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Ultra-High Strength and Ultra-High Modulus Fibers from Polyethylene

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SUMMARY

Using the method of hot drawing developed earlier, an attempt has been made to obtain ultra-high modulus and ultra-high strength PE filaments from original filaments produced by the "surface growth" technique. The average tensile strength of the drawn fibers reaches 5.5 GPa and the value of modulus measured in a dead loading creep experiment is estimated to be 44 GPa. 13 % of the drawn specimens had extremely high tensile strength close to theoretical estimates. The great scatter of the tensile strength data is attributed to the kink-band formation in the specimens due to their bending during preparation or during drawing.

INTRODUCTION

In the last decade the possibility to obtain high modulus and high strength flexible polymers with the help of different techniques has been demonstrated (1, 2, 3). Especially high values of both tensile strength (σ = 4.75 GPa) and modulus (E = 120 GPa) have been obtained for high-molecular weight PE by hot drawing of "surface grown" fibers (4).

In this paper we describe an attempt to further increase the tensile strength and the modulus of these fibers using the drawing technique (2).

EXPERIMENTAL

The original filaments (20–50 μm thick and 100–300 μm wide) were produced by the above technique (4) from 0.5 % xylene solution of linear polyethylene of two different molecular weights: MW = 200 x 10^3 (PE1) and MW = 1.5 x 10^6, commercial grade GUR (PE2). The specimens of PE1 were crystallized at T_{cr} = 100 °C (PE - 100), but the specimens of PE2 were crystallized at three different temperatures T_{cr}: 108, 110, and 115 °C (PE2 - 108, PE2 - 110, and PE2 - 115, respectively).

Hot drawing of these filaments under the very short action of high temperatures was carried out by pulling the loaded specimen past a narrow polished strip of metal at 10 cm/min. The region of intimate mating of orienting specimens with this strip is less than 1 mm. It enables a reduc-

tion of the exposure of oriented specimens at high temperature and minimizes the mechanical destruction process which takes place during drawing. The tensile strength (σ) of drawn and original filaments was measured on the 10 mm long specimens at room temperature. The Young's moduli (E) were measured on 120 mm long specimens by a dead loading creep experiment, the values quoted referring to the secant modulus at a strain (ε) of 0.4 % calculated from a 10 s isochronal stress-strain curve.

RESULTS AND DISCUSSIONS

The values of σ and E of the specimens under investigation are given in Table 1. Considering primarily the characteristics of original samples it become evident that the mechanical characteristics of PE1 are significantly worse (σ = 0.47 GPa) than those of PE2 (σ = 3 GPa), the scatter in the data being very large. 45 % of the specimens had σ = 3.3-3.9 GPa. Besides, there is some discrepancy between our results related to the weak effect of crystallization temperature on σ and the data published earlier (4) which demonstrate a considerable influence of crystallization temperature on the tensile strength of spinned fibers. Young's modulus of PE1 is also well below that of PE2 and only reaches 3.2 GPa.

TABLE 1. Mechanical characteristics of PE filaments

Specimen	Draw ratio	σ [GPa]	$\frac{\Delta\sigma}{\sigma} \cdot 100$	E [GPa] at ε [%]
PE1-100	1.0	0.47 ± 0.01	21	3.2 at 0.4
PE2-108	1.0	3.03 ± 0.39	13	22 at 0.1 17 at 0.1 - 0.4
PE2-110	1.0	3.06 ± 0.29	10	22 at 0.1 17.5 at 0.1 - 0.4
	1.8	4.20 ± 0.54	13	80 at 0.5
	2.0	4.63 ± 2.17	49	92 at 0.5
	2.8	4.45 ± 0.67	15	116 at 0.5
	4.4	4.21 ± 0.75	18	128 at 0.5
PE2-115	1.0	2.84 ± 0.30	11	44 at 0.1 24 at 0.1 - 0.4
	1.7	5.55 ± 0.96	17	74 at 0.5
	2.4	4.24 ± 1.19	28	96 at 0.5
	2.6	4.04 ± 0.52	13	88 at 0.5

The magnitude of Young's modulus of PE2 filaments depends strongly on the level of strain ε . In Fig. 1 the typical stress-strain curve is given. One can observe a sharp change in the slope of this curve at ε = 0.05-0.1 %, which implies a plastic deformation under load due to instability of structure. Values of moduli calculated for the curves of dissimilar slopes differ greatly (see Table 1).

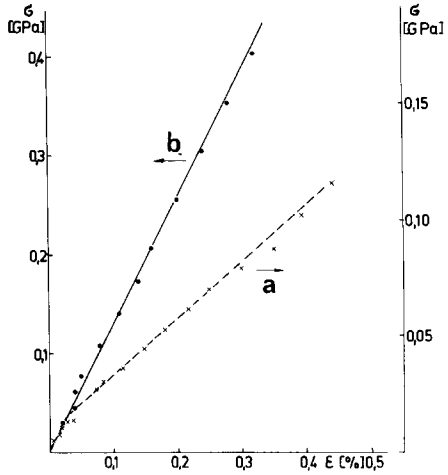


Fig. 1 Stress-strain curves obtained for original filaments of PE2 - 115 (a) and for the filaments of PE2 - 110 drawn 4.4-fold (b)

The values of E calculated at $\varepsilon = 0.1$ % are very high: as high as 44 GPa for PE2 - 115. The relationship between E and T_{cr} agrees with the results of SMOOK et al. (4); however, the moduli of our original samples are approximately 1.75 times less than those cited by SMOOK for the same T_{cr}. This discrepancy may be due to the technique of measurement, which will be discussed below.

The additional drawing was carried out for the PE2 - 110 and PE2 - 115 samples in three stages at the drawing temperature 130, 140, and 150 °C. We succeded in the drawing of PE2 - 110 4.4-fold, while the PE2 - 115 filaments could be drawn only 2.2-fold.

In contrast to the original undrawn samples, the stress-strain curve of the drawn filaments (the typical curve for all drawn samples is shown in Fig. 1b) is linear up to 0.45 %. This fact indicates that drawn filaments have a more stable structure than the original ones.

The relationship between Young's modulus E and draw ratio λ for PE2 samples is demonstrated in Fig. 2 (a, b). The significant increase (from 2.2 up to 5.8 times) of the E values is observed. The ultimate figures reach 128 GPa, which are slightly greater than the values of E, given by SMOOK et al. (4). One should note that the technique of E measurement used gives the lowest values of E in comparison with any other dynamic (in particular acoustic) test.

It follows from Fig. 2 that the Young's modulus of the filaments produced at $T_{cr} = 110$ °C grows more rapidly with increasing draw ratio than E of those produced at $T_{cr} = 115$ °C reaching a value as high as 128 GPa. However, both curves demonstrate a plateau at definite draw ratios. It might be caused by the intense development of a molecular

scissions process, which always occurs during the drawing of the melt crystallized specimens (MARICHIN et al. (5)).

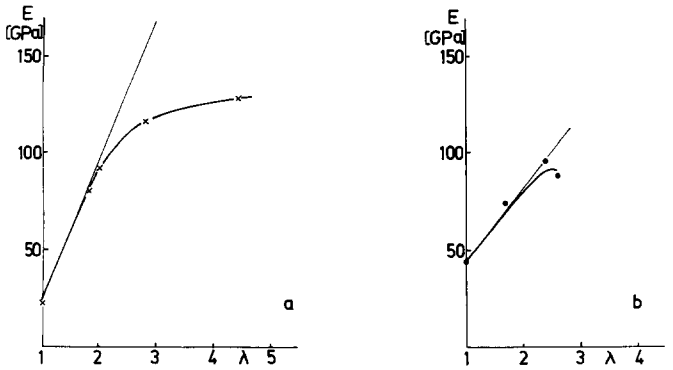


Fig. 2 Young's modulus of PE fibers as a function of draw ratio (a - PE2 - 110, b - PE2 - 115). The E values at $\lambda = 1$ correspond to E of original surface growth fibers.

The tensile strength of drawn samples also considerably increases with draw ratio (see Table 1), σ =4.65 GPa (PE2 - 110; $\lambda = 2.0$) being close to the highest value of tensile strength ($\sigma = 4.75$ GPa) given by SMOOK et al. (4), while the tensile strength of PE2 - 115 with $\lambda = 1.7$ is far greater ($\sigma = 5.56$ GPa) than those values.

The highest tensile strengths have been observed for filaments with intermediate draw ratios ($\lambda = 1.7 \div 2$). With the further increase of the draw ratio the tensile strength tends to decrease (see Table 1) although the moduli keep growing with draw ratio (Fig. 2). The highest tensile strength is observed for the drawn filament of PE2 - 115, when the moduli of these filaments are lower than those of PE2 - 110 filaments. It is seen from Table 1 that the scatter in the tensile strengths of drawn specimens is greater (up to 50 %) than for undrawn ones. The analysis of these data shows that approximately 13 % of the drawn filaments (from the 70) give very high figures of σ : 9.90; 8.42; 7.20; 6.30; 6.00; 5.80; 5.72; 5.70 GPa. These values are close to the theoretical estimate of the tensile strength of a polyethylene macromolecule. They are the maximum values of σ of flexible polymers published in the literature. The probability of observing tensile strengths of this magnitude is high enough (13 %).

The foregoing shows that the additional stepwise hot drawing of original fibers obtained by the surface growth fiber technique (4) may yield specimens of paticularly high tensile strength and modulus.

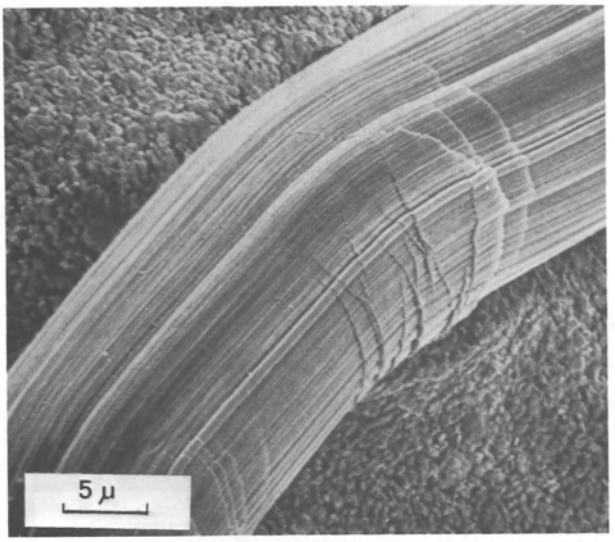
At the same time, not so strong fibers ($\sigma = 3.5 \div 4$ GPa)

are frequently involved in the measured samples (30 %). We assume that this is due to kink-band formation in the ultra-oriented fibers (6). The results of structural investigations of these specimens will be published in the nearest future. However, on the basis of preliminary studies one can maintain that the drawn fibers consist of some extended-chain crystals (or the crystals with partly extended chains) and microfibrils. The first ones are the central threads of original shish-kebab structure (shishs) while the latter are formed during the recrystallization process of kebabs under the action of orienting forces during drawing. Due to the very high degree of orientation of tie molecules in amorphous regions of these microfibrils, the whole specimen behaves like a strong anisotropic crystalline substance. The plastic deformation during compression, bending, elongation, ...etc. causes a specific kink-band formation.

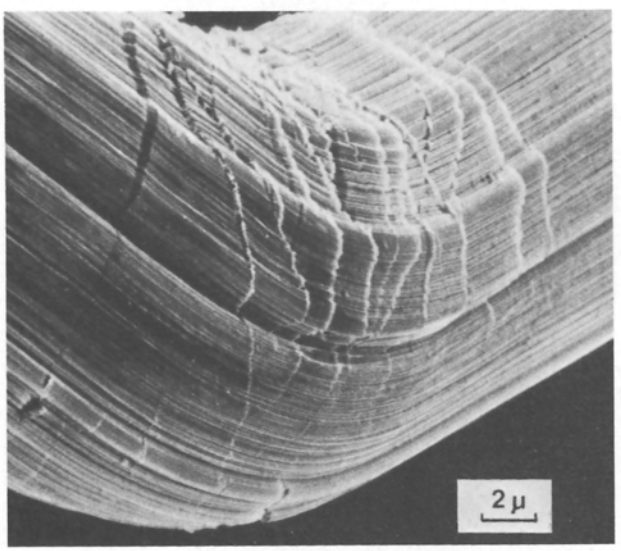
Indeed, the micrographis (Fig. 3) show a great number of kink-bands formed on the surface of our drawn sample during bending. Recently the development of kink-bands was found to cause a large number of microcracks, which results in a considerable loss of strength and drawability of these ultra-oriented materials.

These data were lacking when the original samples were obtained by surface growth fiber technique. No thought was then given to keeping the fibers from the strong bending during winding. This accounts for all the original fibers under investigation having many defects. We assume that the mechanical characteristics of the original as well as the drawn fibers were strongly affected by these defects.

Experiments are now in process aimed at obtaining defectless original fibers. With the above method of drawing used for defectless fibers, it is believed that material of enhanced modulus and strength may be obtained.



a



b

Fig. 3 Formation of kink-bands under weak (a) and strong (b) bending of ultraoriented fibers

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