

Some Observations Concerning the Behavior of Polypropylene Polymers and Fibers

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Synopsis

Data are presented which characterize the behavior of fibers produced from polypropylene polymers under experimental conditions designed to investigate the effect of extrusion temperature on various properties. At high extrusion temperatures molecular weight degradation takes place which results in a lowering of the average molecular weight and a narrowing of the molecular weight distribution. The orientation and crystallinity characteristics of the undrawn fibers also vary with extrusion temperature. The crystal structure of the fibers shows a gradual transformation from a highly ordered monoclinic crystal structure to a paracrystalline structure of lower orientation as the extrusion temperature is increased. Drawing of the undrawn fibers of various molecular weights has been characterized by dynamic stress-strain curves and followed by sonic velocity measurements, the results of which suggest in agreement with other methods that the reduction in crystallinity during drawing is a function of the undrawn crystal structure, the drawing rate, and the drawing temperature. Drawn fibers produced from 21 isotactic polymers have been compared for tensile strength behavior by selecting fibers at the same average molecular weight but with different molecular weight distributions and also with similar molecular weight distributions but at different average molecular weights. These comparisons have shown that at a common draw ratio the tensile strengths of the fibers are lower for those fibers with broad molecular weight distributions when compared to fibers with narrow molecular weight distributions at same average molecular weight. The data also show that the tensile strengths of the fibers of the same molecular weight distribution and crystal structure increase with increased average molecular weight.

Introduction

It has been well recognized by investigators in the field of producing fibers from polymers that the tensile behavior and other fiber properties can be varied over a rather wide range depending upon a number of polymer and process variables. Factors such as polymer molecular weight, molecular weight distribution, extrusion and quenching or coagulation conditions, polymer and fiber crystallinity relationships, orientation, and various other considerations all contribute in exhibiting their effect on the fiber properties.

Recently, studies concerning the effect of some of these variables on the tensile and other properties of melt spun polyolefin fibers have been reported. Higgins and Bryant have reported the effect of melt-spinning

variables on the properties of high-density polyethylene fibers.¹ Ziabicki and Kedzierska have reported the effect of spinning conditions on the orientation of polyethylene and polystyrene fibers.² Capuccio, Compostella, Coen, Bertinotti, and Conti have discussed the effects of polymer molecular weight, fiber crystallinity, and conditions of orientation on the tenacity of polypropylene fibers.^{3,4} Sheehan and Cole have also examined the effect of polymer molecular weight as well as a number of the variables previously mentioned on the tensile characteristics of polypropylene fibers.⁵ One purpose of the study reported here has been to characterize the behavior of polypropylene fibers produced under experimental conditions where the temperature of fiber formation is the major process variable and in which the fibers are obtained from a polymer of given characteristics of isotacticity, molecular weight, and molecular weight distribution.

It has been observed that during the process of fiber spinning from a specified parent polymer that undrawn fibers with widely different properties have been obtained. Examination of the fiber characteristics has shown that the properties of molecular weight, distribution, undrawn fiber orientation, and crystallinity vary as a function of the extrusion and quenching conditions. These, in turn, have been responsible for differences in tensile behavior of the drawn fibers. Another purpose of this study has been to examine the behavior of fibers obtained from a group of 21 isotactic polypropylene polymers of various molecular weights and to describe some observations regarding the effects of molecular weight and molecular weight distribution on tensile properties.

Experimental and Test Methods

The polypropylene polymers used during these studies were obtained from Enjay Chemical Company. Polymers ranging in molecular weight from 374,000 to 125,000 were examined which represent melt index values of approximately 1-100. The isotactic content of all the polymers ranged from 93 to 97%. For the sake of ease of identification, the polymers are designated A through V and their properties are shown in Table I. Extrusion of the polymers was carried out by means of a conventional extruder supplying a metering pump. In one series of experiments the polymer was extruded through a spinneret containing 50 holes of 400 μ diameter at a spinning rate of 62 g./min. In another series of experiments the polymer was extruded through 34 holes of 400 μ diameter at a spinning rate of 20 g./min. The filaments were air-cooled by a flow of conditioned air perpendicular to the direction of filament travel. Spinning temperatures ranged from approximately 238 to 320°C. Filaments were wound on bobbins at 690 m./min. in the first case at a denier of 820 and at 280 m./min. in the latter case at a denier of 630 preparatory to drawing.

Fibers were oriented by stretching using different conditions of speed and heating. In one case, fibers were drawn with the use of conventional drawing equipment over a heater plate at 120°C. and wound at a delivery

TABLE I
Summary of Polymer Properties^a

Group 1			Group 2			Group 3		
Polymer designation	Inherent viscosity ^b	Melt index ^c	Polymer designation	Inherent viscosity ^b	Melt index ^c	Polymer designation	Inherent viscosity ^b	Melt index ^c
A	2.88	1.2	K	2.56	2.7	T	2.60 (1.68)	1.5 (18.3)
B	2.72	1.6	L	2.42	3.5	U	1.96 (1.66)	9.9 (18.7)
C	2.40	2.2	M	2.38	2.8	V	1.72	20.4
D	2.07	7.1	N	2.28	3.9			
E	2.03	5.3	O	2.26	3.6			
F	2.03	5.9	P	1.94	10.6			
G	1.78	10.9	Q	1.88	14.3			
H	1.63	23.8	R	1.82	12.4			
J	1.20	100.	S	1.60	20.3			

^a All polymers had boiling heptane insolubilities of 93–97%.

^b Inherent viscosity: ASTM-D-1601-58-T, polymer concentration 0.1% in decalin, 135°C.

^c Melt index: ASTM-D-1238-57-T, g./10 min., 230°C., 2160 g. load.

speed of approximately 180 m./min. Fibers were also stretched at 15 m./min. both with and without a heater plate. When used, the heater plate was also set at 120°C.

Tensile testing of the fibers was carried out with the Instron Model TM at a testing rate of 100%/min. Testing was also carried out using the Scott IP-4 tester. All fibers were previously conditioned to 70°F. and 65% R.H.

Sonic velocity measurements were made by use of the Pulse Propagation Meter Series Four (manufactured by KLH Research and Development Corp.) on 200 mm. lengths of conditioned fiber.

Birefringence measurements were made with the use of a calibrated quartz wedge compensator in conjunction with a polarizing microscope. Birefringence was calculated from the retardation and the filament diameters measured at the same point.

The x-ray diffraction patterns of the undrawn yarns were measured with the samples in a symmetrical transmission position and the samples were rotated in a plane perpendicular to the plane of the x-ray beam. Nickel-filtered copper radiation was used.

Dilute solution viscosities of the polymers and fibers were determined in accordance with ASTM D-1601-58-T. Conversion to molecular weight from intrinsic viscosity in decalin at 135°C. was made by using the equation derived by Chiang:⁶

$$[\eta] = 1 \times 10^{-4} \bar{M}_w^{0.80}$$

Melt flow properties of the polymers were determined as indicated in ASTM D-1238-57-T. Densities of polymers and fibers were determined by the density gradient method outlined in ASTM D-1505-60-T, ethylene glycol-isopropanol being used as the liquids.

Isotactic content of the polymers and fibers was determined by extracting samples for 3-hr. periods with boiling heptane. Polymer samples were extracted in ground form. Samples were extracted in vapor-jacketed Soxhlet extraction chambers.

Results and Discussion

Fibers of different molecular weights can be obtained from the same parent polymer by varying the temperature of extrusion of the polymer. The rate of thermal and oxidative degradation is known to be dependent upon the temperature of extrusion, the presence of impurities in the polymer, the residence time in the molten state, and the original molecular weight of the polymer. It is therefore also possible to obtain fibers of the same molecular weight from different initial molecular weight polymers. This is illustrated in Figure 1, which shows the molecular weights of fibers produced from three polymers of different initial molecular weights when extruded under identical conditions.

In addition to the variety of molecular weight fibers which can be produced from each of the polymers, the undrawn fiber orientation as measured by birefringence also decreases with decreasing fiber molecular weight (Fig. 2). This reduction in undrawn fiber orientation can be ascribed to

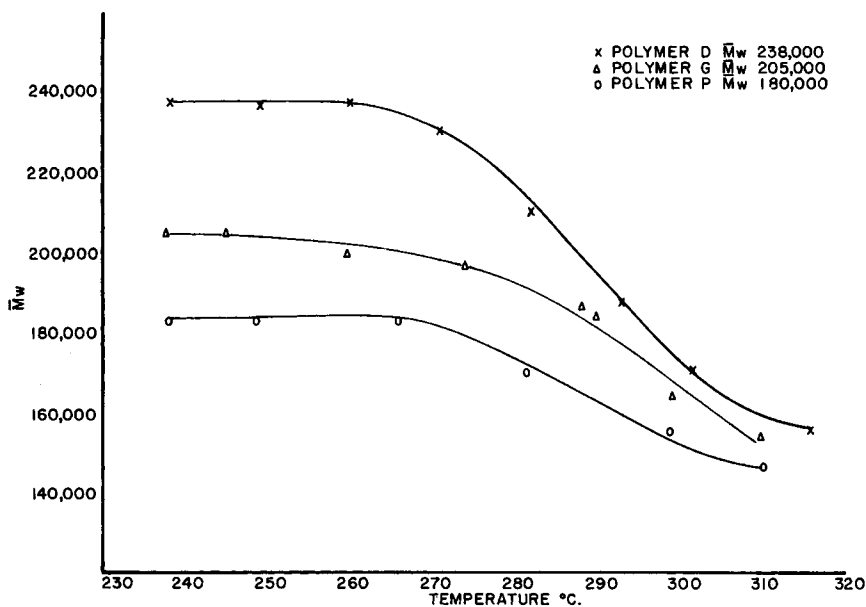


Fig. 1. Fiber molecular weight as a function of extrusion temperature.

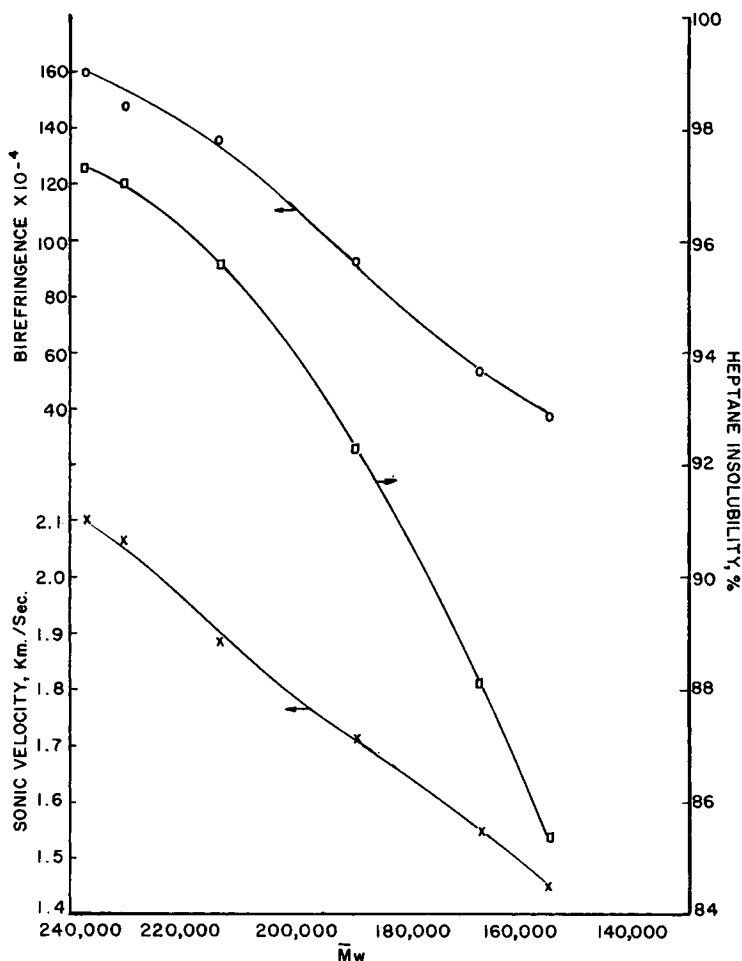


Fig. 2. Fiber molecular weight vs. various undrawn fiber properties (polymer D).

the lower melt viscosity of the filaments emanating from the spinneret orifices. The birefringence is reduced in approximate proportion to the reduction of tension exerted on the filaments during drawdown.

An additional change which occurs during this process is the change in heptane insolubility of the fibers. Heptane insolubility has been widely used as a measure of isotacticity. If one examines the heptane insolubility of the undrawn fibers, it is found that the heptane insolubility decreases with increased extrusion temperatures (lower molecular weight). For polymer D shown in Figure 2, the heptane insolubility was found to decrease from 97.3 to 85.4% with decreasing molecular weight of the undrawn fibers. It has been shown that as the fibers are oriented the insolubility of each molecular weight fiber increases. The highest degree of insolubility is attained by the highest molecular weight fiber.⁷

In addition to these characteristics is the factor of crystallinity which is important not only in the undrawn fiber but which also has an effect on the drawn fiber. The crystalline structure of polypropylene has been reported by various investigators. A three-phase model has been proposed by Natta, Peraldo, and Corradini⁸ and by Wyckoff⁹ which consists of a noncrystallizable amorphous phase, an orientable paracrystalline phase which involves short-range order, and a crystalline phase. The paracrystalline phase, which has been referred to by Natta as the mesomorphic smectic modification,⁸ has been reported by Sobue and Tabata to have the polymer chains parallel to the fiber axis in a hexagonal arrangement.¹⁰ Natta has reported the unit cell of the crystalline phase to be monoclinic and the molecules to be arranged in a threefold helix.¹¹

The particular crystalline structure which is obtained in an undrawn fiber depends upon several variables, of which the extrusion temperature, the method of quenching, and the degree of drawdown are important. Capuccio et al. have shown diffractometer traces illustrating the paracrystalline and monoclinic crystal structures which have been obtained as a function of the rate of cooling from the melt.³ Their concept was that conditions of slow cooling in which crystallization and orientation could occur simultaneously favored the monoclinic crystalline structure. Conditions under which the filament was allowed to draw down dimensionally while fluid favored the paracrystalline structure. Sheehan and Cole also obtained both types of crystal structure as a function of the melt temperature and the manner of quenching. Under their extrusion conditions which involved low drawdowns and speeds, the monoclinic structure was obtained when the filaments were air-quenched. The paracrystalline structure was obtained by quenching in water at low temperature. The use of lower extrusion temperatures required lower water bath quench temperatures in order to obtain the paracrystalline structure.⁵ Rapid quenching of a melt from 270°C. into Dry Ice-methanol at -67°C. was reported to give the paracrystalline structure as compared to the monoclinic structure obtained by means of air quenching.¹² Presumably, the time period over which the polymer is held in the molten condition and the degree of shear and mechanical agitation to which the melt is subjected are additional factors which also have an effect on the crystalline structure obtained under certain specified sets of otherwise constant conditions. In general, it is known that slow cooling as opposed to rapid quenching from the melt favors the development of crystallinity.

The x-ray diffraction patterns of fibers spun from polymer D at several temperatures were determined and are shown in Figure 3. The polymer was spun at temperatures ranging from 238 to 316°C. under otherwise constant conditions to give fibers ranging in molecular weight from 238,000 to 155,000. An air quench was used in all cases. The differences in crystalline structure resulting from differences in the extrusion temperature conditions are clearly seen. The lower extrusion temperatures favor the monoclinic crystalline structure and higher crystallinity levels. As the

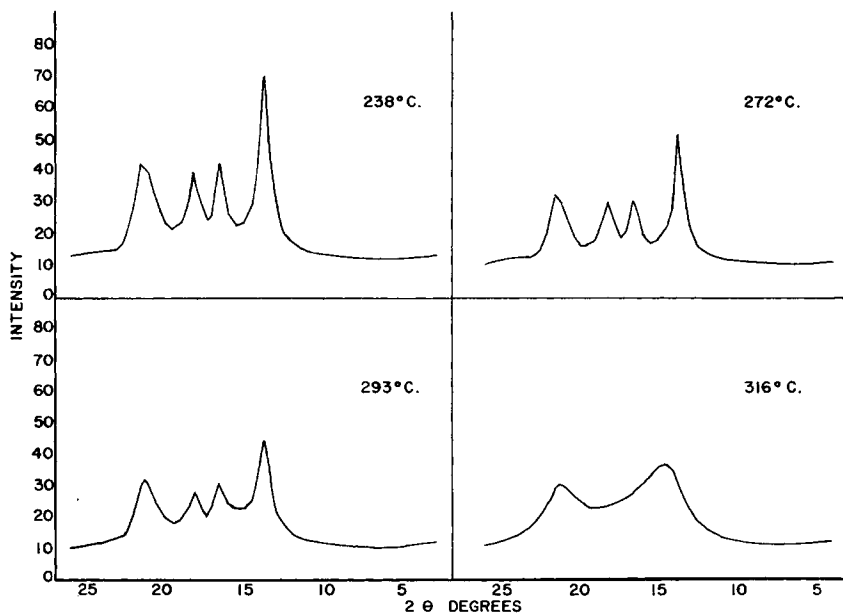


Fig. 3. Diffractometer traces of undrawn fibers produced at various extrusion temperatures (polymer D).

extrusion temperature is raised there is a gradual shift in the crystal structure which results in a change from the predominantly monoclinic crystal form to a state exhibiting both forms and finally to the paracrystalline form at the highest temperatures. The crystallinity at the lowest temperature was found to be 57% and diminished with increasing temperature. Fiber densities determined for these samples were found to decrease from 0.904 to 0.893 g./cm.³ with increasing extrusion temperatures. The differences in the degree of orientation of these fibers can also be clearly seen from the intensities of the peaks of the diffractometer traces.

The monoclinic crystal structures observed are, for one, explainable on the basis that crystallization nuclei in the melt have not been destroyed at the lower melt temperatures. Although these melts are more rapidly cooled through the temperature range of maximum crystallization rate, the nuclei serve to increase the crystallization rate, increase the crystallinity and alter the crystalline structure. Alternatively, high internal viscosities associated with the lower extrusion temperatures cause orientation and crystallization to occur simultaneously thereby resulting in a highly ordered crystalline structure. At the higher extrusion temperatures the fiber is drawn down with less tension due to its greater fluidity before crystallization can occur, with the result that orientation is lower and the paracrystalline structure is formed. One additional consideration is that for each of the higher extrusion temperatures the molecular weights and molecular weight distributions of the fibers are different and might have different

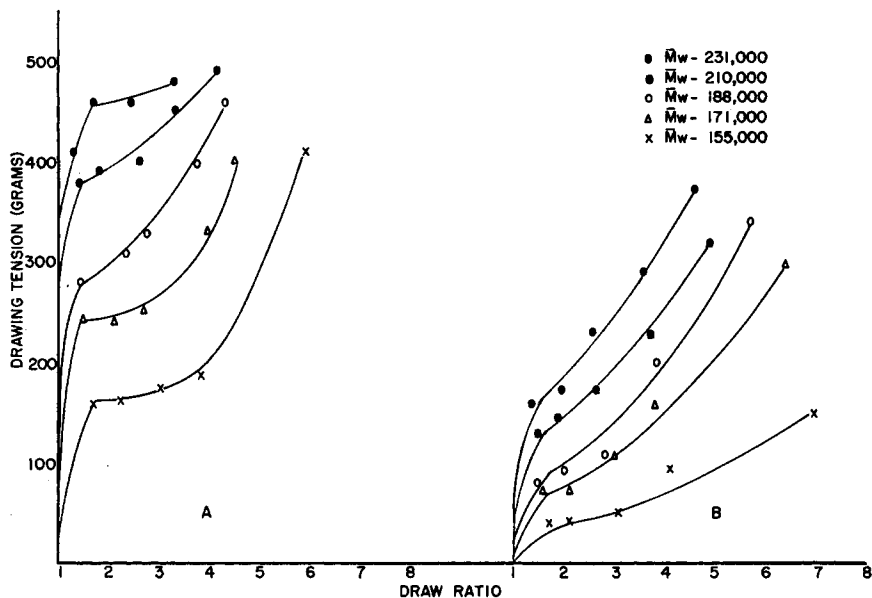


Fig. 4. Dynamic stress-strain curves of various molecular weight fibers from polymer D: (A) cold-drawn; (B) hot-drawn. Fibers were drawn at 15 m./min.

crystallization tendencies. Thus it is possible to obtain undrawn fibers from the same parent polymer which differ in molecular weight, distribution, orientation, crystallinity, and crystalline structure.

Dynamic stress-strain curves for several of the undrawn fibers just described were obtained by stretching the fibers both cold and with the use of a heater plate at a stretching speed of 15 m./min. In both cases tension measurements were made with an electronic tensiometer. These curves are shown in Figure 4. The tensions developed during drawing are considerably higher for the fibers spun at lower temperatures which have the monoclinic crystal structure. Also, the drawing tensions developed during cold drawing are considerably higher than those developed while drawing over a heated plate. Observable also is the fact that the extent of drawing is greater with the fibers extruded at the higher temperatures. From the shapes of these curves, it appears that there is a greater tendency for the filaments to neck when cold-drawn as compared to hot-drawn.

The effect of drawing on the crystallinity of polypropylene structures has been reported in the literature. Capuccio et al. have presented data to show that highly crystalline undrawn fibers undergo a reduction in crystallinity due to the fact that crystallites behave like vulcanized zones.³ These zones are organized into tridimensional lattices which oppose orientation. The effect was stated to be less pronounced when orientation was carried out at higher temperatures. Capuccio et al. also found that undrawn fibers with the paracrystalline structure increase in crystallinity when stretched. The degree of increase depended upon the stretching

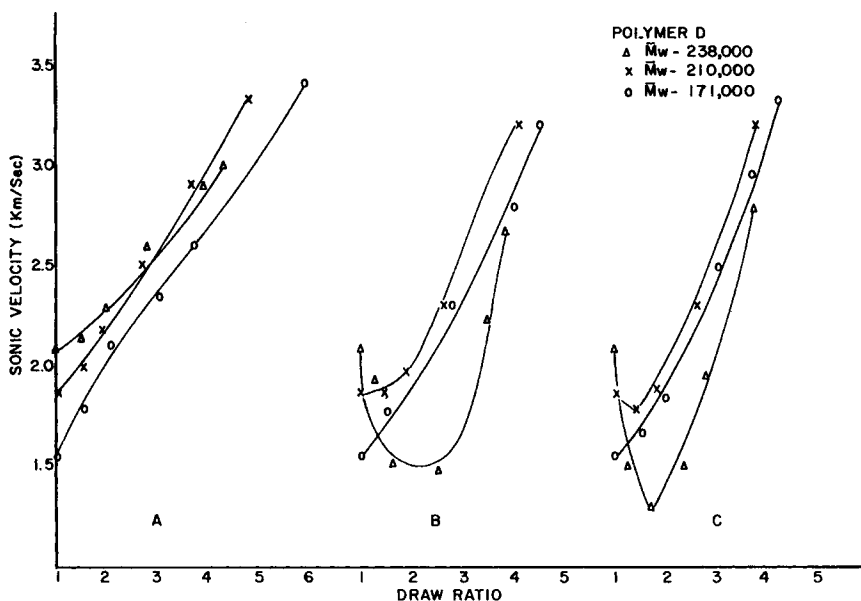


Fig. 5. Sonic velocity as a function of molecular weight, draw ratio, and speed of drawing of fibers from polymer D: (A) hot-drawn, 15 m./min.; (B) cold-drawn, 15 m./min.; (C) hot-drawn, 180 m./min.

temperature. Sheehan and Cole reported the crystallinity of polypropylene fibers to decrease up to a certain ratio and then to level off.⁵ They also reported the filaments with the paracrystalline structure to orient more rapidly than filaments with the monoclinic crystal structure. Wyck-off has reported that orientation of annealed film in the crystalline form resulted in breaking up of the crystallites and reduced them to the paracrystalline state. On heating between 70 and 160°C. the paracrystalline phase could be converted to the crystalline form.⁹ Sobue and Tabata also observed conversion of the crystalline form to the paracrystalline form on stretching of oriented filaments at room temperature or in water below 70°C.¹⁰ Studies conducted in our laboratories indicated that reductions in sonic velocity, which is sensitive to crystallinity at temperatures above the second-order transition temperature,¹³ could be observed during drawing of fibers possessing the monoclinic crystal structure, although the orientation measured by optical birefringence continued to increase.¹⁴ In contrast, undrawn fibers with the paracrystalline structure showed increases in both birefringence and sonic velocity. It was proposed that the reductions in sonic velocity were related to the decrease in crystallinity and were observable despite the increases in molecular orientation as determined by optical birefringence.

The sonic velocity-drawing relationships were further investigated for the fibers described in Figure 4. In addition to these fibers drawn at

15 m./min. both cold and with a heater plate (calculated contact time of approximately 1 sec.); fibers were also drawn at 180 m./min. with a calculated heater contact time of 0.06 sec. The sonic velocity-draw ratio relationships for three different molecular weight fibers are shown in Figure 5. These data show that there are minima in the sonic velocity-draw ratio curves for the cold-drawn fibers and for the fibers drawn with

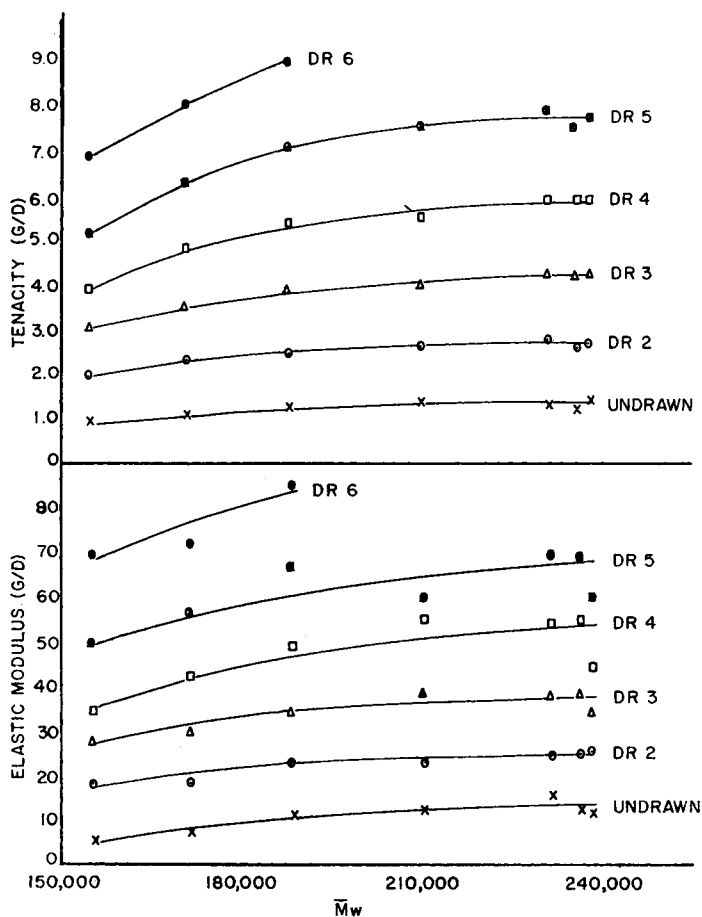


Fig. 6. Tenacity and modulus as a function of molecular weight of fibers from polymer D at various draw ratios.

the shorter heater contact time during the higher speed drawing. In both cases the minima are observed for the highest molecular weight fibers with the predominantly monoclinic crystal structure and there is some suggestion of a small reduction in sonic velocity for the middle molecular weight fiber drawn at the high speed. It is interesting that no minimum in the sonic velocity-draw ratio curve is observed for the yarns drawn at the slower speed with the use of a heater plate. If the sonic velocity observa-

tions are, in fact, reflecting crystallinity changes in the fibers, this would suggest that under certain conditions of drawing the overall loss of crystallinity can be kept at a minimum either by reducing the disruption of crystallinity or by allowing recrystallization to occur or a combination of both. This is consistent with the observations of other investigators with regard to the fact that changes in crystallinity which occur on drawing are affected by the extent of drawing, the temperature and the rate of drawing. Studies on the effect of heat on the crystallinity of fibers have shown that crystallinity increases are at a maximum at temperatures of 120–130°C. and are accompanied by increases in crystallite size.^{15–17}

The tensile properties of the polypropylene fibers drawn under this latter set of drawing conditions are shown in Figure 6. The tenacity is plotted as a function of fiber molecular weight at various draw ratios. The elastic modulus of the fibers is also shown in this figure. These data show that for any given draw ratio the tenacity and modulus increase with increasing molecular weight of the fiber, and the rate is greater at the higher draw ratios. These data also indicate that higher draw ratios are obtained with the lower molecular weight fibers from the same polymer which, of course, have a lower degree of orientation and the paracrystalline structure. The principle of using very high extrusion temperatures to obtain fibers of low orientation and to draw them at high draw ratios to obtain fibers of high tenacity has been discussed in the patent literature.¹⁸ The difficulty in orienting fibers with the monoclinic crystal structures as compared to paracrystalline structures has also been reported. The interesting observation can also be made that there are several combinations of molecular weight and draw ratio which will give a fiber of any intermediate tenacity level, since a decrease due to molecular weight can be compensated by an increase in orientation. It can be appreciated that fiber properties other than tenacity and elastic modulus will vary as a function of molecular weight and degree of orientation. However, it is noteworthy that a range of fiber properties can be obtained from a single polymer although the level of properties will vary depending upon the polymer molecular weight.

Sheehan and Cole have considered a similar type of relationship for polypropylene fibers of molecular weights of 67,000–405,000.⁵ In several comparisons their results showed that the tenacity values fell into several groups of fiber molecular weights, the higher molecular weight fibers exhibiting higher tenacities at any common draw ratio. It was also pointed out that the higher molecular weight fibers were made from broad molecular weight distribution polymers which were not degraded during extrusion thereby maintaining their broad distribution. The lower molecular weight polymers were of a narrower distribution as a result of molecular weight changes which occurred during extrusion. Extrapolation of the data suggested the possibility that narrow molecular weight distribution fibers would have a higher tenacity at any given average molecular weight and draw ratio than the broad distribution fibers. However, this could not be confirmed with the range of polymer molecular weights avail-

able to them. Some of these considerations have been investigated in some detail in this work.

The molecular weight distribution of isotactic polypropylene has been investigated and reported by Davis et al.¹⁹ Their data has shown that thermal degradation of the polymer proceeds by a random process and results in a narrowing of the molecular weight distribution. During the early stages of this process the tail of the distribution curve is broken down with a resultant increase in polymer in the middle and lower molecular weight ranges. The narrowing of the molecular weight distribution was related to the degree of degradation which could be described in terms of a ratio of the final to the initial polymer molecular weight. This index, \bar{M}_w/\bar{M}_{w0} , has been used in this work as an indicator of the molecular weight distribution. A large value indicates a broad distribution and, conversely, a low value a narrow distribution. It was also shown that there is little change in the number-average molecular weight (\bar{M}_n) over a wide range of degradation. This factor, \bar{M}_w/\bar{M}_{w0} , is essentially, therefore, a ratio of the weight-average to number-average molecular weight.

The importance of the effect of molecular weight and molecular weight distribution on the properties of polymers has been recognized, and these are acknowledged to be important factors in their mechanical behavior. The relationship between the molecular weight distribution and some properties of unoriented polypropylene structures has been reported.^{20,21} For example, properties such as flow and impact strength have been shown to be adjustable as a function of the molecular weight distribution. Natta et al. have reported that the tenacity of polypropylene fibers at maximum draw increased with decreasing polydispersity ratio and also increased with number-average molecular weight. The elongation at break of the fibers decreased with decreasing polydispersity ratio.²²

In order to further clarify some of these relationships regarding the dependence of molecular weight and molecular weight distribution on fiber behavior, comparisons of the tensile strengths of a series of fibers from various polymers were made. Data for these comparisons were obtained from experiments during which polymer melts were extruded at various temperatures as previously described and the fibers drawn at various draw ratios. As indicated earlier, it is inherent in this particular process of extrusion and quenching that undrawn fibers produced with broad molecular weight distributions are also characterized as having the monoclinic crystal structure and those with narrower distributions the paracrystalline structure. Additional experiments describing the effect of molecular weight distribution at constant crystalline structure and molecular weight are described later in this paper.

As shown in Figure 1, in addition to obtaining various molecular weight fibers from the same parent polymer, fibers of the same molecular weight can be obtained from polymers of different molecular weights. These fibers in the undrawn state will have different characteristics of orientation, degree of crystallinity, type of crystal structure, and molecular weight

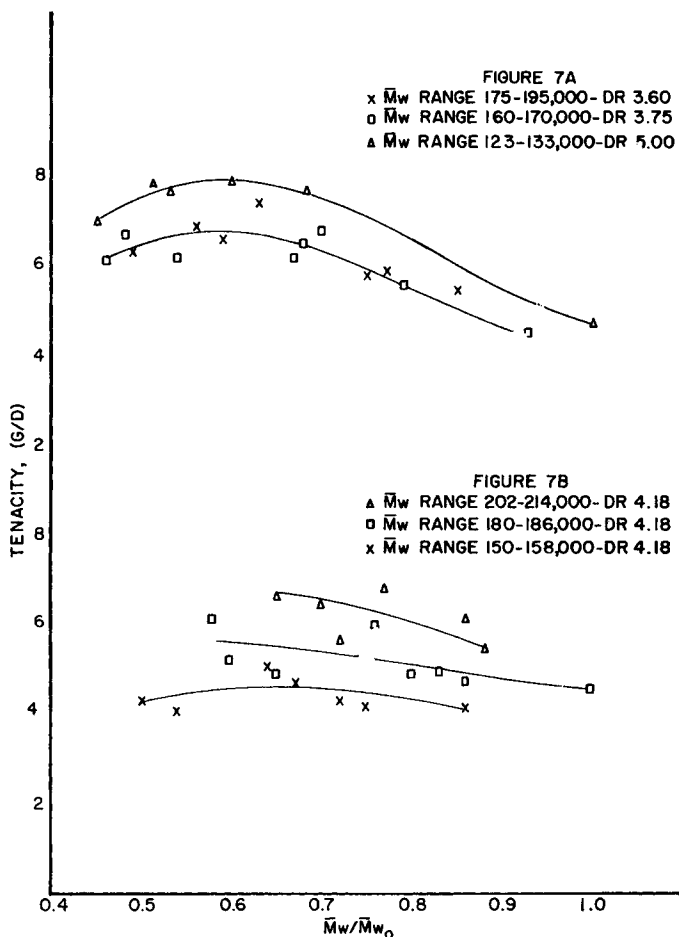


Fig. 7. Tenacity vs. \bar{M}_w/\bar{M}_{w0} at various fiber molecular weights, each at a common draw ratio for fibers from 18 polypropylene polymers.

distribution. A third possibility is to obtain from polymers of different molecular weights fibers with different average molecular weights but which have similar molecular weight distributions.

The tensile strength relationships for several molecular weight fibers produced from the same parent polymer were shown in Figure 6. The fibers in that case differed both in molecular weight and distribution. The tensile strength relationships for fibers having the same average molecular weight but with different molecular weight distributions as expressed by \bar{M}_w/\bar{M}_{w0} are shown in Figure 7 for several levels of average molecular weight and draw ratio. The fibers shown in Figure 7A were spun at the higher spinning throughput and take-up speed described in the experimental section for the production of 50-filament bundles from polymers A through J. Those shown in Figure 7B were produced at

the lower spinning rate described for the 34-filament bundles from polymers K through S. In both cases the fibers were stretched at 180 m./min.

The data showing the relationship of \bar{M}_w/\bar{M}_{w_0} to fiber tenacity for three molecular weight ranges of fibers drawn at various common draw ratios are shown in Figure 7A. These data which represent nine polymers indicate that there is a reduction in tenacity level for the fibers which have high values of \bar{M}_w/\bar{M}_{w_0} , and this reduction appears to be consistent for all three molecular weight ranges considered. Data representing three molecular weight ranges drawn at the same draw ratio are shown in Figure 7B. These data which also represent nine polymers also show a lower tenacity level at higher \bar{M}_w/\bar{M}_{w_0} ratios, although this relationship is less obvious at low tenacity levels resulting from low draw ratios or low molecular weights. In this case all the fibers at the three different molecular weight ranges were drawn at an identical draw ratio, so that the effect of not only \bar{M}_w/\bar{M}_{w_0} can be seen but also the contribution of higher molecular weight itself to higher tenacity.

One of the obvious difficulties in comparing fibers made from polymers with a wide range of molecular weights is that all the fibers are not likely to be similarly oriented at a common draw ratio. In all cases, however, those fibers having high \bar{M}_w/\bar{M}_{w_0} ratios are more highly oriented in the undrawn state and, therefore, it would be expected that they would be more fully drawn (drawn closer to the break point) at a draw ratio also common to fibers with a low \bar{M}_w/\bar{M}_{w_0} at the same average molecular weight. Whether the tendency toward lower tenacity levels at the higher \bar{M}_w/\bar{M}_{w_0} ratios is attributable to the broader molecular weight distribution or to crystallinity or orientation considerations resulting from the fact that these fibers in the undrawn state were highly ordered and had the monoclinic crystal structure is not evident. As previously shown in Figure 6, the response of tenacity to draw ratio for fibers of various molecular weights from the same polymer is greater for fibers of lower molecular weight, particularly at the higher draw ratios. If this consideration is applied to the data of Figure 7 it would be expected that fibers with intermediate \bar{M}_w/\bar{M}_{w_0} ratios would exhibit higher tenacities at any given molecular weight level. This might be logical on the basis that orientation is more efficiently accomplished where the narrower molecular weight distribution and the paracrystalline structure characterize the fibers. At very low values of \bar{M}_w/\bar{M}_{w_0} , the very low orientation of the undrawn fibers might result in a lower drawn fiber tenacity at any given draw ratio. There does, in fact, appear to be an indication of a drop-off in tenacity at the low \bar{M}_w/\bar{M}_{w_0} ratios in Figure 7. If the draw ratio of these fibers were increased, however, the tenacity level would not exhibit this drop-off.

Although the 21 polymers used in this study were extruded at a series of temperatures, it was not possible to degrade the polymers to values of \bar{M}_w/\bar{M}_{w_0} lower than approximately 0.4. In order to do this would have required extremely high temperatures or inordinately long residence times in the melt.

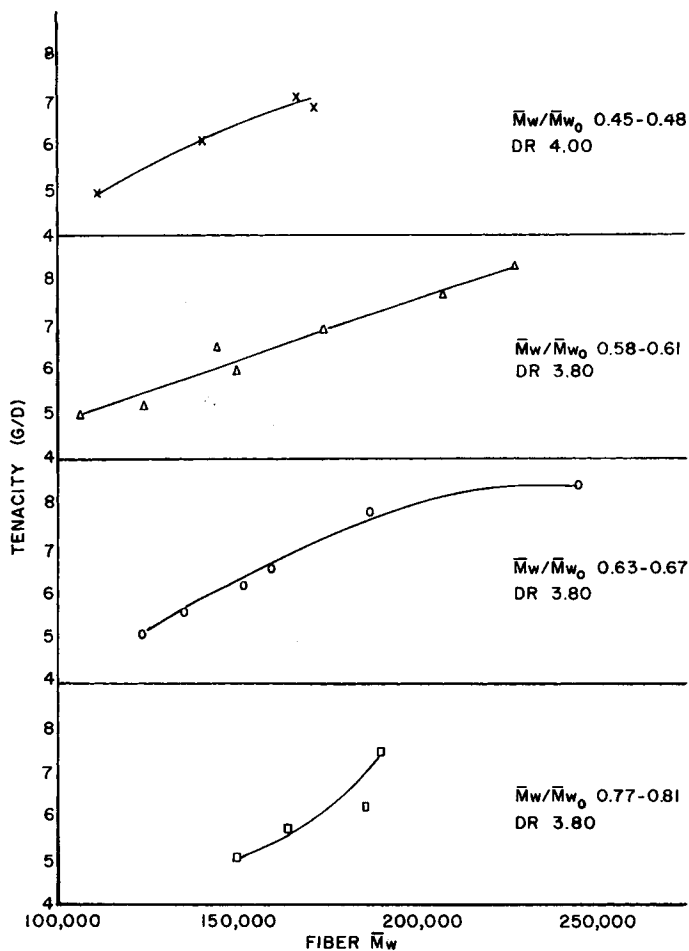


Fig. 8. Tenacity vs. fiber molecular weight at four \bar{M}_w/\bar{M}_{w0} ratios for 50-filament bundles.

Additional comparisons representing eighteen of the polypropylene polymers are shown in Figures 8 and 9. In this comparison, fibers with the same \bar{M}_w/\bar{M}_{w0} ratio were selected, and tenacity levels of the fibers compared. Those shown in Figure 8 are the 50-filament bundles and represent four ranges of \bar{M}_w/\bar{M}_{w0} . Those shown in Figure 9 are the 34-filament bundles and represent three ranges of \bar{M}_w/\bar{M}_{w0} . As previously indicated, these fibers have different average molecular weights ranging from 245,000 to 107,000. From these data it can be clearly seen that there is a good correlation of tenacity with molecular weight at all levels of \bar{M}_w/\bar{M}_{w0} , with the tenacity increasing with increased molecular weight.

A comparison of the level of tenacity at the various \bar{M}_w/\bar{M}_{w0} ratios shows a slightly lower level of tenacity for the \bar{M}_w/\bar{M}_{w0} ratio 0.77-0.81 of Figure 8 and also a slightly lower level for the \bar{M}_w/\bar{M}_{w0} ranges which include 0.70-0.86 of Figure 9. Although the fibers in each of the \bar{M}_w/\bar{M}_{w0}

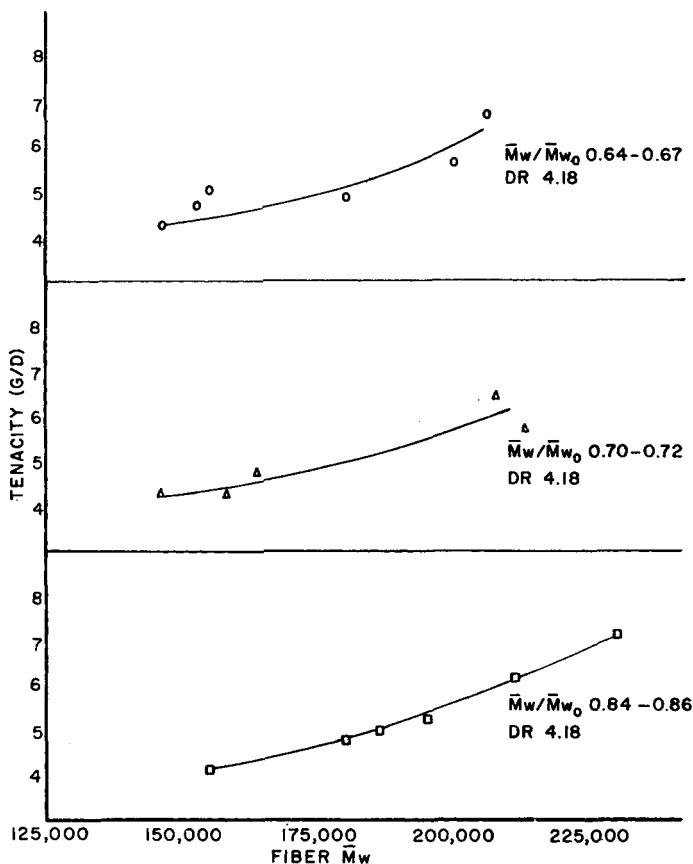


Fig. 9. Tenacity vs. fiber molecular weight at three \bar{M}_w/\bar{M}_{w_0} ratios for 34-filament bundles.

ranges in this comparison differ in average molecular weight and in undrawn fiber orientation, there are experimental data which indicate that they resemble one another with regard to undrawn fiber crystallinity and therefore would be expected to respond similarly to drawing. The correlation of tenacity with molecular weight at each \bar{M}_w/\bar{M}_{w_0} range is good. The observations describing the comparisons of the \bar{M}_w/\bar{M}_{w_0} ranges again do not distinguish between the effect of molecular weight distribution and the effect of undrawn fiber crystallinity on drawn fiber tenacity.

In order to determine the effect of molecular weight distribution on the tensile strength of fibers at a given draw ratio produced from undrawn fibers with the same average molecular weight, degree of orientation, and crystal structure, an experimental device was used whereby polymers of different molecular weights were pre-degraded to approximately the same average molecular weight level. All the polymers were then extruded at the same temperature (245°C.) to yield undrawn fibers of the same crystal

structure (monoclinic) and approximately the same degree of orientation. The fibers were then drawn at several draw ratios and the tensile properties compared.

These data are summarized in Table II. The tenacities at the various draw ratios are consistently higher for those fibers with the lower \bar{M}_w/\bar{M}_{w0} values (narrower molecular weight distributions). This would indicate that molecular weight distribution has an effect on the tensile behavior independent of undrawn fiber crystallinity considerations.

TABLE II
Effect of Fiber Molecular Weight Distribution on Tenacity

Polymer ^a	Original molecular weight	Spinning polymer molecular weight	Fiber molecular weight	\bar{M}_w/\bar{M}_{w0}	Tenacity at various draw ratios, g./den.		
	\bar{M}_{w0}	weight	\bar{M}_w		3.70	4.20	4.70
T	330,000	190,000	170,000	0.51	5.8	7.1	7.7
U	230,000	185,000	172,000	0.75	5.1	6.1	6.6
V	195,000	195,000	180,000	0.92	4.7	5.4	6.4

^a Polymers T and U were pre-degraded to the spinning polymer molecular weights shown. All polymers were then extruded at 245°C. to form fibers with the monoclinic crystal structure.

Consideration of the effect of molecular weight distribution and crystalline structure has only been given to tenacity levels in these comparisons. There are a number of other fiber properties which are related to these characteristics. Studies now in progress have shown that properties such as creep and stress relaxation at elevated temperature are highly dependent upon the molecular weight distribution. Fibers with broad molecular weight distributions have been shown to perform better than fibers with narrow molecular weight distributions.

Summary and Conclusions

The tensile properties of polypropylene fibers can be varied over a wide range by the selection of polymer and the choice of extrusion and orientation conditions. At sufficiently high extrusion temperatures, molecular weight degradation takes place which results in a lowering of the average molecular weight and a narrowing of the molecular weight distribution. In addition, differences in orientation and crystallinity of undrawn fibers are observed as a function of the extrusion conditions. These have been shown by x-ray diffraction patterns and indicate that for fibers extruded under the experimental conditions described, the crystal structure changes from a highly oriented monoclinic structure to a lesser oriented paracrystalline structure as the extrusion temperature is increased. Dynamic stress-strain curves have been determined for fibers of different molecular weights from a given polymer which have been both cold-drawn and drawn in the presence of heat. These stress-strain curves have shown

that considerably higher drawing tensions are developed for cold-drawn fibers compared to hot-drawn fibers. The higher molecular weight fibers which also have the monoclinic crystalline structure and which are more highly oriented in the undrawn state develop higher drawing tensions regardless of the drawing method used. These results are consistent with the conclusions drawn based on sonic velocity measurements regarding the effect of drawing conditions on the changes in crystallinity which occur during drawing. The literature has shown that cold-drawing of monoclinic crystalline structures is accompanied by a reduction in crystallinity, which by these measurements is manifested by a minimum in the sonic velocity-draw ratio relationship.

Fibers spun from 21 isotactic polypropylene polymers covering a range of fiber molecular weights of 245,000 to 107,000 were compared for tensile strength behavior. One comparison was based on a series of fibers produced at various extrusion temperatures from a given polymer. Undrawn fibers produced in this manner were therefore dissimilar with regard to average molecular weight, molecular weight distribution, orientation, and crystallinity. Tenacity and elastic modulus relationships indicated that for any given draw ratio the fibers produced at the lower extrusion temperature (higher molecular weight) had higher tenacities and moduli than those produced at the higher extrusion temperatures.

However, it was also shown that the fibers of lower molecular weight could be drawn to a greater extent with a concomitant increase in tenacity and modulus. A second comparison was based on a series of fibers of the same average molecular weight but having different molecular weight distributions (\bar{M}_w/\bar{M}_{w_0}) by virtue of the fact that they were obtained from polymers of different initial molecular weights. Two such sets of comparisons were made with each set comprised of nine polymers and at several average fiber molecular weight levels.

These results indicated a lower tenacity at a given common draw ratio for fibers with a high \bar{M}_w/\bar{M}_{w_0} ratio (broad molecular weight distribution) produced from polymers with a small amount of molecular weight degradation and from undrawn fibers possessing the monoclinic crystal structure and a high degree of orientation compared to those with an intermediate \bar{M}_w/\bar{M}_{w_0} ratio produced from polymers with a greater amount of molecular weight degradation and from undrawn fibers possessing the paracrystalline structure and a lesser degree of orientation. There was an indication that undrawn fibers with low \bar{M}_w/\bar{M}_{w_0} ratios would also yield lower drawn fiber tenacities by virtue of the very low degree of orientation of the undrawn fibers.

A third comparison was based on a series of fibers which had similar \bar{M}_w/\bar{M}_{w_0} ratios but which had different average molecular weights. These data clearly indicated higher tensile strengths for the higher molecular weight fibers compared to the lower molecular weight fibers at any given common draw ratio. This relationship was found to be consistent at all \bar{M}_w/\bar{M}_{w_0} ratios. The reduction of tenacity at high \bar{M}_w/\bar{M}_{w_0} ratios was also

demonstrated in this comparison, although, as in the earlier comparison, it could not be determined whether this was the result of the effect of molecular weight distribution or the crystal structure of the undrawn fibers.

Finally, an additional comparison was made of the tensile strengths of drawn fibers which were produced from undrawn fibers of the same average molecular weight, monoclinic crystal structure, and approximately the same level of orientation but differing in \bar{M}_w/\bar{M}_{w0} ratios. This was accomplished by the experimental device of pre-degrading polymers of different molecular weights to approximately the same molecular weight prior to extruding them under the same temperature conditions. These results showed that as the \bar{M}_w/\bar{M}_{w0} decreased, the tenacities of the fibers increased thereby indicating a dependence of tenacity on molecular weight distribution independent of crystalline structure.

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Résumé

On présente des données qui caractérisent le comportement des fibres produites à partir de polymères de polypropylène dans les conditions expérimentales conçues pour étudier l'influence de la température d'extrusion sur les différentes propriétés. A des températures d'extrusion élevées, il y a dégradation du poids moléculaire ce qui provoque un abaissement du poids moléculaire moyen et un rétrécissement de la distribution des poids moléculaire. Les caractéristiques d'orientation et de cristallinité des fibres non étirées varient également avec la température d'extrusion. La structure cristalline des fibres présente une transformation graduelle allant de la structure cristalline monoclinique bien

ordonnée jusqu'à une structure paracrystalline possédant une orientation plus faible lorsqu'on augmente la température d'extrusion. L'étirage des fibres non étirées de différents poids moléculaire a été caractérisé par des courbes dynamiques de tension-élongation et a été suivi par des mesures de la vitesse du son. Les résultats obtenus suggèrent en accord avec d'autres méthodes, que la diminution de cristallinité pendant l'étirage est une fonction de la structure cristalline non étirée, de la vitesse d'étirage et de la température d'étirage. Des fibres étirées obtenues à partir de 21 polymères isotactiques ont été comparées du point de vue de leur comportement à la force de tension en choisissant des fibres de même poids moléculaire moyen mais de distribution différentes du poids moléculaire et également en choisissant des fibres de mêmes distributions du poids moléculaire mais de poids moléculaires différents. Ces comparaisons ont montré que pour un même rapport d'étirage, les forces de tension des fibres sont plus faibles pour les fibres possédant de larges distributions du poids moléculaire avec le même poids moléculaire moyen. Les résultats montrent également que les forces de tension des fibres de même distribution du poids moléculaire et la structure cristalline augmentent avec une augmentation du poids moléculaire moyen.

Zusammenfassung

Daten, welche die Charakterisierung des Verhaltens von Fasern, die aus Polypropylen unter Versuchsbedingungen erzeugt wurden, die den Einfluss der Extrusionstemperatur auf verschiedene Eigenschaften zu untersuchen gestatten, werden vorgelegt. Bei hohen Extrusionstemperaturen findet ein Molekulargewichtsabbau unter Verengung der Molekulargewichtsverteilung statt. Auch die Orientierungs- und Kristallisationscharakteristik der ungereckten Fasern hängen von der Extrusionstemperatur ab. Die Kristallstruktur der Fasern zeigt mit Erhöhung der Extrusionstemperatur eine graduelle Umwandlung von einer hochgeordneten monoklinen Kristallstruktur zu einer parakristallinen Struktur von niedrigerer Orientierung. Reckung der ungereckten Fasern mit verschiedenem Molekulargewicht wurde durch dynamische Spannungs-Dehnungskurven charakterisiert und durch Schallgeschwindigkeitsmessungen verfolgt; die Ergebnisse zeigen in Übereinstimmung mit anderen Methoden, dass der Kristallinitätsrückgang während der Reckung eine Funktion der Kristallstruktur im ungereckten Zustand, der Reckungsgeschwindigkeit und der Reckungstemperatur ist. Gereckte Fasern aus 21 isotaktischen Polymeren wurden bezüglich ihrer Zugfestigkeit verglichen, wobei Fasern mit gleichem mittlerem Molekulargewicht, jedoch verschiedener Molekulargewichtsverteilung sowie solche mit ähnlicher Molekulargewichtsverteilung, aber verschiedenem Molekulargewicht ausgewählt wurden. Dieser Vergleich zeigte, dass bei gleichem Reckungsverhältnis die Fasern mit breiter Molekulargewichtsverteilung eine geringere Zugfestigkeit besitzen als diejenigen mit enger Molekulargewichtsverteilung bei gleichem Molekulargewicht. Weiters zeigen die Ergebnisse, dass die Zugfestigkeit von Fasern mit gleicher Molekulargewichtsverteilung und Kristallstruktur mit steigendem mittlerem Molekulargewicht zunimmt.

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