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The property-performance differences between two blended polypropylene fibers[1]

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Abstract

The purpose of this study was to characterize two polypropylene copolymer materials which have similar melt viscosities (melt indices) but behave very differently both during and after processing into fibers. Although the two materials were generated by two different synthetic routes, it was felt that the materials should process similarly because of the similar melt viscosities. The first material, a reactor product, processed normally. With the second material, a physical blend, the spinline tended to break at the spinneret, shutting down the fiber spinning process. These materials are analyzed using optical microscopy (OM), differential scanning calorimetry (DSC) and thermomechanical analysis (TMA), to examine the source of excessive spin breakage. The source of the spinline breakage is found to be "gels" or globular masses on the otherwise smooth surface of the physical blend fibers. Several observations of physical characteristics, such as melting behavior and tensile stiffness, show that the two materials differ in crystallization rates, fraction, and orientation of crystals, and internal stress states. Much of the evidence points to differences in microstructure, molecular weight and molecular weight distribution between the two materials as the root cause of the differences in processability and performance. This conclusion is supported by gel permeation chromatography recently performed on the materials.

Keywords: Polypropylene fiber; Property-performance difference; TMA; DSC; Microscopy

1. Introduction

The morphology of polymers strongly influences the mechanical properties of the fi-

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nal product. This is particularly true of synthetic fibers, which are subjected to a host of thermal and mechanical treatments to achieve particular physical and mechanical states. These treatments can affect the microstructure in both the amorphous and crystalline phases. Without control over the microstructure, or at least insight into it at each step, downstream processability and final appearance of the product are difficult to predict.

Two polypropylene copolymer fiber bundles were examined in this study. One bundle was from reactor synthesized material, the other physically blended. Both were subjected to similar processing, yet show different behavior. These materials were analyzed using optical microscopy (OM), differential scanning calorimetry (DSC) and thermomechanical analysis (TMA), to examine the source of excessive spin breakage in one of the materials. The evidence shows that the more susceptible blend has a higher degree of orientation and is likely to have less complete mixing and a broader molecular weight distribution.

2. Experimental

The materials used in this study were from two stocks of blended polypropylene fibers. Material 1 was a polypropylene copolymer that was a reactor product directly polymerized to a melt flow rate of 20 g min^{-1}; material 2 was a physical melt blend of 9–10 melt flow homopolymer and low melt flow copolymer which was visbroken to the melt flow rate of 20. The fibers were spun at a low draw ratio under equivalent thermal and physical stresses. The materials have a similar linear density of 3 tex per filament (tpf) and microscopy shows that the materials have similar diameters at 65–80 μm.

DSC experiments were performed using the TA Instruments DSC 2920 with a heat-cool-heat cycle over the range of 30–235°C at 20°C min^{-1}. The fibers were cut to short lengths and 4 mg samples were crimped in standard aluminum pans.

TMA experiments were performed with the TA Instruments TMA 2940. To achieve a representative sampling yet ensure high quality clamping, 10 fibers were removed from each bundle and crimped into split aluminum shot in a method similar to that used in ASTM D1294-86 [1]. Thermal expansion/contraction was measured at 3°C min^{-1} under a load of 50 mN (1.6 mN tex^{-1}). Stress–strain measurements were made at room temperature under a constant rate of load (CRL) of 50 mN min^{-1} from a pre-tension of 5 mN (0.16 mN tex^{-1}) to 1000 mN (32 mN tex^{-1}). Constant strain experiments, otherwise known as shrinkage force or thermal stress analysis (TSA), were performed using a pre-tension of 50 mN (1.6 mN tex^{-1}) and stretching the samples 1.5–2.0% to achieve similar initial stress levels in the samples. The samples were heated at 3°C min^{-1}. The above experimental conditions were similar to those used by other investigators [2,3] and ASTM standards [4–6], although the heating rates are somewhat slower.

3. Results and discussion

Optical microscopy offers insight into the cause of the spin breakage. The most prominent features seen in these materials (Fig. 1) are the expansions of the fiber diame-

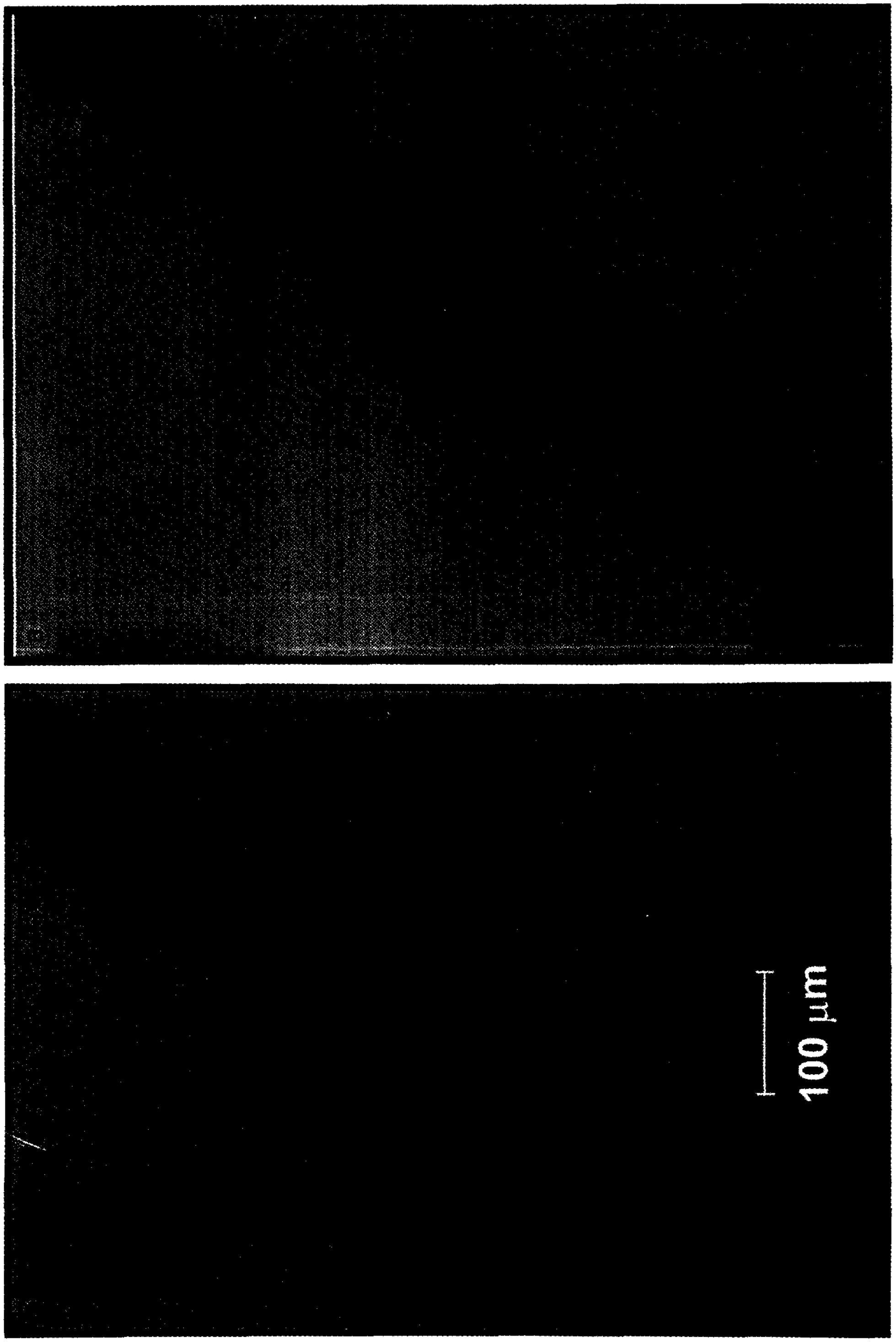

Fig. 1. Optical micrograph of as-received fibers at 310× magnification. (a) Reactor product (material 1) and (b) physical blend (material 2) showing a gel.

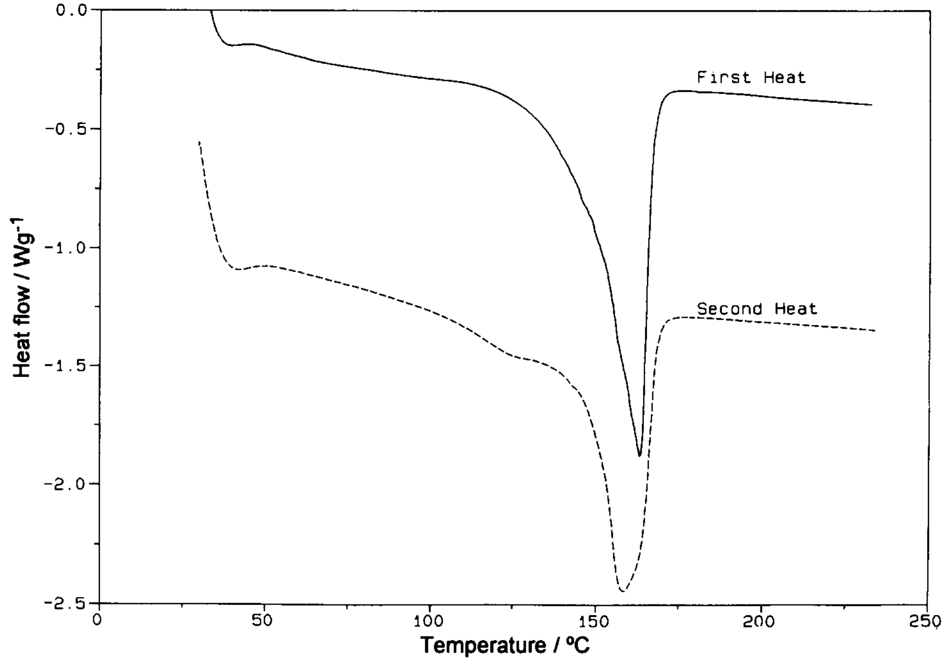

Fig. 2. DSC thermal curves for the physical blend fibers. First and second heating at 20°C min^{-1}.

ter, called gels, which appear in the physical blend (material 2) but not in the reactor product (material 1). The gels appear at a rate of 10–20 gels per 2 cm of fiber bundle, in a random pattern along the fibers. It is unlikely that the gels are formed by the phenomenon of spin resonance. Rather they are formed in the melt and enhance breakage of the fibers by clogging the spinneret. It has been thought that the gel phase is a higher molecular weight component separating from the main phase of the physical blend copolymer (material 2). However, the gels are a small fraction of the total fiber mass and volume and have been difficult to analyze.

Fig. 2 shows the DSC thermal curves of the first and second heatings on material 2. Material 1 showed very similar results, although there are subtle differences. The first heats (as received material) of both materials show single, although somewhat broad melts, with small transitions occurring on the onset slopes. The melt peak temperature and enthalpy of fusion for material 2 are higher than for material 1, although material 1 has a higher melt onset temperature. A summary of the DSC results is given in Table 1.

The single-peaked curves of the first DSC heats indicate that the as-received materials are macroscopically single phase. The curve shapes of the two materials are very similar, with only subtle differences in the leading edge of the melt peak, indicating that the gel structures have little effect on the overall phase structure of the material. The long leading edge and small transitions show there may be some breadth in the crystal perfection (orientation) of the two materials. Correlation has also been drawn between orientation and the DSC melt peak temperature [2]. The reactor product (material 1) has lower crys-

Table 1
DSC onset (Te) and peak (Tp) temperatures and enthalpies (ΔH)

Sample	First heat			Cooling			Second heat		
	Te/°C	Tp/°C	ΔH/(J g^{-1})	Te/°C	Tp/°C	ΔH/(J g^{-1})	Te/°C	Tp/°C	ΔH/(J g^{-1})
1 (reactor product)	148.3	162.2	72.7	114.3	111.6	74.0	146.8	119.6 157 161.3	72.3
2 (physical blend)	143.4	163.2	76.9	116.8	114.0	77.8	147.5	122.8 157.5 161	75.2

Note: there are two peaks on the second heat, the second is a split peak (two maxima).

tallinity (lower melt enthalpy) than the physical blend (material 2) and the lower melt temperature of material 1 may be indicative of smaller crystallites being formed in this material. These observations can be explained by material 1 having a lower molecular weight and/or molecular weight distribution and perhaps more intimate mixing of the copolymers.

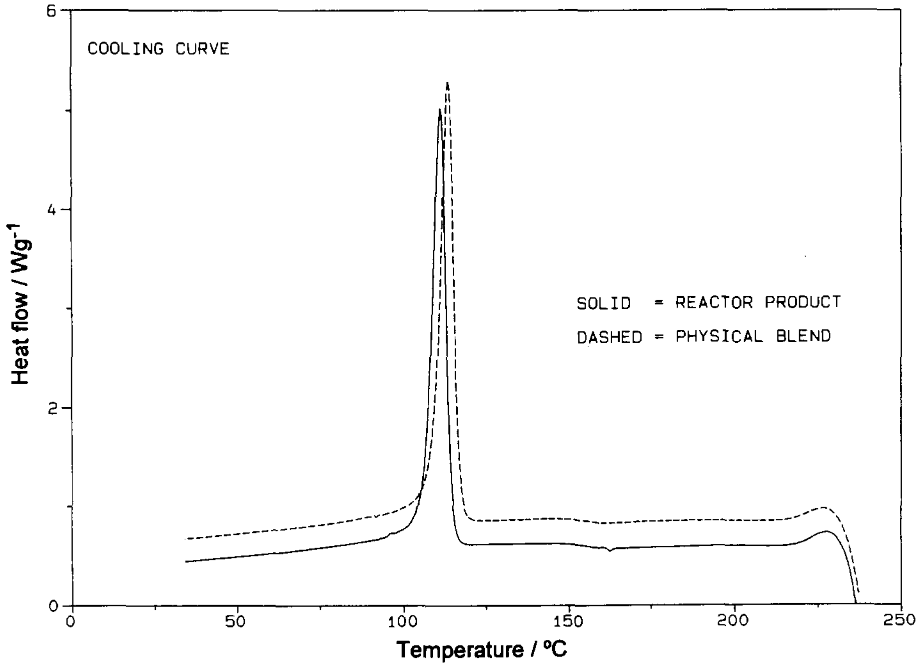

Fig. 3. DSC thermal curves for the cooling (20°C min^{-1}) of the reactor product and physical blend polypropylene copolymer fibers.

The crystallization peak during cooling (Fig. 3) is very sharp, and the slope of the baseline increases dramatically after crystallization. The crystallization peak temperatures follow the same order as the melt peak temperatures, with material 2 being more easily crystallizable. Preliminary isothermal crystallization studies at 116°C also show a similar trend. It has been shown that the crystallization rate increases as both molecular weight and molecular weight distribution increase [7], as well as with the stress state of the polypropylene fibers [8].

The second heat is somewhat more difficult to interpret with three overlapping melt transitions. There are also changes in baseline slopes before and after the transitions that are similar to those seen during the cooling ramps. The reactor product (material 1) has a lower melt temperature on the first peak than does the physical blend (material 2). Both materials have similar peak temperatures for the split main peak, indicating crystallization induced similar stress states for this phase [8]. Integration between 92 and 175°C yields total melt enthalpies of 72 and 75 J g^{-1} for materials 1 and 2, respectively, which are lower than for the respective first heats. The limits of peak integration, however, can be defined several ways, with some definitions yielding higher melt enthalpies than those seen in the first heat. There is much discussion as to whether drawing increases or decreases crystallinity of polypropylene [9].

Several authors have seen multiple melting peaks in polypropylene, and there is the suggestion of multiple crystalline forms in the polypropylene [2,3,9]. It is alternatively suggested that the low temperature melting is caused by a less perfect crystalline order and not from different crystal phases [10]. With very sharp crystallization peaks, it is likely that the low temperature phase is induced at the crystallization temperature. Similar phenomena have been observed for isothermal crystallization [11] and this probably explains the difference in peak temperature between the two materials. It is plausible that the different polymer fractions do not co-crystallize simultaneously, and that the lower

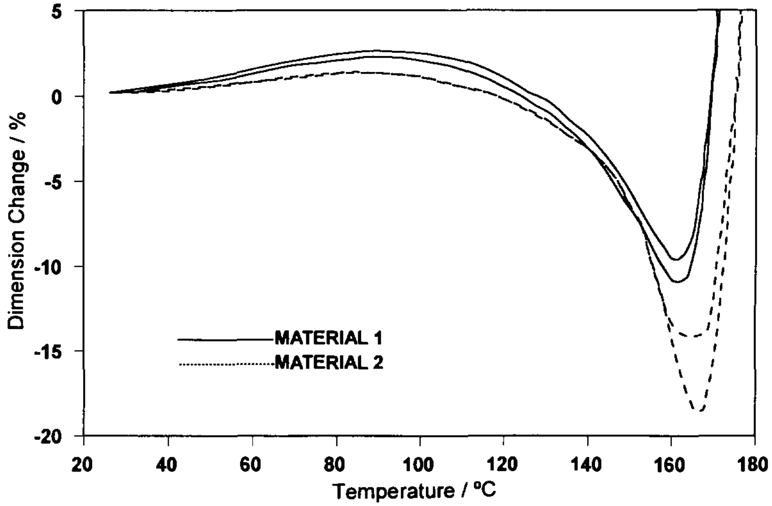

Fig. 4. Thermal expansion/shrinkage of polypropylene fibers.

Table 2

TMA, TSA, stress/strain results

Sample	TMA				Stress/strain		TSA	
	Expansion/ %	Tp/ °C	Contraction/ %	Tp/ °C	Crimp/ %	Compliance/ % N^{-1}	TSA Fp/ N	Tp/ °C
1 (reactor product)	2.5	89	10–11	162	2	6.7	0.09	132
2 (physical blend)	1.2	84	14–19	167	3	5.0	0.10	140

Note: for expansion, contraction and TSA, the Tp is the peak temperature for the associated transition. The three peak temperstures roughly correspond to the onset of shrinkage, melt and softening, respectively.

temperature melt is due to morphological effects. It is possible that the higher melt temperature of material 2 implies the molecular weight of the secondary phase is greater than for material 1.

The peak temperatures in thermomechanical analysis follow similar trends as the DSC results, giving good agreement between the two techniques. But TMA gives much further insight into the physical properties and structure of the polypropylene copolymers, with distinct differences between the two materials. In the expansion/contraction measurements (Fig. 4), material 1 has greater expansion until the initiation of shrinkage around

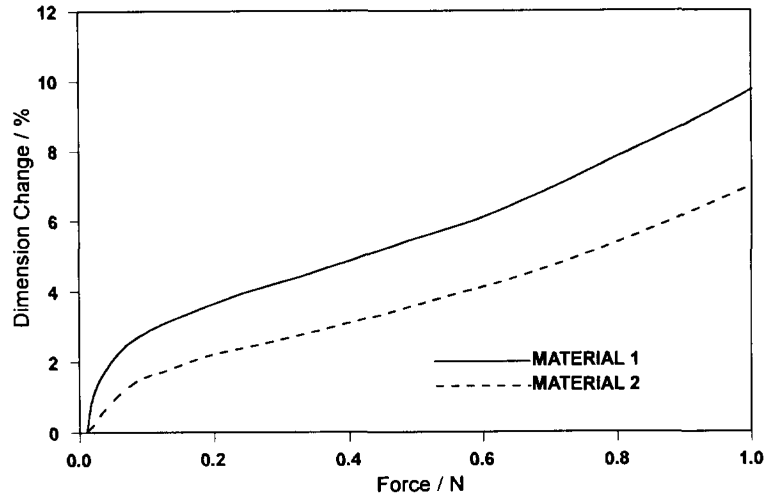

Fig. 5. Stress/strain curves for reactor product and physical blend fibers. The force is ramped 0.05 N min^{-1} isothermally at 25°C.

85°C. It also contracts to a lesser degree and "melts" at a lower temperature. The TMA experiments are summarized in Table 2.

In the stress–strain measurements (Fig. 5), two effects can be seen. First, the expansion at low force levels is a good measure of the relative crimp of the two materials. Second, the slope of the dimension change versus force line is a measure of the material compliance. The reactor product (material 1) shows greater expansion, as expected, and is more compliant (therefore a weaker material) than the physical blend (material 2).

The shrink force measurements (Fig. 6) confirm that material 1 is a weaker material, with a lower overall shrink force. Furthermore, the peak temperature in the force curve is significantly lower than for material 2. The shrink force measurements show finer structures than can be seen in TMA expansion or DSC curves. A secondary relaxation occurs in the materials prior to the melt at around 160°C. In material 2 this relaxation is more prominent.

Lower thermal expansion, and greater shrinkage and shrink force are indicative of a material with greater crystallite orientation [2,12]. These experiments confirm that material 2 has greater orientation than material 1. The extra stresses placed on the amorphous inter-crystalline tie molecules lead to the material being more difficult to deform (less compliant in the stress–strain experiments). Similar results have been seen with the texturing of polyester yarns [10]. It is likely that extra stresses placed on material 2 by the gels in the spinning step are translated to greater orientation in the final fibers.

The shoulders in the thermal stress analysis at around 160°C indicate that the materials have differing strengths in the melt region. Material 2, with the more prominent shoulder, has greater melt strength in this region. It is likely that the gels contribute to the greater melt strength with several possible causes. First is two-phase behavior caused by incomplete mixing of the components of the physical blend. It is also likely that there are re-

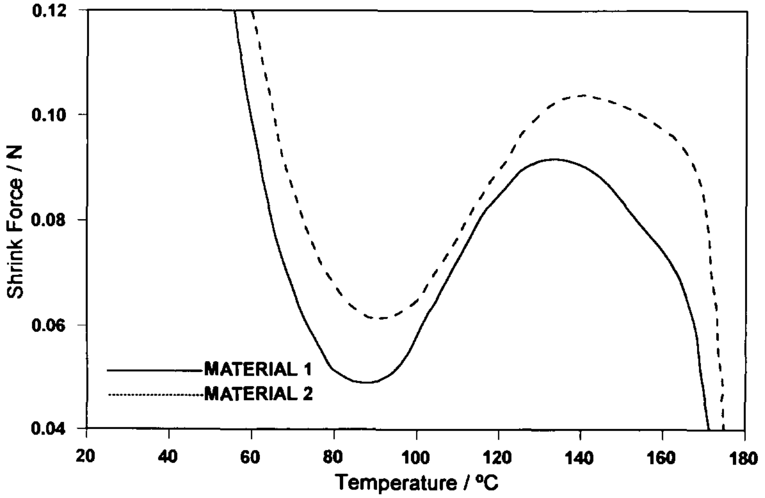

Fig. 6. Thermal stress analysis of reactor product and physical blend fibers. Initial strain 1.5%, heating rate 3°C min^{-1}.

gions of higher crystalline perfection, as suggested by higher orientation and the DSC results. Finally, there may be differences in the melt strength of the material caused by entanglements in the material, or by crosslinking brought about by the visbreaking process. These reasons are not mutually exclusive, and all can be related to greater molecular weight and/or molecular weight distribution in material 2. Gel permeation chromatography performed elsewhere on these materials has recently confirmed that material 2 does indeed have a greater molecular weight and weight distribution.

4. Conclusions

The two polypropylene copolymer fibers have very different appearance and physical properties. Thermomechanical analysis shows that the materials are in two different stress states caused by differences in crystalline orientation. Higher viscosity and stresses due to the presence of the gels in material 2 create higher spinline stresses that lead to the orientation. DSC shows that the materials differ in crystallization rates, crystallite fraction, and most likely molecular weight. Much of the evidence indicates that the physical blend fibers (material 2) have a higher molecular weight and weight distribution and less complete mixing occurs in the blending process. Gel permeation chromatography has confirmed the molecular weight and weight distribution differences between the two materials.

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