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The Model of Polymer Orientation Strengthening and Production of Ultra-High Strength Fibers

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Summary

A model of junction network that is deformed upon drawing has been used to calculate maximum attainable draw ratios (X) and corresponding values of tensile strength (F) for different conditions of polymer film and fiber forming. Experimental data for melt-spun samples of polyethylene (PE), polycaproamide and polyoxymethylene and solution-cast films of polyvinylalcohol appeared to be in good agreement with calculated values. Considered also are methods for the increase of X and F due to polymer molecular weight enhancement in samples forming from "poor" solvent with subsequent orientation drawing under optimal conditions. Values of X = 130 - 230 and those of F = 7 GPa with a Young's modulus E ≈ 144 and sonic modulus E_s = 200 GPa, approximating theoretical, have been obtained for monofilaments of PE with m.w. $2 \cdot 10^6$.

Introduction

Ultra-high modulus and superstrength films and fibers of flexible and rigid chain polymers have been produced in recent years, primarily, by orientation drawing (CIFERRI and WARD 1979; KALASHNIK et al.1980; SAVITSKY et al.1983; SMOOK et al.1980; ZHURKOV et al. 1969). However, a number of problems of fundamental importance for futher progress in the field still remain obscure, despite numerous works and considerable advances in laboratory and industrial technology. The basic questions among them are those of the limit of polymer orientation strengthening and of possibilities for its enhancement by modification of polymer characteristics or processing conditions. The present study was undertaken with a view to provide an answer to these questions in terms of the model of molecular junction network rearranging during drawing (LEVIN et al.1967; HEISE et al.1980; SMITH and LEMSTRA 1979).

Calculated and experimental data

Two assumption were made for quantitative estimation of maximum attainable draw ratio X_0:

1) X_0 is determined as ratio of contour length L of chain between two adjacent junctions to the nearest distance between them l in the initial unoriented state (junction spacing).

2) The junction network is formed at the very onset of melt - elasticity transition when macromolecules are basically in liquid state (except for the sections incorporated in the junctions). The section of the chain between the junctions, as follows from configuration statistics, has, therefore, the shape of a statistical coil, the value L being related to l by ratio

$$L = l^2/A \qquad (1)$$

where A is the length of the statistical segment. Then

$$X_0 = L/l = L/A \qquad (2)$$

The values of l were calculated from those of strength F_0 of unoriented samples at temperature T = 77 K. It was assumed that 1) F_0 is supported by macromolecules binding the network junctions and breaking at the stress reaching theoretical strength of bond (f); 2) taut tie chain concentration is equal to junction concentration. Then $fs = F_0 l^2$, where s is cross-section of bond, and

$$l = (fs/F_0)^{1/2} \qquad (3)$$

The values of A used for calculating X_0 (Table 1) were chosen for polymer melts (or concentrated solution in the case of polyvinylalcohol) in terms of concepts presented in the works of BUSSE (1967), EGOROV and ZHIZHENKOV (1982). The values of F at 77 K were calculated as

$$F^* = F_0 X \qquad (4)$$

since a linear relationship has been observed between F and X for some semicrystalline polymers (SAVITSKY et al.1973). The strength at room temperature (F) was calculated from Zhurkov formula using experimentally obtained values for activation energy of fracture (SAVITSKY and DEMICHEVA 1977). Experimental data of ZHURKOV et al. (1969), also those obtained in a similar manner are in good agreement with the results of calculation (Table 1), which enable us to use the proposed model for a purposeful modification of polymer drawability. A most obvious possibility to increase X is through variation of L and l by reducing probability of junction formation due to introduction of a solvent that causes the molecular coil to move apart. To calculate X for solution-formed samples an assumption was made that probability of junction nucleation is proportional to the degree of macromolecules overlap which is, in turn, dependent on polymer volume concentration (C) being determined by the mode of polymer (P) - solvent (S) interaction in the system. Fig. 1 shows the number (N) of overlapped units (per 1 mole of monomer units) against C plotted for constant density of chains within the equivalent sphere. Solid line represents what is known as the "poor" solvent case with P - P interaction being more preferential than P - S at temperatures $T <$ θ-temperature. Solid line in fig.2 shows constitution diagram of the system. Dash-dot lines in fig. 1 and 2 represent N dependence on C and constitution diagram for the "good" (strong) solvent case when P - S interactions at all temperatures are more preferential than P - P.

At $C < C_{cr}$ macromolecules do not overlap, the critical value of C (C_{cr}) being determined from the condition of packing the entire system volume with unoverlapped macromolecular coils of the diameter D_s:

$$C_{cr} = (v/D_s^3)(M/m) \qquad (5)$$

where v and m are the volume and the weight of monomer unit, M is the polymer molecular weight;

$$D_s^2 = Z\,A_s \qquad (6)$$

where Z is the macromolecule contour length, A_s is the length of statistical segment in a given solvent at given temperature.

For "poor" solvent affine swelling was assumed to occur at $1 > C > C_s$ and N equal to that of pure polymer (N_0). With the decrease of C from 1 to C_s macromolecular coil diameter shows increase of D to D_s; it, however, remains constant upon futher dilution.

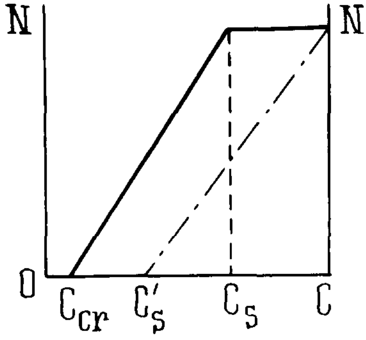

Fig.1. Variation of number of overlapping units with polymer concentration in the system for "poor" (solid line) and "good" (dash-dot line) solvent.

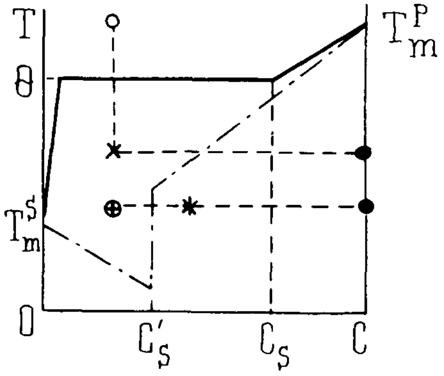

Fig.2. Constitution diagram of polymer - solvent system for "poor" (solid line) and "good" (dash-dot line) solvent.

The value of A_s can be expressed as $A_s = AC_s^{-2/3}$, taking account of (6) and assuming that $D_s^3 = DC_s^{-2/3}$. In transition of o—x, as is shown in fig.2, junction concentration of n may be correlated with that of n_o in the melt-formed sample if n is assumed to be proportional to N which is, in turn, dependent on C, as can be seen from fig.1. Then for $C_{cr} < C < C_s$

$$n = n_o k, \text{ where } k = (C - C_{cr})(C_s - C_{cr})^{-1} \qquad (7)$$

Junction spacing of the network thus formed is determined from the junction concentration and the degree of macromolecule swelling in the solvent. Due to this latter l_c shows $C_s^{-1/3}$ times increase:

$$l_c = (C_s n)^{-1/3} = l(kC_s)^{-1/3} \qquad (8)$$

Contour length L_c of the chain between adjacent junctions in polymer - solvent system may be expressed by the formula of the type (1):

$$L_c = l_c{}^2/A_s = Lk^{-2/3} \qquad (9)$$

It was futher assumed that removal of the solvent at $T_m > T > T_g$ (where the indexes denote melting and glass transition of the system), which is shown as x-● transition in fig.2, does not lead to junction destruction; nor does it result in the formation of new junctions; the occuring affine shrinkage and crystallization do not appear to have any noticeable effect on network averaged dimensions. As a result, the contour length of the chain between adjacent junctions does not change: $L_{sr} = L_c$ (sr denoting the state of the system after solvent removal). Junction spacing diminishes as a result of system volume decrease caused by solvent removal:

$$l_{sr} = l_c C^{1/3} = l(C/kC_s)^{1/3} \qquad (10)$$

Subject to eq.(2), maximum attainable draw ratio may be expressed as:

$$X_c = X_o(C_s/kC)^{1/3} \qquad (11)$$

It is evident that $X_c > X_o$ when $C_s > C > C_{cr}$. To calculate the maximum value of X_c (X_m) which can be achieved through dilution, one has to estimate the limiting concentration of C_{min} when macromolecules are still held together while the number of junctions appears to be minimum (n_m):

$$C_{min} = C_{cr} + l^3(n_m - 1)^{3/2}(AZ)^{-3/2}(C_s - C_{cr}) \qquad (12)$$

The formula, however, fails to regard variance of dimensions of L and l, as well as the junction structure, although it is evident that whatever their influence on C_{min}, the latter is invariably greater than C_{cr}.

As in the case of melt-formed samples, the strength (at 77K) of unoriented solvent free samples is determined by density of taut tie chains which in our model is equal to the density of junctions:

$$F^*_{sr} = fs/l_{sr}^2 = F_o\,(kC_s/C)^{2/3} \qquad (13)$$

After orientation drawing the strength is bound to increase owing to decrease of cross-section per one taut tie chain from S_o to S_f. In the simplest case the number of junctions and their structure are assumed to show no variation upon drawing, S_o consists of taut tie chain cross-section which remains constant and the area of $(S_o - s)$ occupied by coiled sections of macromoleculæs. If $(S_o - s)$ is believed to decrease upon drawing with the volume before and after drawing remaining constant, then after drawing to X the area per one taut tie chain

$$S_f = (S_o - s)/X + s, \quad \text{where } S_o = l_{sr}^2$$

and the strength at 77 K

$$F^* = fs/S_f = fF^*_{sr}\,X\left[f + F_{sr}(X - 1)\right]^{-1} \qquad (14)$$

The values of F at other temperatures may be calculated as described above for melt-formed samples. Taking into account (13) and (11) one can express F* in terms of polymer chain parameters and polymer - solvent system characteristics:

$$F^* = f\left[1 + fc(F_oX_oC_s)^{-1}k^{-1/3} - X_o^{-1}(kC/C_s)^{1/3}\right]^{-1} \qquad (15)$$

Allowing for $C_s - C_{cr} = C_s$ one can simplify eq.(15) and find that F* as the function of C has the maximum at $C = 1.5\,C_{cr}$. Substitution of this value of C into (11) gives the computed value of maximum attainable draw ratio for the given polymer:

$$X_m = 1.1(C_s/C_{cr})^{2/3}\,X_o \qquad (16)$$

According to (5), C_{cr} is proportional to $M^{-1/2}$, hence, X_m is proportional to $M^{1/3}$.

No junction occur in the case of "good" solvent at $C \;\; C_s$. For $1 > C > C_s$ (dash-dot line in fig.1 and ●-✱ - ● transition in fig.2) we get the following equations:

$$n' = n_ok_1, \quad \text{where } k_1 = (C - C'_s)(1 - C'_s)^{-1} \qquad (17)$$

$$l'_c = l(k_1C)^{-1/3}; \quad L'_c = Lk_1^{-2/3}; \quad X_c = X_ok_1^{-1/3} \qquad (18)$$

$$F^{*\prime} \approx F_0 X_0 k_1^{1/3} \qquad (19)$$

Here primed symbols denote the same quantities that unprimed ones denote in the case of "poor" solvent. As follows from eq. (19), in the case of "good" (strong) solvent, reduction of C results in the lowering of $F^{*\prime}$. In producing of fibers or films from polymer solution in "poor" solvent considerable enhancement of strength can be achieved through the increase of polymer molecular weight and decrease of its concentration; orientation drawing (which should be performed avoiding destruction) being an essential step of processing. The proposed model was tested in experiments on PE with m.w. $2\cdot10^6$. Monofilaments spinning, drawing and testing were similar to those described by SMITH and LEMSTRA (1980), ZHURKOV et al. (1969) and LEVIN et al. (1967), respectively. The results are presented in Table 2 and in. fig. 3.

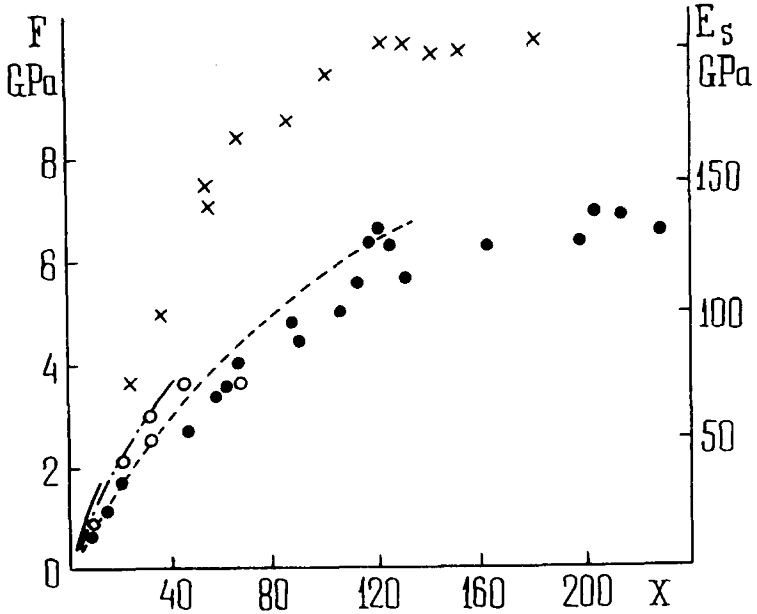

Fig. 3. Tensile strength (o and •) and sonic modulus (x) measured at room temperature versus draw ratio for PE samples: melt-formed (solid line) and decalin solution spun with PE concentration of 10 % (O and dash-dot line) and 2 % (dashed line, • and x). The lines represent calculated data, the points show experimental values.

TABLE 1

Initial data, calculated and experimental results for maximum attainable draw ratio X_o and strength at 77 K and at room temperature (F* and F) for several polymers

N	Polymer	$M \cdot 10^{-4}$	f*) GPa	F_o MPa	$A \cdot 10^{10}$ m	$1 \cdot 10^{10}$ m	Calculated			Experimental		
							X_o	F* GPa	F GPa	X_o	F* GPa	F GPa
1	Polycaproamide	2	25	300	4.5	34	7.5	1.9	1.5	7.5	2.3	1.7
2	Polyethylene	280	27	270	2.52	35	13.7	3.7	1.8	12–32	3.2	1.5
3	Polyethylene	7	27	270	2.52	35	13.7	3.7	1.8	12–32	3.0	1.5
4	Polyvinylalcohol	5	22	300	2.52	36	14.5	6.0	3.0	11–18	5.6	2.75
5	Polyoxymethylene		23	270	2.0	38	19	5.2	2.7	16	4.0	2.5

*) Data of PEREPJOLKIN (1970)

TABLE 2

Calculated (with $C_{cr} = 0.005$ and $C_s = 0.5$) and experimental data of tensile properties of maximum drawn solution spun monofilaments of polyethylene (m.w. $2 \cdot 10^6$)

N	C %	calculated			experimental			
		X_c	F_{sr}, GPa	F, GPa	X_c	F, GPa	E, GPa	E_s, GPa
1	100	14		1.8	12 - 32	1.5	23	60
2	20	25	0.14	2.65				
3	10	41	0.13	3.7	40 - 80	3.45	98	190
4	5	65	0.13	4.7	60 - 90	4.1		
5	2	134	0.10	6.7	140 - 230	7.0	144	200

Good agreement between calculated and experimental data, as well as the values of F and E for PE close to theoretical values, lead us to regard the proposed principle of strengthening as promising for other polymers.

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