusion coefficients, two main groups may be distinguished, one in which diffusion is followed through films made of the pure material, i-PP in our case[3] [Diffusion or permeation through polymer films or layers from an additive source (type I experiment), and the other, in which there is desorption of the additive from the polymers monitored (type II experiment). This second type of experiment is used in the present paper.

In general, it has been assumed that additives distribute uniformly in amorphous polymers, where they form microheterogeneous phases dispersed in the polymeric matrix according to their thermodynamic interactions.[6] Frank and Lehner[7] confirming ideas of some others authors found that in semicrystalline polymers the additive is rejected from growing crystallites during cooling and accumulates in the amorphous phase between the spherulites and in noncrystalline regions of the spherulites. Additives produce changes in the rate of the polymeric matrix crystallization. The additive is rejected into the amorphous regions on the boundaries of spherulites.[8−11] The average concentration in a spherulite (between radial crystalline fibrils)—i.e. its amorphous regions—is reduced by about 30%.[9] Thus, the regions of greatest concentration correspond to spherulite boundaries. Therefore, when the film is prepared from a blend, a change in the rate of crystallization of the polymer component is produced. Changes in the rate of cooling affect only the size of crystallites and not the nonuniform distribution of the additive in a polymer. The geometrical distribution of the amor-

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Table 1. Diffusion Coefficient (*D*) and Correlation Coefficient (R^2), for the Best Fitting to Eq 2, and Activation Energies of the Process for Every Blend

		T (K)						
		345		360		371		
sample	composition erucamide (% by weight)	D (cm^2 s^{-1})	R^2	D (cm^2 s^{-1})	R^2	D (cm^2 s^{-1})	R^2	E_a (kJ mol^{-1})
1	4.6	2.05×10^{-8}	0.992	6.11×10^{-8}	0.992	8.25×10^{-8}	0.989	58
2	8.0	2.62×10^{-8}	0.988	4.90×10^{-8}	0.987	1.04×10^{-7}	0.986	55
3	24.0	3.22×10^{-9}	0.946	1.10×10^{-8}	0.743	6.23×10^{-8}	0.980	118
4	44.0	4.08×10^{-10}	0.940	1.97×10^{-9}	0.900	1.55×10^{-8}	0.500	146

phous component is substantially modified by the presence of the additive during crystallization.

From the hole theory[12] of diffusion, it is known that the diffusion depends on (i) the number and size distribution of pre-existing holes and (ii) the ease of hole formation. This must be taken into account when considering Type II experiments.

On the contrary, when we are dealing with Type I experiments, the geometrical distribution of the film before the diffusion experiments is only governed by the thermodynamic properties of the polymer and kinetic conditions imposed. In Type II experiments, the additive participates in both the creation of the structure and in the transport during the diffusion experiments, whereas in Type I experiments the additive only participates in the diffusion experiments. The available structure to transport in both cases must be quite different and so are the diffusion coefficients which are obtained. Furthermore, polypropylene itself also offers some very peculiar characteristics which can affect the transport of the additive.[13,14]

In a previous paper[2] we found that for blends containing up to 10% erucamide, this is completely located in the amorphous regions and/or in the surrounding amorphous regions of the spherulites of i-PP. However, above this concentration erucamide starts to form globules or droplets, as independent domains inside the polymeric matrix. In this case, we may assume that the diffusion may be controlled by a releasing process from the globules or droplets to the amorphous inter- and/or intraregions which together with the crystalline regions form the polymeric matrix of i-PP. The additive will diffuse through these amorphous regions to the surface and from the surface to the outside.

Theoretical Considerations

According to Fick's second law:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

where C is the concentration, x is the distance, t is the time, and D is the diffusion coefficient.

Let us consider diffusion through a sheet of thickness $2l$, with a concentration of additive C_0, distributed homogeneously at the start of the experiment. The diffusant arriving at the surface is eliminated so rapidly that we can consider the concentration at the surface to be zero. The initial and boundary conditions are then

$$t = 0 \quad l > x > -l \quad C = C_0$$

$$t \geq 0 \quad x = l = -l \quad C = 0$$

$$t \geq 0 \quad x = 0 \quad (\mathrm{d}C/\mathrm{d}x) = 0$$

Equation 1 can be solved by means of a great variety of procedures. A solution by using the Laplace transform[15] leads to

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\left(\sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2\pi^2 Dt}{4l^2}\right)\right) \tag{2}$$

where M_t is the mass of diffusant desorbed at time t, M_∞ is the mass desorbed at $t = \infty$, l is the polymer film thickness, and D is the diffusion coefficient. (i) The approximation for short times is

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{\pi l^2}\right)^{1/2} \tag{3}$$

(ii) and the approximation for long times is

$$M_t = M_\infty \tag{4}$$

i.e. when all the additive has diffused out of the film.

Very recently, Balik[16] proposed a quite rapid, precise, and easily applied method to calculate diffusion coefficients by means of sorption data. This method has been called a "hybrid one-term method". It is represented by a weighted sum of the two first-term approximations for short-time terms given by eq 3 and the first term of eq 2:

$$\frac{M_t}{M_\infty} = \Phi(x)\,f(x) + [1 - \Phi(x)]g(x) \tag{5}$$

where $x = Dt/4l^2$, $f(x) = 4(x/\pi)^{0.5}$ (the short-time approximation), $g(x) = 1 - (8/\pi^2)\exp(-\pi^2 x)$ (the long-term approximation), and $\Phi(x)$ is the weighting function.

Experimental Section

Materials. Polypropylene. Hostalen PPN 1060 additive-free isotactic polypropylene in pellet form was supplied by Disper, S. A. Sant Andreu de la Barca (Barcelona, Spain). It has a nominal melt index MFI = 9 g/10 min at 230 °C and 5 N, a nominal density at 23 °C of 0.905 g cm^{-3}, and 54.2% of crystallinity. Some other characteristic properties such as the isotactic pentad fraction (IPF = 0.92) and molecular weight averages have been given elsewhere.[2,3]

Erucamide (13-*cis*-Docosenamide) ($H_3C(CH_2)_{11}HC{=}CH\text{-}(CH_2)_7\text{-}CO\text{-}NH_2$). A commercial sample of ARMOSLIP (EXP) beads with 96.5% purity (estimated by capillary gas−liquid chromatography (CGLC)), which has been used as standard material for CGLC testings and calibrations, was kindly supplied by AKZO Chemicals, S. A. División Química, El Prat de Llobregat (Barcelona, Spain), and was used as received.

Preparation of Mixtures. Blends of erucamide/i-PP having the compositions shown in Table 1 were prepared by dry-mixing. Mechanical blending was done in a home made mechanical dry blender where i-PP was melted at 200 °C, and then erucamide was added and the content mixed for 10 min. A small quantity (less than 0.1% w/w of polymer) of an antioxidant additive, IRGANOX 1076 (Ciba-Geigy, Basel/Switzerland), was added to protect against thermal oxidation and degradation. Nitrogen was used as a purging gas. Films were made by compression moulding at 200 °C, a temperature exceeding the melting one of i-PP as well as of erucamide, using a Collin press Model 300 with the following pressure program applied to the plates. Firstly, a 5 bar pressure was applied during 3 min; immediately afterward, the pressure was elevated to 35 bar during 2 min; and in a third stage, the pressure was raised to 120 bar during 3 min. Finally, the sample was quenched between the two plates refrigerated with cool water (10 °C) at a pressure of 35 bar during 3 min. The real composition for each one of the blends was estimated as follows.

Measurement of Erucamide Content. The erucamide content of each blend was determined by solvent extraction. After the sample was removed from the mixing chamber and cooled to room temperature, it was extracted by refluxing in a Soxhlet extractor with 100 mL of dry chloroform during 2–3 h, sufficient for a complete extraction of the additive. The extracted material was dried under reduced pressure.

Polymer coupons were molded with dimensions 1 × 10 × 20 mm using a brass mold and a sheet of brass as embolus. These dimensions provide the minimum weight of 0.100–0.150 g required by the sensitivity of the balance. The two-sided surface area of each coupon was around 1–2 cm^2 (edges neglected), and the thickness was calculated from the coupon weight. A small hole was punched in the top center of the coupon so that it could be held on a stainless steel wire which stand the sample from the balance arm. In this manner, the coupons were suspended in the balance arm and prevented from touching the walls. Erucamide was eliminated by evacuation (6×10^{-5} mmHg) and a trap immersed in liquid nitrogen was placed near the desorption chamber, in order to secure a low residual erucamide vapor pressure in the neighborhood of the sample.

Procedure. The kinetics of erucamide desorption were monitored microgravimetrically using an apparatus that was described previously.[17,18] All desorption experiments were made with a recording Electrobalance (Model RG, Cahn Division, Ventron Instruments Corp., Paramount, CA) with a sensitivity of 10^{-6} g). The balance was mounted in a glass vacuum chamber connected to a conventional high vacuum line with a turbomolecular device as diffusion pump. The temperature in the sample arm was maintained constant by an electrically controlled furnace. Both the temperature and weight of the sample were continuously monitored on a microcomputer and then processed apart. Four samples were studied. Their compositions are shown in the first column of Table 1.

Experimental Results

Desorption isotherms as a function of temperature and erucamide content of the thin film are shown in Figure 1a–c as plots of M_t/M_∞ against $t^{1/2}$. Plotting desorption data as a function of the square root of time, therefore, provides valuable information for inferring the controlling transport mechanism. The normalized amount of diffusant desorbed, M_t/M_∞, where M_∞ is the initial weight of additive in the blend, is plotted against time over several hours. The overall shape of the desorption curves are therefore concave downward with respect to the time axis.

Discussion of Results

Model for the Lower Erucamide Content Blends. Because our system behaves as an incompatible system,[2] when the amorphous regions of spherulites are saturated with the additive, the additive is segregated from the polymeric matrix as globules or droplets. Let us assume that our additive, in excess of its *equilibrium solubility*, is segregated from the polymeric matrix as globules.[2] In Figures 2 and 3 are shown the reduced curves as a function of M_t/M_∞ against t, for the desorption of erucamide from four erucamide/i-PP blends of 4.6, 8.0, 24.0, and 44.0% of erucamide at the temperatures of 345, 360 and 371 K. If the diffusion is Fickian, for short times of diffusion we can apply eq 3, and in the early stages the plot must be linear. Plots of the experimental data as a function of M_t/M_∞ against $t^{1/2}$ are shown in Figures 1a–c. The samples with the lower erucamide content, namely those of 4.6 and 8.0% erucamide, show a similar behavior at the three temperatures studied. However, the respective plots of the

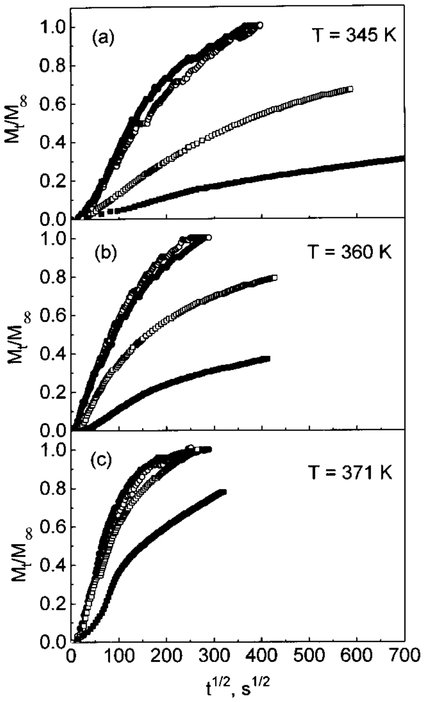

Figure 1. Desorption kinetic curves of erucamide from erucamide/i-PP blends as a plot of M_t/M_∞ against $t^{1/2}$ for blends of: 4.6% erucamide (○); 8.0% erucamide (●); 24.0% erucamide (□), and 44.0% erucamide (■) at temperatures of (a) 345 K, (b) 360 K, and (c) 371 K.

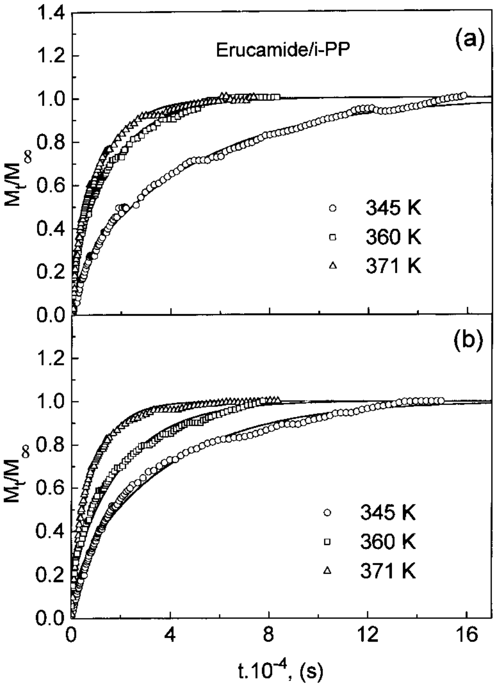

Figure 2. Plot of M_t/M_∞ against t of the experimental data at 345 K (○), 360 K (□), and 371 K (Δ) for samples with erucamide content of a 4.6% and (b) 8.0%. The full line (—) represents the estimated values calculated by means of eq 2. Parameters for this equation have been calculated by means of the best fitting of the equation to experimental data.

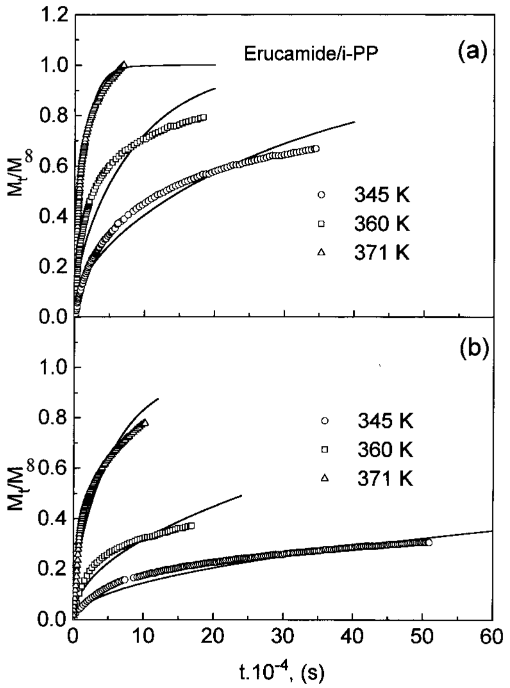

Figure 3. Plot of M_t/M_∞ against t of the experimental data at 345 K (○), 360 K (□), and 371 K (Δ) for samples with an erucamide content of a 24.0% and (b) 44.0%. The full line (—) represents the estimated values calculated by means of eq 2. Parameters for this equation have been calculated by means of the best fitting of the equation to experimental data.

data from the 24.0 and 44.0% erucamide content have a lower slope, which indicates that their diffusion coefficients are smaller than those found for the samples with a lower erucamide content, specially at the lower temperature of diffusion (345 K).

It is not very clear that our desorption isotherms present sigmoidal shape. This would indicate that we are not dealing with a case II diffusion. However, we can say that in the case of the sample with 44.0% erucamide at the temperature of 371 K, the curve does not show the normal tendency. In Figures 2a,b and 3a,b are shown plots of M_t/M_∞ against the time of diffusion t, for each of the samples at the three studied temperatures for each of the blends. The experimental data were fitted to eq 2 by means of a program package which considers fifteen terms of the summatory and to eq 5 proposed by Balik.[7] In fact, the second method is simpler and faster, although both yield the same value for D.

The diffusion coefficients obtained for every sample and the correlation coefficient R^2 for each fitting are summarized in Table 1. As can be seen in Figures 2a,b and 3a,b and as is concluded from the correlation coefficient, the experimental results deviate from the theoretical curves for the six isotherms of the two samples with the higher erucamide content. The respective activation energies of diffusion for each of the samples have been calculated assuming an Arrhenius type plot. The results are given in Figure 4 as a plot of ln D against $1/T$; the slope is larger in the case of the sample of 44.0% erucamide content. The apparent activation energies for the samples with lower erucamide content are similar, around 56 kJ/mol, whereas in the case of the higher composition the activation energy is 118 and 146 kJ/mol, respectively.

Model for the Higher Erucamide Content Blends. We must consider here a quite different situation in which the polymer matrix also contains additive as a heterogeneous component dispersed in the matrix forming globules as macrodomains. From these globules the additive can be released to the matrix as an apparently homogeneously dissolved component forming microdomains in the amorphous regions of spherulites and migrating to the polymer surface where it is removed so suddenly that the additive concentration immediately above the surface is zero.

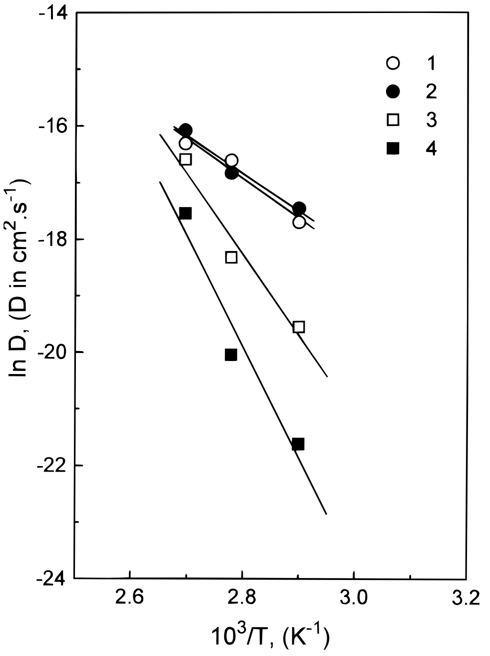

Figure 4. Plot of the diffusion coefficient as ln D against $1/T$ according to the Arrhenius equation for (○) 4.6% erucamide, (●) 8.0% erucamide, (□) 24% erucamide, and (■) 44% by weight erucamide content.

In Figure 5 are shown some details of an idealized schematic representation of the overall process of desorption for the samples with the higher erucamide content. Part i shows a schematic representation of a cutting of the film in which is shown the effect of surface cooling on crystallite and spherulite growth in a semicrystalline polyolefin according to a model given by Muccigrosso and Phillips.[19] The excess of erucamide in the sample forms a separate phase as globules or droplets as independent domains. They are represented by open circles. Part ii represents an enlarged area of i. And part iii gives a detail of a spherulite showing the intra- and inter-amorphous regions of a spherulite. Therefore, in Figure 5 are shown schematically the three zones in which erucamide molecules may be present namely, as a separate crystalline phase forming globules or droplets (1), in the amorphous regions of the spherulites (inter- and intra-spherulites) (2) at the external surface of the film (3). Under vacuum conditions the molecules which are dispersed in the amorphous regions of the i-PP spherulites diffuse to the film surface of i-PP (r_3) where they are removed very rapidly. The rate constant for the removal of erucamide molecules from the surface to the surroundings must be higher than the transport rate or erucamide molecules along the amorphous regions of the spherulites (r_2) so that erucamide does not accumulate on the film surface. On the other hand, we assume that for the transport of erucamide molecules from the globules to the inter- and intra-amorphous regions of spherulites is slower, i.e. the rate r_2 is much higher than r_1.

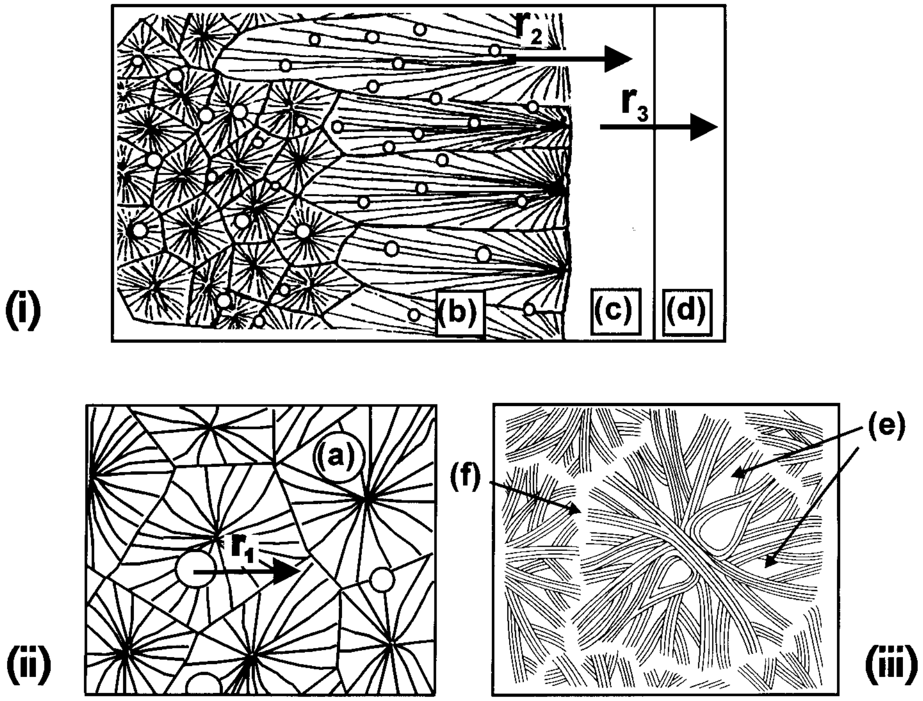

Figure 5. Idealized schematic representation of the diffusion model for the higher erucamide content blends: (i) Schematic representation of a cutting of the film in which is shown the effect of surface cooling on crystallite and spherulite growth in a semicrystalline polyolefin according to a model given by Muccigrosso and Phillips.[19] The excess of erucamide in the sample forms a separate phase (macrodomains) as globules or droplets (independent domains). They are represented by open circles. (b) The erucamide/i-PP blend film, (c) the film surface, and (d) the surroundings (r_2 and r_3 are the transport rates from the film to its surface and from the surface to the surroundings, respectively) are shown (ii) An enlarged region of part i to show the globules (a) as open circles and the transport rate from globules to the amorphous regions of spherulites (r_1). The spherulite's interphases are represented by solid lines; they are actually formed by the inter-amorphous regions (see iii). (iii) The detail of a spherulite[13] to show their intra- (e) and inter- (f) amorphous regions. Erucamide molecules that are located in these regions form a separate crystalline phase[2] (microdomains) quite different from that adopted by erucamide in globules or droplets (macrodomains).

The erucamide forming the globules or droplets must pass through the amorphous regions in order to diffuse to the surface of the films. As the rate of release from the amorphous regions to the surface of the film is very high, it is not the rate-controlling step of the overall process. If the release of the erucamide from the globules to the amorphous regions of the spherulites is faster than its transport to the film surface, i.e. if $r_1 \gg r_2$, the overall transport of erucamide would appear purely diffusional and the kinetics of desorption would be described according to a simple Fickian model. However, if the rate of release from the globules to the amorphous regions is slow, i.e. if $r_2 \gg r_1$, this will be the rate-controlling step which will limit the transport of erucamide to outside the film surface.

The release of erucamide from the globules to the amorphous regions of the spherulites is determined by the rate r_1. This rate depends on temperature and on the ratio of erucamide to i-PP in the sample, since the size of the globules increases as the erucamide content increases in the blend.[2] When the size of the globule is increased, the surface/volume ratio decreases with the subsequent decrease of the rate. If we assume that the release of erucamide from the globules or droplets to the polymeric matrix takes place according to first-order kinetics, it can be expressed by

$$\frac{\mathrm{d}M_t}{\mathrm{d}t} = k(M_{\mathrm{release}} - M_t) \tag{6}$$

where k is the constant of release from globules or droplets to the amorphous regions of the spherulites which form part of the polymeric matrix, M_t is the amount of additive released at time t, and M_{release} is the amount of erucamide which is released at a time $t = \infty$, namely, the total amount of erucamide contained in the globules. By integrating eq 6 we obtain

$$M_t/M_{\mathrm{release}} = 1 - \exp(-kt) \tag{7}$$

Thus, the overall diffusion process should be considered as the sum of two processes: first, we have the diffusion of erucamide which is located in the amorphous regions and/or surrounding the spherulites on the outside of the polymeric matrix, which occurs very rapidly, and a slower process in which the erucamide contained in the globules or droplets is released to the polymeric matrix and later on it diffuses to the film surface and very suddenly to the outside. Then, the overall process can be described as

$$M_{\mathrm{t}} = M_{\mathrm{Fick}}\left(1 - \frac{8}{\pi^2}\left(\sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2\pi^2 Dt}{4l^2}\right)\right)\right) + M_{\mathrm{release}}(1 - \exp(-kt)) \tag{8}$$

The first term of the right hand of eq 8 represents the amount of erucamide diffusing from the amorphous regions of the spherulites at time t, and the second represents the amount of erucamide releasing from the globules to the amorphous regions of spherulites.

This model for the higher concentrations of erucamide, with separate terms for diffusion from the polymer and release of diffusant from diffusant domains, is only mathematically identical to a model used by Berens and Hopfenberg[20] because of a two-term equation. However,

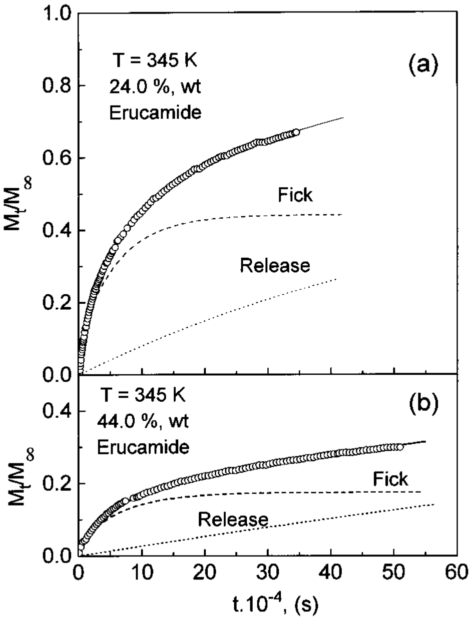

Figure 6. Plot of M_t against t of the experimental data at 345 K for blends with (a) 24.0% and (b) 44.0% erucamide content. Open circles (○) represent experimental results. The full line (—) have been calculated by means of eq 8. The dashed line (— — —) represents the contribution of the pure Fickian diffusion and the line (• • •) the controlled diffusion by release from globules or droplets.

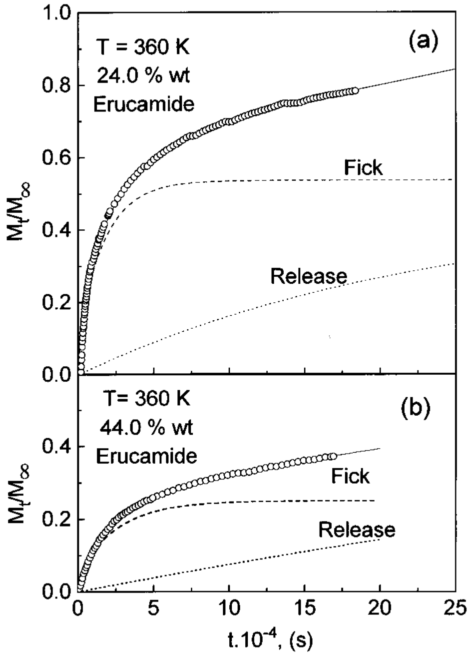

Figure 7. Plot of M_t against t of the experimental data at 360 K for blends with: (a) 24.0% and (b) 44.0% erucamide content. Open circles (○) represent experimental results. The full line (—) was calculated by means of eq 8. The dashed line (— — —) represents the contribution of the pure Fickian diffusion and the dotted line (• • •) the controlled diffusion by release from the globules or droplets.

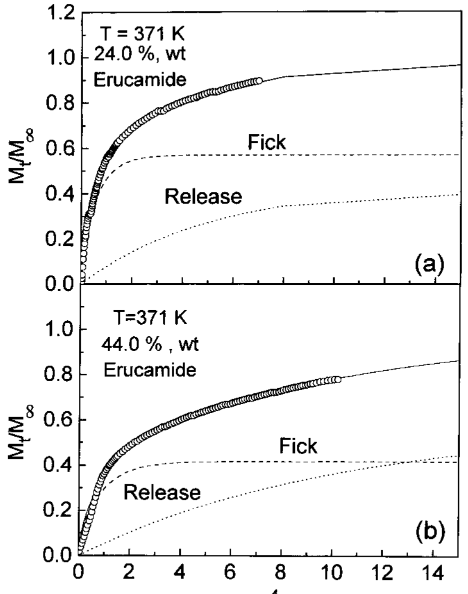

Figure 8. Plot of M_t against t of the experimental data at 371 K for blends with (a) 24.0% and (b) 44.0% erucamide content. Open circles (○) represent experimental results. The full line (—) have been calculated by means of eq 8. The dashed line (— — —) represents the contribution of the pure Fickian diffusion and the line (• • •) the controlled diffusion by release from the globules or droplets.

they used it to interpret gravimetric sorption measurements in glassy polymer powders (vinyl chloride monomer, acetone, or methanol on poly(vinyl chloride). They used their model to simulate excess sorption brought by polymer relaxation, which was modeled as a first-order kinetic process. In the present paper, a model is used to simulate "excess desorption", if we adopt the same terminology to describe the process caused by the presence of diffusant domains in the polymer. We do believe, however that the physical meaning is a bit different. We have employed a first-order kinetic process to describe the transport of erucamide from the globules or droplets to the amorphous region of spherulites because it yields to the best fitting of our experimental results. We have also tested a second-order kinetic to describe the delivery process; nevertheless, the fitting was not as good as that obtained by using a first-order kinetic. The first term of the hand right of eq 8 (Fick contributions) is conditioned because of the boundary conditions of our system. The coincidence of a two-terms overall equation seems to be only fortuitous.

In the Figures 6, 7, and 8, the amount of the desorbed erucamide (M_t) is plotted against the time of diffusion (t) for the samples of 24.0% and 44.0% erucamide content at temperatures of 345, 360, and 371 K. The experimental results have been adjusted to eq 8. In these Figures we can see that the full line which is the resultant of the overall process of diffusion agrees quite well with our experimental data. The dashed line represents the contribution to the diffusion process and the dotted line the contribution due to the release of erucamide from the globules or droplets to the polymeric matrix, i.e. to the amorphous regions and/or to the surroundings of the spherulites which really form the part of the permeable part of the matrix. Table 2 summarizes the diffusion coefficients and the release constants as well as the amount of erucamide released according to a Fickian-type diffusion mechanism and the amount of erucamide released from the globules or droplets to the matrix. Parts a and b of Figure 9 display the Arrhenius plot for the release constant and the diffusion coefficient, respectively, of these two samples.

The diffusion coefficients obtained are higher than those obtained by diffusion (absorption) of erucamide through films made from pure i-PP (Type I).[2] Moreover, in the present series of experiments (Type II experiments), we have not been able to detect the existence of two diffusion coefficients. In this latter case, the geometric morphology of i-PP is completely different

Table 2. Diffusion Coefficient (*D*), Transfer Constant *(k)*, and Relative Ratio of Erucamide for Each One of the Mechanisms and the Activation Energies (*E*), for Both Processes

composition erucamide, (% by weight)	T (K)	D (cm^2 s^{-1})	erucamide (% by weight)	E_a (kJ mol^{-1})	k (s^{-1})	erucamide (% by weight)	E_a (kJ mol^{-1})	R^2
4.4	345	2.05×10^{-8}	4.4	58	–	–	–	0.992
	360	6.11×10^{-8}			–	–	–	0.992
	371	8.25×10^{-8}			–	–	–	0.989
8.0	345	2.62×10^{-8}	8.0	55	–	–	–	0.988
	360	4.90×10^{-8}			–	–	–	0.987
	371	1.04×10^{-7}			–	–	–	0.986
24.0	345	1.67×10^{-8}	10.6	90	1.55×10^{-6}	13.4	102	0.998
	360	5.64×10^{-8}	13.0		4.30×10^{-6}	11.0		0.994
	371	1.51×10^{-7}	15.2		2.01×10^{-5}	8.8		0.997
44.0	345	1.48×10^{-8}	7.7	74	3.34×10^{-7}	36.3	68	0.999
	360	3.88×10^{-8}	11.0		1.06×10^{-6}	33.0		0.996
	371	8.86×10^{-8}	33.0		1.73×10^{-6}	11.0		0.955

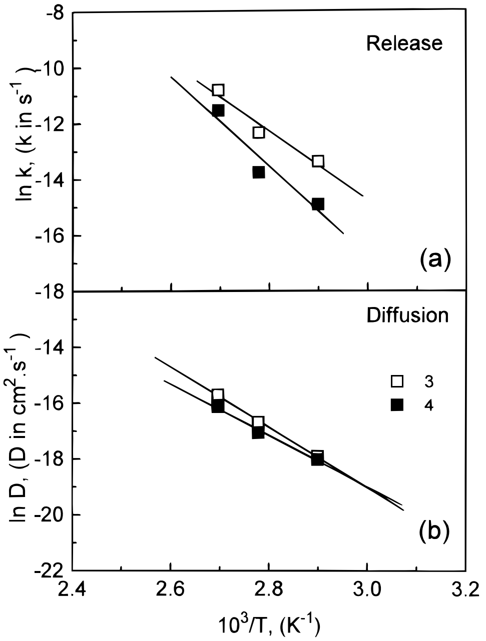

Figure 9. (a) Plot of the transfer constant as ln k against $1/T$ and (b) the plot of the diffusion coefficient as ln D against $1/T$ according to the Arrhenius equation for two samples of (□) 24% and (□) 44% by weight erucamide.

from that of i-PP films which have been made from pure i-PP, as mentioned in the Introduction. Small changes in the spherulite texture, size of the spherulites, or geometric morphology, caused by the presence of an additive during the crystallization, may exert some small but appreciable influence on the mode of transport.

Conclusions

(1) The kinetics of erucamide desorption from films of i-PP within incompatible blends of erucamide/i-PP were studied over a well-defined temperature window and composition of the blends. The desorption process from blends depends on the composition range studied. Thus, for example, for blends with an erucamide content of 4.6% and 8.0%, the diffusion obeyed a Fickian diffusion process. However, for blends with 24.0% and 44.0% erucamide content, the overall process of diffusion is quite different. This may be indicative of two types of behavior according to the composition of the blends.

(2) We have explained this behavior and we have solved it from a practical point of view. If we assume for the overall transport process two terms, one diffusional and other of release, we can formulate an equation which can fit all our experimental data for blends with 24.0% and 44.0% erucamide content. The model provides a good fit even for the most complex experimental desorption data. The model, however, is not limited to the quite good fitting of our experimental results with the three parameters M_{Fick} or M_{release}, D, and k. More surprisingly, it provides an intuitively defining separation of diffusional- and transference-controlled effects which can be satisfactorily explained by taking into account the blend morphology of each of the samples studied.

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