

Mechanical Properties of Polypropylene Filaments Drawn on Varying Post Spinning Temperature Gradients

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(Received February 27, 2006; Revised April 20, 2006; Accepted May 8, 2006)

Abstract: High Modulus and high tenacity polypropylene fibers have been prepared by drawing on a gradient heater. Results show that fiber properties are significantly affected by temperature profiles of final stage drawing on a gradient heater. The gradient drawn filaments showed superior mechanical properties when compared to filaments drawn over a constant temperature heater. Fibers with initial modulus of 16.4 GPa and tenacity of 670 MPa have been manufactured in the process. The nature of the gradient drawing had a significant effect on end properties. The superior mechanical properties are attributed to the high crystal perfection and crystallinity and low void fractions obtained at high draw ratios when drawn over a gradient heater.

Keywords: Drawing, Fiber, Polypropylene, Heater, Post-spinning

Introduction

The success of polypropylene as an industrial fiber lies in its versatility. Excellent chemical resistance, low density and highest melting point in the family of olefin fibers coupled with moderate cost makes it an important fiber in industrial applications. Their relatively good mechanical properties like strength and toughness has made them useful in technical applications. Like other synthetic fibers, the starting material as well as 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 of iPP result in chain slip through crystals, sliding and breakage of tie chains and activation of constrained amorphous regions driven by lamellar disintegration [1,2]. In the post yield region, these alterations of the microstructure result in cavitation, formation of fibrils and stress induced crystallization [3]. There has been considerable work on the production of high modulus and high tenacity fibers through melt spinning and further drawing processes [4-6].

Drawing of as-spun fibres has been done in several ways starting from single stage to three stage drawing. Several references [7,8] 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 being at relatively lower temperature of 60 °C and subsequently at 140 °C when compared to single stage drawing. They showed that morphology created in the first stage of drawing is critical for properties achieved after second stage drawing [9].

Generally heaters for drawing have uniform heating temperatures along the length. This paper reports experiments

on a heater (Indian patent pending 07/DEL/2004/DTD-1 Jan 2004) having a gradient of temperature along the length.

Experimental

Material

Isotactic PP homopolymer was supplied by Reliance Industries Ltd. The material used were tested according to ASTM D 1238 (190 °C/2.16 kg) and the obtained MFI of the material was 35.

Sample Preparation

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

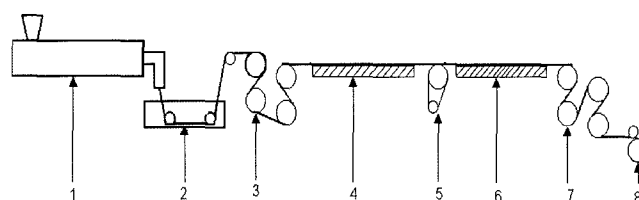


Figure 1. Schematic diagram of extruder and two stage drawing; 1. extruder, 2. quench bath at 70 °C, 3. godet roller, 4. 1st heater, 5. godet roller, 6. 2nd heater, 7. godet roller, 8. take-up device.

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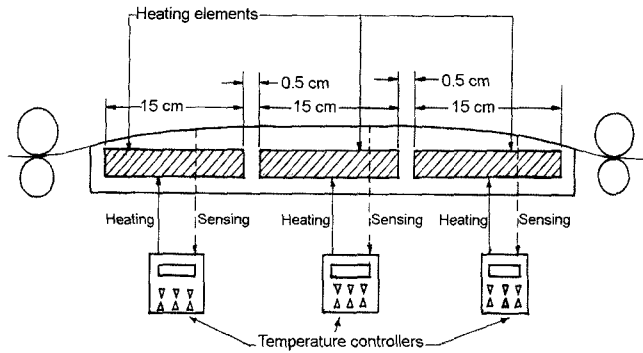


Figure 2. A three element gradient heater.

Table 1. Sample nomenclature of selected gradients

Sample ID	Gradient (°C)
GD1	140-140-148
GD2	140-145-155
GD3	140-148-148
CT	148-148-148

Two stage drawn filaments are used as feed material for ultradrawing over the gradient heater as shown in Figure 2. A gradient heater, fabricated in the lab after initial experiments, (Figure 2) is a continuous steel plate on a series of heating elements coupled with temperature controllers. The heating elements are separated by air gap so that heating of one element is not affected by another. When heating elements are kept at different temperatures, the upper plate being continuous in nature, show a gradient of temperature along its surface.

The drawing process was carried out with different gradients on the heater. Several gradients have been tried out in the lab and gradients outlined in Table 1 were finally selected on the basis of improvement in mechanical properties. The filament is drawn to the maximum before whitening and the draw ratio determined accordingly.

As denoted in the Table 1, GD denotes gradient drawn samples while CT denote constant temperature drawn sample.

Static Mechanical Properties

Tensile properties are measured vide ASTM D638 at 23-25 °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 out 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 the Bragg’s angle in WAXD diffractogram. Amorphous pattern of PP was superimposed on the sample

WAXD pattern. After segregating the crystalline contribution, weight fraction crystallinity “χ_c” was calculated using the following formula:

$$\chi_c = \frac{\int_0^\infty s^2 I_c(s) ds}{\int_0^\infty s^2 I_s(s) ds}$$

Where, χ_c: mass fraction crystallinity, I_c: intensity of crystalline scattering, I_s: intensity of total scattering, S = 2sin(θ/λ), λ = 1.54 Å, θ: Bragg’s angle

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, cos² φ_{c,z} = 1 - 1.099 cos² φ_{110,z} - 0.901 cos² φ_{040,z}

The cos² φ_{110,z} and cos² φ_{040,z} were obtained from azimuth intensity distribution measurements of (110) and (040) reflections according to the equation [10]

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

where, I(φ) is the intensity diffracted from the (hkl) planes normal to 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 method [11].

Birefringence and Amorphous Orientation Function

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

The birefringence is 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 is calculated using the equation [12]

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

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 [13].

Volume Fraction of Voids

The volume fraction of voids (φ_v) in the drawn filament is

estimated from the X-ray crystallinity and density values as per the relationship proposed by Bodaghi *et al.* [14].

$$\Phi_v = \frac{1 - \rho_s \chi_c}{\rho_c} - \frac{\rho_s(1 - \chi_c)}{\rho_{am}}$$

Where, ρ_s , ρ_c , ρ_{am} and χ_c is measured sample density, density of crystalline PP, density of amorphous PP and sample X-ray crystallinity respectively. ρ_c and ρ_{am} values are taken as 0.936 g/cc and 0.857 g/cc respectively.

Results and Discussion

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

Initial modulus of drawn polymer as seen from Table 2 is a unique function of the draw ratio quite independent of the initial morphology and the molecular weight. Gradient drawn polypropylene samples are characterised by high draw ratios coupled with high initial modulus. While tensile modulus reflects the average structure, tensile strength relates to the weakest position in the structure. The tensile strength of fibers is determined by intrinsic parameters like the intrinsic elastic modulus of the parent polymer, the intermolecular bonds and the chain length distribution. Post spinning operations improves the mechanical properties but also introduces defects like inhomogeneities and voids. Thus generally at very high draw ratio though the modulus increases, strength suffers. In case of gradient drawing however, high modulus coupled with high tenacity values are obtained due to the unique microstructure developed which is discussed subsequently.

Table 2. Filament tensile properties

Sample ID	Draw ratio	Initial modulus (Gpa)	Tenacity (Mpa)	Energy (kg-mm)	Elongn. (%)
GD1	17.4	14.4	670	675	7
GD2	16.4	14	540	560	6
GD3	18.7	16.4	640	541	6
CT	16	13.1	460	500	5

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

Sample ID	Birefringence	Xray crystallinity (%)	f_c	f_a
GD1	0.033	65	0.96	0.73
GD2	0.032	62	0.97	0.71
GD3	0.034	71	0.98	0.80
CT	0.031	61	0.94	0.68

Microstructure

As 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 had been made by Yamada [15].

The amorphous orientation values increase remarkably and reach a maximum of 0.8 for GD3 sample. The high modulus and tenacity values of the sample GD1 and GD3 are a result of the very high amorphous orientation values. Stretching of filaments cause chain slip through the crystals, sliding and breakage of tie chains and 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 transmit effectively the stress between crystallites.

In gradient drawing process, the heater plate acts as if consisting of a series of a large number of heaters with increasing temperature. With each increase of temperature some molecules become mobile, get oriented under stress and tend to crystallize. In the process, filaments get gradually stabilized with the increased temperature profile. In constant temperature drawing, where a filament was exposed to a sudden 'shock' of temperature, the draw stresses are high with resultant inferior properties. Thus gradient drawing is a superior method than constant temperature drawing for producing filaments with superior mechanical properties.

Table 4 gives the values of void fractions of the gradient drawn and constant temperature drawn sample. The very low void fractions for almost all the gradient drawn samples have been their noticeable characteristic.

Gradient drawing allows high draw ratios with low void content. It is interesting to note that inspite of the high draw ratio of GD3 it shows a very low void fraction. The incremental drawing over the gradient heater approaching the melting point results in low drawing stress characterised by near absence of voids (9×10^{-4}) and is one of the main reasons behind the high tenacity values of GD3 sample. Samples drawn over a constantly increasing temperature gradient had a relatively higher void fraction value.

Effect of Nature of Gradient

Gradients which tend to stabilise over the initial or the

Table 4. Density crystallinity, X-ray crystallinity and Void fraction

Sample ID	Density crystallinity (%)	Xray crystallinity (%)	Void fraction ($\times 10^{-4}$)
GD1	58	65	34
GD2	55	62	72
GD3	67	71	9
CT	52	61	112

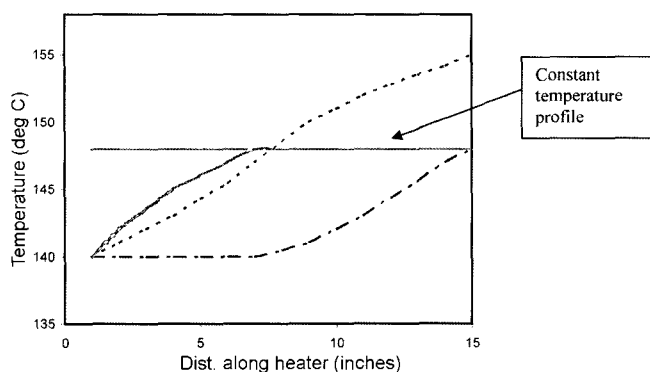


Figure 3. Different gradients tried on the heater vs the constant temperature profile.

final zone resulted in better filament properties. This may be because of the fact that the heat transfer is not proper for a continuously increasing temperature field. A stable temperature field on the start prepares the filament for an increasing temperature gradient, which happens for GD1 while the oriented filament as a result of an initial temperature gradient get a chance to be stabilised at the end for GD3. Overall GD3 showed the best properties. This shows that the filament which gets more time to be in the higher temperature regime results in a superior structure. In a gradient heater with an end stabilising zone, drawing and heat setting take place simultaneously. Thus even thermal properties are better for such filaments. For a full discussion on the thermal properties and effect on a different MFI polypropylene the reader is referred to separate communications [16,17].

Conclusion

The gradient drawing process has achieved higher modulus values compared to the normal temperature drawing of filaments. Highest tenacity of 670 MPa and modulus of 16.4 GPa has been achieved by the gradient drawing process. Gradient drawing process has achieved a high crystallinity of 71 % and amorphous orientation factor of 0.80 resulting in superior mechanical properties compared to the constant temperature drawing on comparable temperature scales. The advantage of the gradient heater lies in the fact that it allows

the filament to be drawn on a higher temperature range with minimum void formation and consequently superior mechanical properties. The process has the greatest advantage of being continuous in nature.

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