Studies on Production of Polypropylene Filaments with Increased Temperature Stability

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ABSTRACT: High Modulus high tenacity polypropylene filaments have been prepared by drawing them on a heater with a gradient of temperature. The thermal properties have been analyzed, and the effects of nature of the gradient and end temperatures on thermal properties of the filament have been investigated for such filaments. Low shrinkage values even at 150°C, high retention of storage modulus in dynamic mechanical analyses and very low change in length in thermomechanical analyses have been the characteristic of the gradient drawn filaments. The filaments have high crystallinity, crystal perfection, and crystal orientation. In addition, the reported process has the advantage of being continuous in nature. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 838–842, 2006

Key words: polypropylene; filament; drawing

INTRODUCTION

Polypropylene (PP) filaments, due to their low cost and excellent mechanical properties, are widely used in carpet backing, ropes, and many other domestic and industrial applications, where a medium tenacity is required. Polypropylene filaments have the shortcoming of having poor thermal stability. The softening point of polypropylene filaments is around 130°C, which is often very low for most applications. Because of their low cost, PP filaments can also be used as reinforcement in composite materials, but even in such applications a high thermal stability of PP is required. There has been some work[1,2] directed to produce filaments having better thermal stability but all of them were batch processes. This study describes a continuous production of polypropylene filaments with higher thermally stability.

EXPERIMENTAL

Polypropylene fibers are extruded from 35 MFI homopolymer sourced from Reliance (India) in a single-screw extruder having an L/D ratio of 20. The temperature profile used for the extrusion was 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 was 15.8 m/min. The monofilament was quenched by ice cooled water kept at 4°C and at a distance of 2 cm below the spinneret level. The as-spun filament was drawn in sequence over heater plates at temperatures of 60 and 120°C to the maximum permissible draw ratio without whitening. Additional drawing step was carried out on a heater having a gradient of temperature which was the novelty of the process.

The gradient heating arrangement[2] (Fig. 1) consists of three heating elements separately sensed by K-type thermocouples and controlled by PID type controllers, which controls temperature to an accuracy of 0.1°C. A small air gap between the heating elements ensures that the heaters act independent of each other. The top heater plate, overlaying the heating elements, being continuous, shows a gradient of temperature. The filament was drawn at a draw rate of 2 m/min and, thus, was subjected to a total time of around 14 s on the gradient heater, the length of the gradient heater being around 47 cm.

The temperature of the heating elements can be raised to control end temperatures and nature of gradient on the heater plate. The temperature on the heater plate was physically sensed every time with a contact type temperature sensor before experiments, since the room temperature and humidity affects temperature of the heater plate.

Several gradients of temperature in terms of starting, middle, and end temperatures have been tried, but only those gradients that resulted in filaments having excellent thermal properties are reported. To compare gradient drawing process with constant-temperature-drawn samples, the filaments were drawn over constant temperatures of 140°C (35W), 150°C

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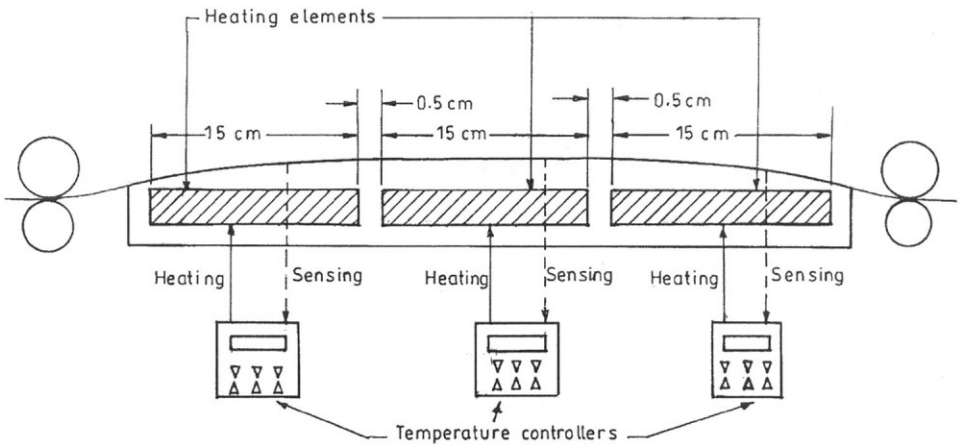

Figure 1 Schematic representation of a gradient heater.

(35X), and 160°C (35Y). Above 160°C, drawing was not possible because of filament breakage or high unevenness in the drawn filament.

Free shrinkage

Free thermal shrinkage was measured by treating 10 cm of the filament in constant temperature silicon oil bath for 5 min. Temperatures selected for free shrinkage measurements are 120 and 150°C. Ten readings are taken for each test and the average values reported.

X-ray crystallinity, crystallite width, and 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:

$$\chi_c = \frac{\int_0^\infty s^2 I_c(s) ds}{\int_0^\infty s^2 I_0(s) ds}$$

where, χ_c = mass fraction crystallinity; I_c = intensity of crystalline scattering; I_s = intensity of total scattering;

$S = 2 \sin\frac{\theta}{\lambda}$; $\lambda = 1.54$ Å; θ = Bragg's angle.

The average lateral crystalline thickness was estimated from the broadening observed in the WAXD pattern recorded for 2θ range of 10–35°, at a scanning rate of 2° min^{-1}. The integral breadth of the diffraction intensity arising from the imperfection of crystallites was measured in terms of $\beta_{1/2}$ (*hkl*).

Apparent crystalline size was determined according to the Scherer's equation:

$$D_{(hkl)} = \frac{K\lambda}{\beta \cos\theta}$$

where, β is the half width of the diffraction peak in radian, K is taken to be unity, θ is the Bragg's angle, and λ is the wave length of the X-rays. The values of $D_{(hkl)}$ for (110) reflection was calculated.

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 equation[3]

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

where, $I(\phi)$ 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.

Thermomechanical analysis

Thermomechanical analysis was done in a Perkin–Elmer TMA 7 analyzer at a force of 60 mN from 50 to

TABLE I
X-ray Microstructure, Melting, and Shrinkage Values

Sample ID	Temperature gradient	X-ray peak half width (degrees)	X-ray crystallinity (%)	Crystallite orientation	Shrinkage at 120°C (%)	Shrinkage at 150°C (%)
35 W	140–140-140	6	56	0.93	8	14
35 L	140–160-160	3.6	62	0.97	7	9
35 X	150–150-150	5.3	58	0.95	4	12
35 Y	160–160-160	5.1	60	0.96	4	11
35 N	160–160-165	5.3	66	0.97	3	9
35 Q	160–168-168	5.5	70	0.98	2	7

150°C at a heating rate of 5°C/min. The linear coefficient of expansion "α" is given by

$$\alpha = \Delta L/(L\,\Delta T)$$

where, L is the original length of the sample, ΔL is the change in length of the sample and ΔT is the temperature change.

Dynamic mechanical properties

The dynamic mechanical properties have been analyzed with Perkin–Elmer DMA7, at 1 Hz frequency, strain amplitude of 0.02%, and as a function of temperature from −50°C to 155°C with a heating rate of 10°C/min. The gauge length of the sample was 5 mm. The storage modulus (E′) and loss factor E″/E′ (tan δ) were recorded with temperature, where E″ is the loss modulus.

RESULTS AND DISCUSSION

Thermal shrinkage

The thermal shrinkage of select samples with designated gradient is reported in Table I. Shrinkage experiments have been conducted at 120 and 150°C respectively. Low shrinkage values are observed for gradient drawn samples. Sample 35Q showed a very low value of 7% shrinkage at 150°C, indicating very high dimensional stability of the sample.

It is observed that low shrinkage values may be associated with high values of X-ray crystallinity. High crystallinity is due to drawing carried out at fairly high temperatures enabled by the gradient drawing process. Such high crystallinity along with high crystalline orientation of ~0.97 for most of the samples and 0.986 for sample 35Q probably leads to the formation of lateral crystal bridges restricting molecular movement in the amorphous zones. Such filaments are expected to have low shrinkage values.

The gradient drawing process leads to mobility of chains at each incremental temperature and stabilizing the filaments at that temperature. This allows the drawing process to be accomplished at comparatively higher temperatures. It is suggested that the gradient heater acts as a combination of infinite numbers of heaters each having a discreet temperature working in sequence. In this way, the filaments are drawn on a gradual manner in a steadily increasing temperature field.

Qin et al.[1] have reported a value of 18.3% at 150°C for pure PP filaments. Kar[2] has reported a relatively low value of 7.8% at 160°C for a PP sample prepared by the Draw Heat Set process. The gradient drawing process, however, results in better thermal stability of PP filaments with a continuous process when compared to batch processes of Qin et al. and Kar.

Thermomechanical properties

To observe the thermal stability of the filaments, thermomechanical (TMA) experiments were conducted with a load of 60 MN applied during the heating process. The TMA observations are shown in Figure 2.

It was observed that length of the samples is stable upto temperatures of around 105°C for samples 35L and ~112°C for samples 35N and 35Q exposed to higher end temperatures on the gradient heater. All of the gradient drawn samples are characterized by very low coefficient of expansion "α" values as shown in Table II, indicating very high dimensional stability. 35Q had a total nominal change in length of 0.52% upto 150°C and a very low coefficient of thermal expansion of -9.49×10^{-5} from 86 to 150°C. 35Q being

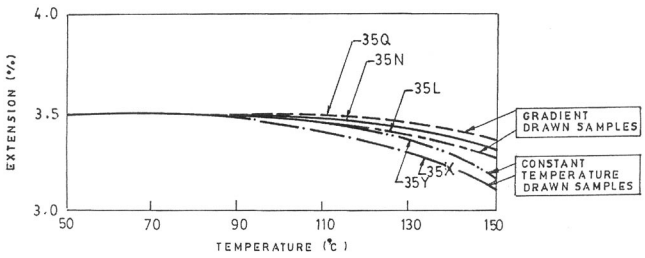

Figure 2 Thermomechanical properties of gradient drawn vis-à-vis constant temperature drawn samples.

TABLE II
Thermomechanical Properties of Filaments

Sample ID	Temperature range for heating scan in TMA (°C)	α (°C)
35L	50–105	No change
	105–150	-2×10^{-4}
35X	50–82	No change
	82–150	-7.26×10^{-4}
35Y	50–88	No change
	88–150	-4.5×10^{-4}
35N	50–111	No change
	111–150	-2.6×10^{-4}
35Q	50–113	No change
	113–150	-1.3×10^{-4}

drawn at relatively high end temperature results in more perfect crystals stabilized at such high temperature. These findings are similar to observations reported by other authors.[4,5]

For the constant-temperature-drawn samples, 35X and 35Y there was relatively high change of length in the scale of observations. The temperature of inflection was 82°C for the constant-temperature-drawn sample at 140°C and increases to 88°C for the sample drawn at 150°C. Even this value was quite low when compared to the gradient drawn sample, which shows temperature stability till a minimum temperature of 105°C. The thermal expansion values for the constant-temperature-drawn samples on average are higher than the gradient drawn samples, which was indicative of lower thermal stability.

Dynamic mechanical properties

The storage modulus for the filaments is shown in Figure 3. Sample 35Q showed a very high modulus of 26.5 GPa. It retains very high value of storage modulus of 12 GPa even at temperature of 140°C, which is better than the storage modulus of 10 GPa, reported by Kar[2] for the best draw-heat set polypropylene filament at 140°C. Even at 155°C, sample 35Q has a relatively high storage modulus of 950 MPa. Samples 35Q and 35N drawn at the same starting temperature of 140°C showed a similar behavior in terms of storage modulus. A similar trend was observed for 35L, which were drawn on a gradient starting at 160°C. Secondary crystallization is observed for the constant-temperature-drawn sample in the heating scan. This is due to lower organized constant-temperature-drawn sample gets a chance to reorganize in the heating scan.

The tan δ curve of PP generally exhibits relaxations localized in the vicinity of -80°C (γ), 10°C (β), and 100°C (α). The β-transition in the interval between $T = -20$°C and 10°C is associated with the glass transition in the most mobile part of the amorphous phase,

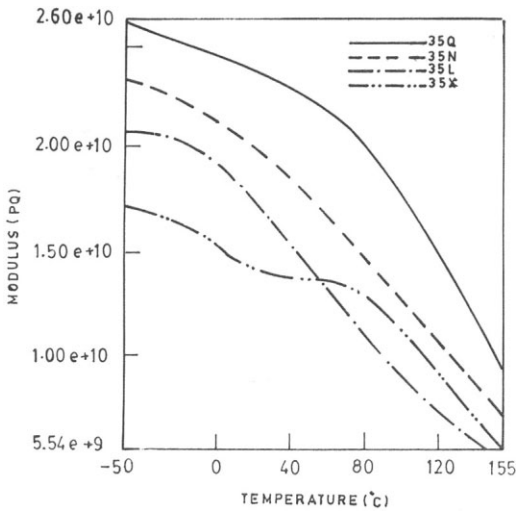

Figure 3 Storage modulus of gradient drawn vis-à-vis constant temperature drawn samples.

whereas the other maximum (α-transition in the interval between $T = 70$ and 110°C) is attributed to the glass transition in the remaining part of the amorphous phase—the rigid amorphous fraction.

As evident from Figure 4, 35X show a β transition peak at around 45°C. The constant-temperature-drawn sample having a higher amorphous content and less hindrance of movement for the amorphous material because of lower crystal orientation shows a distinct β transition. The tan δ curves of the gradient drawn samples are marked by the absence of the β-transition, which is due to the high crystallinity achieved through the gradient drawing process. They also indicate that the residual amorphous content in the gradient drawn samples are majorly 'rigid'.

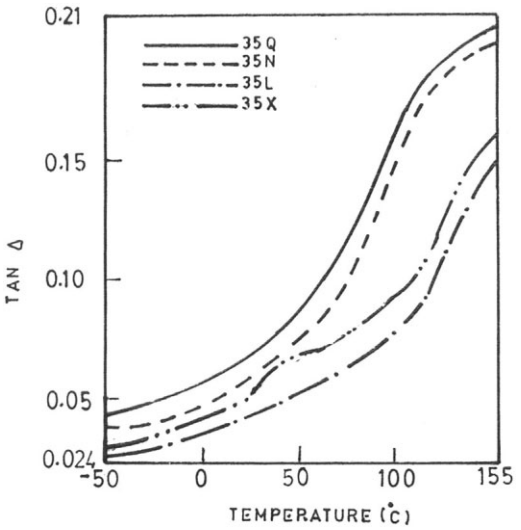

Figure 4 Tan δ spectra of gradient drawn vis-à-vis constant temperature drawn samples.

For filaments drawn over constant temperature heater, it can be observed that there is higher free shrinkage and lower modulus retention properties. No drawing was possible over a constant temperature heater at 168°C, but gradient heater allows drawing filaments with end temperatures of 168°C. In gradient drawing process, the heater plate can be considered as 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. Further in this process, filaments get stabilized with each increase of temperature. There may be partial melting and recrystallization of polymeric molecules at such high temperatures resulting in the formation of more perfect crystallites. The ultimate result was a structure having high crystallinity and crystals bridges. In a 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 proves to be superior to constant temperature drawing for producing filaments with superior thermal properties.

CONCLUSIONS

Gradient drawn filaments are characterized by low free shrinkage value of 7% at 150°C and a very high modulus of 26.5 GPa. The gradient drawing process results in high levels of crystallinity and dimensional stability for filaments. The half width of melting of around 4°C shows a very narrow range of crystal sizes. Thermomechanical analysis carried out attained a low α values of -1.3×10^{-4}. High thermal stability indicate existence of crystal bridges restricting the disorientation of amorphous zones, which is further supported by delayed and faint tan δ transitions and absence of transitions in case of the highest crystallinity achieved. Remarkably low shrinkage values for gradient drawn samples have been obtained.

The advantage of the gradient heater lies in the fact that it allows the filament to be drawn on a higher temperature range in which drawing on a constant temperature heater is not possible. In addition to all the properties, the process has the advantage of being continuous in nature.

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