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THE STRENGTH AND STIFFNESS OF POLYMERS

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Preface

The development of polymers of high mechanical performance has been a subject of rapid growth in the last decade. Studies with flexible, semiflexible, and rigid-rodlike polymers have led to (1) a better understanding of the molecular structure of such polymers and the relation to strength and other properties, and (2) the development of processing techniques for preparing high-modulus polymers. Solid and melt processing have been used effectively to orient and extend flexible polymers. The consequent polymer morphology and the processing conditions are very important for the achievement of high mechanical performance. The elastic modulus of a drawn polymer can increase markedly with the extent of deformation. Morphological and theoretical models have been proposed to interpret small- and large-strain deformations for semicrystalline and amorphous polymers, respectively.

The need for polymers with greater thermal and oxidative stability has led to the development of polyaromatic (semiflexible and rigid-rod) polymers. In many cases, these polymers form anisotropic (liquid crystalline) melts or solutions. These systems have been processed to high-modulus fibers using fiber-forming techniques.

The diverse approaches described in this book show that a properly designed polymer, when processed by the appropriate technique, may result in a lightweight polymer with a tensile modulus comparable to that of metals.

Anagnostis E. Zachariades
Roger S. Porter

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Solid-State Extrusion of Thermoplastics

ANAGNOSTIS E. ZACHARIADES and ROGER S. PORTER

It has long been recognized that the theoretical tensile modulus of a polymer chain should approach the modulus of steel. Until a decade ago, these theoretical approaches were considered unlikely to be achieved because all known polymers had moduli about two orders of magnitude lower. The reason for the low modulus is that polymer chains fold in a series of folded-back chains and assume a random entangled and twisted configuration which has a low load-bearing capacity. It was realized that the greatest strength results from a structure of highly oriented, extended, and densely packed chains. Indeed, some polymers (e.g., Kevlar and X-500) have been processed into fibers that exhibit moduli of approximately 200 GPa, indicating that the earlier theoretical values can be approached. The possibility of developing human-made organic materials of high strength-to-weight ratio has opened inroads on their resistant competitors, the metals.

Polymer researchers have pursued the problem of making polymers with well-aligned, extended, and closely packed chains by two basic approaches: (1) chemical construction of rigid rod-like polymers by synthesizing polymers containing aromatic rings in the chain backbone, and (2) processing existing conventional flexible chain polymers in such ways that a permanent deformation of the internal structure may occur. In the second approach, a highly oriented and extended chain configuration with substantially increased modulus may be achieved by solid-state deformation using the extrusion or drawing techniques, by extrusion of supercooled melts, and by drawing from dilute flowing solutions.

The method of solid-state extrusion has been studied extensively recently for the deformation of various semicrystalline and amorphous polymers. However, the compositionally simple high-density polyethylene (HDPE) has been used preferentially in most studies in order to understand the concurrent morphological transformation and because it presents one of the highest theoretical tensile moduli (see Table 1).

In this chapter, we review the solid-state extrusion process in structural and morphological terms. The review includes the evaluation of the extrusion variables, their effect on the physical and mechanical properties of high-density polyethylene extrudates, and the development of new approaches by which the solid-state extrusion may be used for a wider range of polymers.

THEORETICAL MODULUS

In attempting to produce polymers with high modulus, it is essential to have a knowledge of the modulus at the microscopic level; that is, the modulus of a perfect polymer crystal. Theoretical calculations for the modulus of well-known crystalline polymers have been reported by various workers [1,2]. For a linear straight-chain

Table 1. Limiting Modulus Values for Some Polymers and Other Materials

Material	Modulus (GPa)
Polyethylene	240
Polypropylene	42
Polystyrene	12
Polyoxymethylene	53
Poly(vinyl alcohol)	250
Poly(ethylene terephthalate)	137
Carbon steel	208
Aluminum	69
Glass fiber	69-183

hydrocarbon polymer, the theoretical modulus was calculated to be 240 GPa. Dulmage and Contois [3] were the first to determine the extensional modulus of macroscopic fiber by an X-ray diffraction method which was used subsequently by Sakurada [4-7] and his co-workers to measure the modulus of many crystalline polymers. In addition, Sakurada et al. have shown that the extensional crystalline modulus is 60 times higher than the transverse crystalline modulus, thus emphasizing the dependence of the macroscopic modulus on the covalent character of the highly aligned and extended polyethylene. Similar studies to those of Sakurada and his co-workers were undertaken by Britton et al. [8] on a number of oriented polyethylene films. Their results suggest that with increasing draw ratio the parallel lamellar structure changes to a continuous crystal with randomly distributed defects throughout the polymer. Consequently, the theoretical calculated and X-ray determined moduli should show agreement. Such limiting moduli values for some polymers and other materials are shown in Table 1.

METHODS FOR MAKING HIGH-MODULUS FIBERS

One way of making high-modulus polymers is by chemically constructing polymers with rigid backbone chains. A second feasible method, mentioned previously, is by processing the polymer in ways that result in an extended rigid chain configuration. Before we dwell on solid-state extrusion, we shall discuss briefly the various processing approaches that are used for the preparation of polymers with a high degree of chain orientation and modulus.

Construction of Rigid Macromolecules

Organic fibers with very high moduli have been made independently at the laboratories of the Monsanto and DuPont companies and are composed essentially of oriented para-substituted aromatic units, as shown in Fig. 1. These result in a rigid backbone chain; however, they confer high melting points and poor solubility. As a result, the fabrication of these polymers into fibers is difficult and can only be spun from solution. The reader interested in high-modulus aromatic fibers is referred to a detailed review written by Black [9].

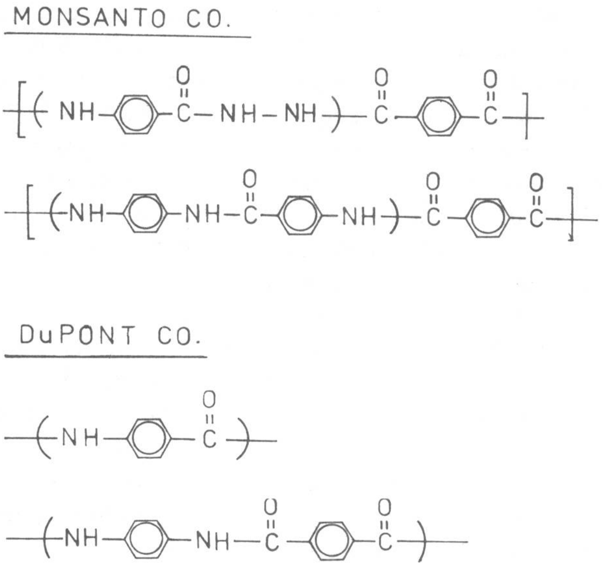

Figure 1. Examples of rigid rod-like polymers.

Drawing

Early attempts to produce high-modulus fibers were initiated with tensile drawing of linear polyethylenes at elevated temperatures.
In a typical tensile drawing experiment, dumbbell or rod samples are mounted and drawn on a tensile testing machine. Apart from the molecular characteristics of the polymer (molecular weight and molecular weight distribution), the draw temperature and rate are important variables and must be selected carefully for maximum effective draw. Takayanagi [10] produced polyethylene fibers with modulus 35 GPa by drawing melt-extruded films. Peterlin [11] and his co-workers obtained linear polyethylene fibers of draw ratio 20 and with modulus 27 GPa. Also, Fischer [12] and his co-workers reported the preparation of drawn polyethylene fiber at a draw ratio greater than 15 and having a dynamic modulus of 38 GPa. In 1973, Capaccio and Ward [13-15] reported that linear polyethylenes could be drawn up to draw ratio 30. These highly drawn samples had moduli up to 70 GPa, which is 25 to 30% of the estimated limiting modulus value.

Clark and Scott [16] developed a two-step drawing process for the preparation of polyoxymethylene, polypropylene, and polyethylene fibers. The polymer was first drawn up to the natural draw ratio at a fast rate and subsequently was slowly superdrawn at a temperature that depended on the crystalline dispersion temperature.

Other synthetic linear aliphatic polymers have been drawn to produce high-modulus fibers, but these will not be considered because they fall outside the scope of this review.

Solution Stirring

This technique has been developed by Pennings et al. [17] to produce an ultra-high-modulus polyethylene. It involves the longitudinal growth of fibrillar polyethylene crystals ($M_w = 1.5 \times 10^6$) from xylene solution subjected to Couette flow above 100°C and at growth rates up to 150 cm/min. The growth process was found to be affected by the take-up speed of the growing microfiber; that is, fibrillar crystals with diameters in the range 50 μm, the rotor surface and speed, the polymer concentration, and the crystallization temperature. The X-ray diffraction results and the mechanical performance of the macrofibers together with the possibility of growing them at a temperature far above the thermodynamic equilibrium solubility temperature for ideal polyethylene crystals indicate the effective extension of polymer chains during the crystallization process. These macrofibers have a remarkably high modulus of 100 GPa, about 40% of the theoretical value for perfect polyethylene crystals, which indicates a large percentage of fully extended chains. The tensile strength at break is 4 GPa.

Extrusion

The extrusion technique has become a widely studied technique for processing polymers. It was realized as early as 1968 that oriented extrudates could be obtained from the melt by extruding through a capillary rheometer with a conical die [18]. Work forwarded by Southern and Porter [19,20] lead to the development of transparent and fibrous linear polyethylene extrudates. These were obtained by extruding the polymer in the molten state (132 to 136°C) above a critical shear rate in a capillary rheometer and through a conical die. As a result of the rising extrusion pressure, the polymer underwent supercooling, which combined with the high elongational velocity gradient lead to the massive crystallization of the polymer in the conical die. This process was subsequently modified [21,22] by processing the polymer in the solid state (i.e., the polymer was in the solid state before entering the die). This modification of the extrusion technique produced transparent fibers with moduli in the range of 30 to 70 GPa for linear polyethylene. Predecki and Statton [23] also obtained transparent and rigid polyethylene extrudates of extrusion draw ratio up to 36 using conical dies with a tapered die angle not greater than 8°. In spite of the high extrusion draw ratio, there was only a five-fold increase in the modulus of their extrudates compared with the undrawn material. The direct ram extrusion of polyethylene has also been studied more recently by Kolbeck and Uhlmann [24] in the United States and by Farrell and Keller [25] in England. The first authors studied the extrusion of high-density polyethylene at 100 to 110°C through conical and slit dies to obtain fiber and film extrudates of maximum extrusion draw ratio up to 36 and 26, respectively. The second authors studied the dependence of the mechanical performance on the extrusion condition for a series of extrusions at maximum extrusion draw ratio 20 and in the temperature range 90 to 120°C.

Hydrostatic extrusion is an alternative approach to the direct ram extrusion process, in which the pressure is transmitted to the polymer through a pressure transmitting fluid (e.g., caster oil), and has been studied by various workers. Davies [26] investigated the hydrostatic extrusion of high-density polyethylene at maximum extrusion draw ratio 9. He studied the effect of pressure on extrusion and observed that practical extrusion draw ratios are limited by the shear failure of the polymer in the die rather than the excessive applied pressures. Gibson et al. [27,28] also investigated the hydrostatic extrusion of high-density polyethylene and studied the effects of extrusion pressure, molecular weight, and product size. They extruded at 100°C and the extrudates, of maximum extrusion draw ratio 25, had a tensile modulus of ~46 GPa. The hydrostatic extrusion of high-density polyethylene has also been investigated by Nakayama and Kanetsuna [29] and by Inoue and Nakayama [30]. The first two authors, in a series of papers, reported on the effects of extrusion conditions on the molecular orientation of the extrudates. The other authors studied the extrusion of 10 different engineering polymers at room temperatures.