Oriented PP–PS Composites Obtained by Polymerization of Styrene Inside Oriented PP Matrices. I. Dispersion of PS and the Composites' Orientation

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SYNOPSIS

Dispersion of polystyrene (PS) and the molecular orientation of the polypropylene–polystyrene (PP–PS) composites acquired by the *in situ* polymerization of styrene in the oriented PP matrices were characterized by microscopic observations, birefringence measurements, and differential scanning calorimetry. It has been shown that applied processing of the "envelope" polymerization leads to obtaining oriented composites with large contents and the specific dispersion of PS. Some composites exhibit a substantial gradient of PS concentration and a gradient of molecular orientation, both strongly dependent on the initial structure of the oriented PP matrix. The modification of the PP structure taking place during processing does not disturb the orientation of the matrices deformed to the higher draw ratios. The structural changes of the oriented PP induced by processing are reflected in the shrinkage behavior and mechanical properties discussed in the second part of this paper. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Multicomponent polymer systems have recently attracted a great deal of interest as materials with beneficial properties and interesting structure. One of the methods of obtaining such systems is *in situ* polymerization, meaning the polymerization of a monomer diffused into a host polymer matrix. Both processing and the structure–properties relationship of the composites prepared in this way have been reported in many papers (e.g., Refs. 1–5), but the majority of the materials have been acquired from isotropic (unoriented) matrices. Nevertheless, the application of oriented polymers as matrices seems to be very interesting. Such composites may join the benefits characteristic of oriented materials with features arising from the high dispersion of another component inside the matrix. However, if oriented polymers are to be used as matrices, employed pro-

cessing must be carefully managed to avoid significant relaxation of the orientation of the matrix. The diffusion of the monomer and the subsequent polymerization will, then, be controlled to a great extent by the initial arrangement of macromolecules in the matrix. For this reason, the investigation of the obtained composites may provide information not only on the resultant samples but also on the initial molecular architecture of the employed matrices.

Swelling of oriented polymers is much lower than that of the unoriented ones[6–8] and is associated with the relaxation of molecular orientation due to the solvent-induced[8,9] and thermal shrinkage.[10,11] Then, the processing temperature should be significantly lowered, which results usually in obtaining a composite of the insufficient contents of the guest polymer. This inconvenience can be avoided in some cases by employing specific processing techniques.

In our laboratory, the investigation of the oriented composites prepared by *in situ* polymerization was carried out using oriented isotactic polypropylene (PP) as the matrix and styrene (ST) as the mono-

mer. All details concerning the employed technique together with the discussion of the effects responsible for the high contents and high molecular weight of the guest polymer inside the host matrix have been described in a previous paper.[12] The purpose of this study was to show the physical constitution and some properties of prepared composites that exhibit a specific dispersion of the polystyrene (PS) component. Our attention will be focused on the molecular orientation of the matrices and the obtained composite materials. The presentation is split into two parts: In the first, the microscopic observations, birefringence measurements, and differential scanning calorimetry (DSC) data are analyzed. The second part describes the shrinkage behavior and the results of the dynamic mechanical investigations that were employed for the characterization of the samples; it has been shown that the analysis of shrinkage stresses exerted by the oriented homopolymers and composites can be successfully used as an additional method for material characterization.

To facilitate the understanding of the presented results, it seems to be useful to summarize here the description of the employed processing technique and some important conclusions concerning the polymerization process.

EXPERIMENTAL

Preparation of PP Matrices

Five oriented matrices were made from isotactic PP F401 (Mitsui Petrochemical Industries Ltd., Japan) by drawing 1 mm-thick foils at various temperatures with the rate of 2 cm/min. The matrices denoted by PP1, PP2, and PP4 were drawn with necking to the natural draw ratios, whereas PP3 and PP5 were obtained from PP2 and PP4, respectively, by sub-

sequent drawing to the higher draw ratios. This drawing was carried out with the same rate and at the same temperature as employed for the first drawing procedure. The matrices PP1, PP2, and PP3 contained microvoids, but since the voids were also present in the respective composites,[12] no correction for voids was made in this part.

Preparation of PP-PS Composites

All the details concerning the preparation of the oriented composites have already been presented.[12] Processing was performed in a special "envelope" made from poly(ethylene terephthalate) and filled with liquid ST containing photoinitiator (benzoin isobutyl ether). The oriented matrices in the form of plates (30 × 20 × about 0.2 mm) were used for obtaining the composite materials. After placing the matrix inside and immersing it in ST, the "envelope" was hermetically welded. The matrix was subjected to the initial swelling and then the UV radiation was switched on to induce the polymerization process. Processing parameters such as the temperature (45°C) and the time of initial swelling (2 h) were chosen as a compromise between the required amount of absorbed ST and the structural and dimensional stability of oriented PP. ST contained 7 wt % of the photoinitiator in order to assure a complete polymerization of the monomer inside the "envelope" in a reasonable irradiation time (about 4 h). After the polymerization, the composite sample was cautiously removed from the surrounding PS, carefully cleaned, and rinsed in toluene to extract PS from the surfaces.

Sample Characterization

Direct observation of the morphology was performed with a phase-contrast microscope using 10 μm-thick sections cut parallel to the drawing direction and

Table I Characteristics of PP Matrices

Sample	Drawing Temperature (°C)	Draw Ratio	$\Delta n_0 \times 100$	ST/PP (%)	ΔH_0 (J/g)
PP1	20	5.8	2.63 ± 0.07	11	99.1
PP2	50	7.9	3.36 ± 0.09	3	105.4
PP3	50	10.7	3.44 ± 0.07	2	108.4
PP4	90	8.1	3.19 ± 0.07	1	107.8
PP5	90	12.3	3.23 ± 0.06	2	111.2

Table II   Characteristics of PP–PS Composites

Sample	PS/PP (%)	k_v	$\Delta n_0 \times 100$	$\dfrac{\langle \Delta n \rangle}{\Delta n_0}$	$\langle \Delta n_{PP'} \rangle \times 100$	$\dfrac{\Delta H}{\Delta H_0}$	ΔT_p (°C)
PP1p	74.0	0.61	2.61 ± 0.10	0.45	1.93 ± 0.07	0.85	−1.2
PP2p	26.0	0.82	2.81 ± 0.08	0.63	2.16 ± 0.06	0.94	−0.5
PP3p	15.0	0.89	3.15 ± 0.07	0.88	3.11 ± 0.07	0.97	−0.5
PP4p	27.0	0.81	2.97 ± 0.04	0.88	3.23 ± 0.04	0.91	−1.6
PP5p	2.3	0.98	3.09 ± 0.10	1.00	3.15 ± 0.10	0.97	0.0

perpendicular to the surface of the plate. To evaluate the birefringence of oriented samples, the observations were also realized using a polarizing microscope with a fringed interference field.

Electron microscopy was carried out on the fractures (made in the same direction as the sections) coated with gold, using the scanning microscope Jeol JSM-35C. Thermograms of differential scanning calorimetry (DSC) were obtained using a DuPont 2000 thermal analysis system at a heating rate of 10 degrees/min. The total heat of melting was assessed for all the samples at a peak area from about 60 to 190°C using a sigmoidal base line. The density of the oriented PP matrices and the composite samples was measured in a water–ethanol gradient column stabilized at a temperature of 20°C.

RESULTS

Some parameters characterizing the oriented matrices are summarized in Table I. The draw ratio was determined from changes of the cross-section area of the matrices. The parameter Δn_0 denotes the birefringence of the matrices measured during the microscopic observation of the sections (this value remains constant in the whole volume of the matrix). The parameter ST/PP characterizes the sorption of ST in the oriented matrix at the temperature 45°C. It was calculated as the mass of ST absorbed after 4 h of swelling related to the initial mass of the matrix. These values are useful for the visualization of the differences between the ST sorption of the matrices and the PS contents in the final samples. Since ST affects the matrix both during the initial swelling (2 h) and subsequent polymerization (4 h when the amount of ST decreases continuously), the intermediate time of 4 h was arbitrarily chosen. The detailed results of the kinetics of ST sorption in the matrices have been published

elsewhere.[12] ΔH_0 denotes the heat of melting for the matrices.

The quantities characterizing the oriented composites are compiled in Table II. The parameter PS/PP denotes the contents of PS calculated as a mass of the PS component related to the initial mass of the PP matrix. It is easy to notice that the PS contents in the composite materials obtained by "envelope" polymerization is not comparable with the ST sorption of the host matrices (the values ST/PP in Table I). The parameter k_v is the mean vol-
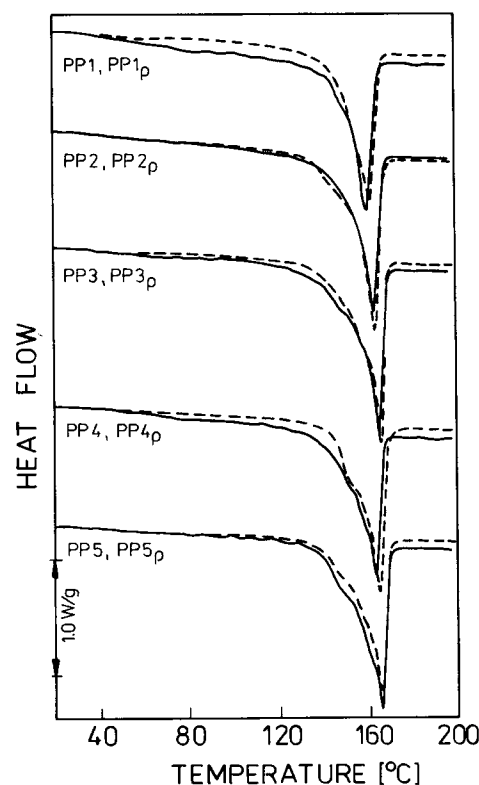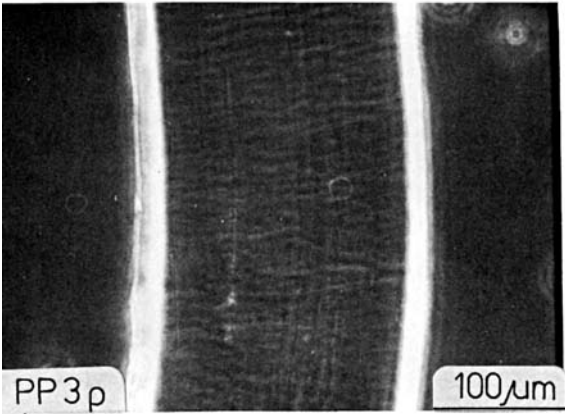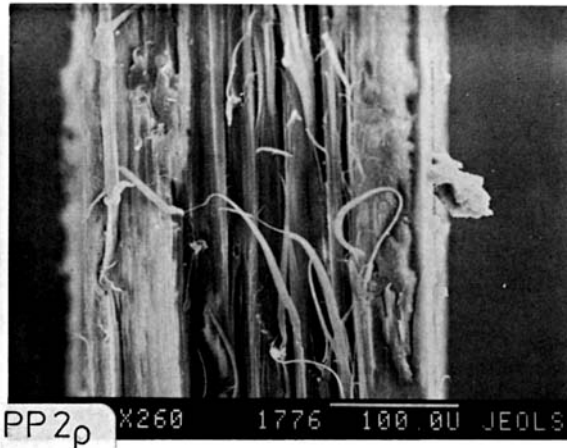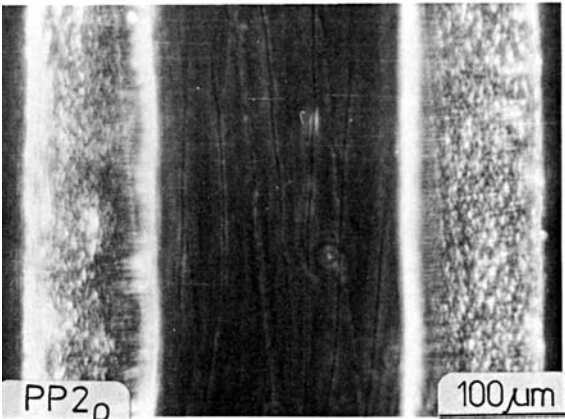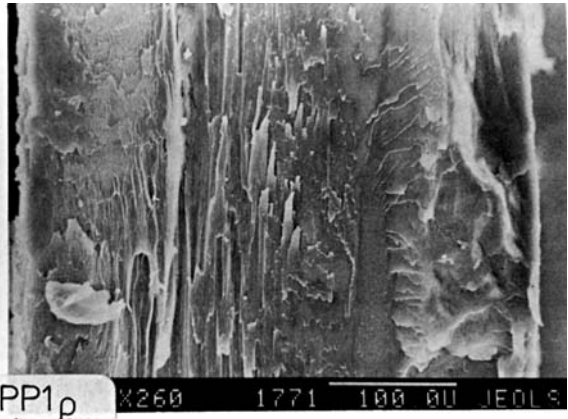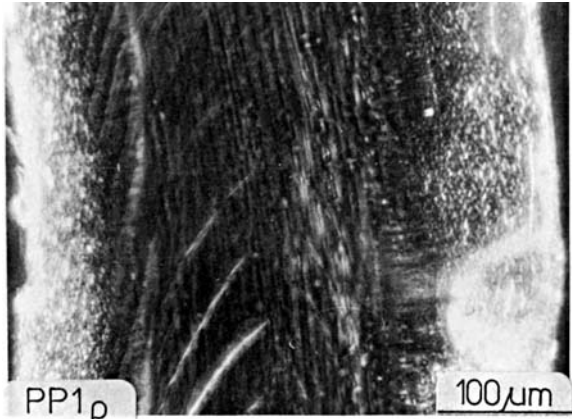

Figure 1   DSC thermograms for the composites (continuous) and matrices (dash); the heat flow is related to the mass of the PP contained in the sample.

a   b

Figure 2   (a) Phase-contrast micrographs of the sections of the composites and (b) SEM micrographs of the corresponding fractures.

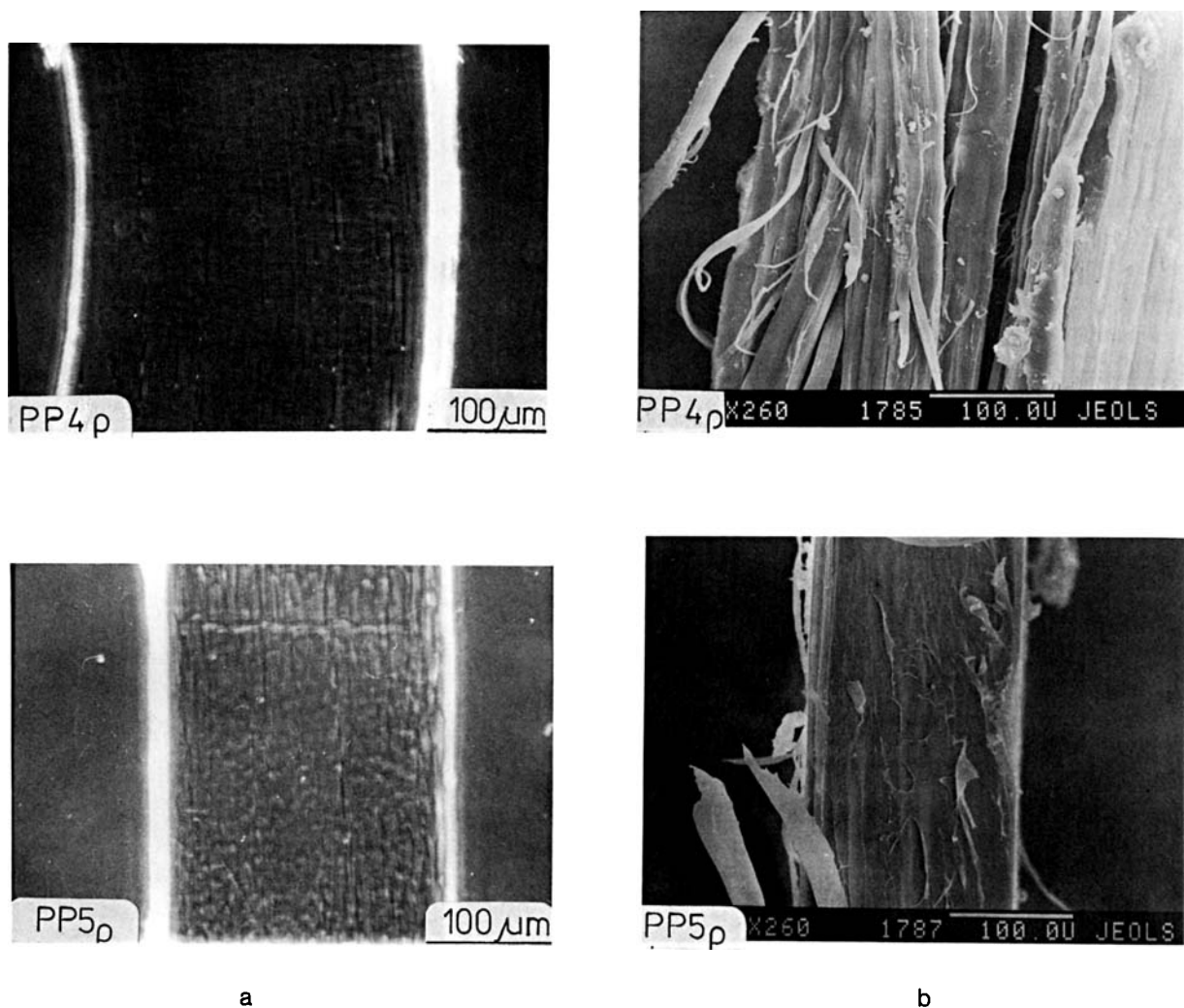a   b

Figure 2 (*Continued from the previous page*)

ume fraction of PP in the composite calculated on the basis of the parameter PS/PP, measured densities of the matrices, and the density of PS extracted from the composites.[12] The meanings of the birefringences gathered in Table II are explained in the text below. $\Delta H / \Delta H_0$ is the ratio of the melting heat of the PP component of the composite to the value for the corresponding, oriented matrix, and ΔT_p denotes the difference in their melting peak temperatures.

It is seen that the value of the melting heat for PP in the composite is lower than that recorded for the matrix. The decreased perfection of the crystalline structure of the PP component in the composites is also reflected in the temperature differences ΔT_p. The values of ΔH and ΔT_p enable only

a rough comparison of the thermal behavior close to the melting temperature T_p. The complete DSC traces of the composites and the matrices are shown in Figure 1 (for the composites, the values of heat flow have been related to the mass of the PP component). It is seen that significant differences resulting from the structural changes can be observed also at low temperatures starting from about 50°C.

Figure 2 presents the phase-contrast micrographs of the sections of the oriented composites and the SEM micrographs of the surfaces of sample fractures. It is seen that the concentration of the PS component is very inhomogeneous inside the composite; nevertheless, no clearly separated grains are detected. The lack of such inclusions was also confirmed by SEM observations performed with a

higher magnification. It is possible to distinguish two characteristic regions—the external shell and the internal core; however, the line between them is not evenly clear for all the samples. The relative thicknesses of these regions are also different and cannot be directly related to the amount of PS inside the composites (compare the samples PP2p and PP4p of nearly the same PS contents).

A typical pattern observed in a polarizing microscope with a fringed interference field is shown in Figure 3(a) with the example of the PP2p sample. The changes of birefringence in the volume of each composite, calculated on the basis of such patterns, are illustrated in Figure 3(b). It is seen that the

birefringence changes from the maximum value Δn_0 in the middle to the lower values in the outer regions of the composites. The absolute values of the maximum birefringence Δn_0 for each composite are specified in Table II. The mean birefringence $\langle \Delta n \rangle$ along the thickness of each composite was calculated on the basis of the birefringence profile. The values are presented in Table II in the form of $\langle \Delta n \rangle / \Delta n_0$.

DISCUSSION

In the previous paper[12] concerning the oriented PP–PS composites obtained by the *in situ* polymeriza-
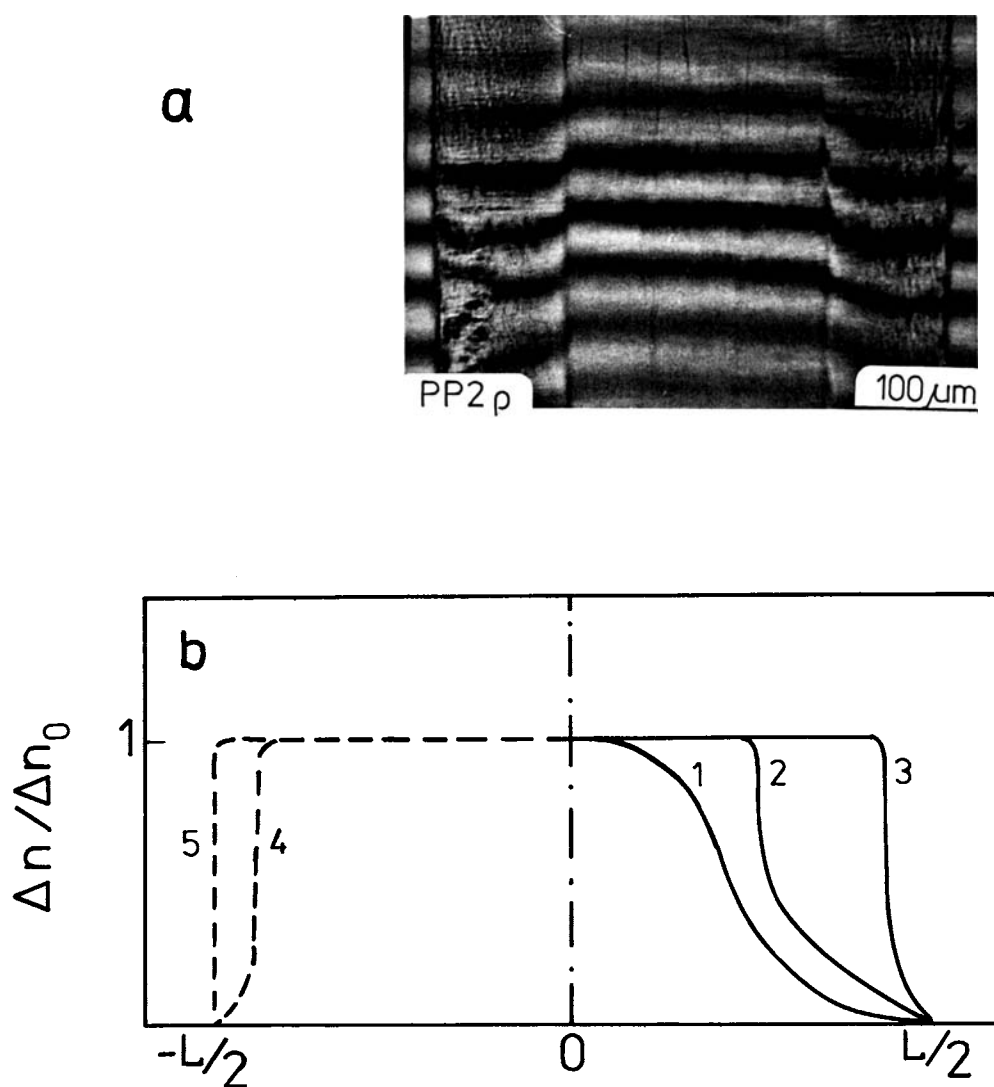

Figure 3 (a) Section of the PP2p composite observed in a polarizing microscope with a fringed interference field and (b) the changes of relative birefringence in the volume of each composite. Only one-half of each symmetric curve is presented; L denotes the thickness of the sample.

tion of ST, it was reported that the employed "envelope" technique is determined by the following transport processes taking place during initial swelling and subsequent polymerization: (i) diffusion of ST into the host polymer; (ii) diffusion of the initiator; (iii) osmosis of ST into the PS regions just formed in the matrix; and (iv) extraction of PS from the swollen matrix. The relative efficiency of these processes, strongly dependent on the PP structure and the processing conditions, determines the contents and the molecular weight of PS formed inside the matrix. The diffusion of the initiator is lower than the diffusion of ST, so the molecular weight of PS formed inside is much greater than the molecular weight of PS from outside the matrix.[12]

The characteristic constitution of the composites presented in Figure 2 results from the employed processing of the "envelope" polymerization. When polymerization starts (after the initial swelling), the ST diffusion inside the PS regions newly formed in the matrix is the most pronounced process and this effect is responsible for the high PS contents in the composites. A high flow of ST from outside and a nonuniform distribution of the initiator inside the matrix lead to obtaining the PS component concentrated preferentially in the outer parts of the sample, independently of the thickness of the matrix. Nevertheless, no clearly separated grains of pure PS are observed inside the composites (compare Fig. 2); hence, the arrangement of PS is very specific and is not comparable with the dispersion obtained during classical mixing of two components. Despite the high content of the guest polymer, there is no distinct glass transition of PS recorded on the DSC thermograms of the composites (compare Fig. 1). The glass transition temperature of PS extracted from the composites was about 100°C.[12] This glass transition in the composite is smeared probably due to the influence of the matrix on the molecular mobility of PS chains (indicating the high dispersion of the guest polymer). However, it can also be superimposed on the thermal effects of shrinkage[13] or on the changes of the molecular structure of the modified matrix during heating.

The analysis of the DSC thermograms presented in Figure 1 shows that the perfection of the crystallites in the composites PP1p, PP4p, and PP3p is substantially decreased with regard to the respective matrices. The thermal behavior of the composite PP5p is different (in comparison with the matrix) only at higher temperatures, but in PP2p, the structural changes influencing the DSC trace are not so pronounced. The thermograms even indicate that, within a certain temperature range, the structure of

the PP2p composite seems to be more stable than is the structure of the matrix. It is shown in the next part that a similar conclusion results from the analysis of the shrinkage measurements of the composites and the matrices.

The complex processing leads to changes in the structure and orientation of the matrix. The birefringence of the composites, determined by the overall molecular orientation,[14] is not constant in the whole cross section of the sample but shows a characteristic profile, different for each composite (Fig. 3). To obtain composite materials with a stable molecular orientation and to achieve a better insight into the process of "envelope" polymerization, it is necessary to analyze in detail the causes responsible for the observed changes.

The measurements of the birefringence of oriented PP swollen with ST at 45°C prove that the gradient of birefringence cannot result from ST diffusion into the matrices. Figure 4 shows the changes of the birefringence of the PP matrices plotted vs. the square root of the swelling time divided by the sample thickness. The data for the PP5 matrix have not been presented because the value of its birefringence remains constant during swelling and is the same (to the accuracy of the experimental error) as that for the nontreated matrix. Figure 4 demonstrates that the birefringence of the matrices changes significantly due to the variety of involved processes such as ST-induced structural changes, ST- and temperature-induced shrinkage, and closing the voids during swelling. However, despite the changes of the value, the birefringence remains constant in the whole cross section of the matrix. Thus, the gradient of the birefringence observed in the composite materials results from the relaxation of molecular
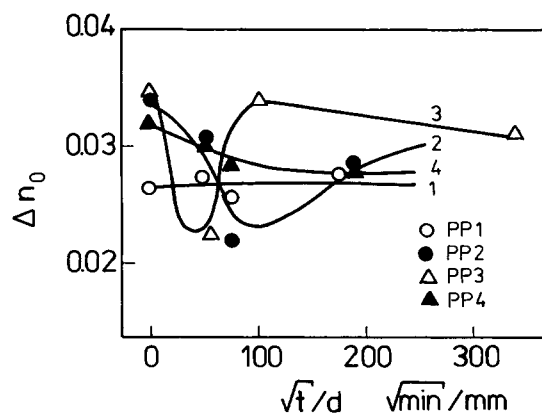

Figure 4 Changes of the birefringence of the PP matrices during swelling with ST (45°C) plotted vs. square root of the swelling time divided by the sample thickness.

orientation in certain regions of the matrix during the polymerization process or from the gradient of the concentration of the PS component.

To assess the influence of the presence of the PS component on the birefringence of the composites, the calculation of the mean birefringence, $\langle \Delta n_{PP} \rangle$, of the PP component was performed according to the relation $\langle \Delta n_{PP} \rangle = \langle \Delta n \rangle / k_v$. The estimated values are gathered in Table II. The comparison of these values with the maximum birefringence, Δn_0, of the composites and with the birefringence of the matrices during ST swelling (Fig. 4) indicates the following:

- In the composites PP3p, PP4p, and PP5p, the content of PS is sufficiently high to be responsible for the observed changes of birefringence. This means that in the corresponding matrices only minor relaxation of orientation is expected during the polymerization process.

- In the composite PP4p, PS is present not only in the shell but also in the core (the value $\langle \Delta n_{PP} \rangle$ is significantly higher than the Δn_0 of the composite). Since the volume fraction of the core for this composite is 0.86 [Fig. 3(b)] and the mean volume fraction k_v of PP is 0.81 (Table II), it is easy to assess the mean volume fraction of PP in the core and in the shell as being 0.92 and 0.13, respectively.

- In the PP1p and PP2p composites, the polymerization process must be associated with the significant relaxation of the molecular orientation of the corresponding matrices taking place in the regions rich in PS (the value of $\langle \Delta n_{PP} \rangle$ is profoundly decreased).

The molecular orientation in PP is maintained at the employed temperatures only due to the presence of the crystalline structure.[14,15] However, it is seen that due to the large differences in the initial structure of the oriented matrices and due to the presence of the guest polymer the relation between changes of the orientation and changes of structure is not straightforward. The analysis of the DSC data presented in Figure 1 together with the results of the similar DSC measurements for the matrices swollen with ST[12] show that the high relaxation of the molecular orientation revealed in the matrices PP1 and PP2 during polymerization is associated with the significant decrease of the perfection of the crystalline structure only in the former sample. In the matrix PP2, the structural changes induced dur-

ing initial swelling are maintained during polymerization, contrary to the molecular orientation, which significantly relaxes in the regions rich in PS. Such behavior seems to be unusual because of the large shell region in the PP2p composite (where the mean volume fraction of the PP component is only about 0.62, assuming the lack of PS in the core).

Opposite behavior is seen in the case of the PP4p composite that contains nearly the same amount of PS as does the PP2p sample. In the matrix PP4, significant structural changes occur during the polymerization process without the coinciding changes of the molecular orientation. This suggests that the amorphous phase of the PP4 matrix is rather relaxed and oriented macromolecules form the crystalline regions of varying perfection. This supposition agrees with the mechanical properties presented in the following part.

CONCLUSIONS

The results show that the oriented PP–PS composites obtained by *in situ* polymerization of ST in the oriented PP matrices exhibit the large contents and specific dispersion of the PS component. No clearly separated grains of PS are detected inside the composites. The constitution of the final composite strongly depends on the initial structure of the oriented host PP matrix that controls the diffusion of ST and influences the following polymerization. The gradient of the PS concentration and the gradient of molecular orientation appear in the composites. The gradient of orientation results from the presence of PS dispersed in a specific way and, in the case of the matrices deformed to the lower draw ratios, from the relaxation of the orientation of the PP matrix during the polymerization process. The modification of the structure of the matrices during processing takes place in all investigated samples, but the orientation of the matrices deformed to the higher draw ratios is well preserved and is not affected significantly by the employed processing.

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