Hot Nip Drawing: A Rapid Method of Producing High Modulus Polypropylene Films

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Synopsis

There are many methods currently producing high modulus and high strength films and fibers in industry. This publication examines the results of a hot nip drawing process to produce high modulus PP films at a relatively rapid production rate. The effects of both temperature and rate of draw on the drawn material will also be examined.

INTRODUCTION

The production of high modulus films and fibers by various deformation methods carried out on thermoplastics has become common place. Deformation processes such as roller drawing,[1] hydrostatic extrusion,[2,3] solid state extrusion,[4] gel spinning/hot drawing,[5-7] superdrawing,[8,9] and zone annealing[10] have been employed to try and achieve the highest possible strength and modulus through orientation. The gel spinning/hot drawing technique currently produces the highest strength and modulus fibers of polyethylene (PE). The moduli of these fibers have been reported to be as high as 120 GPa[6] with a breaking tensile strength just over 4.0 GPa.[7] A similar technique, drawing dry gels crystallized from dilute solution, currently produces the highest strength and modulus polypropylene (PP) films with a Young's modulus of 36 GPa and a tensile strength of 1.03 GPa.[11]

Gel spinning and drawing of dry gels are both excellent methods for producing high strength fibers and films, but they have a number of inherent problems. Generally speaking, the techniques are high technology methods requiring specific polymer molecular weights and distributions. In addition, the gel spinning technique requires extensive solvent removal schemes such that the cost for these polyolefin fibers is comparable to that of acid spun high temperature aromatic polyamides. Methods which avoid solvents typically produce materials with significantly lower mechanical properties and/or the rate of production do not offer much hope of being commercial in the forseeable future.

Recently Kaito et al.[1] have proposed a hot roller-drawing method of forming high modulus high strength films. An attempt is being made to produce PE films with large draw ratios that can be controlled by roller spacing and draw velocity. Another group of researchers, Kunugi et al.,[10] have

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proposed a "zone-annealing" method to improve the mechanical properties of various polymers including PP.[10,12-16]

For the past 4 years we have been producing films with similar properties through tensile drawing with a heating device. It is desirable that such a process be both continuous and applicable to either thin or thicker sheets. Certainly our method can be readily modified to accomplish this goal; furthermore, control of the draw ratio is possible by adjusting draw velocity and/or draw temperature.

EXPERIMENTAL

Material

The samples in these hot draw experiments were strips (20 cm long by 5 cm wide) cut from translucent extruded sheets of polypropylene (PP) approximately 0.80 mm thick. The PP designated as PP 5225 (M_n = 50,000 M_w = 600,000) was produced by the Shell Development Co. and contains no plasticizers but does contain small amount of stabilizers.

Hot Nip Drawing

After samples were cut from extruded sheets of PP, each was marked with a felt tip pen every centimeter along its length so that a draw ratio ($\lambda = l/l_0$) could be obtained at the end of the experiment. These samples were then creased across their width and mounted in specially designed grips. Once mounted, a heating device (Fig. 1) was attached to the top of the sheet so that it rode on the slight indentation made by the crease. The sheet was then drawn at a constant rate (10, 25, 50, or 100 cm/min) by an Instron Tensile Tester. The neck produced traveled downward presumably because of the weight of the heating device, which stayed in contact with the newly forming neck. The drawing load was measured by an Instron 500 kg reversible load cell.

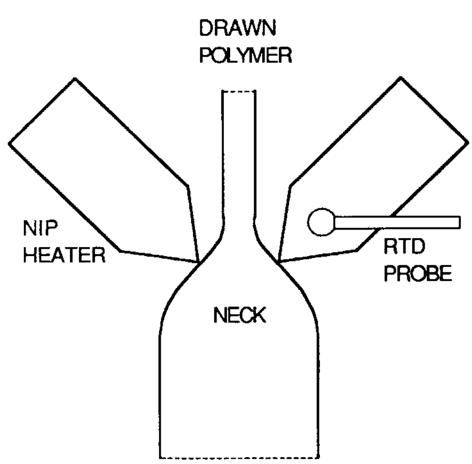

Fig. 1. Schematic diagram of the not nip apparatus.

This drawing procedure was repeated several times at each of the four crosshead speeds while varying the temperature of the hot nip apparatus. To determine the draw ratio (λ), we took two or three measurements of the new separation of marks from near the center of the drawn sample and averaged them. After λ was determined, strips 10.0 cm long by 0.60 cm wide were cut out of the drawn material. The thicknesses of these films were measured, and then samples were remounted into the Instron grips so that their modulus could be determined. The moduli tests were carried out at 23°C with a draw velocity of 1 cm/min, a gage length of 2.0 in., and were drawn to approximately 1% deformation.

To obtain draw ratios greater than 12–13, a second draw or a redraw was necessary. Since a film that has already been drawn once cannot easily be creased, the heater did not have an indentation to ride on and a new method of attaching the hot nip apparatus had to be devised. During the redraw process the heating device was attached to the moving crosshead. To avoid sample failure, crosshead speed had to be slow (1 cm/min) and the temperature of the hot nip apparatus had to be near the melting temperature of the PP sheet. The cross sections of these films were remeasured and remounted into the Instron for moduli measurements.

RESULTS AND DISCUSSION

Appearance

The optical properties of the hot drawn films ranged from transparent to opague depending on the draw temperature. Lower draw temperatures yielded opaque films while higher draw temperatures produced transparent material. The opaqueness of drawn sheet is presumably due to the formation of microvoids in the deformation region which allows large length increases with little to no cross-sectional area reduction.[17] Transparent films produced at higher temperatures presumably never had these microvoids, or the voids are closed soon after they are formed due to the lower viscosity/higher polymer mobility at these higher draw temperatures.

Previously drawn films, when redrawn to $\lambda > 16$, tended to fibrillate or split during the redraw process. A possible explanation, on a molecular or microscopic level, is that because the films and molecules are oriented in the draw direction, only weak van der Waals interactions are present between molecules which serve to hold aligned elements together. In the low to completely unoriented undrawn sheet, the initial presence of strong chemical bonds in all directions will tend to reduce the possibility of fibrillation or splitting.[18]

Draw Ratio

The λ's of the films were measured and plotted against draw temperature (Fig. 2); the temperature used was that measured by an RTD probe (platinum resistance thermocouple) in a hole drilled into the heating device. The maximum λ with a single draw (12.5) occurred at approximately 115°C with a draw velocity of 100 cm/min. Below 115°C, films broke across their width presumably due to an increase in the drawing stress due to the inability of polymer chains to reorganize and accommodate the imposed strain. As temperature is

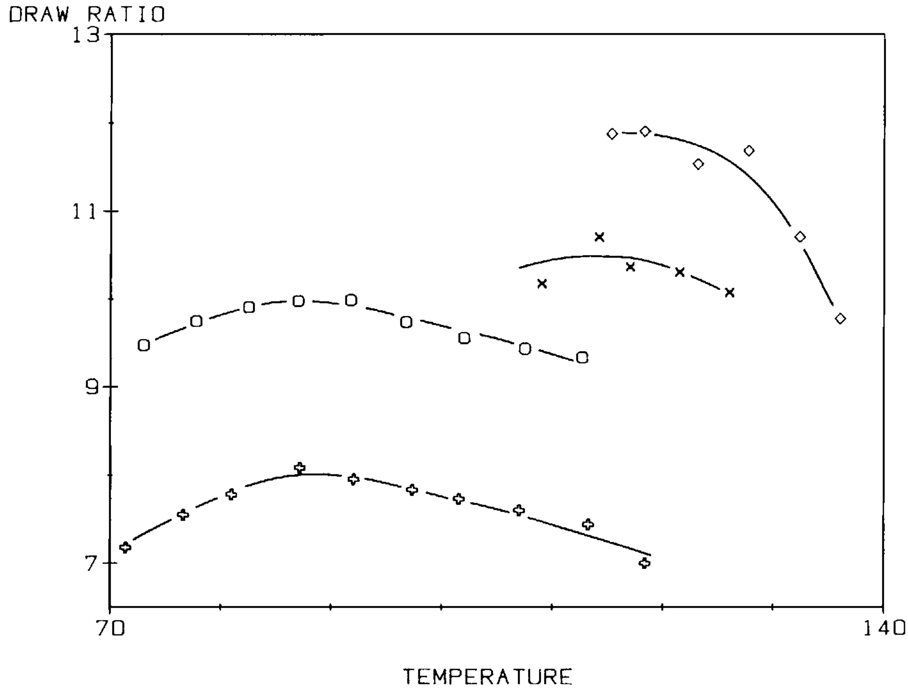

Fig. 2. Draw ratios (λ's) of PP 5225 at various temperatures for the following deformation rates (cm/min): (+) 10; (○) 25; (×) 50; (◇) 100.

increased above 115°C, chain mobility is enhanced, and one might expect more rapid disentanglement and a corresponding ease of chain alignment; this is not found to be the case. The increased chain mobility at higher temperatures also causes an increased tendency to randomization of chain orientation. At higher temperatures there is a higher driving force to return to the undeformed state (elastic recovery) before recrystallization "sets" the structure. Therefore, the drawing temperature which produces the maximum λ is determined by a delicate balance between elastic recovery, chain slippage, and a "setting" of the structure by recrystallization.[17]

Tensile Properties

The tensile properties of drawn PP sheet are shown in Figures 3 and 4; both Young's modulus and tensile strength increase with increasing draw ratio. The maximum value for Young's modulus is 13.2 GPa for a film with a draw ratio of approximately 26 (twice drawn). Young's modulus for our highest single draw (λ = 12.5) was 4.5–5.0 GPa. Kunugi et al.[10] reported a maximum Young's modulus of 17.2 GPa for their "zone-annealing method." This method requires five zone drawing steps at relatively slow drawing rates (4.0 cm/min) accompanied by 12 zone annealing steps. When Kunugi et al.[10] prepared a fiber by a one-step zone-drawing method, Young's modulus was 3.82 GPa. This value is slightly lower than our best once drawn film, which we can produce at 100 cm/min; this is approximately 25 times faster than the zone-draw method.

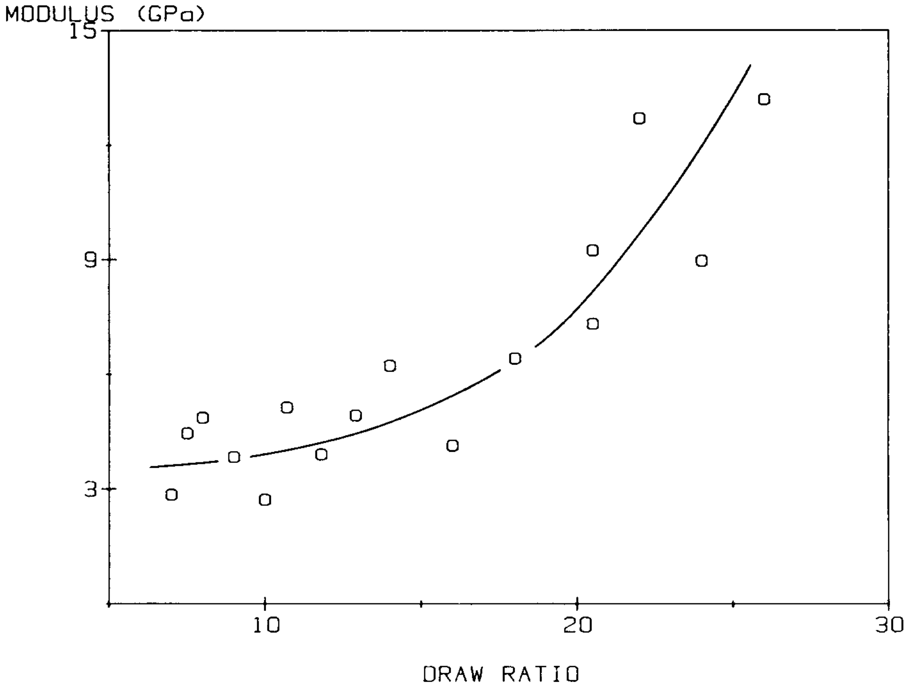

Fig. 3. Young's modulus (GPa) vs. draw ratio for PP 5225 tested at 1.0 cm/min at 23°C.

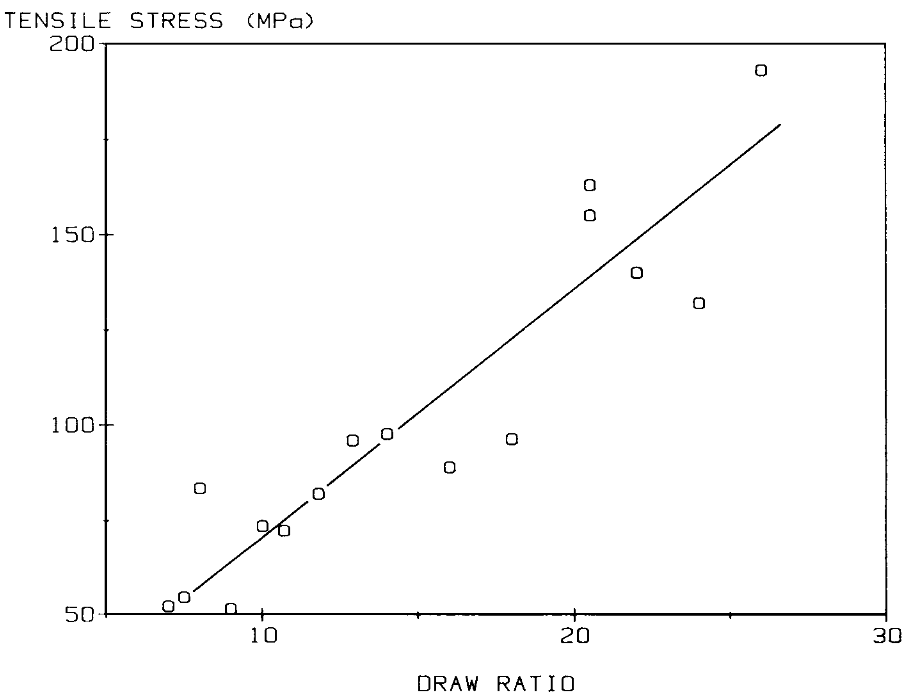

Fig. 4. Tensile strength (MPa) vs. draw ratio for PP 5225 tested at 1.0 cm/min at 23°C.

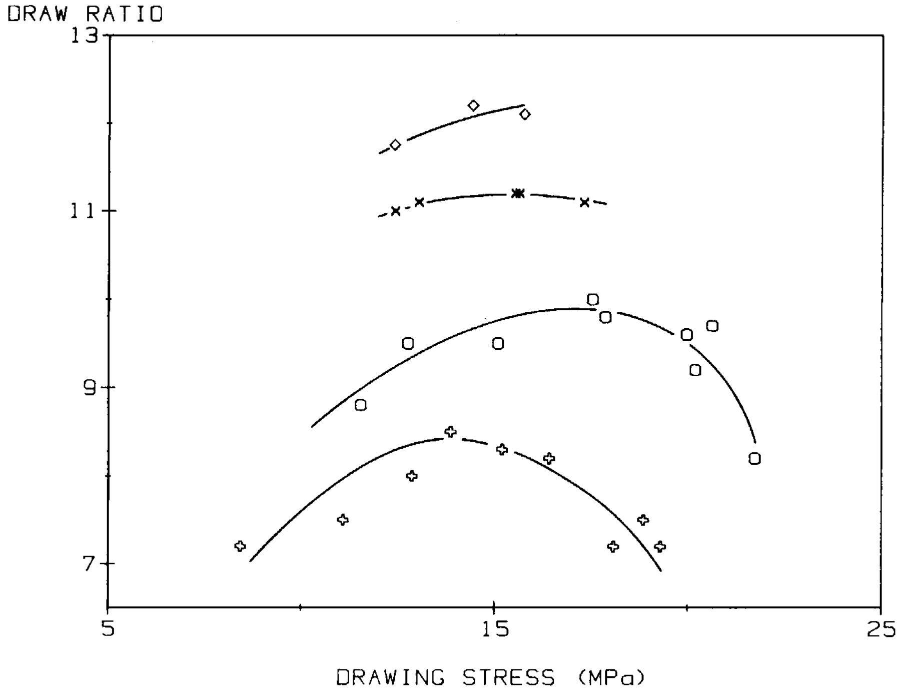

Fig. 5. Draw ratio (λ) vs. drawing stress (MPa) for PP 5225 for the following deformation rates (cm/min): (+) 10; (○) 25; (×) 50; (◇) 100.

In Figure 5, draw ratios are plotted against drawing stress for each of the four crosshead rates. It is seen that the drawing stress does not increase substantially when the rate of film production and/or draw ratio is increased. However, as one goes to higher drawing rates, the temperature range at which one can operate and stay within these drawing stresses becomes narrower. This means that at higher drawing rates one must operate as close to the optimum drawing temperature as possible or risk catastrophic failure.

CONCLUSION

There are several different methods of producing high modulus high strength films and fibers, with each method having its own merits and drawbacks. The process described in this publication can help increase the "natural" draw ratio by controlling the temperature at the neck at a given draw rate. The draw ratio is a function of the temperature of the heating device, with the highest draw ratio produced at an optimum temperature for a particular rate of draw. This method can be easily applied to either thin film or thicker sheet. The hot nip draw method currently does not produce the highest modulus or strength films. However, this method has a number of advantages namely; it is free from solvent handling problems; it has relatively fast production rates (presently 100 cm/min); and it produces film with little "neck-in" from the original sheet. Studies are currently underway to improve both the speed of production and the draw ratio/modulus of the film produced.

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