

Stereoblock Polypropylene/Isotactic Polypropylene Blends.

II. Mechanical Behavior

S. V. CANEVAROLO,^{1,*} F. DE CANDIA,^{1,†} and R. RUSSO²

¹Dipartimento di Ingegneria Chimica ed Alimentare, Università di Salerno, 84081 Fisciano (Sa), Italy;

²Istituto di Ricerca e Tecnologia delle Materie Plastiche CNR, 80072 Arco Felice, Napoli, Italy

SYNOPSIS

The mechanical properties of stereoblock polypropylene/isotactic polypropylene blends have been analyzed at different temperatures and at large deformations. The samples at a lower content of isotactic polypropylene show good elastic properties, both in terms of deformation reversibility and in terms of energy dissipation in the hysteresis cycles. Considering the dependence of the elastic behavior on the temperature, the model that can be suggested is based on the presence of a physical network in which the cross-linking is due to cocrystallization between the matrix (the stereoblock polypropylene) and the crystalline domains of isotactic polypropylene. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In a previous article,¹ we described the phase organization of stereoblock polypropylene/isotactic polypropylene blends; the obtained results indicate that both the components segregate a crystalline phase. Moreover, the thermal analysis and the thermal microscopy seem to suggest that, at least for the blends at lower content in isotactic component, cocrystallization phenomena are present. This is a crucial aspect because the cocrystallization means, in principle, the presence of a physical network whose thermal stability is ruled with a great probability by the component having the higher melting point, in this case, the isotactic polypropylene. On the other hand, as underlined in the previous article, this aspect concerns not only the practical applications of this class of blends, but can also contribute to better understanding of the physical behavior of different classes of elastomeric polypropylenes obtained by blending or by direct synthesis.²⁻⁵ In the present article, we report the results obtained by analyzing the mechanical behavior at large mono-

axial deformations; different samples, in a wide composition range, were analyzed, but attention was focused mainly on samples at a lower content of the isotactic component. The use of large deformations can give a great contribution to verify the presence of a physical network, to analyze the elastic behavior, and to test its thermal stability. Of course, this information can be used to support a structural model.

EXPERIMENTAL

The stereoblock polypropylene (sbiPP) used in this work is the same material used in previous papers,^{6,7} synthesized by the Zambelli' group at Salerno University, using a soluble Ziegler-Natta catalytic system, according to the Ewen' procedure.⁸ This polymer presents a low crystallinity, a little more than 10%, as a consequence of its steric disorder; the melting point is in the range 40 to about 60°C, depending on the thermal history. The isotactic polypropylene (iPP) was obtained from RAPRA. The blends were made initially by dissolving the two components in hot xylene and casting at 80°C. The dry films were then pressed at 190°C in a Carver press using Teflon sheets; the pressure molding was followed by rapid quenching to 0°C in an ice-water bath. As in the previous article,¹ the blends are herein indicated by the code sbiPP/iPP followed by

* Permanent address: Materials Engineering Department, Universidade Federal de São Carlos, 13560 São Carlos (SP), Brazil.

† To whom correspondence should be addressed.

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a number that is the weight percentage of isotactic polypropylene, i.e., sbiPP/iPP20 is a blend containing 20% of isotactic polypropylene.

Mechanical properties were analyzed at various temperatures with an Instron 4301 dynamometer equipped with an Instron temperature chamber 3119; the deformation speed was 10 mm/min. Samples were cut from films, as strips of about 4 mm wide by 30 mm long and 0.6 mm thick; a gauge length of 10 mm was defined on the central part of the sample with ink reference marks. The deformation was followed by measuring, at regular time intervals, the distance between the two marks, according to a procedure previously described.⁹

RESULTS

The stress-strain behavior of the blends, as obtained after the two-stage procedure (solvent casting and pressure molding) is shown in Figure 1; the engineering stress, i.e., the tensile force over the undeformed cross section, is reported as a function of the nominal strain as obtained by the ink reference marks. The nominal strain is here indicated as λ and was calculated as the actual distance between the marks over the initial one. Data of Figure 1 were detected at room temperature; for each sample, more than one stress-strain plot was detected, and in the figure, the range of fluctuation is shown. The curves are typical of a plastic behavior, characterized by the presence of the yielding, fol-

lowed by a plastic flow in which a mature neck propagates over all the sample (except sample sbiPP/iPP50) and then by a stress hardening. It is evident that the yield point, which is observed at about 20 MPa in the pure iPP, decreases on decreasing the iPP content, reaching about 4 MPa in the pure sbiPP. This effect is simply related to the overall sample crystallinity, which decreases on decreasing the iPP content.¹

In particular, if the yield stress is reported as function of the crystallinity, as given, for instance, by the thermal analysis,¹ a linear correlation is obtained. The deformation range corresponding to the neck propagation and following the yielding also depends on sample composition. It is extended up to λ 5.5 in the pure iPP, it is reduced to λ 4.7 in sample sbiPP/iPP80, whereas it is only 3.2 in the pure sbiPP. The necking is not so evident in sample sbiPP/iPP20, whereas it is totally absent in sample sbiPP/iPP50, which, after yielding, shows a continuous hardening up to the fracture. In the isotactic polypropylene, the necking range was correlated with the crystal thickness,^{10,11} whereas in samples characterized by very small crystals, any visible neck can be absent.^{12,13} If the same correlation is assumed in the present case, one could conclude that the crystal thickness decreases from the pure iPP to the pure sbiPP, going through a minimum in sample sbiPP/iPP50. Although it seems very reasonable that the crystal thickness decreases on decreasing the iPP content (see Ref. 1), it is difficult to find an explanation for sample sbiPP/iPP50;

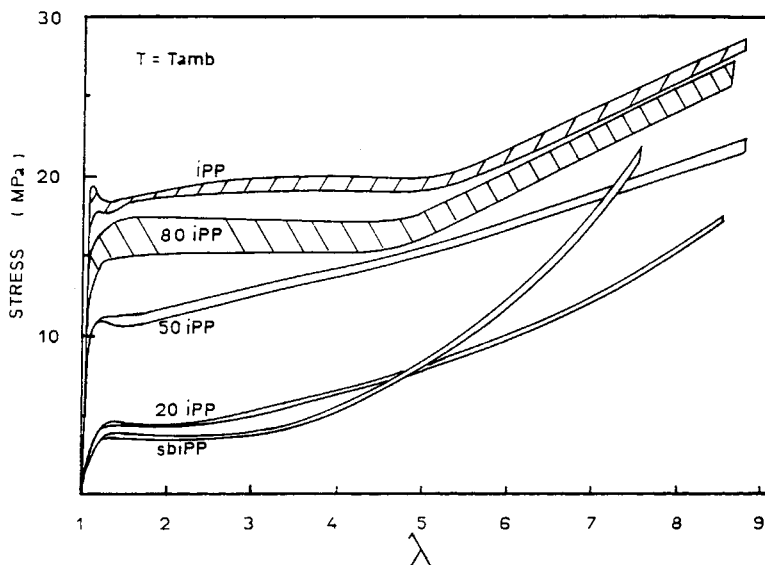


Figure 1 Tensile behavior at room temperature of the sbiPP/iPP blends with various iPP concentrations as shown.

some role could be played by the inversion of the matrix between the two components, probably occurring at intermediate compositions. However, this aspect is not particularly relevant for the purpose of the present article. As for the fracture behavior, it occurs substantially at the same strain value for all the samples (about $\lambda 8$) with the exception of the pure sbiPP, which breaks at about 7.2. The tensile strength decreases on decreasing the iPP content, again with the exception of the pure sbiPP.

The mechanical behavior at 80°C is reported in

Figure 2(a) and (b); the stress-strain plots are divided in two parts, the stress scale being 10 times smaller in Figure 2(b). It is important to point out that 80°C is widely above the melting of the sbiPP component and that, therefore, in the analyzed samples, any segregated crystalline domain of this component is absent. To test the reversibility of the axial deformation, the samples were tested cyclically with an initial deformation up to 500%, a rapid return to the starting point, with a resting period of 5 min, and then a second run with a deformation of

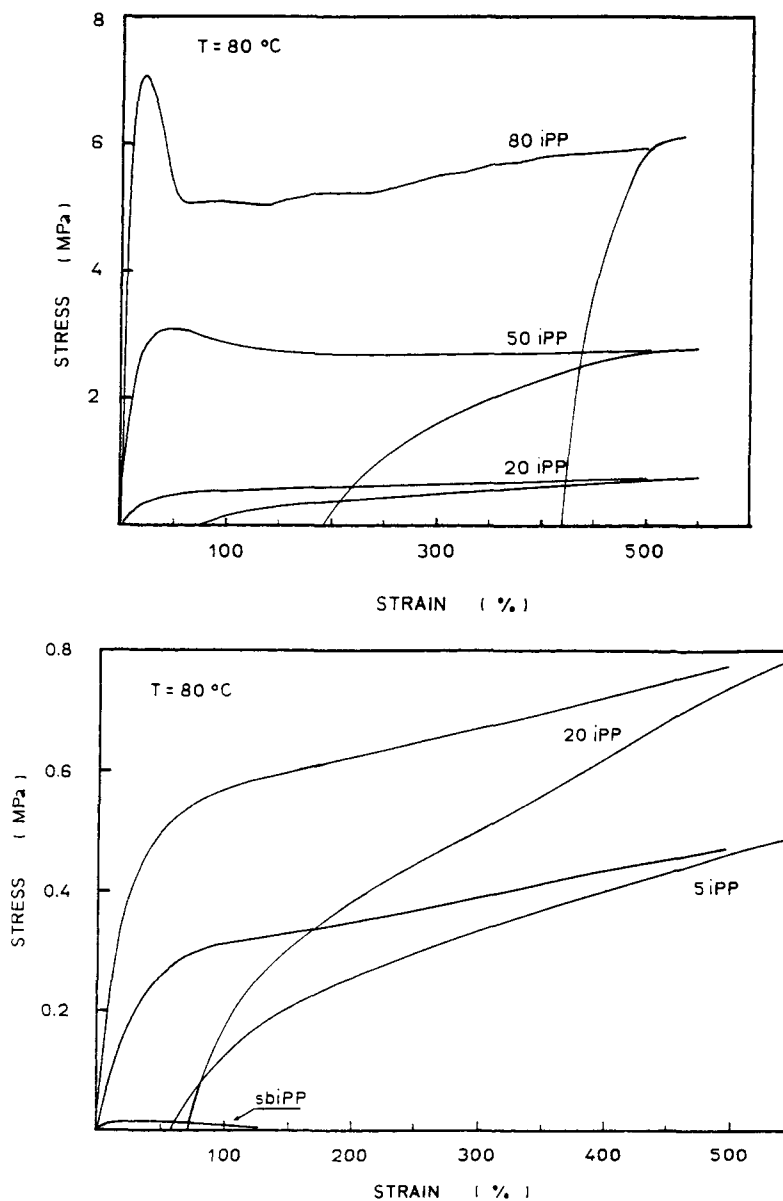


Figure 2 Cyclic tensile behavior at 80°C of the sbiPP/iPP blends with various iPP concentrations: (a) samples sbiPP/iPP80, sbiPP/iPP50, and sbiPP/iPP20; (b) samples sbiPP/iPP20, sbiPP/iPP5, and sbiPP.

550%, just above the first. This experimental procedure gives the permanent set, i.e., the residual deformation, after the first run. The permanent set is nearly total in sample sbiPP/iPP80, it is reduced to 200% in sample sbiPP/iPP50, and it is less than 100% in samples at lower iPP content. It is about 50% in sample sbiPP/iPP5, which indicates a very good elastic behavior; the elastic behavior of this sample is maintained also at higher temperatures, up to 140°C. The data regarding the pure sbiPP are also shown in Figure 2(b), but, as evident, the mechanical properties at this temperature are very poor.

The elastic behavior was also analyzed as a function of the temperature for sample sbiPP/iPP20, which, within the samples showing a good elastic behavior, is that at higher iPP content. The temperature was in the range 25–140°C. In particular, the information on the sample elasticity was obtained analyzing the hysteresis behavior; at each temperature, a deformation cycle was carried out with a deformation limit of $\lambda = 4$, and then the fraction of dissipated mechanical energy was calculated as the ratio between the area delimited by the two curves of stretching and relaxing and the total area under the stretching curve. The so-obtained results are reported in Figure 3, where the fraction of dissipated energy, indicated as Φ , is reported as a function of the temperature. A trend with a minimum at 80°C is quite evident. In Figure 4, the permanent set after each hysteresis cycle is also reported as a function of the temperature. The data in Figure 4 regard two classes of samples: The first is the same used in all the experiments, and the

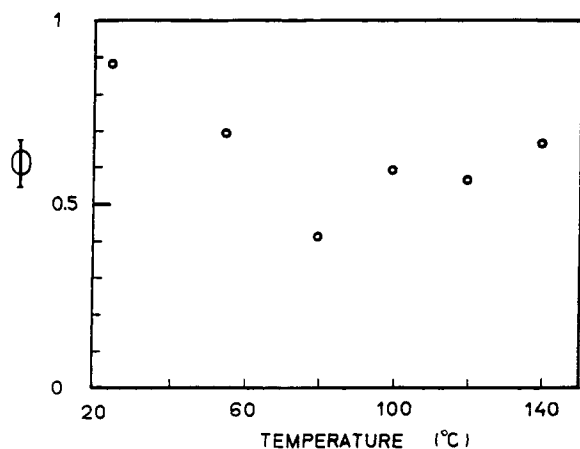


Figure 3 The fractional mechanical energy Φ dissipated in the hysteresis cycles is reported as a function of the temperature. The reported data refer to sample sbiPP/iPP20.

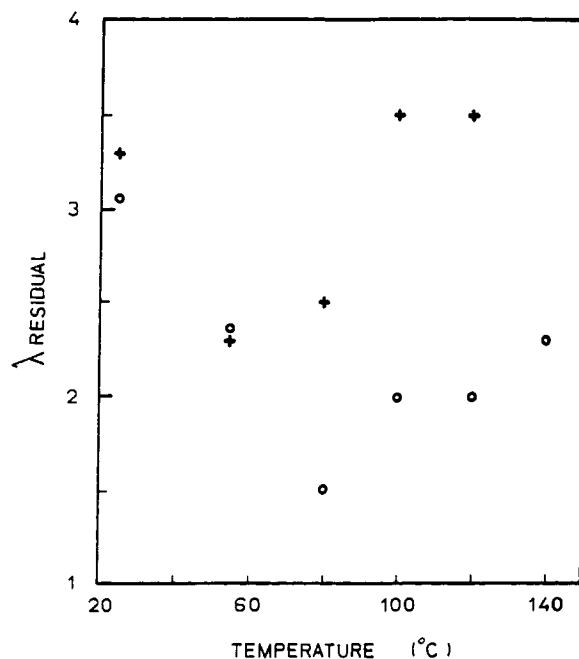


Figure 4 Residual permanent set detected after each hysteresis cycle at different temperatures: (O) conventional sbiPP/iPP20; (+) sample sbiPP/iPP20 obtained by slow cooling after the pressure molding.

second corresponds to samples that after the pressure molding were slowly cooled to room temperature, instead of the rapid quenching to 0°C. The first class gives results in agreement with Figure 3, with a minimum at 80°C, where the permanent set is only $\lambda = 1.5$. In the second class, the reversibility of the deformation is strongly reduced, the permanent set is 2.5 at 80°C, and it is 3.5 at 120°C, compared with 2.0 observed at this temperature for the other samples.

These last data clearly indicate the dramatic influence that the thermal history plays on the mechanical behavior, and this aspect is considered in more detail in Figure 5. In this figure, the behavior of two samples of sbiPP/iPP20, characterized by different thermal histories, are compared with the standard hot-pressed sample Q. A first sample (SC) is a film as obtained after the solvent casting; a second sample (HT) was obtained from sample SC by melting it at 180°C with 5 min of rest, by rapid cooling to 125°C with a rest at this temperature of 5 minutes more, and then by cooling to room temperature. In the same figure, for the purpose of comparison, the behavior of a blend still containing 20% in iPP is also shown, in which the sbiPP was substituted for by atactic polypropylene (sample aPP/iPP20).

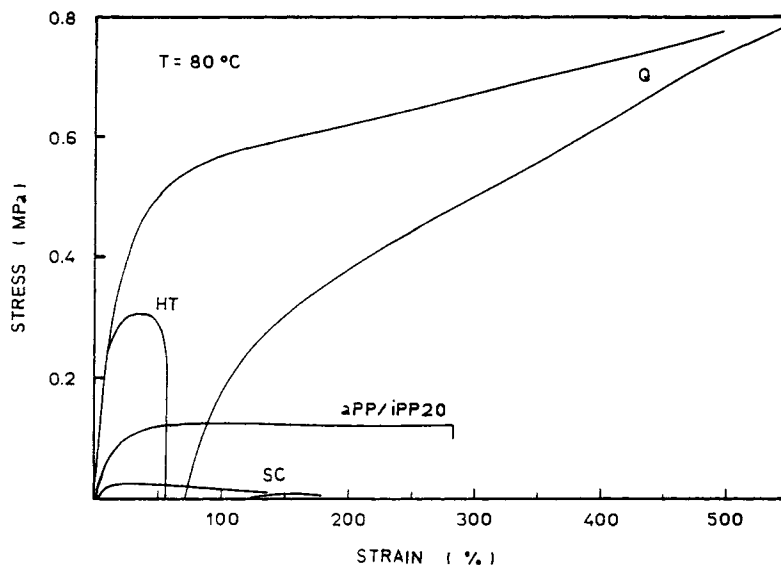


Figure 5 Cyclic tensile behavior at 80°C of various blends. Curve Q: standard sbiPP/iPP20. Curve SC: sbiPP/iPP20 obtained by solvent casting. Curve HT: sample SC after heat treatment. Curve aPP/iPP20: the sbiPP component was substituted by atactic polypropylene.

Sample SC shows a very low stress level, and the deformation is nearly all plastic and also small at the fracture; sample HT does show an appreciable improvement of the stress level, but the deformation at the fracture is still very low. Sample aPP/iPP20 does show low values of stress and strain at the fracture.

DISCUSSION

The stress-strain behavior at room temperature indicates the influence of the overall order degree on the drawing parameters. The yield point is linearly dependent on the crystallinity. Similarly, the mechanical energy spent to draw the samples up to the fracture (defined by the area under the stress-strain plot) also decreases on increasing the sbiPP content, again as a consequence of the reduced crystallinity, which reduces the physical constraints to the plastic flow. The deformation range, corresponding to the neck propagation, wide in the pure iPP, appreciably decreases on increasing the sbiPP content, being totally absent in sample sbiPP/iPP50 (for reasons to be eventually analyzed), and it is only weakly visible in the other samples. This trend could be correlated with the morphological organization,¹⁰⁻¹³ and in the first approximation, it seems to indicate a reduced crystal thickness in samples at lower iPP content, as reasonably expected.

However, although the data at room temperature are not surprising, the mechanical behavior observed at 80°C is of great importance to draw some conclusions on the structural organization. In fact, at this temperature, the sbiPP is widely above its melting temperature range, and, therefore, the presence of crystalline domains of this component can be categorically excluded. The results of Figure 2 indicate that an appreciable elastic behavior is shown by the samples at low iPP content; the permanent set is below 100% in sample sbiPP/iPP20 and it is only 50% in sample sbiPP/iPP5. For these samples, at this temperature, the thermal microscopy and the calorimetric analysis indicate that a crystalline iPP phase is still present.¹ At this temperature and at these low iPP contents (up to 20%), the model that can be suggested is a dispersion of iPP crystalline domains in a fluid sbiPP matrix. There are only two possible explanations for the observed elastic behavior: The first assumes a physical cross-linking between the matrix and the iPP crystalline domains, and this can occur assuming co-crystallization of sbiPP and iPP being formed at least on the surface of the iPP crystals. The second possibility assumes a physical network only due to the iPP component dispersed in the sbiPP matrix that does not play any role in the elastic behavior.

This second hypothesis seems less reasonable, mainly because it is difficult to explain the drawability (up to 550%) shown, for instance, by sample

sbiPP/iPP5. In fact, if the chains responsible for the elastic behavior are the iPP molecules, connecting the different crystalline domains, these chains, at this very low dilution, should be few and far from the random coil conformation, unable to justify the observed elastic behavior. So, the only reasonable hypothesis seems to be the first, taking also into account the behavior observed for samples SC, HT, and aPP/iPP20, which will be considered later. Data of Figure 3 give a further support to the first hypothesis; in fact, the minimum at 80°C (maximum in elasticity) can be explained considering that this temperature is just above the melting temperature range of the sbiPP matrix, which, therefore, can assume an elastic behavior, and still too low to compromise the thermal stability of the iPP domains. Thus, an increase of temperature in the direction of the melting of the iPP reduces the stability of the physical cross-links with an increase of the dissipated energy, as indeed observed. The same interpretation can be given to the data in Figure 4 for the conventional hot-pressed samples. However, in this figure, the first element needed to understand another crucial aspect is given, i.e., the relevant role played by the sample preparation, i.e., pressure molding followed by rapid quenching.

When the pressure molding is followed by slow cooling, the elasticity of the system is reduced and, in fact, the permanent set for these samples is widely higher than in the conventional samples. The slow cooling allows a better crystallization of the iPP phase, which, on growing, can exclude the sbiPP less regular sequences. The behavior of sample SC (shown in Fig. 5) points in the same direction; this sample, obtained by simple solvent casting, shows very poor mechanical properties, because the slow solvent removal allows the growing of well-segregated crystalline phases. Also, sample HT shows very poor mechanical properties; the procedure followed to obtain this sample can explain the observed behavior. The first stage is the melting of sample SC, the second is the cooling to 125°C (this temperature allows a complete crystallization of the iPP phase, excluding any possibility of cocrystallization with the sbiPP component), and the third is the cooling to room temperature (which allows the crystallization of the sbiPP matrix). So, the adopted procedure avoids any physical cross-link based on cocrystallization. The last sample, aPP/iPP20, obtained following the conventional two-stage procedure, also shows very poor mechanical properties. All this evidence strongly supports the model based on the cocrystallization of iPP and sbiPP, which is

possible only if a pressure flow is present in the molten state and if the following quenching is so rapid to avoid any possibility of slow and ordered crystallization, which, of course, moves into the direction of totally segregated crystalline phases. In fact, the annealing of the quenched samples at temperatures just below the melting of the iPP phase removes any elastic behavior.

To conclude, the analysis of the mechanical properties shown by sbiPP/iPP blends obtained by pressure molding followed by quenching supports a model based on the cocrystallization and shows the conditions to induce this phenomenon. Moreover, it gives a strong, and we believe definitive, support to the evidence of cocrystallization based on the thermal analysis already presented.¹

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REFERENCES

1. S. Canevarolo and F. de Candia, *J. Appl. Polym. Sci.*, to appear.
2. J. W. Collette, C. W. Tullock, R. N. McDonald, W. H. Buck, A. C. L. Su, J. R. Harrell, R. Mulhaupt, and B. C. Anderson, *Macromolecules*, **22**, 3851 (1989).
3. D. T. Mallin, M. D. Rausch, Y. G. Lin, S. Dong, and J. C. W. Chien, *J. Am. Chem. Soc.*, **112**, 2030 (1990).
4. R. Mulhaupt, J. W. Collette, D. W. Ovenall, and W. H. Buck *Prep. Polym. Mater. Sci. Eng.*, **53**, 488 (1985).
5. A. C. L. Su and C. K. Shih, in *Thermoplastic Elastomers*, N. R. Legge, G. Holden, and H. E. Schroeder, Eds., Hauser, New York, 1987.
6. F. de Candia, R. Russo, and V. Vittoria, *Makromol. Chem.*, **189**, 815 (1988).
7. F. de Candia and R. Russo, *Thermochim. Acta*, **177**, 221 (1991).
8. J. A. Ewen, *J. Am. Chem. Soc.*, **106**, 6355 (1984).
9. L. Araimo, F. de Candia, V. Vittoria, and A. Peterlin, *J. Polym. Sci. Phys.*, **16**, 2087 (1978).
10. F. de Candia, R. Russo, and V. Vittoria, *J. Appl. Polym. Sci.*, **34**, 689 (1987).
11. F. de Candia, G. Romano, R. Russo, and V. Vittoria, *Colloid Polym. Sci.*, **265**, 696 (1987).
12. F. de Candia, P. Iannelli, R. Russo, and V. Vittoria, *Polym. Eng. Sci.*, **28**, 974 (1988).
13. V. Vittoria and R. Russo, private communication.

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