Oriented PP–PS Composites Obtained by Polymerization of Styrene Inside Oriented PP Matrices. II. Shrinkage Behavior and Mechanical Properties

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SYNOPSIS

Thermal shrinkage and the mechanical properties of oriented polypropylene–polystyrene (PP–PS) composites obtained by *in situ* polymerization of styrene in the oriented PP matrices were examined by the analysis of shrinkage stress curves and dynamic mechanical data. It has been shown that by changing the structure of the oriented matrices it is possible to control the properties of the obtained oriented composites. Some composites reveal an increased stability of the molecular network at higher temperatures and the modulus of the material obtained from the matrix drawn at 90°C to the natural draw ratio is significantly increased. It is also shown that the differences between the untreated matrices and the PP component of the respective composites observed in the relaxation of the shrinkage stresses correspond very well with the differences seen in the mechanical loss in the frequency range of about 0.02 Hz. Such behavior suggests that similar molecular motions are involved both in the relaxation of shrinkage stresses and in this part of the mechanical loss. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In the first part of this presentation,[1] it was shown that the polypropylene–polystyrene (PP)-(PS) composites prepared by *in situ* polymerization of styrene (ST) in oriented PP matrices exhibit the large contents and the specific dispersion of the guest polymer. The molecular orientation of the matrices is preserved during processing, although the initial diffusion, subsequent polymerization of ST, and the presence of PS influence the physical constitution of the host polymer. In this part, the results of shrinkage behavior and dynamic mechanical measurements are presented. Modification of the oriented matrices produced by employed processing have been evaluated by comparison of the properties of the nonmodified matrices and the final composites. It has also been shown that the analysis of the shrinkage behavior of oriented homopolymers and composites can be successfully used as an additional method for polymer characterization.

EXPERIMENTAL

The preparation of the oriented PP matrices and PP–PS composites has been described in detail in the first part of this presentation.[1] The oriented matrices were initially swollen with ST at the processing temperature before polymerization. To assess the influence of such swelling on the shrinkage behavior, a set of matrices swollen for 3.5 h in ST at 45°C and vacuum-dried was also prepared.

Sample Characterization

The shrinkage behavior was examined by the measurement of the shrinkage forces exerted by the oriented sample kept at a constant length and heated with a constant heating rate. The apparatus has been described in detail elsewhere.[2] The distance between the fastening clamps was 25 mm and a heating rate of 3 deg/min was employed in all the experiments. The curves' shrinkage stress (the shrinkage force

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related to the initial cross section of the sample) vs. temperature were recorded for the nontreated matrices, the swollen-and-dried matrices, and the composites. Then, the differential curves were calculated according to the procedure described below.

The investigation of the dynamic mechanical properties were performed at 21°C in a wide range of deformation frequencies, using the apparatus described elsewhere.[3] The samples were subjected to a static elongation of 1% superposed on the sinusoidal strain of an amplitude of 0.5% and frequencies in the range from 10^{-3} to 10 Hz. The results are presented in terms of the real Young's modulus E' and loss factor $\tan \delta = E''/E'$ for each deformation frequency.

RESULTS

Some parameters characterizing the oriented matrices and composites are gathered in Tables I and II, respectively. Drawing of PP in the conditions specified for the matrices PP1, PP2, and PP3 leads to the characteristic whitening of the samples caused by voiding.[1,4] In any case, when the correction for the voids was required, the cross section S_p of the polymer was assessed according to the relation $S_p \approx S \cdot \rho/\rho_p$, where S is the cross section of the sample, while ρ_p and ρ denote the densities of the oriented bulk polymer (without voids) and the sample, respectively. The values of ρ_p/ρ are specified in Table I. The parameter PS/PP in Table II denotes the mass quotient of the two polymers constituting the composite, while k_V is the volume fraction of PP in the composite (the volume of PP divided by the volume of the whole composite). In both tables, the storage modulus represents the values obtained from the dynamic measurements for the lowest frequencies used.

As an example of the curves of shrinkage stresses, the traces for the two matrices, PP2 and PP4, and for the respective composites, PP2p and PP4p, are presented in Figure 1(a). The analysis of such curves enables a direct qualitative comparison of the shrinkage behavior between the host matrices and the composite samples. It is seen that despite nearly the same PS content in both composites their shrinkage is significantly different in comparison with the matrices. To obtain the most comprehensive information, all the results are presented in the form of differential curves $\sigma(T)$, according to the formula

Table I Characteristics of the PP Matrices

Sample	Drawing Temperature (°C)	Draw Ratio	ρ_p/ρ	Storage Modulus E' (GPa)
PP1	20	5.8	1.019	2.33
PP2	50	7.9	1.009	4.04
PP3	50	10.7	1.088	5.68
PP4	90	8.1	1.000	2.69
PP5	90	12.3	1.000	4.21

Table II Characteristics of the PP–PS Composites

Sample	PS/PP (%)	Density (g/cm^3)	k_V	Storage Modulus E' (GPa)
PP1p	74.0	0.947	0.61	1.60
PP2p	26.0	0.927	0.82	3.04
PP3p	15.0	0.870	0.89	4.31
PP4p	27.0	0.930	0.81	3.37
PP5p	2.3	0.906	0.98	4.20

$$\sigma(T) = \frac{\sigma_M(T) - \sigma_{CM}(T)}{\sigma_{M\max}} \qquad (1)$$

where $\sigma_M(T)$ is the shrinkage stress of the matrix; $\sigma_{M\max}$, the maximum value of this stress; and σ_{CM}, the shrinkage stress of the composite related to the PP component according to the relation

$$\sigma_{CM}(T) = \frac{\sigma_C(T)}{k_V} \qquad (2)$$

where σ_C denotes the measured values of the shrinkage stresses exerted by the composite, and k_V, the calculated volume of the fraction of PP in the composite sample (Table II). Two sets of curves were calculated for two sets of matrices—the first, for nontreated ones [Fig. 1(b)] and, the second, for the swollen-and-dried matrices [Fig. 1(c)]. The shrinkage behavior of the PP component in the composites is significantly different from the behavior of both comparative PP matrices. The differences, however, do not exceed 50% of the maximum stresses of the matrices.

The absolute values of some characteristic points on the shrinkage stress–temperature curves recorded for each investigated material are gathered in Table III. T_0 is the temperature of stress commencement and $T_{\max}$ denotes the temperature of the maximum shrinkage stress $\sigma_{\max}$. For the composite samples, the values of this stress have been related to the PP components according to eq. (2).

Figure 2 shows the dynamic mechanical proper-

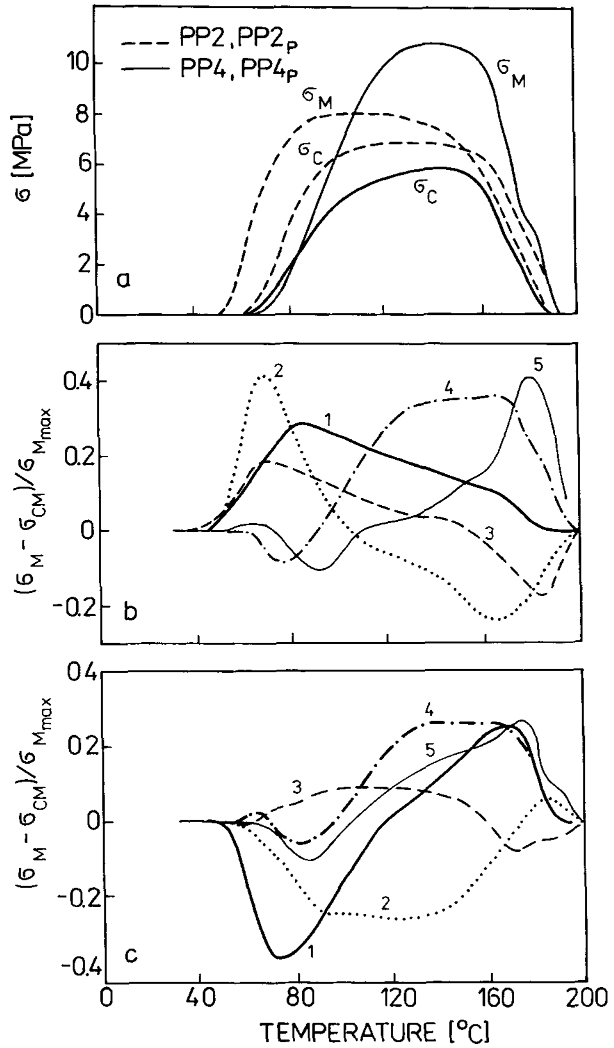

Figure 1 (a) The temperature dependence of shrinkage stresses recorded for the PP2p and PP4p composites (σ_C) and for the respective matrices (σ_M). The differential curves of shrinkage stresses calculated according to eq. (1) for the (b) nontreated and (c) swollen-and-dried matrices taken as the reference; the numbers near the lines are referred to the respective matrices and composites.

ties recorded at room temperature for the oriented matrices and final composites. The tan δ and the real part E' of the Young's modulus are plotted against the logarithm of the deformation frequency. Similar plots were also recorded for PS; both E' and tan δ were found to be nearly constant in the whole range of frequencies used, being equal about 3.0 GPa and 0.03, respectively. On the basis of the data recorded for the composites, the values of E' and tan δ for the PP components were assessed according to the parallel and series model. For the former, $E = k_V E_{PP} + (1 - k_V) E_{PS}$, whereas for the latter, $1/E = k_V/E_{PP} + (1 - k_V)/E_{PS}$, where E, E_{PP}, and E_{PS} denote complex dynamic moduli of the composite, PP, and PS, respectively. The calculated results are marked in Figure 2 with continuous and dashed lines.

Figure 2 shows that the Young's modulus of the composites is generally decreased in comparison with the matrices except for one sample—PP4p. This composite reveals a substantial increase of the modulus to the value that is greater than the moduli of both components. The traces of tan δ for the composites are changed in comparison with those obtained for the matrices, indicating significant changes in the structure of PP during processing.

DISCUSSION

Before the discussion of the current results, it seems to be useful to recall some features of the prepared composites presented in the first part of this article.[1] It was shown that in the samples PP1p, PP2p, PP3p, and PP4p the external shell and internal core can be discerned; however, the line between these regions is not evenly clear. The shell is rich in PS but the guest polymer is also present in the core; particularly, the PP4p composite contains the significant amount of PS in the core region. The employed processing, i.e., the swelling and subsequent polymerization, imposes the changes both in the crystalline structure and in the molecular orientation of the matrices. These changes were analyzed on the basis

Table III Shrinkage Parameters of the Oriented Matrices and Composites

Sample	T_0 (°C)	T_{max} (°C)	σ_{max} [Mpa]
PP1	48	101	5.9
PP2	50	110	8.1
PP3	37	116	11.6
PP4	65	138	10.7
PP5	53	163	12.6
PP1 s-a-d[a]	58	125	4.5
PP2 s-a-d	64	138	6.8
PP3 s-a-d	49	124	12.1
PP4 s-a-d	56	141	9.6
PP5 s-a-d	72	156	13.5
PP1p	53	109	4.5
PP2p	58	123	8.5
PP3p	50	140	11.0
PP4p	64	140	7.0
PP5p	62	147	10.8

[a] s-a-d denotes that the matrix was swollen for 3.5 h in ST at 45°C and dried.

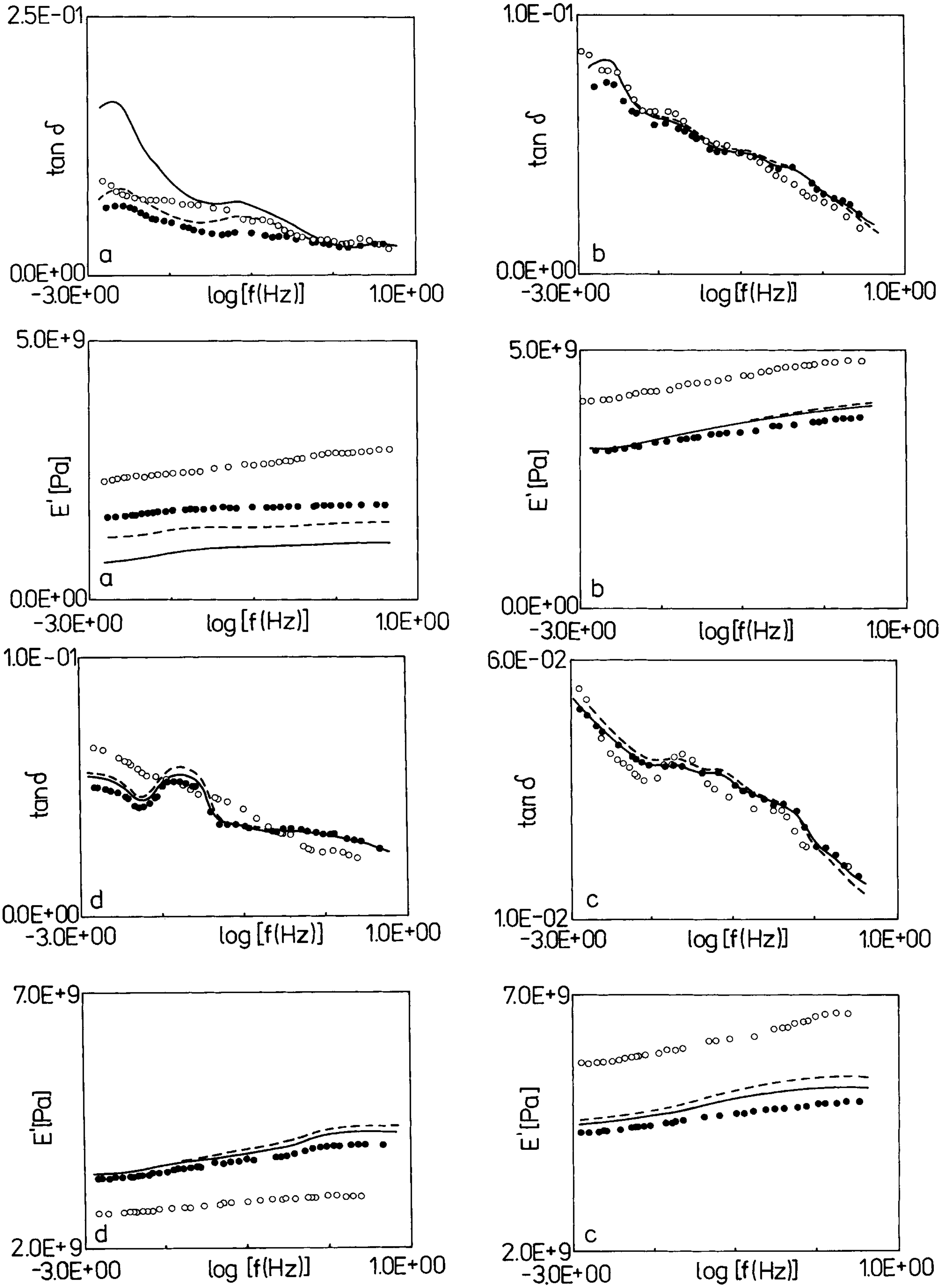

Figure 2 The tan δ and the real part E' of the Young's modulus vs. the logarithm of the deformation frequency for the (○) matrices and (●) composites: (a) PP1, PP1p; (b) PP2, PP2p; (c) PP3, PP3p; (d) PP4, PP4p; (e) PP5, PP5p. The lines denote the values for the PP component of the composites assessed according to the parallel (continuous line) and series (dashed line) model.

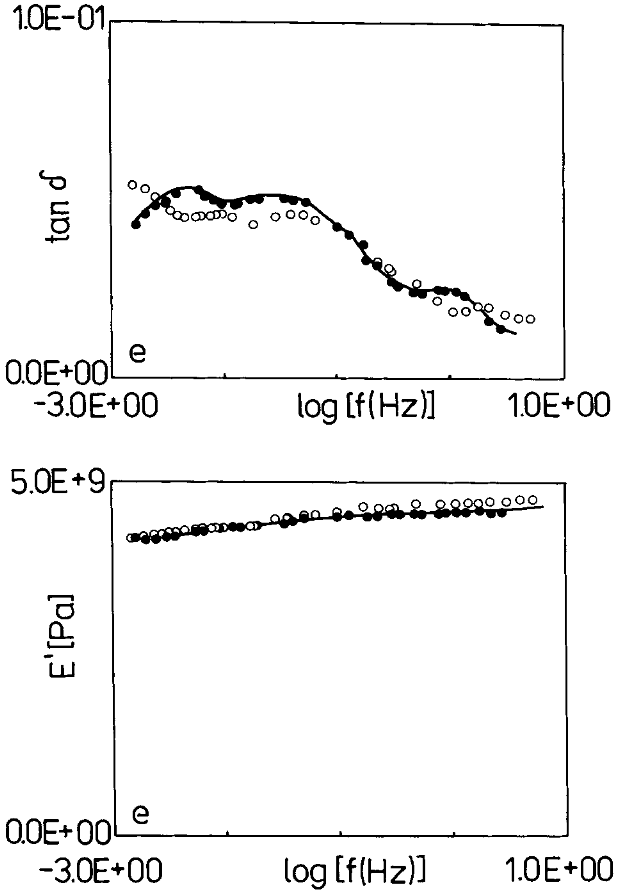

Figure 2 (*Continued from the previous page*)

of the DSC thermograms and the results of the birefringence measurements.

The perfection of the crystallites in the PP1p, PP3p, and PP4p composites is substantially decreased with regard to the respective matrices. However, in the PP2p sample, the structural changes are not so pronounced and the thermograms indicate that at temperatures about 150°C the structure of the composite seems to be even more stable than is the structure of the matrix. The analysis of the birefringence revealed that the polymerization process is associated with the significant relaxation of molecular orientation in the PP1 and PP2 matrices. In the matrices PP3, PP4, and PP5, only minor relaxation of orientation takes place during the polymerization.

The attachment of the guest polymer to the matrix is mainly of a physical nature; the composites are completely soluble[5] and precipitated PP does not show the presence of connected PS chains.

Shrinkage Behavior

It has been pointed out in many articles (e.g., Refs. 6–11) that the measurement of shrinkage stresses delivers interesting information on the stability of molecular orientation and on the changes in the molecular network of oriented plastics. The externally recorded traces are the resultant effects of the two local processes: The contraction of extended immobilized chain elements resulting in local forces in the material and the local relaxation of these forces, most likely due to intermolecular slipping.[11,12] If the shrinkage stresses are recorded as a function of temperature [Fig. 1(a)], the low-temperature part of the obtained curve is significantly dependent on the rate of local contractions. The high-temperature region of this curve is, in turn, profoundly influenced by the possibility of the local relaxations of generated shrinkage stresses and reflects the stability of the molecular network.

The shrinkage of the composite results from the contraction of its oriented PP part that is modified by the processing (swelling at elevated temperature and polymerization) and by the presence of PS. Some aspects of this modification may be qualitatively characterized by analyzing the shrinkage stress curves presented in the form of differential traces [Fig. 1(b) and (c)]. However, since the investigation of the shrinkage stresses is not routine in the studies of oriented polymers, it seems to be useful to introduce an illustrative analysis on the basis of the curves shown in Figure 1(a). The composites presented, PP2p and PP4p, show entirely different shrinkage behavior in relation to the respective matrices, although their PS content is nearly the same.

The shrinkage of PP2p starts at higher temperature than does the shrinkage of the matrix due to the partial relaxation of internal stresses during processing. However, despite this relaxation and decreased molecular orientation,[1] the maximum value of the shrinkage stresses of the composite is relatively high. The recorded shrinkage force has been related to the cross section of the whole sample; the maximum value of the shrinkage stress related to the oriented PP component exceeds by more than 30% the expected value and becomes comparable with the stresses exerted by the untreated matrix (Table III). It is also seen that at higher temperatures the stresses of the composite relax more slowly than do the stresses of the matrix. Such behavior indicates the decreased possibility of local relaxation (intermolecular slipping) and the increased stability of the molecular network of the composite sample at higher temperatures.

The shrinkage of the PP4p composite starts at the same temperature as does the shrinkage of the respective matrix [Fig. 1(a)]. However, due to the substantially increased Young's modulus of the material [compare Fig. 2(d)], the exerted shrinkage stresses are higher at the beginning. Then, the rate of the stress growth decreases at a temperature of about 100°C (T_g region of PS) and the relatively low maximum value of the stresses is reached, although the orientation of the PP4 matrix does not relax significantly during processing.[1] The stresses of the composite also relax at significantly lower temperatures than do the stresses exerted by the untreated matrix, indicating the decreased stability of molecular network of the composite. Since in this composite the guest polymer is dispersed not only in the shell but also in the core,[1] the observed behavior may result from the high attachment of the PS to the host matrix. This attachment is probably associated with the formation of the additional connections between the crystallites, decreasing their perfection but increasing the stiffness of the material below the glass transition of PS (increased Young's modulus, higher initial shrinkage stresses) and influencing the shrinkage above about 100°C.

The observed shrinkage behavior of the composites remains in good agreement with the DSC data presented previously.[1] Their analysis shows substantially decreased perfection of the crystallites in the PP4p composite and slightly increased stability of crystals at a certain temperature region in the PP2p sample (in comparison with the respective matrices). The crystalline elements constitute junction points of the physical network, so their changes must influence the relaxation of the shrinkage stresses observed at higher temperatures.

The discussed changes of the shrinkage behavior are more distinctly seen in the differential curves [compare, e.g., traces 2 and 4 in Fig. 1(b)]. The use of swollen-and-dried matrices enables the qualitative assessment of the influence of the initial swelling on the shrinkage behavior of the composites. The significant changes between the curves in Figure 1(b) and (c) revealed in the low-temperature region show that swelling of the matrices for 3.5 h produces high relaxation of internal stresses in oriented PP. This relaxation is particularly pronounced in the matrices PP1 and PP2, which also show the highest contraction during ST swelling.[5] Nevertheless, the swelling process only slightly affects the possibility of intermolecular slipping; the high temperature parts of the curves in the Figure 1(b) and (c) remain similar.

A detailed examination of the differential curves 1, 3, and 5 of the composites indicates that

- The shrinkage stresses exerted by the PP1p composite are exactly of the value that could be estimated considering the change of the orientation during polymerization.[1] The polymerization process and the presence of PS induce the changes in the matrix that are responsible for the slightly increased local relaxation processes (intermolecular slipping).
- The internal stresses of the PP3p composite are lower than those of the PP3 matrix. Nevertheless, the composite exhibits an increased stability of the molecular network at higher temperatures; it is seen that the shrinkage stresses exerted by the composite are higher than those of both untreated and swollen-and-dried matrices.
- The decreased stability of the molecular network reported in PP4p at higher temperatures results from the presence of PS; it is seen that the high-temperature parts of curves 4 in Figure 1(b) and (c) remain unchanged. Such behavior, together with observed changes of the shrinkage of the composite at the temperatures close to the T_g of PS, gives further evidence for the high attachment of PS to the matrix.
- In PP5p, the stability of the molecular network is significantly decreased; the most dominant shrinkage effect in the composite is related to the substantially increased relaxation of the stresses at higher temperatures in comparison with both the untreated and swollen-and-dried matrices. The decreased perfection of the crystalline structure of the PP5p sample is also seen on the DSC thermograms presented previously.[1] Also, small changes of shrinkage occur in this composite at the region of T_g of PS; however, the PS content in this sample is very low.

Mechanical Properties

The analysis of the mechanical properties is directed not only toward the presentation of the features of the obtained composites, but also mainly for showing the differences between the composites and the matrices and for revealing the changes of the oriented PP during the processing. The results of the calculations performed on the basis of the parallel and series model are then helpful, and however simplified, they enable the assessment of the properties of the modified PP component. The differences between the calculated values and the values measured for the untreated matrix were related to the structural changes of the matrix analyzed in the first part. If a poor correlation is found, the composite cannot be treated as a simple mixture of the two components and the other effects must be included in the explanation of the material constitution.

Table I shows that the storage modulus of the untreated matrices does not correspond with the draw ratio. The modulus is, however, well correlated with the birefringence of the samples (compare the first part of this paper[1]), increasing with the increase of the molecular orientation. Since the employed processing generally leads to a decrease of both molecular orientation and the perfection of the crystalline structure, the moduli of the composites are expected to be lower than the moduli of corresponding matrices. Figure 2 illustrates this tendency for all the composites except for PP4p. The structural changes of the matrices and the relaxation of orientation during processing[1] are responsible for the decrement of the modulus of the PP1p, the PP2p, and, to some extent, the PP3p composite. Considering the magnitude of these changes, the calculated moduli of the PP component of the PP1p and PP2p samples seem to have reasonable values. In PP3p, however, the calculated modulus of the PP component is slightly too low, probably indicating the weaker adhesion of both components in the shell region.

The storage modulus of the PP4p composite is greater than the moduli of both its components. The calculations show that the modulus of the matrix after the modification should exceed by 30% the modulus of the untreated one. Such changes are unlikely to be caused without the physical interaction of the components. As mentioned above, in this composite, the guest polymer is highly attached to the matrix and, most likely, it forms the additional connections between the crystalline elements of the oriented PP. Additionally, the higher increase of the modulus with the deformation frequency observed for PP4p (in comparison with the matrix) remains in agreement with the proposed constitution of the composite.

The description of the loss behavior is more complicated due to the complex structure of the composites and to the fact that PP alone shows a number of mechanical relaxation processes (e.g., Refs. 13 and 14). In the frequency range studied, the mechanical loss expressed in terms of tan δ corresponds to the α relaxation process,[15] which, in isochronal measurements, occurs above room temperature. Although the nature of the α relaxation is not clearly understood, there is general agreement that it exists only in the presence of the crystalline phase[14] and occurs in regions where the interlamellar shear is the predominant effect of the mechanical deformation.[16] The process presumably incorporates such phenomena as the intracrystalline relaxations and the sliding of the tie molecules inside the crystalline blocks.[16]

Figure 2 shows that a characteristic of loss traces recorded for the composites is significantly different from that observed for the untreated matrices (see, e.g., samples PP4p and PP5p). The revealed changes cannot be interpreted merely as the result of the addition of a noncrystalline component of the lower loss factor, but they confirm a strong modification of the structure of the oriented PP matrices by the processing conditions and by the presence of PS. At low frequencies, the composites containing the highest amounts of PS (PP1p, PP2p, PP4p) exhibit a decreased mechanical loss in comparison with their matrices. This behavior results from the presence of PS mostly in the interlamellar regions, where it hampers effectively the mobility of the noncrystalline phase, decreasing in this way the interlamellar shearing processes. On the other hand, the composites of the lower PS content (PP3p, PP5p) display an increased loss in this frequency range because of a decreased perfection of the interlamellar regions being penetrated by ST but not stiffened enough by a small amount of PS.

The results of the model calculations show the likelihood of a significant increase of the mechanical loss for the PP component in the PP1p composite resulting from the changes of the structure and molecular orientation during processing. For the other samples, the calculations of the loss factor of the PP component show only a minor increase of tan δ in comparison with the respective composites. In general, the calculated values of the loss factor exceed the values measured for the matrices. In the case of the PP2p and PP3p samples, there is, however, a certain frequency region of about 0.02 Hz (from about -2 to -1.4 on the logarithm scale) where the loss of the modified matrix is lower. The opposite behavior is observed for the specimen PP4; the loss of the modified matrix is higher than that of the untreated one just in this frequency range (and also in the region of the highest employed frequencies). For the other frequencies, the composite shows a decreased loss in comparison with the matrix due to the modification of PP with the attached PS component. The decreased loss is consistent with the stiffening of the sample revealed in the increased storage modulus; therefore, the occurrence of the higher damping in the frequency range of about 0.02 Hz demonstrates the enhancement of a certain relaxation process related to the crystalline phase.

It is remarkable that the relation between the composites and the respective matrices found in the mechanical loss in the frequency of about 0.02 Hz corresponds very well with the shrinkage behavior. The composites that exhibit lower stability of the molecular network at higher temperatures than the matrices also show increased damping in this frequency range. On the other hand, the tan δ for the samples of the increased stability of the network is more or less decreased in comparison with the respective matrices.

The comparative assessment of the stability of the molecular network was performed on the basis of the relaxation of the exerted shrinkage forces. This relaxation results from the intermolecular slipping, which in the oriented semicrystalline polymer above the T_g is realized mostly by pulling the extended chain elements of the amorphous phase out from the crystallites that constitute the cross-linking points of the molecular network. Since such slipping is related to the presence of the crystalline phase, it should give rise to the broad spectrum of the α mechanical relaxation and influence the trace of tan δ. However, when the intensity of the loss processes of the composites is considered, their oriented components should be analyzed because these components are involved in the relaxation of the shrinkage forces. This is particularly important for the PP1p sample containing the highest amount of PS; for the others, the difference between the calculated values and the values measured for the composites is less significant.

Figure 2 shows that the PP4p sample exhibits the most pronounced loss change in the considered frequency range. For this composite, the possibility of the stronger attachment of the oriented PP structure with the PS chains was revealed. This attachment could be realized by entangling of the PS chains around the PP chain elements on the surfaces of the PP crystallites leading to the increase of the described intermolecular slipping and to the decreased stability of the molecular network observed in the shrinkage behavior at higher temperatures.

CONCLUSIONS

The results presented show that by changing the structure of the oriented matrices it is possible to control the properties of the obtained oriented composites. The shrinkage force measurements demonstrate that the shrinkage behavior of the oriented composites is determined by the modification of the structure of the oriented PP matrices by the ST diffusion and the following polymerization. The shrinkage analysis revealed that some composites show increased stability of the molecular network at higher temperatures in comparison with the respective untreated matrices.

The mechanical properties are also dependent on the structural changes of the matrices; however, the influence of PS (as the component of the blend) is seen, particularly for the composites with the highest PS contents. Generally, the storage modulus of the composites are decreased in comparison with the matrices because of the structural reorganization of PP. Opposite behavior shows the composite obtained from the matrix drawn at 90°C to the natural draw ratio (PP4p); its significantly increased modulus is due to the stronger attachment of PS with the host PP matrix.

The mechanical loss of the composites differs significantly from the loss of the matrices, indicating structural changes during the processing. The comparison of the results of the shrinkage stress measurements with the results of the mechanical loss leads to an interesting observation. The differences between the untreated matrices and the oriented PP component of the composites observed in the relaxation of the shrinkage stresses correspond very well with the same differences seen in the mechanical loss in the frequency range of about 0.02 Hz. Such behavior suggests that the effects of intermolecular slipping that are responsible for the relaxation of the shrinkage stresses at higher temperatures are also involved in that part of the α relaxation process.

REFERENCES

1. M. Trznadel, M. Pluta, and M. Kryszewski, *J. Appl. Polym. Sci.*, to appear.
2. T. Pakula and M. Trznadel, *Polymer*, **26**, 1011 (1985).
3. T. Pakula and Z. Soukup, *J. Polym. Sci. Polym. Phys. Ed.*, **12**, 2437 (1974).
4. G. A. Gallagher, R. Jakeways, and I. M. Ward, *J. Appl. Polym. Sci.*, **43**, 1399 (1991).
5. M. Trznadel, P. Milczarek, and M. Kryszewski, *J. Appl. Polym. Sci.*, **43**, 1125 (1991).
6. N. Kahar, R. A. Duckett, and I. M. Ward, *Polymer*, **19**, 136, (1978).
7. P. R. Pinnock and I. M. Ward, *Trans. Faraday Soc.*, **62**, 1308 (1966).
8. J. H. Nobbs, D. I. Bower, and I. M. Ward, *Polymer*, **17**, 25 (1976).
9. J. H. Nobbs, D. I. Bower, and I. M. Ward, *J. Polym. Sci. Polym. Phys. Ed.*, **17**, 259 (1979).
10. F. Rietsch, R. A. Duckett, and I. M. Ward, *Polymer*, **20**, 1133 (1979).
11. M. Trznadel and M. Kryszewski, *J. Macromol. Sci. Rev.*, **C32** (3,4), 259 (1992).
12. M. Trznadel, *J. Macromol. Sci.-Phys. B*, **28**, 285 (1989).
13. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967.
14. R. H. Boyd, *Polymer*, **26**, 323 (1985).
15. M. Pluta and M. Kryszewski, *Acta Polym.*, **38**, 42 (1987).
16. A. J. Owen and I. M. Ward, *J. Macromol. Sci.-Phys. B*, **7** (3), 417 (1973).

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