

# High Modulus Polypropylene Fibers. I. Mechanical Properties

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**ABSTRACT:** Extensive studies concerning the spinning and drawing of polypropylene resulted in a method for production of high modulus fibers under industrially feasible conditions. The fibers were produced in a conventional melt spinning and drawing process that was optimized in order to increase the elastic modulus of fibers. By such optimization of the process, a tensile strength of around 8 cN/dtex, an elastic modulus up to 14.7 GPa, and a dynamic modulus up to 19 GPa were attained. In this study the mechanical properties of polypropylene fibers were investigated, which were spun from fiber grade controlled rheology (CR) polymers and from the blends of a fiber grade CR polymer with a molding grade polymer in the composition range of 10–50 wt %. The addition of the molding grade

polymer to the fiber grade CR polymer resulted in lower tensile strength and moduli, with one exception. By blending a CR polymer with 10% of the molding grade polymer, maximization of the elastic and dynamic modulus was achieved. The predicted modulus of a two-phase blend, calculated from several representative equations, was compared with the elastic modulus of drawn fibers, determined from the specific stress versus strain curve, and the dynamic modulus, obtained from the sound velocity measurements. The best fit was achieved with the Kleiner simplex equation. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1–8, 2005

**Key words:** polypropylene; mechanical properties; elastic modulus

## INTRODUCTION

A number of techniques and methods have been developed to produce high modulus polypropylene (PP) fibers and films.<sup>1–13</sup> The gel spinning/hot drawing technique<sup>9,10</sup> currently produces the highest strength and modulus fibers of polyethylene and PP. A similar laboratory technique, drawing dry gels crystallized from dilute solutions,<sup>12,13</sup> gives PP films with an elastic modulus of 40.4 GPa and a tenacity of 1.6 GPa. Gel spinning is an excellent method for producing high modulus fibers, but it requires a specific polymer with a very high molecular weight (from 1 to several millions) and extensive solvent removal, resulting in a high price for these fibers. Other methods that avoid solvents are based on melt spinning and drawing under special conditions,<sup>1–5</sup> which is slow stretching on a tensile testing machine or in an oven resulting in an elastic modulus in the range from 10 to 22 GPa, and on solid state extrusion,<sup>6–8</sup> which is hydrostatic extrusion or die drawing followed by slow stretching, giving PP fibers with values of 17 and 20 GPa. The common deficiency of all these methods or more ex-

actly laboratory processes is the extremely low rate of production connected with high costs. That is why the aim of our work was to develop a more economical method based on an improved melt spinning and drawing process under industrially feasible conditions. We also investigated the possibility of producing high modulus PP fibers from binary polymer blends of different molecular weights. The tensile properties of these fibers are presented, whereas the structure of these fibers will be presented in Part II of this series.

## EXPERIMENTAL

### Preparation of PP fibers

Fibers were spun from a blend of two commercial PP chips, Hostalen PPU 1780F2, a fiber grade controlled rheology (CR) polymer with a melt flow rate of 18 g/10 min, and Hostalen PPN 1060F, a molding grade homopolymer with a melt flow rate of 2 g/10 min. Hostalen PPN 1060F is a broad molecular weight distribution polymer with a weight-average to number-average molecular weight ratio ( $M_w/M_n$ ) of 5, whereas Hostalen PPU 1780F2 is a narrow molecular weight distribution polymer (CR polymer) with an  $M_w/M_n$  of 3.3. Five blend samples were prepared by blending the fiber grade polymer with 10, 20, 30, and 50% of the molding grade CR polymer by weight.

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Several fibers were produced by melt spinning from these polymer blends and from the pure fiber grade polymer.

The melt spinning and in-line drawing of PP fibers was carried out on an Extrusion Systems Ltd. laboratory spin-draw device. From preceding experiments<sup>14</sup> the optimal process path variables were established in order to achieve maximal elastic modulus of the fibers that were produced. The polymers were extruded at a rate of 30.1 g/min through a spinneret with 10 holes (0.35-mm diameter each). The temperature of the melt at the spinneret was 245°C. Cooling of the resultant filaments was achieved with cross-flow air quenching at 7°C. The as-spun filaments were three-stage drawn at 50°C, with an overall draw ratio of 15.3, in a continuous spin-drawing process. These series I fibers are termed continuously drawn fibers. Continuously moderately drawn fibers were additionally drawn on a Zimmer laboratory draw device. In this subsequent slower stage the fibers were drawn through a hot plate at 145°C to the limiting draw ratio. No separate heat setting step was carried out. These series II fibers are termed discontinuously drawn fibers.

### Tensile testing

The tensile properties of the PP fibers of series I (continuously drawn fibers) and series II (discontinuously drawn fibers) were measured with an Instron 6022 tensile testing machine. Samples with an initial gauge length of 25 cm were stretched at a crosshead speed of 1.6 mm/s for discontinuously drawn fibers and 5.5 mm/s for continuously drawn fibers. Conventional specific stress-strain data were obtained under conditions of controlled temperature and humidity ( $T = 21$ , relative humidity = 65%). The mechanical data presented in this article are the average of 50 parallels and specific stress-strain curves of are the average of 20 parallels.

## RESULTS AND DISCUSSION

### Studies of spinnability and drawability

PP melts are noted for their high viscosity. Only polymers with low molecular weight, that is, with high melt flow rate (about 20) and narrow molecular weight distribution, so-called fiber grade polymers, are known for their good spinnability and drawability. With increasing polymer molecular weight, the deviation from Newtonian behavior is more pronounced and the relaxation spectrum of molecules is extended to longer times, which leads to spinline instabilities and ductile filament failure. Because of poor spinnability of high molecular weight polymers, also called molding grade polymers, they are inconvenient for conventional melt spinning. For these polymers the

range of temperatures in which spinning is practically possible can be adjusted by raising the temperature of the melt. In our case the optimum spinning temperature of the fiber grade CR polymer was found to be around 235°C and that of the molding grade polymer was around 285°C. The spinnability of blends was altered when adding the molding grade polymer to the fiber grade CR polymer. The temperature range of the polymer blends was limited at the lower temperature range because of a brittle fracture of the extruded polymer jet and with the polymer degradation and capillary break of the polymer jet at the higher temperature range. The optimum spinning temperature of most blends was found to be 245°C. When the blend composition reached 60/40 fiber/molding grade polymers, the first spinline instabilities were observed at this temperature. The blend composed of 50/50 fiber/molding grade polymers also showed an early stage occurrence of melt fracture. Although some instabilities occurred, the temperature was kept at 245°C to avoid the change of the process path variables.

It is also convenient to keep the melt temperature as low as possible to avoid thermal degradation of the PP macromolecules and a drop in pressure. Higher pressure is desirable because an improved temperature uniformity of the melt can be obtained, resulting in more uniformly spun filaments. The unnecessary degradation of the macromolecules and a loss of longer macromolecules were minimized with the higher mass output rate through the spinneret holes. PP is very prone to the melt spinning instability known as draw resonance and melt fracture. With the raising of the mass output rate the tendency to spinline instabilities increases and limits the spinning speed. To avoid onset of these instabilities, the draw down ratio was kept as low as possible. In contrast, the high mass output rate of 21.7 g/min and the low draw down ratio of 2.1 resulted in a pronounced die swell. The swelling of the emerging jet can cause difficulties in the elongation of the molten filament and affects the speed of spinning. Blends with the higher percent of added molding grade polymer displayed greater die swell and consequently the onset of the draw resonance. Thus, the spinning speed was adjusted for the undisturbed spinning and inline drawing of the blend composed of 50/50 fiber/molding grade polymers. The take-up speed of 425 m/min was then kept constant for spinning all other samples as well.

The rapid cooling of the extrudate jet was achieved with cross-flow air quenching. The air stream temperature was below 2°C, and the temperature of the air in the quench cabinet was 7°C. A high air stream speed can lead to uneven thickness of the filaments, but at given spinning conditions (245°C melt temperature, 21.7 g/min mass output, 2.1 draw down, 1.5-m spinline length) the rapid cooling was unavoidable. The

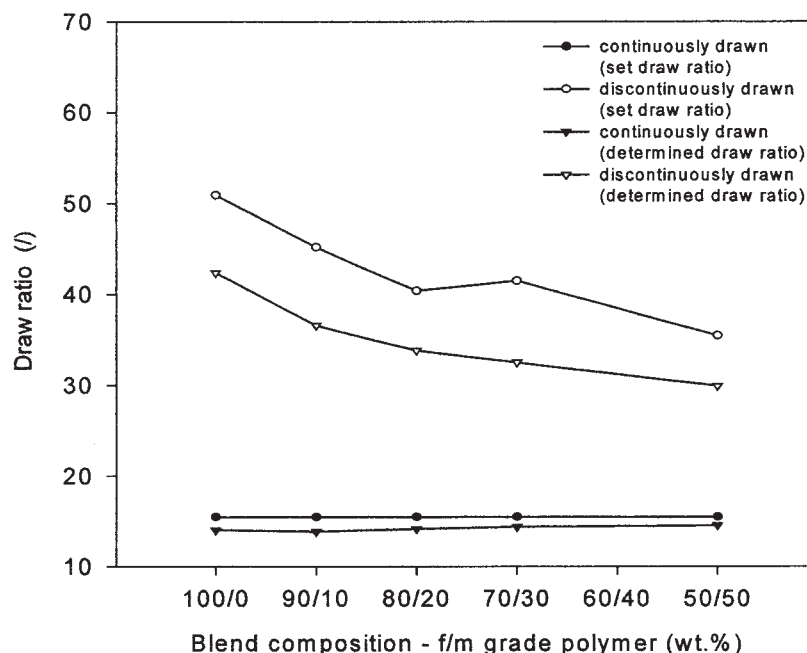


Figure 1 The variation of the draw ratio with the blend composition.

speed of the air stream was set to 0.31 m/s. The measured diameters of the filaments showed that the variation of the thickness was below 7% for all samples.

To attain good mechanical properties, the as-spun fibers were immediately drawn on a spin-drawing device. To avoid the change of the unstable crystalline structure in monoclinic form, immediate drawing was performed. The thermodynamically unstable structure formed by the rapid cooling of the extrudate jet allowed us to attain high draw ratios. Three-stage drawing was conducted so that uniform drawing without the filament breakage was achieved in all steps. A draw ratio of 15.3 was found to be the maximum attainable for filaments spun from the 50/50 fiber/molding grade polymer blends, and it was then kept constant for the other samples as well. The true draw-ratio given by the ratio of the measured linear densities of drawn and undrawn filaments was lower because of spontaneous relaxation of the filaments after the drawing was completed. A value of around 14.4 was determined for all samples, as seen in Figure 1.

It is well known that a higher overall draw ratio can be obtained with multistage drawing. The samples of series I were additionally drawn in a separate step at elevated temperatures. The drawing was carried out in a temperature range between 110 and 150°C to the limiting draw ratio. The highest draw ratio could be obtained at 145°C for all samples. The addition of the molding grade polymer to the fiber grade polymer resulted in the lowering of the drawability of the filaments spun from the blends. The fiber spun from the pure fiber grade CR polymer could be drawn to a

higher limiting draw ratio than fibers spun from the blends. The limiting draw ratio, which could be obtained for a given resin, was lowered almost linearly when raising the content of the molding grade polymer. The same decrease was seen for the true draw ratio determined from the ratio of the measured linear densities of discontinuously and continuously drawn filaments (Fig. 1).

### Mechanical properties

Figures 2 and 3 present the specific stress-strain curves of the continuously drawn and discontinuously drawn fibers, respectively, that were spun from the pure fiber grade CR polymer and from blends of this polymer with added molding grade polymer in the composition range of 10–50 wt %.

The continuously drawn fibers of low tensile strength and high toughness are easily extensible. The shape of the specific stress-strain curves (Fig. 2) shows, after an initial linear portion, a marked yield point, and, up to the break, a region of low slope, where large extensions are produced by small increases in the specific stress. These specific stress-strain curves show the typical characteristics for the ductile polymers, a maxima that corresponds to the initiation of necking, that is, yielding followed by the leveling off of the specific stress-strain curves, which corresponds to the neck propagation and drawing of the necked region. The blending has no effect on the occurrence of yielding, which appears at the extension at around 11.5% for all fibers. In contrast, there is a

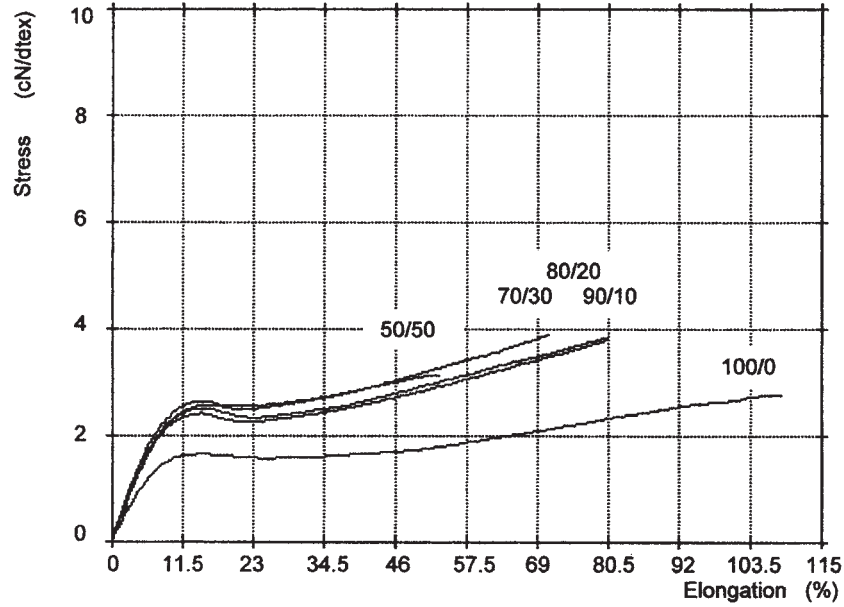


Figure 2 The specific stress versus strain curves of continuously drawn fibers.

pronounced effect of blending on the specific stress at which yielding occurs. The yield stress of the fibers spun from the blends with a value of around 2 cN/dtex, which represents more than 50% of the breaking specific stress, is much higher than the yield stress of the fiber spun from the pure fiber grade CR polymer. Figure 2 shows that the fiber spun from the pure fiber grade CR polymer is the most extensible and of least tenacity among all fibers. The addition of the molding grade polymer to the fiber grade CR polymer resulted in achieving higher stresses at the same percent of

extension for the fibers spun from the blends than for fibers spun from the pure fiber grade CR polymer. When increasing the content of the molding grade polymer, the extensibility of the fibers was lowered.

The discontinuously drawn fibers exhibit a brittle mode of deformation behavior, with a short initial period of steep slope and a regime of sharply rising specific stress until fracturing occurred at the extensions between 9 and 12.4% (Fig. 3). These fibers are not so deformable, because their permanent deformation after the onset of yielding occurs at the application of

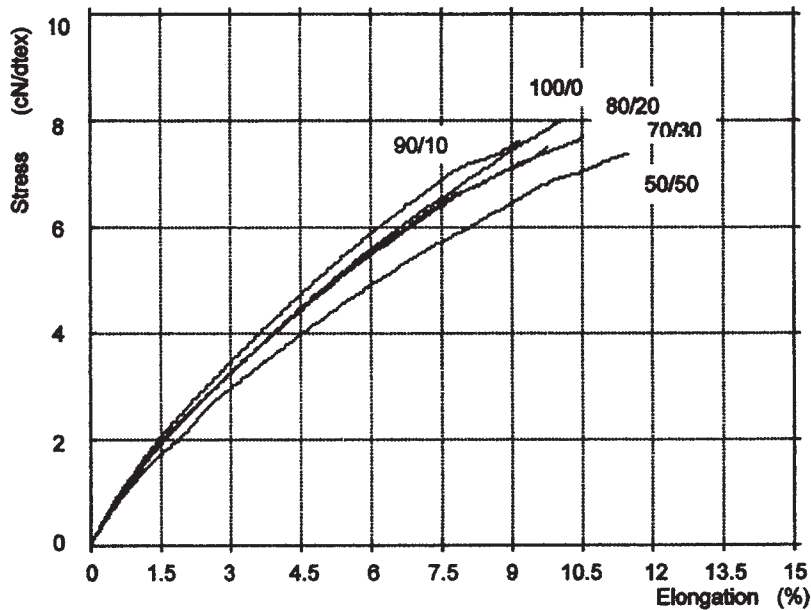


Figure 3 The specific stress versus strain curves of discontinuously drawn fibers.

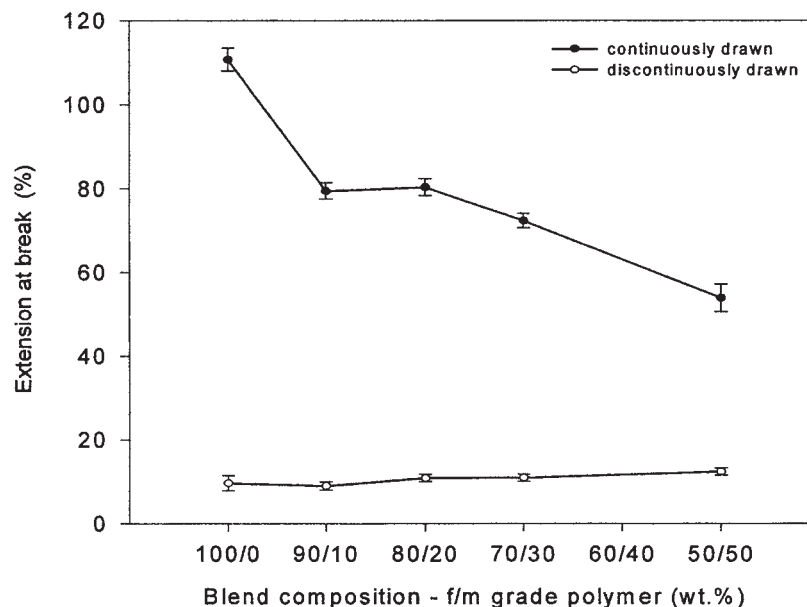


Figure 4 The variation of the extension at break of fibers with the blend composition.

a low specific stress at the extensions at around 0.5%. The yield stress at around 0.8 cN/dtex represents less than 15% of the specific stresses reached at the fracture of these fibers. Similarly, the addition of the molding grade polymer to the fiber grade CR polymer resulted in achieving lower stresses at the same percent of extension for the fibers spun from the blends, especially for the fiber spun from the blend with the highest content of molding grade polymer.

The composition of the blends influences the extension at break of the fibers. Although the continuously drawn fibers were drawn with the same draw ratio, they differed in the measured extension at break. The addition of the molding grade polymer to the fiber grade CR polymer resulted in poorer extensibility of continuously drawn fibers and caused their break to occur at extensions that are 30–50% lower than the extension of the fiber spun from the pure fiber grade CR polymer (Fig. 4). Because the discontinuously drawn fibers were already drawn to the limiting draw ratio in the course of drawing, they are less extensible. Their extension at break is between 9 and 12.4%, increasing with the increase in the content of the molding grade polymer in the blend.

The tensile strength or specific stress of fibers, determined as a tensile force at break over the undeformed cross section (i.e., original weight of fiber per unit area), and the true tensile strength, defined as the ratio of the tensile force at break to the weight of fiber per unit area at the time of breakage, are seen in Figure 5. The continuously drawn fibers show a slight increase in the tensile strength with the addition of molding grade polymer to the 70/30 fiber/molding grade polymer blend, but they drop to a value not

much higher (<10%) than the value of the fiber spun from the pure fiber grade CR polymer with fiber spun from a 50/50 fiber/molding grade polymer blend. The difference between the specific stress and true specific stress is high only with the continuously drawn fibers, where the instantaneous minimum cross-sectional area supporting the load at the time of break is much lower than the underformed cross section of fiber. For the discontinuously drawn fibers the change of the linear density in the course of tensile testing is minor and, because the cross-sectional area supporting the load is not changed much, the true specific stress is higher only at around 10%. The discontinuously drawn fiber spun from the pure fiber grade CR polymer has the highest tensile strength among all fibers. The addition of the molding grade polymer slightly lowers the tensile strength of fibers spun from blends: 5% for fibers spun with 10, 20, and 30% added molding grade polymer, and 10% for the fiber spun with 50% added molding grade polymer.

The elastic modulus, in addition to the tensile strength, is one of the most important properties of technical fibers. The static elastic modulus is determined as the ratio of the specific stress versus strain that is a tangent of the angle between the initial part of the specific stress–strain curve and the horizontal axes. The dynamic elastic modulus is determined as a product of the velocity of sound waves and the density of fibers. The continuously drawn fibers spun from the blends show slight increases in both the elastic and dynamic moduli when adding the molding grade polymer to the fiber grade CR polymer, whereas the moduli of discontinuously drawn fibers slightly decrease, with one exception (Fig. 6). The discontinu-

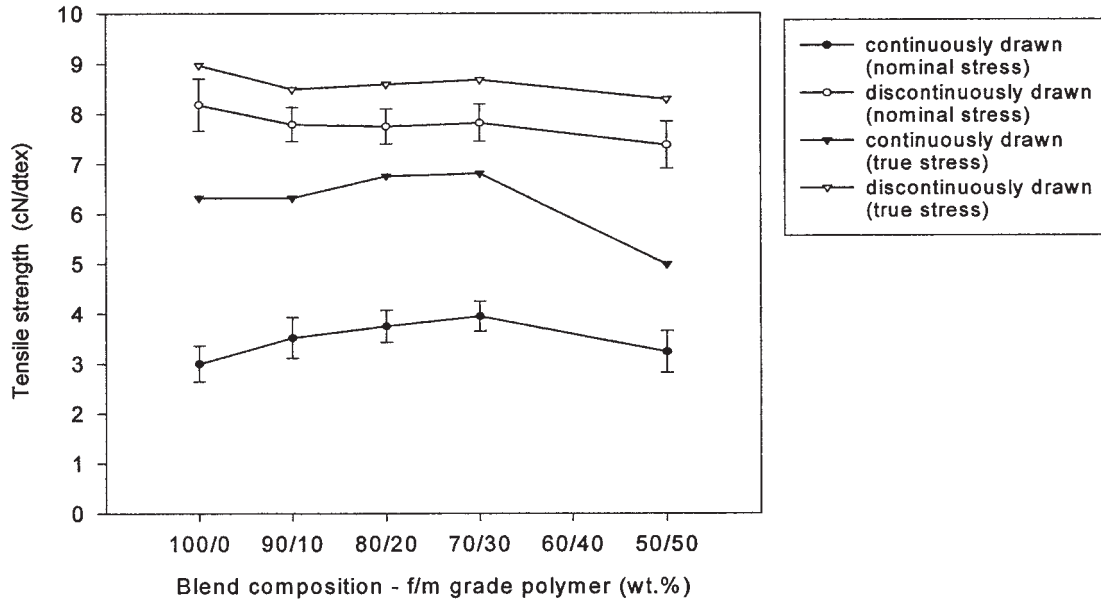


Figure 5 The variation of the specific stress at break (nominal stress, true stress) of fibers with the blend composition.

ously drawn fiber spun from a 90/10 fiber/molding grade polymer blend has the highest modulus (elastic modulus = 14.7 GPa, dynamic modulus = 19 GPa) among all samples.

There are several literature models that describe the moduli of blends as a function of the composition.<sup>15-18</sup> As a first approach to predict the elastic and dynamic moduli, the simple law of mixtures was applied,<sup>15</sup> where the equation for the upper bound of the modulus is

$$E_b = E_1\phi_1 + E_2\phi_2 \quad (1)$$

and the equation for the lower bound is

$$\frac{1}{E_b} = \frac{\phi_1}{E_1} + \frac{\phi_2}{E_2} \quad (2)$$

where  $E_1$  and  $E_2$  are the experimentally determined values of the moduli of fibers spun from the pure components (i.e., the fiber grade CR polymer and the molding grade polymer) and  $\phi_1$  and  $\phi_2$  are corresponding volume fractions of both components.

Kleiner et al.<sup>16</sup> proposed the following empirical equation of the second order:

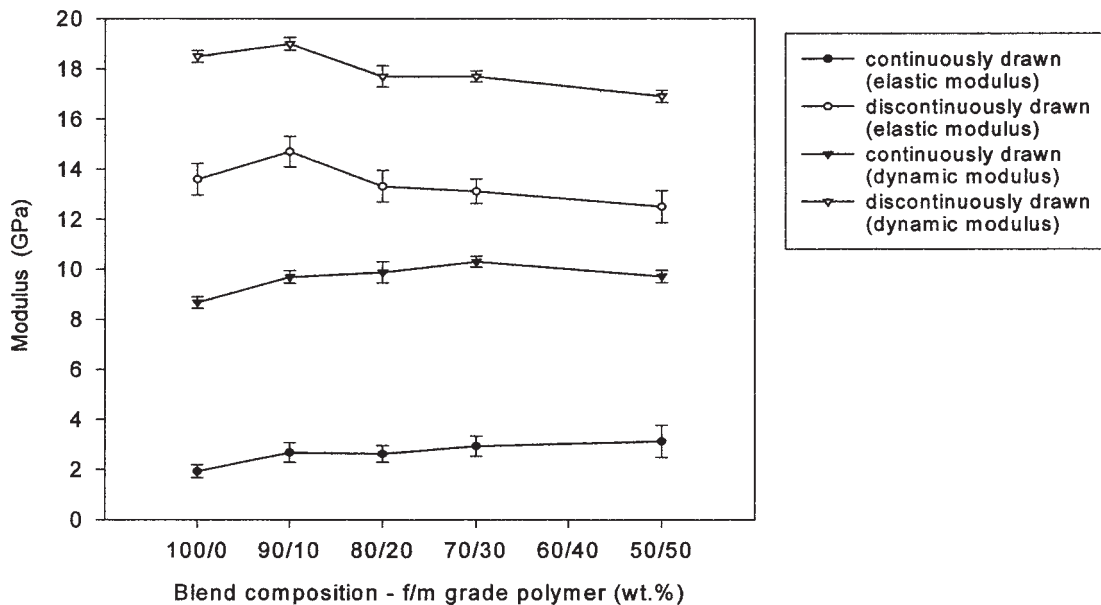
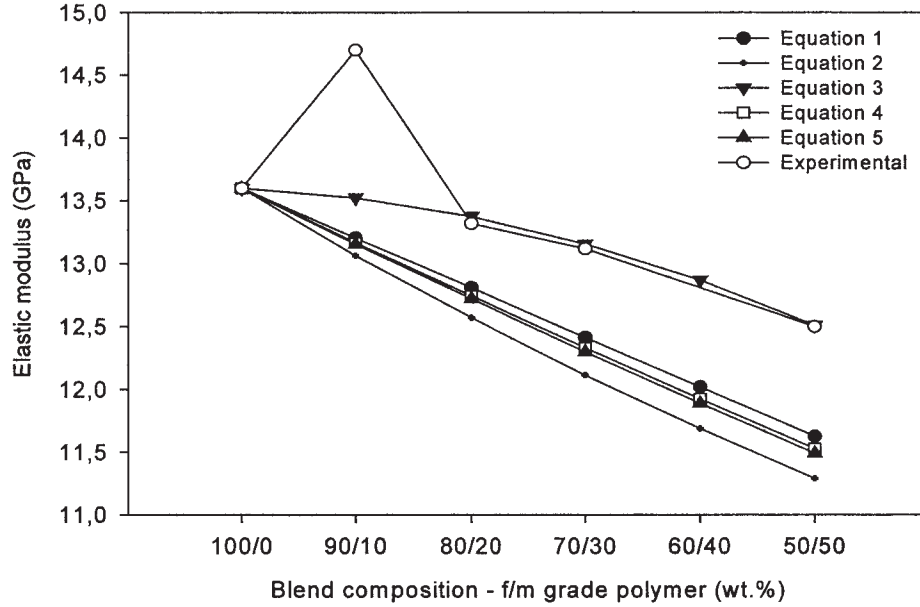


Figure 6 The variation of the elastic modulus and dynamic modulus of fibers with the blend composition.



**Figure 7** The elastic modulus as a function of the blend composition predicted by eqs. (1)–(5) and the experimentally determined elastic modulus of fibers.

$$E_b = E_1\phi_1 + E_2\phi_2 + \beta\phi_1\phi_2 \quad (3)$$

The empirical parameter  $\beta$  is obtained from the following expression  $\beta = 4E_{12} - 2E_1 - 2E_2$ , where  $E_{12}$  is the experimental value of the modulus for the fiber spun from a 50/50 molding/fiber grade polymer.

If we consider the blends as a matrix with inclusions and not as a continuum of two phases, then the equation by Halpin and Kardos<sup>17</sup> is relevant:

$$E_b = E_1 \left( \frac{1 + AB\phi_2}{1 - B\phi_2} \right) \quad (4)$$

with

$$A = 2 \left( \frac{L}{D} \right); \quad B = \frac{(E_2/E_1) - 1}{(E_2/E_1) + A} \quad (4a)$$

where  $A$  is an empirical constant that depends on the stress distribution in the composite and takes into account the shape and geometry of the filler phase. It is obtained from the length to diameter ratio ( $L/D$ ) and is equal to 1 for spherical reinforcement and larger than 10 for orientation in one direction. In our case values between 10 and 50 were taken into account. For the calculated moduli plotted in Figure 7 and Figure 8,  $L/D = 40$  was assumed.

The relation given by Davies,<sup>18</sup> assuming the blend to be macroscopically homogeneous and isotropic, is given by

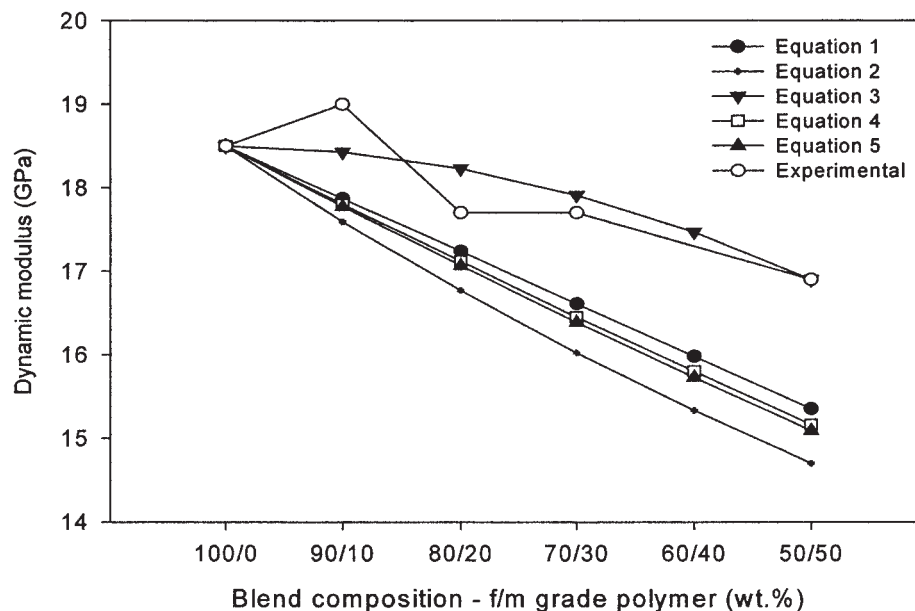
$$E^{1/5} = E_1^{1/5}\phi_1 + E_2^{1/5}\phi_2 \quad (5)$$

The theoretical predictions of the moduli on the basis of the theories cited above [eqs. (1)–(5)] are given in Figure 7 with the experimentally obtained elastic modulus from the tension test and in Figure 8 with the experimentally obtained dynamic modulus from the sonic velocity method. In eqs. (1)–(5) the following values of  $E_1$  and  $E_2$  were used for the calculation of the moduli of fibers spun from the blends:  $E_1 = 13.6$  GPa and  $E_2 = 9.65$  GPa for the elastic modulus,  $E_1 = 18.5$  GPa and  $E_2 = 12.2$  GPa for the dynamic modulus.

From Figures 7 and 8 it is evident that the experimental data for the discontinuously drawn fibers spun from the blends are best represented by the Kleiner equation. In this equation the term  $\beta$  expresses the magnitude of the deviation from linearity, which is from the ideal “rule of mixtures behavior,” and may be a relative measure of the blend compatibility. A positive  $\beta$  represents a nonlinear synergism, which is the criterion for compatibility, whereas a negative  $\beta$  expresses the criterion for incompatibility. The calculated value of  $\beta$  is positive for both moduli, indicating a synergistic effect of blending the different polymer grades on the modulus. For both the static and dynamic elastic moduli the largest positive deviation occurs with the 90/10 fiber/molding grade polymer blend composition, suggesting good compatibility of this polymer mixture.

## CONCLUSION

In the course of our experiments we observed that the blending of the fiber grade polymer with a spinning inconveniently higher molecular weight polymer did not disturb the spinning conditions within a limit. The



**Figure 8** The dynamic modulus as a function of the blend composition predicted by eqs. (1)–(5) and the experimentally determined dynamic modulus of fibers.

onset of spinline instabilities was noted only for blends with 40% or more of the molding grade polymer added. For continuously drawn fibers the addition of the molding grade polymer resulted in the improvement of the mechanical properties. The tensile strength, elastic modulus, and dynamic modulus of these fibers increased when increasing the content of the molding grade polymer in the blend up to the 30 wt %. For discontinuously drawn fibers, drawn to the limiting draw ratio, the addition of the molding grade polymer resulted in poorer drawability and consequently lower tensile strength and moduli, with one exception. By blending a CR polymer with 10% of the molding grade polymer, maximization of the elastic modulus and dynamic modulus was achieved.

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