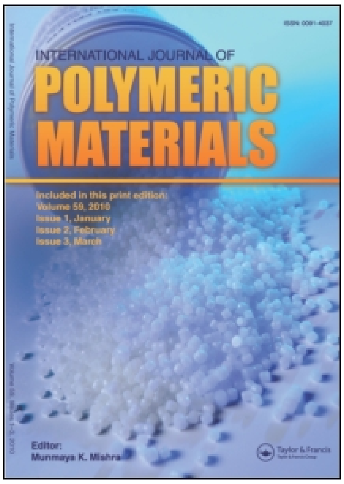

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Maruyama, Seiichiro , Imada, Kiyohisa and Takayanagi, Motowo(1972) 'The True Stress-True Strain Relationship in the Plastic Deformation of some Crystalline Polymers', International Journal of Polymeric Materials, 1: 3, 211 — 221

To link to this Article: DOI: 10.1080/00914037208075285

URL: http://dx.doi.org/10.1080/00914037208075285

Intern. J. of Polymeric Mater., 1972, Vol. 1, pp. 211–221

The True Stress–True Strain Relationship in the Plastic Deformation of some Crystalline Polymers

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(*Received* 5 *October*, 1971)

The relationships between true tensile stress (σ) and true tensile strain (ϵ) for plastic deformation of high density polyethylene (HPDE), its blends with *n*-paraffin, and nylon 6 were formulated in an equation with generalized form. The product of logarithmic σ/σ^* and logarithmic ϵ/ϵ^* is equal to a constant with negative value ($-c$). σ^* and ϵ^* are determined empirically by shifting the doubly logarithmic curves along with the both axes. Constant c is characteristic of polymer species, being independent of melt index, drawing temperature (30–110°C for PE, 80–160°C for nylon 6), deformation rate and blending ratio of paraffin to PE. The value of c is 0.384 for PE and 0.175 for nylon 6. Referring to the idealized system with $c = 0$, σ^* is predicated as the critical yield stress for unfolding molecules from lamellar crystals and ϵ^* is the true strain giving the extended chain conformation, which amounts to stretch ratio of 240 for PE. The fiber structure was assumed to form with contraction of the extended chains thus obtained. The law of volume additivity of σ^* holds for the blend system of HDPE and *n*-paraffin.

INTRODUCTION

There have been many works reported on necking phenomena of crystalline polymers during stretching process. However, few studies on necking process have been reported with consideration of the true stress–true strain relationships in the whole range of stretching.

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In this paper, the true stress–true strain behavior of high density polyethylene (HDPE), its blend material with *n*-paraffin, and nylon 6 has been investigated from a viewpoint of plastic deformation process beyond the extension of necking region. It was found that the true stress–true strain relationship of these materials could be represented by the generalized equation.

EXPERIMENTAL

The polymers used are listed in Table 1. These materials were melted on a hot plate and quenched in cold water. Polyethylene was blended with paraffin (in varying amounts) using a hot roller with a surface temperature 145°C.

TABLE I
Samples used

Sample	Polymer	Grade (Company)
PE-1	High density polyethylene	Hizex 1200J[1] (Mitsui Petrochemical Co.)
PE-2		Sholex 4002B[2] (Nihon Olefin Co.)
PE-3		Novatec JV040[3] (Mitsubishi Chemical Co.)
PE-3a	Blend of PE and paraffin	Novatec JV040 (90%) + paraffin A[4] (10%)
PE-3b		Novatec JV040 (90%) + paraffin B[5] (10%)
PE-3c		Novatec JV040 (90%) + paraffin C[6] (10%)
PE-3d		Novatec JV040 (80%) + paraffin C (20%)
PE-3e		Novatec JV040 (67%) + paraffin C (33%)
NYL	Nylon 6	Amilan CM1031 (Toray Co.)

[1] Melt Index (M.I.) 9.2
[2] Copolymer with butene-1, M.I. 0.2
[3] M.I. 4.0
[4] m.p. 50°C
[5] m.p. 70°C
[6] m.p. 108°C

The blended materials were melted again on the hot plate and quenched in the same way as the straight polymer samples. Three kinds of *n*-paraffins, A, B and C were used, of which the melting points were 50°, 70° and 108°C, respectively. The specimen for tensile testing was cut from the quenched sheet, its dimensions being 20 mm long, 50 mm wide and 0.3–0.6 mm thick.

Tensile testing was conducted using a Tensilon, Model UTM-III, equipped with an air-oven (Toyo Measuring Instruments Co., Ltd.).

The nominal stress (s)–nominal strain (e) curve were obtained at the conditions shown in Table 2. The definitions of s and e are as follows:

$$s = F/A_0 \tag{1}$$

$$e = (l - l_0)/l_0 \tag{2}$$

where A_0 and l_0 are the cross-sectional area and the length of the original, and F and l are the force and the length of the same sample during deformation, respectively. Figure 1 shows an example of the s–e curves.

TABLE II

Drawing conditions and some parameters characterizing the true stress–true strain curves for PE, the blends of PE and paraffin, and nylon 6

Sample	Drawing Temperature (°C)	Elongation Rate* (mm/min)	σ_Y (kg/mm²)	c	σ^* (kg/mm²)	ϵ^*
PE-1	30	5	2.65	0.384	1.28	5.75
	50	5	1.60	0.384	0.84	5.33
	70	5	1.17	0.384	0.63	5.38
	90	5	0.79	0.384	0.46	5.55
	110	5	0.50	0.384	0.27	5.58
	50	50	2.16	0.384	1.26	6.31
	70	50	1.45	0.384	0.82	5.91
	90	50	0.94	0.384	0.56	5.93
PE-2	90	5	0.95	0.384	0.41	4.82
PE-3	50	5	1.48	0.384	0.80	5.55
PE-3a	50	5	1.11	0.384	0.58	5.55
PE-3b	50	5	1.36	0.384	0.68	5.55
PE-3c	50	5	1.43	0.384	0.76	5.55
PE-3d	50	5	1.33	0.384	0.69	5.55
PE-3e	50	5	1.20	0.384	0.62	5.55
NYL	80	5		0.175	1.37	1.70
	120	5		0.175	1.26	1.78
	160	5		0.175	0.89	1.76

* Original length of the specimen is 20 mm.

The use of the nominal stress (s) and nominal strain (e) has generally been adopted in the studies of mechanical properties of polymers. However, in order to study the plasticity or large deformation of polymers, it is more appropriate to use the true tensile stress (σ)–true tensile strain (ϵ) relationship for interpreting the deformation mechanisms. The σ–ϵ curves were obtained with such intentions by the following methods.

The s–e curve was conventionally divided into two regions, O-A and A-B as shown in Figure 1. In the region of O-A, corresponding to the extension up to the beginning of necking, the true stress and the true strain were estimated by means of Eqs. (3) and (4) from the nominal stress (s) and strain (e) values.

$$\sigma = F/A = (F/A_0)(l/l_0) = s(1 + e) \tag{3}$$

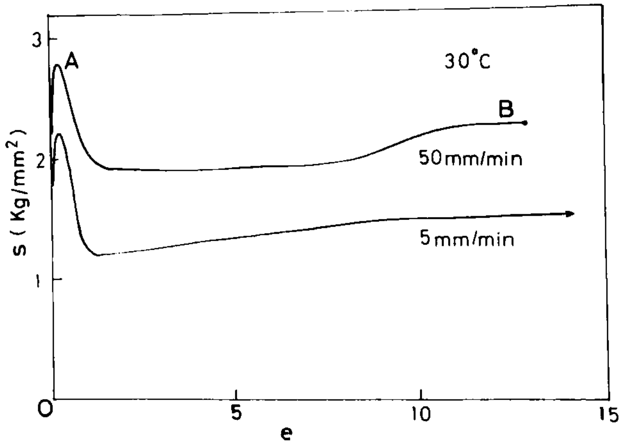


FIGURE 1 Nominal stress (s) vs. nominal strain (e) for PE-1 at the rates of 5 mm/min and 50 mm/min (original specimen length 20 mm). The sample yields at the point A and fractures at the point B.

$$\epsilon = \int_{l_0}^{l} \frac{dl}{l} = \ln (l/l_0) = \ln (1 + e) \tag{4}$$

These relations are based on the assumptions of uniform deformation and constant volume of stressed sample.

In the region of A-B, the true stress (σ) and the true strain (ϵ) were estimated by taking account of the reduction of the cross-sectional area (A) of the specimen accompanied by the increase of sample length. Eqs. (5) and (6) are derived with an assumption of constant volume from Eqs. (3) and (4), respectively.

$$\sigma = F/A \tag{5}$$

$$\epsilon = \ln (A_0/A) \tag{6}$$

where the value of A was evaluated by direct measurements of the cross-sectional dimensions of the specimen at each stage of elongation. Its operation was conducted as follows. At the time when the sample elongation was midway stretching was stopped, the stretching force was instantaneously read and the sample was quenched by air at the fixed length in order to measure the area of the neck part. The specimen seemed to be quenched without any significant change in its size.

Another type of measurement of true strain was conducted for comparison with those obtained by the above method. Gage marks were indicated at 2 mm intervals on the surface of the specimen. The increments of the distance between the neighboring marks were measured, including the neck region.

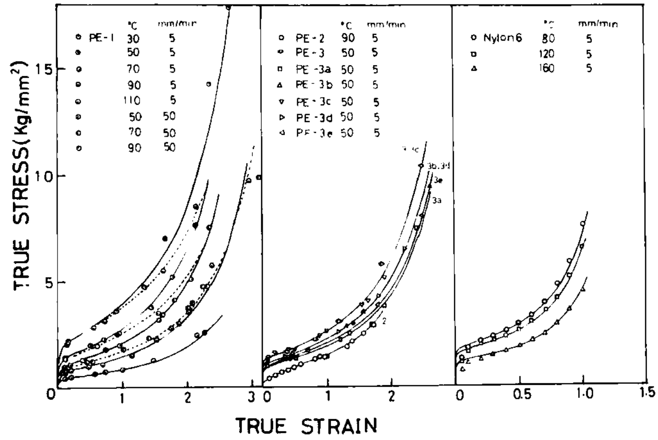
The true strain in this case was calculated by Eq. (4). The agreement among the strain values obtained by both methods was quite good. However, in the case of stretching at low temperatures, which accompanies a remarkable localized neck, the measurement of true strain by the gage length method was more difficult than the method based on the reduction of the cross-sectional area. The neck formation is associated with a complex triaxially stressed state in that region. Eq. (5) represents only an average stress in such a case.

Since, for nylon 6, a neck region was not observed during stretching, it was possible to calculate the true stress and true strain in the whole range of elongation by Eqs. (3) and (4).

RESULTS

Experimental data of true stress and true strain during elongation of each material under different conditions are shown in Figures 2(a), (b) and (c). The symbols of polymers in the figure agree with those listed in Table I.

We made doubly logarithmic plots of the true stress and the true strain for the data belonging to the A-B region in Figure 1, which cover the major parts of the curves in Figure 2. When we adequately shifted these curves parallel to the abscissa and the ordinate by $\log\epsilon^*$ and $\log\sigma^*$, respectively, in order to achieve superposition, we obtained a master curve of HDPE and that



(a) (b) (c)

FIGURE 2 True stress (σ) vs. true strain (ϵ) and the calculated σ–ϵ curves according to Eq. (7), for (a) PE-1, (b) PE-2 and the blends of PE-3 and paraffins A, B and C, and (c) nylon 6. The solid lines and the broken lines denote the calculated σ–ϵ curves at the elongation rates of 5 mm/min and 50 mm/min, respectively.

of nylon 6, respectively, as shown in Figure 3. These composite stress–strain curves are expressed by the generalized form of the following equation.

$$\log(\sigma/\sigma^*)\,\log(\epsilon/\epsilon^*) = -c \tag{7}$$

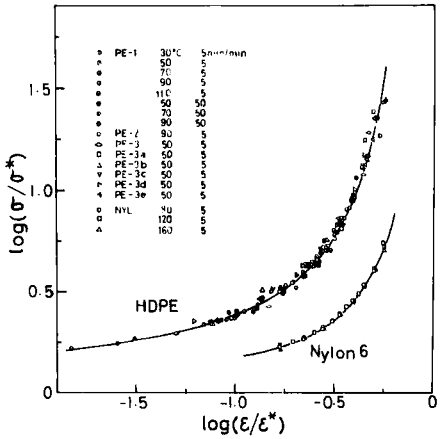


FIGURE 3 $\log(\sigma/\sigma^*)$ vs. $\log(\epsilon/\epsilon^*)$ for PE and nylon 6.

Table II shows the values of the shift parameters σ^*, ϵ^* and the constant c, together with the true stress σ_Y corresponding to the so-called yield point A in Figure 1.

Table II indicates that c is the constant value characteristic of each polymer. The constant c for HDPE is 0.384, which is independent of the grades with different values of melt index or copolymer composition, drawing temperature, and even of the composition of the blends with paraffin. The constant c of nylon 6 is 0.175, which is unaffected at least by the drawing temperature. In spite of the varieties in grades and in elongation conditions, ϵ^* exhibits almost constant values, being around 5.55 for HDPE and 1.75 for nylon 6 as shown in Table II. However, detailed inspection of the dependency of σ^* and ϵ^* of PE-1 on temperature as shown in Figures 4 and 5, respectively, reveals that not only σ^* but also ϵ^* are influenced by the temperature. General tendency is that the temperature dependence of σ^* is more remarkable than that of ϵ^*. The increase in the cross-head velocity for elongation also causes both σ^* and ϵ^* to increase.

It should be noticed that, for the blends of PE and paraffin, no change of ϵ^* could be observed with increasing concentration of paraffin. On the other hand, the addition of paraffin to PE decreases σ^*.

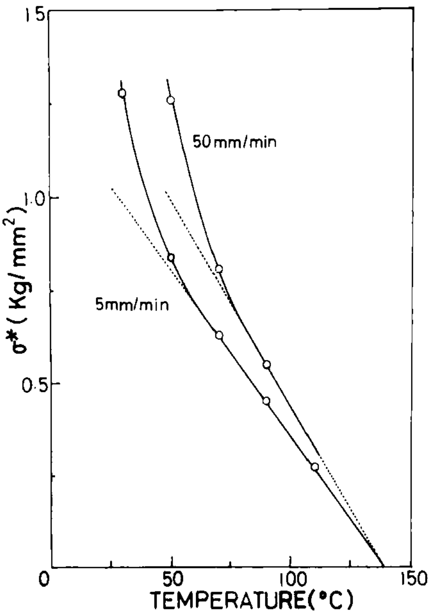


FIGURE 4 Values of σ^* vs. drawing temperature for PE-1 at the elongation rates of 5 mm/min and 50 mm/min.

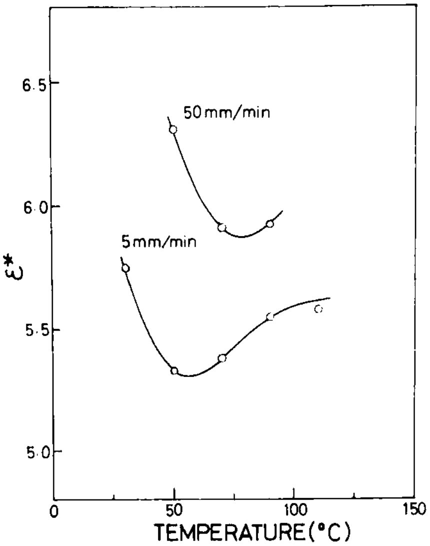


FIGURE 5 Values of ϵ^* vs. drawing temperature for PE-1 at the elongation rates of 5 mm/min and 50 mm/min.

DISCUSSION

According to Eq. (7), σ approaches asympotically to σ^* as ϵ tends to zero. The term σ^* may be associated with the yield stress of the original structure with spherulitic texture or lamellar crystals. The stress contribution from the elastic deformation is considered to be corrected for σ^* in such a limiting case. The fact that the σ^* value of HDPE is almost proportional to σ_Y seems to support this view. Since σ becomes infinite when ϵ tends to ϵ^*, the term ϵ^* expresses the ultimate strain at which the stress is assumed to be infinite. Such relationships are more clearly understood by envisaging the idealized system with $c = 0$ in Eq. (7). On the other hand, the deformation behavior of real system is characterized by the value of c, which measures the deviations from the behavior of the idealized system.

Figure 6 shows the schematic representations of σ–ϵ relationships corresponding with Eq. (7) for (a) idealized ($c = 0$) and (b) real system of crystalline polymers ($c > 0$). Figure 6 reveals that, for the idealized system, as soon as the original structure of lamellar crystal begins to yield or unfold at stress $\sigma = \sigma^*$ in $\epsilon = 0$, it continues to elongate at the constant stress of σ^* up to the ultimate strain $\epsilon = \epsilon^*$. At $\epsilon = \epsilon^*$, the initial fold structure is completely decomposed and the molecular chains are fully extended along with the direction of stress. Thus the stress of deformation rises abruptly to infinite. However, such an idealized process of deformation can not actually be

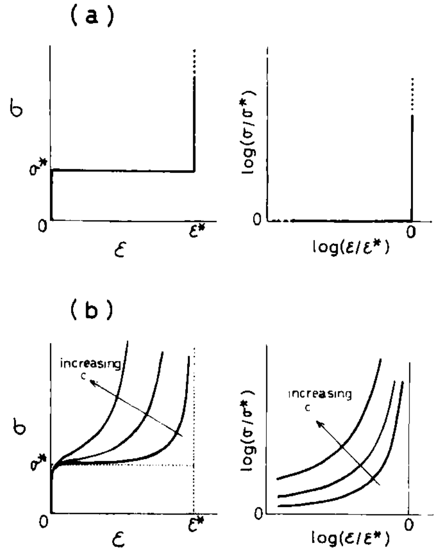


FIGURE 6 Schematic representation of true stress–true strain relationships for (a) idealized and (b) real systems of crystalline polymers.

expected, because the heterogenous micronecking will take place in a complicated fashion, being accompanied by the crystal rotation, interlamellar slip, tilting of molecules in lamellar crystal, crystal transformation, twinning, unfolding and so on. One may theorize that at the final stage of unfolding, some molecules are largely extended and at last become free from the restraint from the surrounding molecular environments owing to their highest retractive force. Once they become free in extended state, they may contract to form folded crystallites, and a fiber type structure. With such a mechanism of fiber formation, so-called interlamellar tie-molecules could form by the interaction of molecules in their contracting processes with different degree of constraint. Thus, the actual stretching process follows a different path apart from the idealized plastic deformation path as shown in Figure 6(a). The constant c represents, as mentioned above, a measure of the deviation of the actual system from the idealized one. For example, nylon 6 has a smaller c value than PE, and the plastic deformation of nylon 6 may be closer to the idealized process than that of PE, while the stress up to the yield point in nylon 6 is larger than in PE.

We will discuss in more detail concerning the temperature dependence of σ^* and ϵ^*. The value of σ^* of PE decreases lineally with increasing temperature. Extrapolation of this linear relation to $\sigma^* = 0$ gives the melting point of polyethylene on the abscissa. In the temperature range below 60°C for 5 mm/min elongation rate or 80°C for 50 mm/min elongation rate, σ^* deflects upwards from the linear relation as shown in Figure 5. The values of ϵ^* exhibit the minimum, when they are plotted against temperature. At this temperature, σ^* deviates from the linear relationship between σ^* and draw temperature. These temperatures are $T_1 = 333$°K with the cross-head velocity $k_1 = dl/dt = 5$ mm/min, $T_2 = 353$°K with $k_2 = 50$ mm/min. The activation energy for plastic deformation, ΔH^*, is evaluated by Eq. (8), which gives 27 $k$cal/mole.

$$1_n\,(k_1/k_2) = (\Delta H^*/R)\,(1/T_1 - 1/T_2) \tag{8}$$

This energy value agrees with the activation energy of 28 $k$cal/mole for relaxation as evaluated from the shift of frequency of the absorption maxima of α_1 against temperature in the mechanical relaxation of PE[1]. The α_1 mechanism has been postulated by Iwayanagi[2] to arise from the slippage between the both surfaces of stacked crystalline lamellae. However, Takayanagi and Matsuo[3] assigned it to the slippage between mosaic blocks, of which a lamella is composed. At present, it seems to be reasonable to consider that the interfaces of mosaic blocks start to slip while being accompanied by the unfolding of molecules at the interfaces of the blocks. Such a process will continue by creating the new slip planes in lamellae. Figure 7 represents a schematical representation of molecular process of unfolding of lamellar crystals. Fully

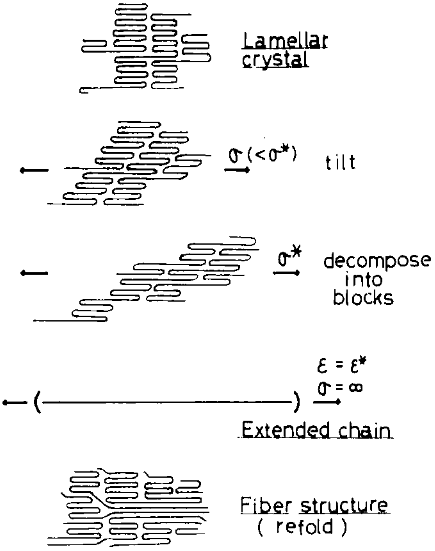


FIGURE 7 Schematic representation of molecular process of plastic deformation of lamellar crystals.

extended molecules are fictitious or only transiently feasible, which contract (due to the heat of drawing) to form a fiber-like structure with stacked crystallites.

Keith[4] has proved the existence of tie-links connecting the lamellae or lamellar bundles. Let us reconsider the above process by taking into account of the existence of interlamellar links. The molecular chains in the folded state in lamellar parts limited by two tie-links could be pulled out continuously, until the chains in the crystal block confined by tie-molecules are exhausted. The unfolding process will cease when $\epsilon = \epsilon^*$. At that time the chains between tie-links are perfectly extended. Although such a situation is fictitious, it is interesting to discuss this limiting case. The stretch ratio, l/l_0, corresponding to the average value of $\epsilon^* = 5.55$, gives the value of 240 by Eq. (2). Assuming that the lamellar thickness is 200Å and tie-link fraction is 1 %, the values of l/l_0 evaluated with such an assumption are around 40 and 100, respectively, for the two cases of the molecular chain arrangements before unfolding being perpendicular to the direction of stress as Kobayashi[5] described and parallel as Garber *et al.*[6] described. The assumption of molecular arrangement parallel to the draw direction seems to be more preferable at present than the perpendicular one, which corresponds with the schematical representation in Figure 7.

The values of σ^* for the blends of PE with paraffin C decrease linearly with increasing paraffin concentration. If the volume fraction of paraffin is denoted by v, we obtain an empirical equation (9).

$$\sigma^* = 0.80(1 - v) + 0.26v \tag{9}$$

Eq. (9) represents the law of volume additivity of stress. This means that the phases of PE and paraffin are subjected to the applied force in parallel with the same strain. Actually, the value of ϵ^* of the blend system is constant, assuming the value of 5.55. This value agrees with the value of unblended HDPE. Unfolding process of lamellar crystals of PE in the blend takes the same courses as in the pure PE.

Acknowledgement

We wish to express our deepest thanks to Mitsubishi Chemical Ind. Co., Ltd. for its financial support to this work.

References

1. H. Nakayasu, M. Markovitz, D. J. Plazek, *Trans. Soc. Rheology*, **5**, 261 (1961).
2. S. Iwayanagi, "Solid State Physics" (Seitz, Turnbull, edit.; Academic Press, New York, 1963) Vol. 14, p. 458.
3. M. Takayanagi and T. Matsuo, *J. Macromol. Sci.-Phys.*, **B1**(3), 407 (1967).
4. H. D. Keith, F. J. Padden, Jr., R. G. Vadimsky, *J. Polymer Sci.*, A-2, **4**, 467 (1966).
5. K. Kobayashi, cited in the book of P. H. Geil, "Polymer Single Crystal", *Interscience*, New York, 1963, p. 473.
6. G. A. Garber, E. S. Clark, *J. Macromol. Sci.-Phys.*, **B4**(3), 499 (1970).