

Property Correlations for Doubly Oriented Polymers Prepared by the Rolltrusion Technique

INTRODUCTION

We have demonstrated¹⁻³ that a highly doubly oriented polymer can be produced stepwise or continuously by a deformation process termed rolltrusion. The technique overcomes some of the processing limitations imposed by die drawing and other well-known procedures.⁴ Besides, highly ordered transparent plastics are produced wherein triaxially oriented crystallites are organized in an orderly manner in three dimensions. The disposition of the interconnecting amorphous regions depends upon the processing conditions for doubly oriented plastics such as polyolefins, polyamides, polyesters, etc., of high quality. Furthermore, the rolltrusion method is superior to the often conventional two step techniques⁵ of (i) drawing followed by (ii) rolling, used to produce doubly oriented polymers. Mechanical properties,⁶ such as tensile modulus and strength, toughness, creep, wear rate,⁷ and so on, have been correlated with morphological parameters (such as birefringence, crystalline, and amorphous orientations factors, crystallinity, density, melting and heat of fusion, etc.).

In this short communication we comment on some of the salient features which have been found for polyethylene and polypropylene and which have not yet been emphasized. Tensile strength and wear behavior are chosen in this short communication, to illustrate relationships. It is apparent that the trends observed in these engineering properties can be related primarily to changes in the "amorphous" intercrystallite regions of the materials, the orientation and properties depending primarily upon processing conditions.

MATERIALS AND EXPERIMENTAL

The properties of commercial polyethylene (\bar{M}_n 13,900, \bar{M}_w 91,900) and polypropylene (\bar{M}_n 65,600, \bar{M}_w = 413,000) used in these illustrations have been reported.^{3,7} Rolltrusion is a unique process () in which commercial polymer of moderate to high molecular weight is passed between thermostatted (hot or cold) rollers (fixed or corotating) in a controlled way, depending upon the nature of the polymer and its physical state. It is a "single pass" process, unlike the normal two step operation^{1,2,3,6} described previously³ in the literature. Figure 1 illustrates the differences between some related modes of processing and schematically illustrates the morphological changes associated with rolltrusion processing. The morphology in Figure 2 essentially a low index plane of the crystalline regions is parallel to the rolling plane even though molecular weight has an influence.³

RESULTS AND DISCUSSIONS

It is well known that polymer birefringence Δn can be expressed⁹ as

$$\Delta n = f_a(1 - \chi_c)\Delta n_a^0 + f_c\chi_c\Delta n_c^0 + \Delta n_f^0$$

where f_a and f_c are the Herman's amorphous and crystalline orientation factors, χ_c the crystalline fraction, and Δn_a^0 , Δn_c^0 , and Δn_f^0 are respectively the intrinsic amorphous, crystalline, and form birefringences of the specimen in different orientation directions. These values have been obtained by several workers¹⁰⁻¹² for the polyolefins studied.

From birefringence and wide angle X-ray measurements, f_a and f_c were evaluated and correlated with some properties already found for doubly oriented polyethylene and polypropylene.

Figures 3(a) and (b) illustrate the dependence of orientation factors on draw ratio. Note that f_c quickly approaches an asymptotic limit whereas f_a monotonically increases with orientation.

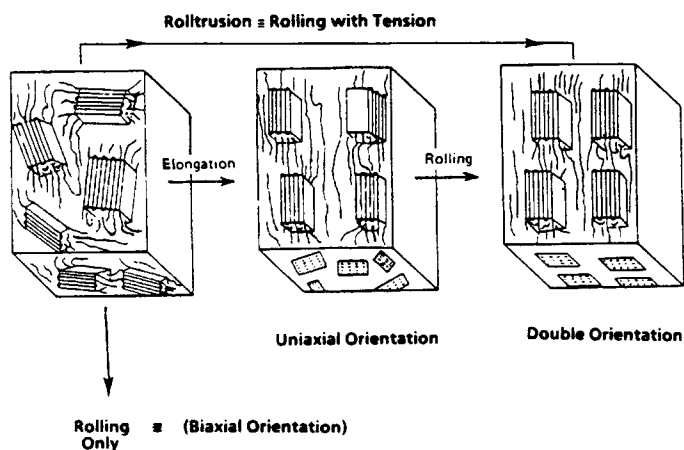


Fig. 1. Schematic illustration of the morphological features involved in some polymer processing operation such as: (a) elongational or uniaxial deformation; (b) rolling following Ref. 1 i.e. double orientation; (c) direct rolling or two-way stretching (biaxial orientation); (d) rolltrusion: one step double orientation process (this work) where the polymer is under tension during rolling.

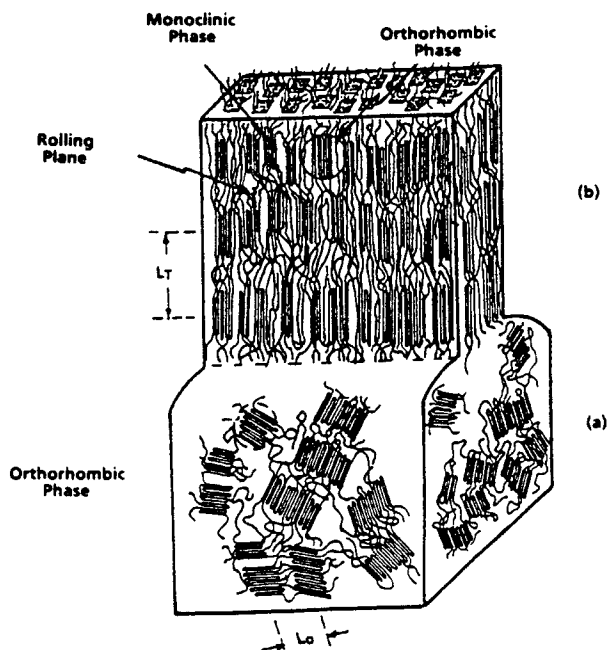


Fig. 2. Illustration of the change in morphology associated with rolltrusion. The diagram does not represent the packing or density changes, but only the enhanced crystalline-amorphous orientation encountered on passing from a disordered texture (magnified view within spherulites) to a well-ordered nonspherulitic texture; herein crystalline and oriented amorphous regions are well ordered and alternate. There is always a low index crystallographic plane lying parallel to the plane of rolling, other planes being ordered with respect to this one. In this diagram the processed end of the workpiece has a larger long period, L_T , than the unprocessed part, L_0 , that is formed initially at a lower temperature.

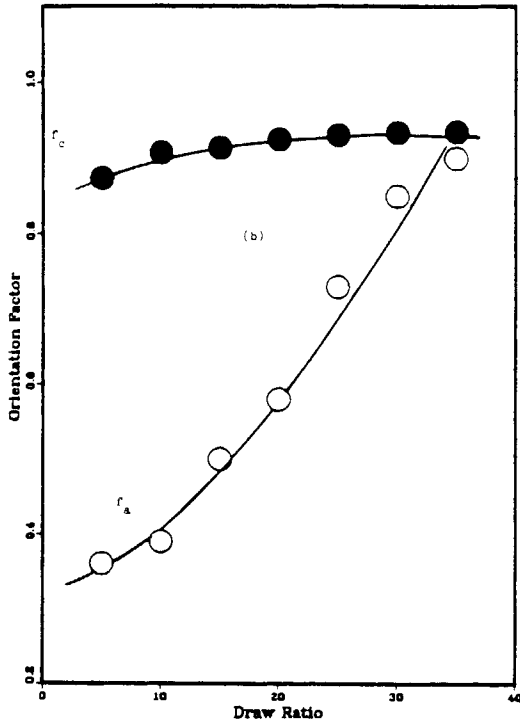
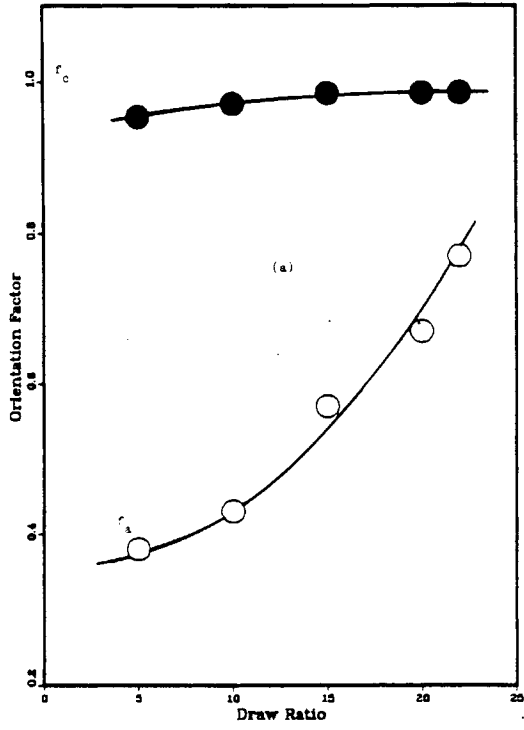


Fig. 3a. Amorphous and crystalline orientation factors f_a and f_c , respectively, for (a) high density polyethylene and (b) isotactic polypropylene as a function of draw ratio.

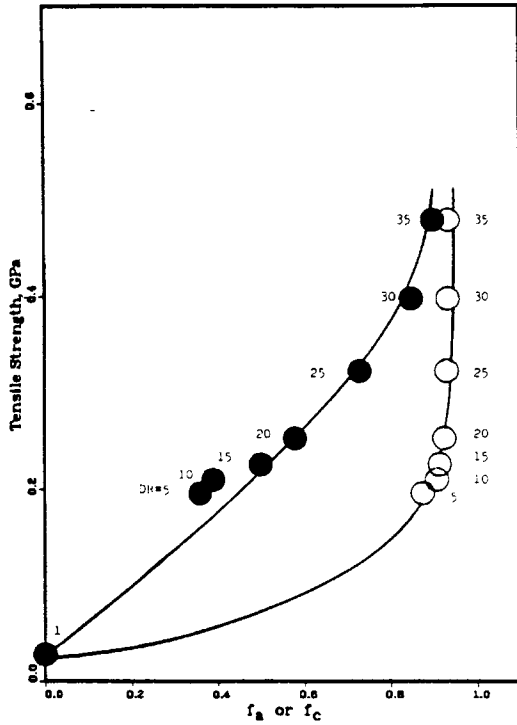
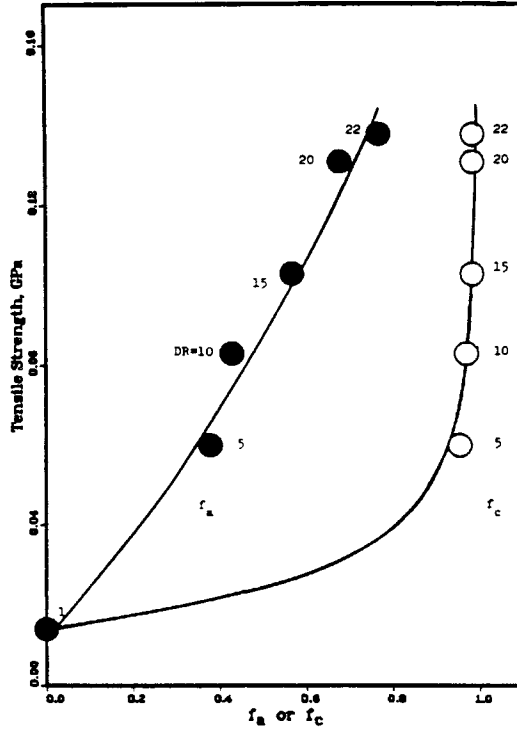


Fig. 4a. Tensile strength vs. orientation factors f_a and f_c for: (a) polyethylene rolltruded at 120°C; (b) polypropylene rolltruded at 158°C; (c) polyethylene produced by roller drawing¹³ at 100°C. Draw ratios are indicated in the figures.

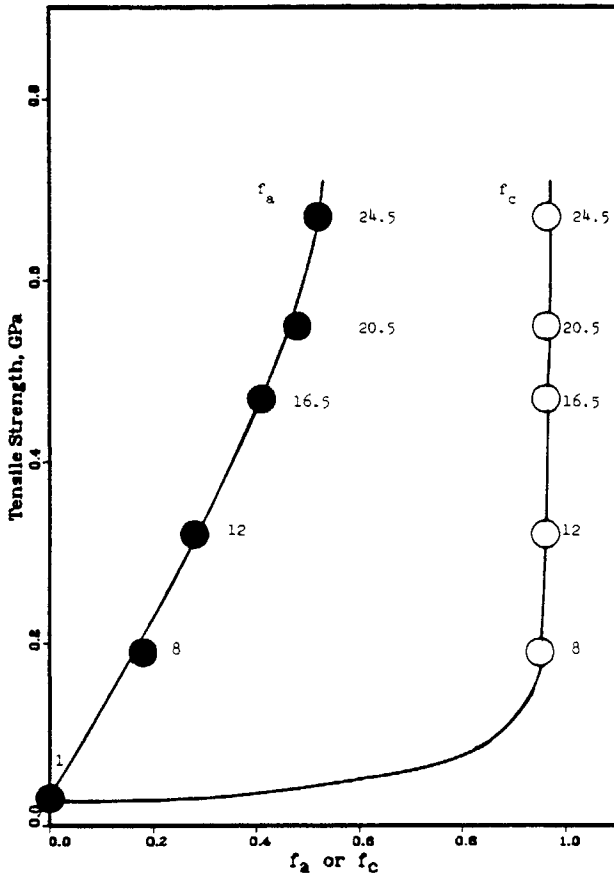


Fig. 4c. (Continued from the previous page.)

These trends show that deformation at the higher draw ratios must occur (primarily) in the amorphous regions. Since tensile mechanical properties also improve considerably with draw ratio, correlation between f_a , f_c and these properties were established. In Figures 4(a) and 4(b) tensile strength vs. f_a and f_c , respectively, are illustrated for doubly oriented polyethylene and polypropylene. Note that the correlation with f_a shows an almost linear relationship over a wide range of deformation whereas the property change with f_c is not well correlated in these plots.

Tensile strength (TS) rather than modulus seems to be a more useful engineering parameter here. Similar analysis of recent literature data¹³ on polyethylene has been analyzed and comparable trends, shown in Figure 4(c), are established.

It is also interesting to describe the wear behavior correlation with f_a for these same materials. Figure 5(a) and 5(b) show that the inverse wear rate is nicely correlated with f_a . Note that similar trends in wear behavior are seen in Figure 5(b) whenever different orientation directions (along and transverse to the draw direction) are employed.

Correlations have been provided for uniaxially oriented polymers by other workers.^{14,15} For example, a linear relationship has been found between the log (TS) and f_a for polypropylene fibers¹⁴ (for samples with draw ratios up to X10), prepared under various conditions. It was found in another study that no simple correlation existed between TS and f_a for polyethylene fibers¹⁵ prepared by a variety of drawing conditions with DR values as high as X25. Note that f_a values are not unique, but depend upon the intrinsic Δn values selected; however, the behavioral trends reported here should not be changed appreciably if other values are selected.

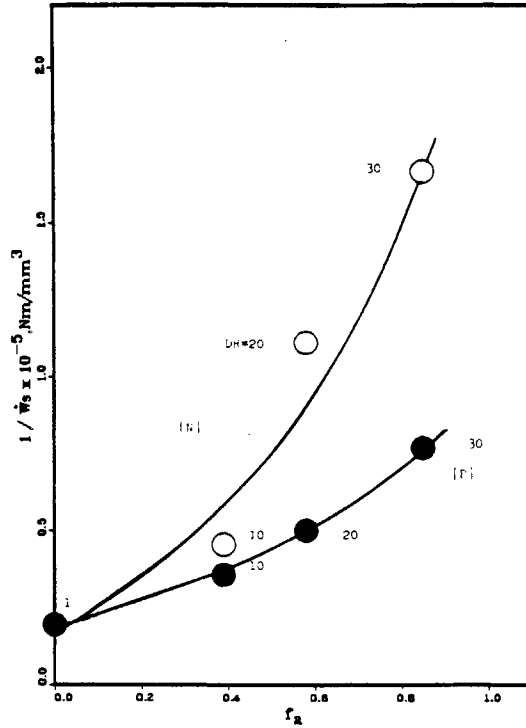
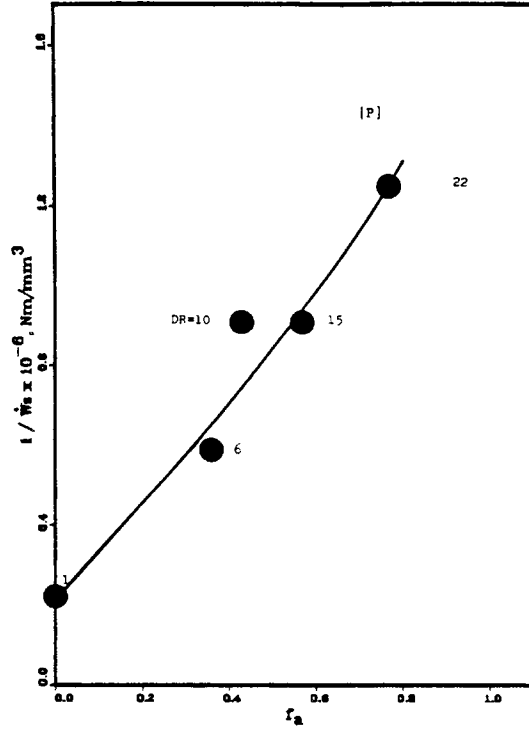


Fig. 5a. Inverse wear rate \bar{W}_s^{-1} (N m/mm^3) as a function of f_a for doubly oriented polyolefins figure for: (a) polyethylene in the rolltruded plane parallel to the draw ratio direction [P]; (b) polypropylene along [P] and transverse [N] to the rolltruded plane.

Trends in properties are accounted for in a morphological model and Figure 2.³ In it the crystallinities are highly oriented along the draw direction (molecular chain axis) following the spherulitic to fibrillar transition that occurs usually in the range DR 5–10, depending upon draw temperature.¹⁶ On the other hand, the disposition of tie molecules between crystallites improves continuously as a consequence of further deformation to higher draw ratios, which is in line with the observed changes in TS reported in this article for both of these polyolefins. Recently, evidence from small angle X-ray scattering measurements¹⁷ shows that several higher order peaks occur parallel and even perpendicular to the rolling plane, attesting to the highly ordered nature of these polymers. Details and analyses of these data are being prepared for several polymers.

CONCLUSIONS

In rolltruded (doubly oriented) polymers the mechanical properties correlate preferably with orientational changes in the tie molecular regions that are located between well-oriented crystallites.

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J. H. MAGILL*

D. C. SUN*

M. J. SHANKERNARAYANAN

Material Science and Engineering Department
School of Engineering
University of Pittsburgh
Pittsburgh, Pennsylvania 15261

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*Also Chemical and Petroleum Engineering Department.