Stereoblock Polypropylene/Isotactic Polypropylene Blends. IV. Cocrystallization and Phase Separation

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SYNOPSIS

The blending process of stereoblock isotactic polypropylene and isotactic polypropylene (sbiPP/iPP) including a well distribution of the components (by solvent mixing), posterior hot pressing (shear mixing), and a final quenching into ice water freezing these blends at room temperature in a particular flow oriented cocrystallized structure. This structure gives rise to a birefringent pattern which is stable up to 170°C when it disappears by melting. In the molten state the two components segregate destroying the original flow oriented structure. In the following cooling the iPP crystallizes in a spherulitic form and the sbiPP phase crystallizes only partially disturbed by the restrictions imposed by the iPP crystals. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Blends of stereoblock isotatic polypropylene and isotatic polypropylene (sbiPP/iPP) have been the subject of various previous publications.[1-5] The properties of the blends are strongly affected by the technique used during blending. Samples obtained by solvent dissolution, evaporation of the solvent, hot pressing, and immediate quenching into ice water freeze the sbiPP/iPP blends at room temperature in a particular flow oriented structure.[3] Samples at these conditions present very good elastic properties, both in terms of deformation reversibility and in terms of energy dissipation in the hysteresis cycles, this effect being more easily noticed in blends with low iPP content.[4] Because these elastic properties hold still for temperatures well above the melting temperature of the sbiPP phase (but below the melting temperature of the iPP component i.e., 80°C $\leq T <$ 170°C) we conclude that the physical network was due to a cocrystallized structure.[4] On the other hand, if the blend is allowed to cool slowly or even to crystallize isothermally the two components separate into two phase and crystallize separately. The isothermal crystallization kinetics of the iPP component[5] have shown that the iPP crystals are nucleated by the sbiPP phase, producing more defective crystals (with lower melting temperature) the higher the sbiPP content. The iPP crystallinity is also affected by the sbiPP phase given lower values than expected in the intermediate compositions reassuring the imiscibility of the two components even in the molten state.

In this paper we continue studying the crystallization phenomena of sbiPP/iPP blends using quantitative polarized light intensity.

MATERIALS AND EXPERIMENTAL

The materials employed in this work are the same already used in previous publications,[1-4] i.e., sbiPP synthesized by the group of Prof. Zambelli (Universita di Salerno) and iPP from RAPRA.

The blending was originally done by dissolving both components in hot xylene, allowing to dry at room temperature under mild vacuum, and finally hot pressing at 190°C between Teflon sheets in a Carver hot press. The amount of sample at each pressing was kept low, being not enough to fill the area left by the spacer, in order to allow a free flow
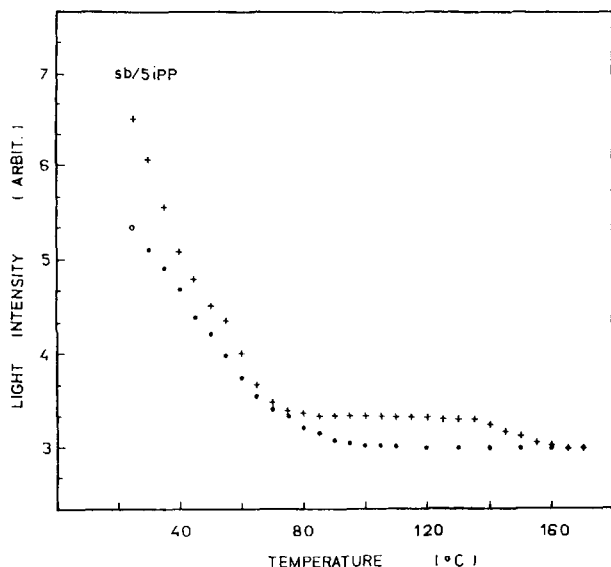

Figure 1   Birefringent light intensity as a function of temperature of hot pressed and quenched sbiPP/iPP blend with 5% of iPP: O, first heating; + second heating.

Figure 2   Same as Figure 1 but for blend with 10% of iPP.

of the molten sample. The films were rapidly cooled by quenching in ice water.

The cross-polarized light intensity was measured using a Jenapol light microscope equipped with a hot stage THMS600 from Linkam and an exposimeter Gossen Lunasix 3. The samples were heat cycled twice between room temperature and 170°C at a rate of 2°C/min. On cooling they were isothermally crystallized at 90°C and 50°C during 1 h in each step in order to allow the crystallization of both components.

RESULTS AND DISCUSSION

Figures 1 to 3 show a two heating cycle of samples with 5, 10, and 20% of iPP, respectively. The first heating was ended at 170°C, minimum temperature for instabilization of the cocrystallized sbiPP/iPP structure which, during the following cooling, allows for the iPP phase segregation and crystallization (which is in the spherolitic form). At this temperature there is disappearance of the weak remaining birefringent structure. This original structure is better visible when using a polarized light field with a lambda plate as a uniform colored field of blue, violet, or yellow, according to the flow direction of the sample being parallel, 45°, or perpendicular to the polarizer, respectively. This orientational behavior, which is radial in the hot pressed and quenched samples, suggest a flow-induced oriented crystalline organization in the sample as already
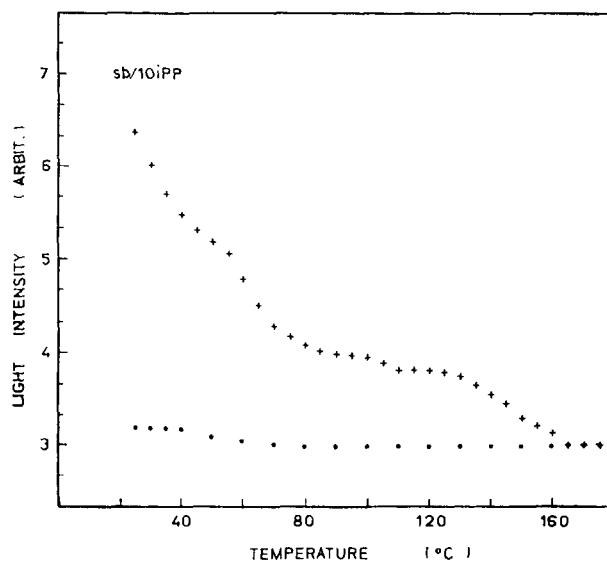
discussed.[3] During the following cooling, down to 25°C, the sample was isothermally crystallized at 90°C and 50°C during 1 h in each step in order to allow the crystallization of both components, and than the second heating cycle was applied.

Still analyzing the results of the first heating one can see that blends with only 5% of iPP initially show a reasonable birefringence value which reduces on heating, reaching a minimum level at about 80°C, due to the melting of the sbiPP component singularly crystallized. If the concen-
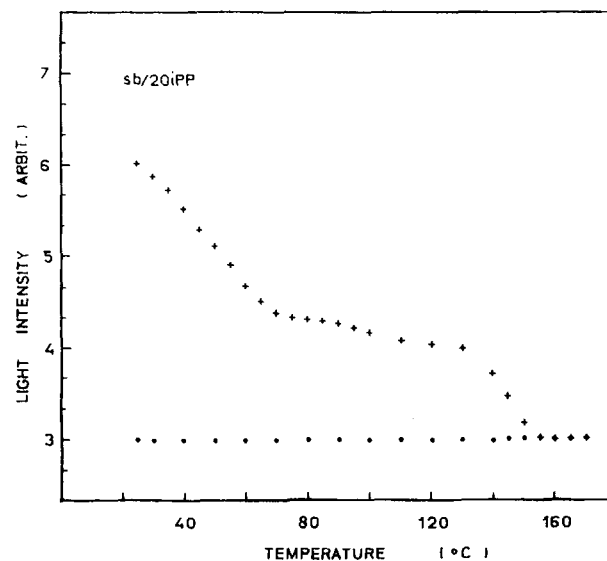

Figure 3   Same as Figure 1 but for blend with 20% of iPP.

tration of the iPP component is increased to 10%, the initial level of light intensity at 25°C (again mainly due to the sbiPP singularly crystallized) almost disappear. Increasing the iPP concentration even further (to 20%) the polarized light intensity level reaches the minimum value, i.e., there is no longer any singular sbiPP crystallization in the hot pressed and quenched blends. The addition of crescent quantities of iPP in the sbiPP/iPP blend changes gradually the normal sbiPP crystallization, which is of the fringed miscel type[5] and so birefringent, into a flow oriented cocrystallized structure.[3,4] This cocrystallized structure is weakly birefringent and, in all cases, is stable up to 170°C, when it totally disappears by melting. At a particular concentration between 10% and 20% of iPP the iPP chains are in sufficient number to form a molecularly mixed blend avoiding any possibility of the sbiPP chains to crystallize singularly.

On the following cooling there will be first, the crystallization of the iPP component which is in a spherulitic form. This crystallization, in the absence of flow and being driven mainly by the iPP component, should be spherulitic, and so loosen the original crystalline structure. The original flow oriented structure is obtained only when the chains of the two components are well mixed together, by shearing, and the structure frozen by a fast cooling (quenching) to the room temperature. The iPP crystallization occurs in the blend in the same temperature range as it happens when in the pure state, i.e., in the range of 130°C to 90°C. Continuing to reduce the temperature also the sbiPP chains will crystallize, again in the same temperature range shown when in the pure state, i.e., 60°C to 40°C. In this work, the choice of the crystallization temperatures for both components is not of great importance (the crystallization kinetics of the iPP phase have already been the subject of another publication[5]), 90°C and 50°C were chosen as the crystallization temperatures for each component taking into account that these conditions need a practical time for maximum crystallization conversion.

Both crystallization processes increase the polarized light intensity of the sample at room temperature and, in the second heating, it is possible to follow the melting of each component as regions in which there is a marked drop in the light intensity. Finally if a second cooling is done, again there will be crystallization of the iPP in the spherulitic form, confirming the definitive lost of the original flow-oriented cocrystallized structure.
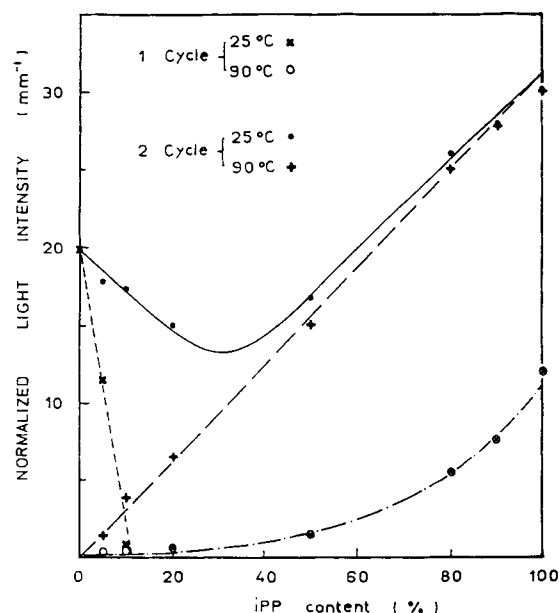

Figure 4 Normalized birefringent light intensity as a function of the iPP content measured at 25 and 90°C during first and second heatings.

These results, extended to all iPP concentrations, are summarized in the diagram of Figure 4. There, it is plotted the normalized birefringent transmitted light intensity at the two particular measuring temperatures (25°C and 90°C) during both heatings as

$$\Phi = \frac{I_T - I_{170}}{t}$$

where Φ is the normalized light intensity (mm^{-1}), I_T is the light intensity at the crystallization temperature T (25°C and 90°C), I_{170} is the light intensity at 170°C, and t is the sample thickness (mm) as a function of the iPP content in the blend. The intensity at 170°C was chosen as the background intensity because at this temperature all crystallinity has already been destroyed. The samples tend to shrink during the first heating in the temperature range of 140°C to 150°C and so, in the equation above, the thickness (always measured at 25°C) was taken as the initial value for the first heating and the final value for the second.

The next four measurements used can give a complete view of the sample transitions. The first was taken at 25°C in the fresh sample and so including the contributions of all birefringent (and so crystalline) phases at room temperature. This value is high for pure sbiPP but reduces rapidly with the increase of the iPP content reaching zero in the range just above 10%. By extrapolation we can get

the minimum amount of iPP to avoid the singular crystallization of the sbiPP in the range of 13%. Increasing the iPP content even further there is a slow growth of the light intensity reaching maximum for the pure iPP. The confirmation of the phase responsible for this behavior is done with the help of the next measurement, at 90°C.

The second measurement was taken at 90°C, temperature just above the melting temperature range of the pure sbiPP phase. The results show a slowly crescent curve, with very low values in the low iPP content side (lower than approx. 13%), which increases for increasing iPP contents. At higher concentrations the data overlaps that obtained at 25°C. This implies that the contribution in the low iPP content range (lower than 13%) is only due to the singular crystallization of the sbiPP phase and in the high iPP content range is due to the cocrystallized sbiPP/iPP blend (which is in a flow-oriented form).

During the cooling from 170°C there is the crystallization of the iPP phase in a spherulitic form and so there is an increase in the birefringent light measured at 90°C. As expected the curve is linear with the increase in the iPP content, extrapolating at both ends to the measured (iPP) or expected (zero for sbiPP) values shown by the pure components.

Finally the fourth measurement was taken at 25°C, after a heat treatment for 1 h at 50°C to allow the crystallization of the sbiPP phase. The curve behavior in the whole range is not additive (i.e., a linear curve interconnecting the data shown by each pure component) but rather presents a minimum in the 30% iPP range. This shows that the crystallization of the sbiPP phase, done after the iPP crystallization and so in an environment of dispersed iPP crystals, is much lower than expected, indicating that it was disturbed by the restrictions imposed by these iPP crystals. The drop in the light intensity is considerable (up to 50% in the range of 30% of iPP) and so, in order to be so effective, part of the sbiPP chains have to have being involved in a way with the iPP crystals possibly cocrystallizing in the outer iPP lamella shell. The cocrystallization mechanism would be similar to that shown by hot pressed and quenched sbiPP/iPP blends.[3,4]

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