

Diffusion and Subsequent Polymerization of Styrene in Oriented Polypropylene Matrix

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SYNOPSIS

Results of investigations of styrene diffusion into oriented polypropylene matrix and subsequent polymerization performed in special conditions are shown for samples drawn at various temperatures to different draw ratios. It is demonstrated that styrene sorption in oriented polypropylene is relatively low, but proposed processing leads to obtaining polypropylene-polystyrene composites with large polystyrene contents.

INTRODUCTION

Physical combination of two or more synthetic polymers is one of the widely used methods for producing new materials interesting both from practical and scientific points of view. Such combinations can be realized by mixing polymers during extrusion from the melt, precipitation from a common solvent, or polymerization of the diffused monomer inside a host polymer matrix. The last method, reported in several early articles,¹⁻⁴ is still very attractive because of the following benefits:

- Better dispersion of the introduced polymer.
- Possibility of obtaining various structures in different samples as well as inside the volume of one sample (gradient polymers) realized by careful control of numerous parameters characterizing diffusion and polymerization processes.

In the case of semicrystalline matrix, initial structure and morphology strongly influence the diffusion of the penetrant and dispersion of the formed guest polymer. The investigation of samples obtained by this method may then provide some information not

only on the resultant component but also on the initial structure of the polymer matrix.

In our laboratories, investigations on the modification of unoriented polyolefins by diffusion of styrene (ST) and its eventual polymerization inside the matrix⁵⁻⁷ have been realized for several years. It was found that obtained polyethylene-polystyrene (PE-PS) and polypropylene-polystyrene (PP-PS) systems show modified structure,^{5,7} high dispersion of guest PS,⁷ and interesting mechanical properties.⁸ Diffusion and polymerization were carried out at a temperature of 65°C, which was sufficient for obtaining a high degree of ST sorption. The same investigations performed on oriented polymers are much more complicated because of significantly decreased diffusion of the penetrant in oriented systems⁹⁻¹¹ and possible relaxation of molecular orientation during diffusion and subsequent polymerization (solvent-induced¹¹⁻¹³ and thermal^{14,15} shrinkage). Considering the stability of molecular orientation, both diffusion and polymerization processes must then be performed at sufficiently low temperature and special techniques during polymerization must be employed to assure relatively high contents of introduced amorphous polymer.

The purpose of this presentation is to show the possibility of such processing. Some results on ST diffusion into oriented polypropylene and changes induced by the swelling agent are presented because these processes play an important role in the described polymerization. Mechanical properties of

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resultant composite PP-PS samples will be published later.

EXPERIMENTAL

Sample Preparation

Isotactic PP F401 produced by Mitsui Petrochemical Industries (Japan) was used in all the experiments. Foils 1 mm thick were oriented by drawing at various temperatures at the rate of 2 cm/min with necking to the natural draw ratios (samples PP1, PP2, and PP4 in Table I). Samples PP3 and PP5 were obtained from PP2 and PP4, respectively, by subsequent drawing with the same rate and temperatures to higher draw ratios. Drawing temperatures and draw ratios determined from changes of sample cross sections are summarized in Table I. Samples PP1, PP2, and PP3 contained microvoids, and cross sections S_p of polymer were estimated from a measured value S according to the relation $S_p \approx S\rho/\rho_p$, where ρ_p and ρ are densities of the oriented bulk polymer (without voids) and sample, respectively.

Styrene Sorption

Diffusion of ST in oriented PP was carried out at 45°C. The temperature was a compromise between the required amount of absorbed ST and the structural and dimensional stability of oriented PP. For each sample, a set of pieces ($20 \times 10 \times$ about 0.2 mm) was immersed in ST and successively each of them was removed from the bath. After quick wiping, its mass decrease during ST evaporation was measured as a function of time. The mass of the swollen piece, m_s , was determined from the extrapolation of that function to zero time. The sorption was expressed in terms of coefficient $N = (m_s - m_0)/m_0$, where m_0 is the initial mass of the piece. As previously reported,⁶ in the case of PP, no polymer ex-

traction takes place during ST treatment; hence, this coefficient describes actual contents of styrene in the sample. If ST sorption was measured for the samples that showed mass extraction during swelling (e.g., for PP-PS composites), m_0 was assumed as a mass after complete evaporation of ST (i.e., after 1 week of vacuum drying). Similarly, if ST diffusion was performed at constant length, the same procedure of estimating m_0 was employed after cutting swollen pieces out from the constraints (to avoid the influence of uncertain diffusion of ST inside the parts of material squeezed in the clamps).

Before further investigations, all pieces of swollen samples were vacuum dried for 1 week.

Polymerization

Both initial swelling and subsequent polymerization were performed in a special "envelope" made from poly(ethylene terephthalate) foils and plates that were styrene resistant and transparent for UV radiation. The hermetically welded "envelope"-containing oriented sample and distilled styrene with 7 wt % of photoinitiator (benzoin isobutyl ether) was placed in a special temperature chamber. The chamber was filled with water thermostated at 45°C, and two quartz windows enabled free exposure of the sample to UV radiation. Two mercury lamps AS 700 (Austria) were switched on for 3.5 h after 2 h of initial swelling. Then, the "envelope" remained 1 h in the chamber at elevated temperature. Such treatment was sufficient for complete polymerization of contained styrene. After cautious removal from the surrounding polystyrene, the sample was carefully cleaned and rinsed in toluene to extract PS from the surfaces. Such prepared samples were vacuum dried for 1 week before further investigations.

To characterize polystyrene formed inside the PP matrix, it was extracted from the composite sample by dissolving the specimen in boiling toluene and precipitation of PP with tetrahydrofuran (THF).

Table I Drawing Parameters of PP Samples

Sample	Drawing Temperature (°C)	Drawing Rate (cm/min)	Draw Ratio	ρ_p/ρ	Birefringence $\times 100$
PP1	20	2	5.8	1.019	
PP2	50	2	7.9	1.009	2.9 ± 0.1
PP3	50	2	10.7	1.088	
PP4	90	2	8.1	1.000	3.0 ± 0.1
PP5	90	2	12.3	1.000	3.4 ± 0.1

After centrifuging, the solution was carefully filtered. Both solvents were evaporated in vacuum, and acquired PS was vacuum dried at a temperature of 100°C for 1 week.

Samples Characterization

Densities of oriented PP and composite samples were measured in a water-ethanol gradient column stabilized at a temperature of 20°C. Thermograms of differential scanning calorimetry (DSC) were obtained using a DuPont 2000 thermal analysis system at a heating rate of 10 deg/min. Total heat of melting was assessed for all samples at a peak area from about 60 to 190°C using a sigmoidal base line.

Gel permeation chromatography (GPC) of obtained polystyrene was performed employing an LKB 2150 HPLC pump, a set of Toyo Soda columns G4000HXL and G2000HXL, and a UV detector. THF was used as an eluent with a flowing rate of 0.8 mL/min, and chromatograms were analyzed according to a calibration on TSK standard polystyrene.

RESULTS

Styrene-Treated Samples

Figure 1 shows the changes of ST sorption N during swelling of oriented samples. Although the thick-

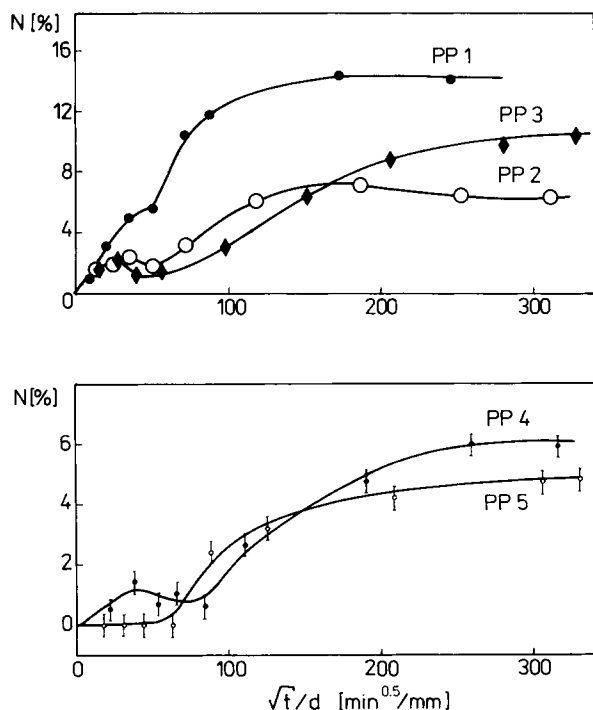


Figure 1 Coefficient N of ST sorption vs. $t^{0.5}/d$ for oriented PP samples.

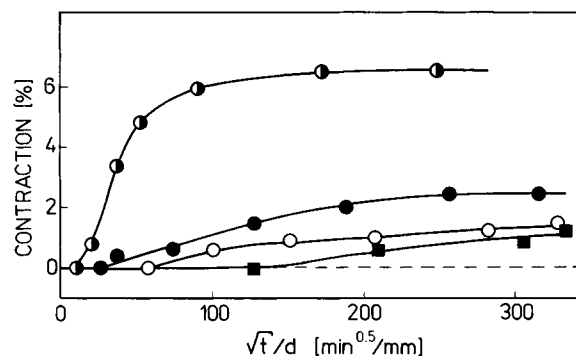


Figure 2 Contraction of ST-treated PP samples vs. $t^{0.5}/d$: (●) PP1; (■) PP2; (○) PP3; (---) PP4; (■) PP5.

nesses of the samples did not differ significantly (from 0.18 to 0.21 mm), the abscissa was scaled in $t^{0.5}/d$, where t and d denote swelling time and sample thickness, respectively. From comparison of these curves with the typical plots of diffusion,^{11,16} it is seen that diffusion of ST in oriented PP is non-Fickian. Figure 2 depicts contraction of the samples during the swelling process. Contraction is relatively low even for high swelling times, but molecular mobility plays an important role in the diffusion process. Figure 3 illustrates the influence of external constraints on the sorption of styrene for the PP1 sample. It is seen that when macroscopical shrinkage is impossible ST sorption is about two times lower. Comparative measurements of thermal contraction in air revealed that thermal shrinkage at the same temperature is several times lower than in the ST environment.

The fact that samples PP1, PP2, and PP3 contain microvoids is very significant for their swelling behavior. These specimens, opaque after deformation, become transparent after a certain time of ST treatment. Such behavior is not observed in air even after long-time annealing until temperatures close to the

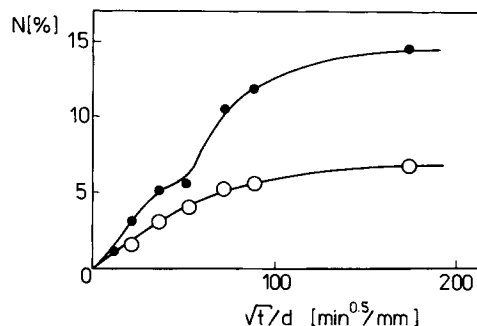


Figure 3 Coefficient N of ST sorption vs. $t^{0.5}/d$ for un-constrained (●) and constrained (○) PP1 samples.

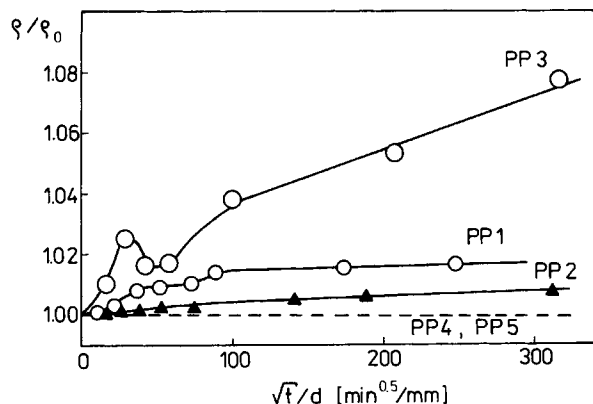


Figure 4 Changes of relative density vs. $t^{0.5}/d$ for ST-treated PP samples.

melting point of PP. Voids closing is also reflected in the changes of density of styrene-treated samples, as shown in Figure 4 (density of each specimen was related to the value for respective unswollen sample). For samples containing voids, besides initial anomalies, density increases with swelling time. It is seen that the higher the void content the greater the change observed; for samples PP4 and PP5 (without voids), density remained constant (to the accuracy of experimental error) and is sketched in the plot with a dashed line.

Anomalities observed on density curves result from the changes of structure taking place during swelling. Figure 5 shows total heat of melting ΔH for ST-treated samples related to the values ΔH_0 of untreated ones plotted against $t^{0.5}/d$. Changes of enthalpy are the most pronounced for PP1, PP2, and PP3; for the remaining two samples, results are close to the value 1.0 for all swelling times. In the case of oriented polymers, true structural changes observed in DSC are superposed to shrinkage effects,¹⁷ so in this work, such measurements are used only for comparative studies. It is seen that ST treatment induces some changes in the structure that correspond very well to the anomalies observed in the density plots (compare Fig. 4).

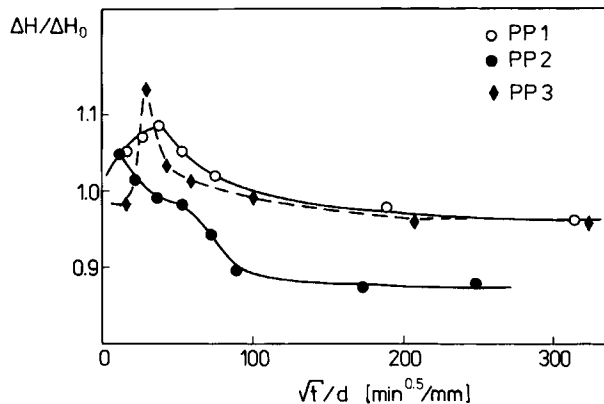


Figure 5 Relative value of melting heat vs. $t^{0.5}/d$ for ST-treated PP samples.

PS-Containing Samples

Data concerning composite samples are compiled in Table II (respective samples are denominated by a letter p). Coefficient K denotes the mass fraction of PS related to the mass of initial, oriented PP sample. $\Delta H/\Delta H_0$ is the ratio of the melting heat for PP in a PS-containing sample to the value for the initial, oriented specimen and ΔT_{\max} denotes the difference of their melting peak temperatures.

Polymerization of the samples, started after 2 h of swelling, was completed in 5.5 h after swelling commencement; hence, the values of $t^{0.5}/d$ varied from about 55 to 90 $\text{min}^{0.5} \text{mm}^{-1}$. Results presented in Figure 1 show that for these values of $t^{0.5}/d$ sorption of monomer changes from less than 10% (PP1) to about 1% (PP4 and PP5). It is easy to notice that for all samples PS contents K is significantly greater than N .

Thermal data presented in Table II show that the heat of melting for PP in composite samples is lower than the value recorded for the respective ST-treated, oriented PP (compare Fig. 5). The observed temperature difference ΔT_{\max} , although slight, also demonstrates decreased perfection of crystalline structure in PS-containing samples.

Table II Characteristics of PS-containing Samples

Sample	K (%)	Density (g/cm^3)	Birefringence $\times 10^2$	$\Delta H/\Delta H_0$	ΔT_{\max} ($^{\circ}\text{C}$)
PP1p	74	0.947 ± 0.007		0.85 ± 0.01	-1.2
PP2p	26	0.927 ± 0.002	2.48 ± 0.07	0.94 ± 0.01	-0.5
PP3p	15	0.870 ± 0.001		0.97 ± 0.01	-0.5
PP4p	27	0.930 ± 0.002	2.38 ± 0.07	0.91 ± 0.01	-1.6
PP5p	2.3	0.906 ± 0.002	3.40 ± 0.10	0.97 ± 0.01	0.0

Table III Characteristics of Obtained PS

PS	Density (g/cm ³)	<i>T_g</i> (°C)	<i>M_n</i>	<i>M_w/M_n</i>
Outer	1.050	80.0	1,500	10.2
From PP1p	1.055	100.0	43,000	5.3
From PP4p	1.055	102.5	76,000	3.7

Polystyrene extracted from composite samples shows rubberlike behavior while heated above 100°C, contrary to outer PS, which is visco-liquid above about 80°C. Table III presents the characteristic of outer PS as well as of PS extracted from two composite samples. Molecular weights were calculated from gel chromatograms according to the calibration described in the Experimental section. It is seen that the properties of outer and inner PS are significantly different.

DISCUSSION

Diffusion of a liquid penetrant into semicrystalline polymeric material is a very complex phenomenon strongly dependent on the temperature. Presented results are limited only to 45°C, because at this temperature, both ST sorption and stability of molecular orientation proved to be satisfactory for further processing. Birefringence, used as a measure of resultant (amorphous and crystalline) orientation, did not change during swelling, and its value for composite samples was also consistent with results calculated for the oriented PP matrix and included an unoriented PS component (compare values in Tables I and II). Also, measurements of shrinkage forces, employed as a sensitive measure of changes of orientation in amorphous regions,¹⁸ confirmed complete firmness of orientation for PP3, PP4, and PP5 samples and sufficient stability for the remaining two specimens after 5 h of ST treatment.

The results presented show that ST sorption is relatively low even in samples containing microvoids. Styrene treatment is responsible for their effective closing, as shown in Figure 4. However, ST appears not to penetrate inside the voids. For instance, the volume contents of voids, determined as $\rho_p/\rho - 1$, in the PP3 sample is above 8% (compare Table I) and complete filling of them with ST would lead to sorption *N* of about 10%, which is reached only after a long swelling time when voids are nearly totally closed. Voids are also observed in PS-containing samples PP1p, PP2p, and PP3p.

If the diffusion into voids can be neglected, distortions on sorption curves observed in Figure 1 re-

sult from structural changes induced by the swelling agent. Comparison with plots of total heat of melting (Fig. 5) indicates that some structural reorganizations occur exactly in the same interval of the abscissa scale. The role of molecular mobility in the swelling process is clearly seen from comparison of sorption curves recorded for unconstrained and constrained samples (Fig. 3). Macroscopical shrinkage is relatively low (compare Fig. 2), but local shrinkage processes in the oriented sample¹⁹ may be active enough to produce structural and orientational rearrangement that changes the sorption ability of the PP matrix. It is seen that when these processes are significantly delayed by external constraints the sorption of the sample decreases.

In semicrystalline polymers, diffusion processes can be considered practically as taking place in the amorphous phase.^{11,20} Hence, introduced PS is fixed in the amorphous regions of PP. The difference between monomer sorption of oriented PP and PS contents in composite samples is remarkable and cannot be explained only by continuous diffusion of the monomer inside the PP matrix during the polymerization process. Let us assume a completely idealized case of an infinite volume of monomer (with initiator) outside the sample, polymerization taking place only inside the matrix, and total conversion of diffused ST to PS. Neglecting small initial distortions of sorption curves, traces of *N* vs. time for several samples can be satisfactorily approached with the simple exponential equation $N = N_0 [1 - \exp(-at)]$, where *N*₀ and *a* are constants. Changes of ST contents inside the matrix are then described by the simple differential equation

$$\frac{dN}{dt} = a(N_0 - N) - \frac{dK}{dt}$$

where the second term depicts the rate of conversion of ST to PS. In the stationary state, independently of the kinetics of radical concentration change inside the sample and of the mechanism of radical recombination,

$$K = a(N_0 - N)t + K_0$$

where K_0 denotes initial fraction of PS and N is constant. The maximum value of the increase of K in time t is then equal to aN_0t . For sample PP1, fitted values $a = 0.0032 \text{ min}^{-1}$, $N_0 = 14.7\%$, so after 4 h of polymerization, K increases only by about 11%.

Even in such idealized conditions, calculated PS contents proved to be about six times lower than those measured experimentally. The only possible explanation of such a discrepancy lies in the assumption that ST diffusion inside already polymerized PS areas is preferred and that such osmosis leads to high sorption of ST during polymerization. This supposition can be verified by measurement of the ST sorption coefficient N for the composite PP-PS sample. By knowing the sorption N_{PP} of the PP matrix and the current value of K of the PS contents during such sorption, it is possible to evaluate the mass of ST sorbed in PS regions fixed inside the matrix. This mass, related to the mass of the PS component, can be expressed in terms of the N_{PS} coefficient and calculated according to the equation

$$N_{PS} = \frac{(K + 1)N - N_{PP}}{K}$$

A separate PP sample drawn at 60°C to the natural draw ratio 6.5, stored 1 week at room temperature, then immersed for 4 h in ST at 45°C (for stabilization) and completely dried in vacuum was prepared for such measurements. Figure 6(a) shows the coefficient of styrene sorption N_{PP} for that sample plotted as a function of $t^{0.5}/d$. It is seen that the initial swelling of the oriented PP (stabilization) is necessary because ST treatment induces structural changes influencing the diffusion properties of the sample. Then, the stabilized sample was swollen with ST and performed polymerization (carried out in the same way as for all PS-containing samples) led to PS contents $K_0 = 18.6\%$. For such a prepared PP-PS composite, ST sorption N at 45°C and current PS contents K were measured as a function of swelling time. Figure 6(b) and (c) shows the results of K and values of N_{PS} (calculated according to the above equation) plotted vs. $t^{0.5}/d$. Changes of PS contents [Fig. 6(b)] indicate that extraction of PS proceeds in two steps—relatively quick at the beginning (related probably to the extraction of oligomeric PS and a high molecular weight component anchored close to the surface) and much slower for longer swelling times. Sorption of ST in the regions rich in PS [Fig. 6(c)] quickly reaches values greater than 200%, indicating that the mass of ST diffused in PS exceeds more than twice the mass of this polymer. Such efficient osmosis is possible most

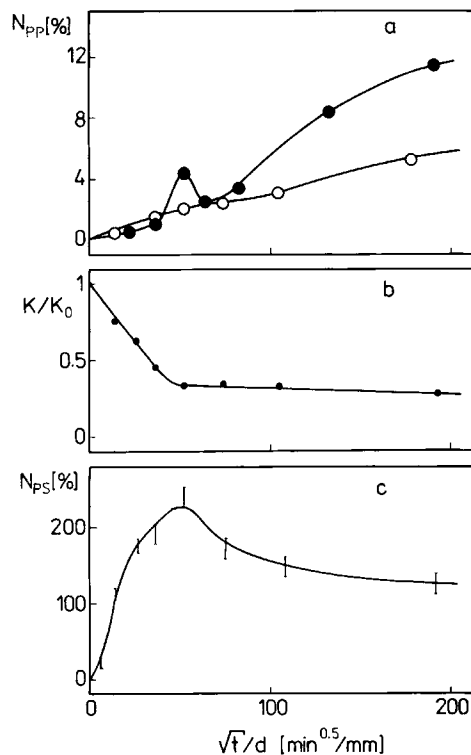


Figure 6 Results of styrene treatment plotted vs. $t^{0.5}/d$ for oriented PP and composite PP-PS samples: (a) ST sorption N_{PP} for untreated (●) and stabilized in styrene (○)-oriented PP; (b) relative value K/K_0 of PS contents in composite sample during styrene treatment ($K_0 = 18.6\%$); (c) ST sorption N_{PS} of PS fixed in PP matrix.

likely because the stiffness of the swollen amorphous phase of PP is very low and limited only by surrounding crystallites. In such a situation, volume deformations of the regions rich in PS, determined by the structure of the matrix, may be large until exerted osmotic pressure is balanced by a reaction of the matrix. The deformations considered may result in distension of the crystalline structure and destruction of some crystallites contributing to lower perfection of the structure observed for composite samples (compare values of $\Delta H/\Delta H_0$ and ΔT_{max} in Table II).

ST penetration in the composite PP-PS specimen is very complex, and observed sorption is a result of three transport processes: diffusion into the PP matrix, osmosis inside the regions rich in PS, and extraction of PS. During polymerization performed in the "envelope," these processes take place in specific external conditions (limited volume and presence of PS both inside and outside the matrix) and another transport process is involved—diffusion of initiator inside the sample. The rate of this diffusion related to the rate of monomer sorption determines the molecular weight of PS obtained inside

the host polymer. Data gathered in Table III show that the molecular weight of PS inside the matrix exceeds several 10s times the molecular weight of outer PS, indicating that diffusion of the initiator into the sample is significantly hindered. The table lists characteristics of inner PS only for two samples of the highest PS contents but various draw ratios and different structures of oriented PP matrix. The relative rate of diffusion of monomer and initiator is different for these samples and results in various molecular weights of formed PS.

The results show that the physical nature of the processing is very complex and may result in different contents and molecular weights of PS inside the matrix dependent on the relative effectiveness of involved transport processes and external conditions. By changing certain parameters characterizing polymerization (e.g., time or the intensity of UV radiation) and parameters determining the efficiency of the diffusion processes, not only the gradient of the PS contents but also the gradient of the molecular weight can be obtained inside the host sample. The effectiveness of the diffusion in the polymer matrix as well as in the composite sample strongly depends on its crystalline structure and molecular orientation so that the structural differences may lead to changes in the relative activity of the transport processes. In the case of PP2p and PP4p samples, which show nearly the same contents of PS, ST sorption in the host matrices is different (compare Fig. 1). Similarly, the PS fraction measured for unoriented PP subjected to initial swelling followed by polymerization is nearly the same as for the PP1p sample, whereas ST sorption in unoriented material reaches about 30% after 2 h of swelling. It is also remarkable that, despite of such a large fraction of PS, the oriented PP1p sample is flexible, contrary to the brittle unoriented one (mechanical properties of oriented PP-PS composites will be published later).

CONCLUSIONS

The results show that the proposed treatment of the polypropylene-styrene system leads to obtaining composite PP-PS samples of large PS contents. The method described is particularly useful in the case of oriented host polymers that exhibit low styrene sorption and their processing temperature cannot be high because of the stability of molecular orientation. The method of "envelope" polymerization is determined by the following transport processes: diffusion of styrene and initiator into the host polymer, osmosis of styrene through the PP matrix into areas rich in polystyrene, and extraction of polystyrene

from the swollen matrix. The relative efficiency of these processes, strongly dependent on the PP structure and processing conditions, determine the contents and molecular weight of polystyrene formed inside the matrix.

Measurements of styrene diffusion into oriented polypropylene revealed that styrene treatment is responsible for the effective closing of the microvoids; however, styrene appears not to penetrate inside the voids. Diffusion shows non-Fickian character, and observed distortions on sorption curves result from styrene-induced structural changes of the crystalline matrix.

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