EFFECT OF DRAWING DIFFERENT MFI POLYPROPYLENE FILAMENTS ON A GRADIENT HEATER

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Abstract

High-modulus and high-tenacity polypropylene fibres were prepared by drawing as-spun filaments on a heater with a temperature gradient. The results on two different MFI PP show that the fibre properties are significantly affected by the temperature profiles at the final stage of drawing on a gradient heater. High crystal perfection and crystallinity at very high draw ratios have been obtained for the gradient drawn fibres. The gradient drawn filaments showed superior mechanical properties when compared to filaments drawn over a constant temperature heater. Fibres with an initial modulus of 16.4 GPa and tenacity of 875 MPa were obtained in the process. The molecular weight of the parent material significantly influenced the mechanical properties of the material. High molecular-weight (low MFI – Melt Flow Index) materials are characterised by comparatively lower modulus but higher tenacity values. High draw ratios were possible for the higher MFI samples, leading to more orientation and modulus.

Key words:

drawing, polypropylene, fibre, heater, gradient heater

Introduction

The success of polypropylene fibres in industrial use lies in its versatility. Their excellent chemical resistance, low density and highest melting point in the family of olefin fibres, coupled with moderate cost, makes them an important fibre type in industrial applications. Their relatively good mechanical properties, such as strength and toughness, has made them useful in technical applications. Like other synthetic fibres, both the starting material and the processing conditions controls the physical structure of polypropylene. The process of drawing depends on molecular weight, molecular weight distribution, initial morphology, drawing temperature and strain rate. It has been proposed that stretching iPP results in chain-slip through crystals, sliding and breakage of tie chains and the activation of constrained amorphous regions driven by lamellar disintegration [1,2]. In the post-yield region, these alternations of the microstructure result in cavitation, formation of fibrils and stress-induced crystallisation [3].Considerable work has been done on the production of high-modulus and high-tenacity fibres through melt spinning and other drawing processes [4,5,6,7,8,9,10].

The importance of molecular weight on filament properties has also been highlighted by researchers. Svetec [11] found that a medium-weight polymer with a narrow molecular-weight (MW) distribution was most suitable for producing high-modulus high-tenacity PP fibres. It has been generally observed that drawability increases with MW up to a certain value, after which it decreases. The importance of molecular weight is also highlighted in the gel spinning process [12,13]. However, it is slow, and requires specific molecular weights & distributions as well as extensive solvent removal schemes.

As-spun fibres have been drawn in several ways, from single-stage to three-stage drawing. Several references [14,15] report that multi-stage drawing produced better results than single-stage drawing. Wang et al. reported better value of polypropylene monofilaments when drawn in two stages (the first at the relatively lower temperature of 60^{o}C, and subsequently at 140 ^{o}C), when compared to single-

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stage drawing. They showed that morphology created in the first stage of drawing is critical for the properties achieved after second-stage drawing [16].

Generally heaters for drawing have uniform heating temperatures along their length. This paper reports experiments on a heater (Indian patent pending, Application No. 07/DEL/2004/DTD-1 Jan 2004) which has a temperature gradient along its length.

Experimental

Material

The isotactic PP homopolymer was supplied by Reliance Industries Ltd. The materials used were tested according to ASTM D 1238 (190^{0}C/2.16 kg) and the obtained Melt Flow Index (MFI) of the material were 3 and 35.

Sample preparation

The monofilament was prepared through extrusion and drawing. The spinning was done in a laboratory-model single-screw extruder with a L/D ratio of 20. The temperature profile used for the extrusion was 180^{0}C at the feed zone, 200^{0}C at the compression zone, 220^{0}C at the metering zone and 240^{0}C at the die. The take-up speed was 15.8 m/min. The filaments in all cases were quenched by ice-cooled water kept at 4^{0}C and at a distance of 2 cm below the spinneret level. The as-spun filaments were drawn through a two-stage drawing process, at temperatures of 60^{0}C and 120^{0}C respectively, as shown in Figure 1, to the maximum permissible draw ratio without whitening.

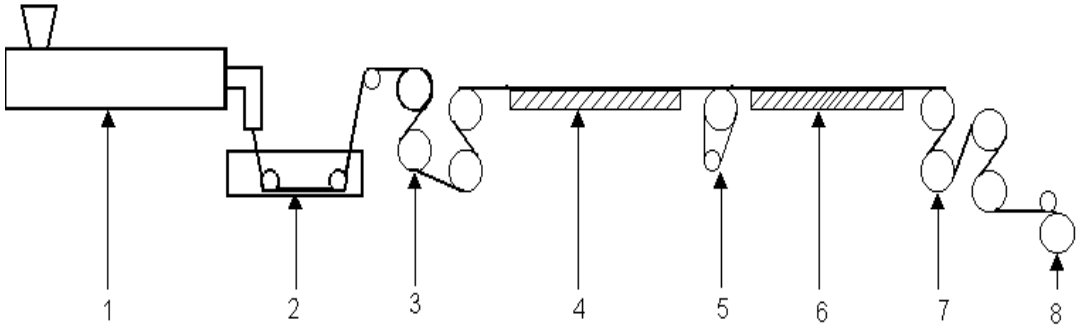

Figure 1. Schematic diagram of extruder and two stage drawing.
1 - extruder, 2 - quench bath at 70C, 3 - godet roller, 4 - 1st heater, 5 - godet roller, 6 - 2nd heater, 7 - godet roller, 8 - take-up device

Two-stage drawn filaments are used as feed material for ultradrawing over the gradient heater, as shown in Figure 2.

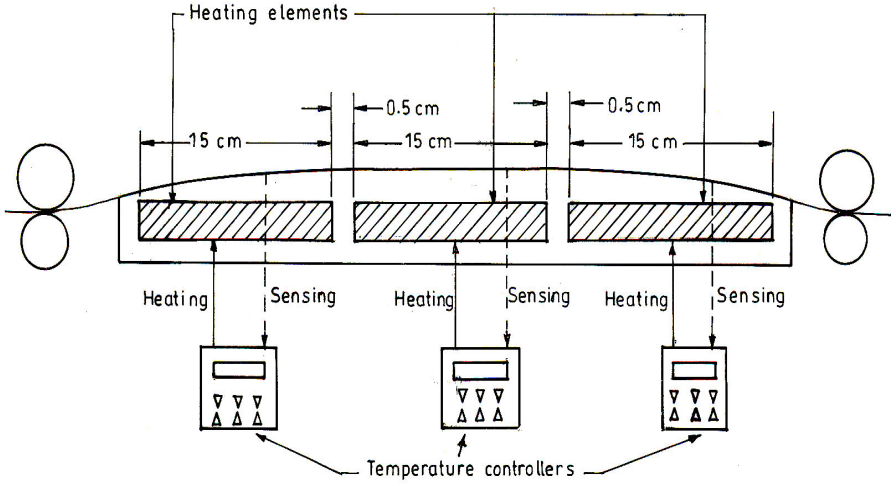

Figure 2. A three-element gradient heater

The gradient heater, constructed in the lab after initial experiments, (Figure 2) was a continuous steel plate on a series of heating elements coupled with temperature controllers. The heating elements are separated by air gaps, so that the heating of one element is not affected by another. When the heating elements are kept at different temperatures, the upper plate being continuous in nature, a gradient of temperature is shown along its surface.

The drawing process was carried out with different gradients on the heater. The selection of gradients was carried out on the basis of improvement in mechanical properties. The filament is drawn to the maximum before whitening, and the draw ratio determined accordingly.

Table 1. Sample nomenclature of selected gradients

Sample ID	Gradient (^{0}C)
GD1	140-140-148
GD2	140-145-155
GD3	140-148-148
CT	148-148-148

As denoted in Table 1, GD denotes gradient drawn samples while CT denotes constant temperature-drawn samples. The number which comes before the alphabet denotes the sample's MFI. For example, a sample denoted as 17GD1 would mean Polypropylene of 17 MFI, drawn over a gradient of (140-140-148)^{0}C.

Static mechanical properties

Tensile properties were measured according to standard ASTM D638 at 23-25^{0}C, 65% RH, on a Statimat at a speed of 20 mm/min with a gauge length of 100 mm. All the tensile properties reported represents the average value of ten readings, the sample being taken from different parts of the package. The overall stress-strain curve was used to determine the initial modulus. tenacity and elongation of the sample.

X-ray crystallinity and crystalline orientation function

Intensity plots of powdered samples were obtained against 2θ, where θ is Bragg's angle in the WAXD diffractogram. The amorphous pattern of PP was superimposed on the sample WAXD pattern. After segregating the crystalline contribution, the weight fraction crystallinity "χ_c" was calculated using the following formula:

$$\chi_C = \frac{\int_0^\infty s^2 Ic(s)ds}{\int_0^\infty s^2 Is(s)ds}$$

where: χ_c = mass fraction crystallinity; Ic = intensity of crystalline scattering; Is = intensity of total scattering;

$$S = 2\sin\frac{\theta}{\lambda};$$

λ = 1.54 Å; θ = Bragg's angle

The crystalline orientation function (f_c) was calculated using the Herman-Stein orientation function:

$$f_C = \frac{(3\cos^2\phi_{c,z} - 1)}{2}$$

where $$\cos^2\phi_{c,z} = 1 - 1.099\cos^2\phi_{110,z} - 0.901\cos^2\phi_{040,z}$$

the $\cos^2\phi_{110,z}$ and $\cos^2\phi_{040,z}$ were obtained from azimuth intensity distribution measurements of (110) and (040) reflections according to the following equation: [17]

$$\cos^2 \phi_{hkl,z} = \frac{\int_0^{\frac{\pi}{2}} I(\phi) \cos^2 \phi \sin \phi \, d\phi}{\int_0^{\frac{\pi}{2}} I(\phi) \sin \phi \, d\phi}$$

where I(ϕ) is the intensity diffracted from the (hkl) planes normal to the x-crystallographic axis. The integrals are evaluated from the intensity distribution of (110) and (040) reflections. WAXD crystallinity (χ_c) was calculated applying the Farrow-Preston [18] method.

Birefringence and amorphous orientation function

A Leitz polarising microscope with a Leitz Wetzler tilting plate-type quartz compensator was used to determine the birefringence (Δn) of drawn fibres. The diameter of the fibres was measured with the help of a projection microscope. At least ten readings were taken for each of the sample.

The birefringence was then calculated using the formula

$$\Delta n = \frac{6.18 \times \text{phase difference in nm}}{1000 \times \text{fibre diameter in } \mu\text{m}}$$

The amorphous orientation function was calculated using the equation [19]

$$f_a = \frac{\Delta n - \chi_c \Delta n_c f_c}{(1 - \chi_c)\Delta n_a}$$

where χ_c = X-ray crystallinity; Δn = birefringence; Δn_c = intrinsic crystalline birefringence; Δn_a = intrinsic amorphous birefringence; f_a = amorphous orientation function; f_c = crystalline orientation function: Δn_c and Δn_a are taken as 0.033 and 0.0468 respectively [20].

Results and discussion

It was observed that the tensile properties of the fibres depend significantly on the temperature gradient. The tensile properties of the selected fibres are given in Table 2**.**

Table 2. Comparative tensile properties of 3, and 35 MFI material

Sample ID	Draw Ratio	Initial Modulus, GPa	Tenacity, MPa	Energy, kg-mm	Elongation, %
3GD1	13	10.4	607	700	7.8
3GD2	14.4	9	875	820	9
3GD3	16.2	13.2	770	520	6
3CT	12	7	620	640	8
35GD1	17.4	14.4	670	675	7
35GD2	16.4	14	540	560	6
35GD3	18.7	16.4	640	541	6
35CT	16	13.1	460	500	5

As seen from Table 2, the initial modulus of drawn polymer is a unique function of the draw ratio, quite independent of the initial morphology and the molecular weight. Lower molecular-weight 35 MFI samples are characterised by high-draw ratios coupled with initial modulus. on the other hand, the 3 MFI sample was difficult to draw due to high entanglements, and consequently higher modulus values

were not achieved. For such high molecular weights, unfolding is more difficult in extension, and scission takes place more easily without an increase of taut-tie molecules.

Tensile modulus reflects the average of the structure, whereas tensile strength relates more to the weakest position in the structure. The tensile strength of fibres is determined by intrinsic parameters such as the intrinsic elastic modulus of the parent polymer, the intermolecular bonds and the chain length distribution. The post-spinning operations improve the mechanical properties but also introduce defects such as inhomogeneities and voids. The ends of the extended chains, formed through the unfolding of the crystallites, lead to defects which form microcracks in the sample when it is stretched. These flaws have little effect on the modulus, which involves low strain, but play a significant role in axial strength, which is measured at the limiting strain of the material.

In higher molecular-weight samples, there are fewer such defective points. and therefore the possibility of extending the original sample of a higher molecular weight to unfold to a greater extent without the formation of microcracks is greater. For a higher molecular-weight sample, with more entanglement density, the chance of stress concentration increases naturally, and the probability of a mass flow of polymer predominates when compared to opening entanglements and further drawing.

Table 3. X-ray crystallinity, crystallite and amorphous orientation functions

Sample ID	Birefringence	X-ray Crystallinity, %	f_c	f_a
3GD1	0.031	62	0.94	0.63
3GD2	0.031	59	0.94	0.62
3GD3	0.032	64	0.96	0.69
3CT	0.029	58	0.95	0.59
35GD1	0.033	65	0.96	0.73
35GD2	0.032	62	0.97	0.71
35GD3	0.034	71	0.98	0.8
35CT	0.031	61	0.94	0.68

As is evident from Table 3, the crystallite orientation values do not change appreciably. as at such high draw ratios, the crystallites are already oriented. Similar observations were made by Yamada [21]. The amorphous orientation values increase remarkably, and reach a maximum of 0.8 for the 35GD3 sample. The high modulus and tenacity values of the 35GD1 and 35GD3 samples are a result of these very high amorphous orientation values. The stretching of filaments causes chain-slip through the crystals, the sliding and breakage of tie chains and the activation of constrained amorphous regions driven by lamellar disintegration. The amorphous phase participates actively in the deformation process, together with crystallites during tensile test. For highly crystalline gradient drawn filaments coupled with high amorphous orientation, amorphous layers and taut-tie molecules effectively transmit the stress between crystallites.

It can also be observed that gradient drawn samples are characterised by higher crystallinity values. In the gradient drawing process, the heater plate acts as if it consists of a series of a large number of heaters with increasing temperature. With each increase of temperature, some molecules become mobile, become oriented under stress and tend to crystallise. In the process, filaments get gradually stabilized with the increased temperature profile. Readers are referred to another detailed article on the concept of gradient drawing for a single MFI polypropylene elsewhere [22]. In constant temperature drawing, where a filament was exposed to a sudden temperature ‘shock’ , the draw stresses are high, resulting in inferior properties. Thus gradient drawing is a superior method to constant temperature drawing for producing filaments with superior mechanical properties.
Overall, the crystallinity of higher MW samples was low for the gradient and constant temperature-drawn samples. The reason may be that the nucleation rate varies inversely with MW, which implies that as-spun fibre from high MW would have a lower degree of crystallinity. The parent crystallinity affects the final crystallinity of the drawn filaments.

Gradients which tend to stabilise over the initial or final zones resulted in better filament properties. This may be because the heat transfer is not appropriate for a continuously-increasing temperature field. A stable temperature field at the start prepares the filament for an increasing temperature gradient, which happens for GD1, while as a result of an initial temperature gradient the oriented filament has the chance to become stabilised at the end for GD3. Comparatively, for both the molecular weights a perpetually increasing gradient has resulted in slightly weaker properties.

Conclusion

The gradient drawing process achieved higher modulus values compared to the normal temperature drawing of filaments. The highest tenacity of 875 MPa and a modulus of 16.4 GPa has been achieved by the gradient drawing process. This process has achieved a high crystallinity of 71% and amorphous orientation of 0.8, resulting in superior mechanical properties compared to the constant temperature drawing on comparable temperature scales. Average initial modulus values have been higher for the 35 MFI samples, while higher tenacity values are obtained for 3 MFI samples. The highest draw ratio is also restricted in case of 3MFI filaments, indicated by premature whitening. Gradients which tend to stabilise over the initial or final zones resulted in better filament properties.

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