Discrete strength levels in polypropylene films

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The mechanical strength of oriented and non-oriented polypropylene films was studied at a deformation rate of 50 mm min^{-1} and room temperature by using a statistical method. For the oriented and non-oriented films, the numbers of discrete strength levels were found to be eight and nine, respectively. The discrete strength levels were attributed to the spectra of the defects in the form of submicro-, micro- and macrocrazes. Oriented films showed higher levels of mechanical strength — an effect attributed to the absence of macrocrazes.

(Keywords: polypropylene films; orientation; discrete strength levels; defect distribution)

INTRODUCTION

The mechanical behaviour of polymers and composites has been systematically studied by Ward *et al.*[1–4] in terms of their structure, with emphasis on the theoretical description of the mechanical anisotropy in oriented polymers, polyethylene in particular. Structural models were developed. They include an aggregate model, which considers the polymer structure to be aggregated into highly anisotropic units, and a composite model for short-fibre-reinforced composites.

According to the statistical theory[5–8], the strength of materials is determined by the most damaging defect. In n different samples of the same series, defects of various damaging degrees can be found. The samples are characterized by different strengths σ_B expressed by the strength distribution curve $\rho(\sigma_B)$. Every maximum on this curve (or distribution function) corresponds to one type of defect with different damaging degree, e.g. microcrazes with different lengths. If the structure of the material has several types of defects — microcrazes, submicrocrazes, structural inhomogeneities — then $\rho(\sigma_B)$ has several maxima, i.e. several strength levels. The maxima on the strength distribution function are the discrete strength levels. The same approach can be applied to the elongations at break (ε_B) of the samples.

Discrete strength levels have been reported in a number of papers[9–17]. They result from the presence of defects of different nature in the polymeric material. Oriented crystalline and amorphous polymer fibres and lamellae (poly(ε-caprolactam), poly(ethylene terephthalate) and poly(methyl methacrylate)) were systematically studied.

Experimental data concerning the strength of non-oriented and oriented polypropylene (PP) films by using statistical methods of investigation have not been reported until now.

Polypropylene is a crystalline polymer with a spherulitic structure in the non-oriented state. On orientation of the crystalline polymer, the spherulite structure is destroyed and fibrils oriented along the direction of the applied force are formed. The fibrils are composed of microfibrils comprising alternating crystalline and amorphous parts[18]. The amorphous parts are the weaker ones in the polymer structure. Therefore, the structure of oriented and non-oriented polypropylene is heterogeneous (discrete).

By using small-angle X-ray diffraction[18,19], circular microcrazes having dimensions of 21, 50 and 150 nm were found to appear in the weak parts of the polymer structure under tension applied to the film. The largest crazes, which cause the breaking of the tested sample, were found to be the most damaging to the material's performance.

In the present work the discrete strength levels of non-oriented and oriented polypropylene films were studied.

EXPERIMENTAL

Isotactic polypropylene (iPP), Buplen 6631 (Neftochim, Bulgaria), $MI = 1$–3 g/10 min at 130°C and loading 21.2 N, density from 899 to 905 kg m^{-3}, was used as starting material.

The non-oriented iPP films were prepared by cold press moulding in the solid state. The oriented iPP tapes were prepared on an industrial line (Barmag, Germany). The preparation of the polymer tapes comprised: extrusion of the 1000 mm wide film, cooling it from 200 to 18°C in a water bth, winding on a roll and cutting the films by using a cutter drum. The tapes obtained were passed through slow-running rolls (30–32 m min^{-1}) and then continuously stretched at 140–150°C to get thin oriented fabrics by passing through fast rolls (170–190 m min^{-1}) and cooling down to 15–17°C. The fabrics thus obtained were wound on spindles. The stretching factor was $f = 6$. All samples prepared by the tapes were 20 mm long (test length), and 2.5 mm wide, 50 μm thick for the oriented films and 7 mm wide, 130 μm thick for the non-oriented films.

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The tensile strength and the elongation at break were measured at 25°C, at different stretching rates, by using a 'Teratest 2200' machine (Germany).

RESULTS AND DISCUSSION

It is well known that the strength of an oriented polymer can significantly exceed that of a non-oriented one. In some publications[19–21] it was pointed out that the strength of polymeric materials depends on the rate of their deformation. We carried out tensile tests on non-oriented PP films at five rates of stretching: 10, 50, 100, 500 and 1000 mm min^{-1} or within 50 to 5000% min^{-1}. *Figure 1* shows that the real stress at break does not increase monotonically with increasing deformation rate (curve 1). Within the rate range where the stress diminished, an abrupt decrease of the elongation at break from 1000 to 12% was observed (curve 2). It could be suggested for the irregularity observed that at small deformation rates there was enough time for the material to become oriented at the beginning of the loading and the dependence of strength on the loading rate in this range was similar to that of oriented material. At higher deformation rates the materials underwent nearly brittle break without achieving orientation. The results obtained correlate well with the data reported for PP[19–21].

The statistical study of the strength of oriented and non-oriented PP films was carried out at a deformation rate of 50 mm min^{-1}. Two hundred samples from each series were subjected to tensile test. The results obtained are presented as differential curves of the distribution of the nominal stress at break (*Figures 2* and *4*) and strain at break (*Figures 3* and *5*) for non-oriented and oriented films, respectively.

The differential curves obtained show a number of maxima corresponding to discrete values of the stress and strain at break.

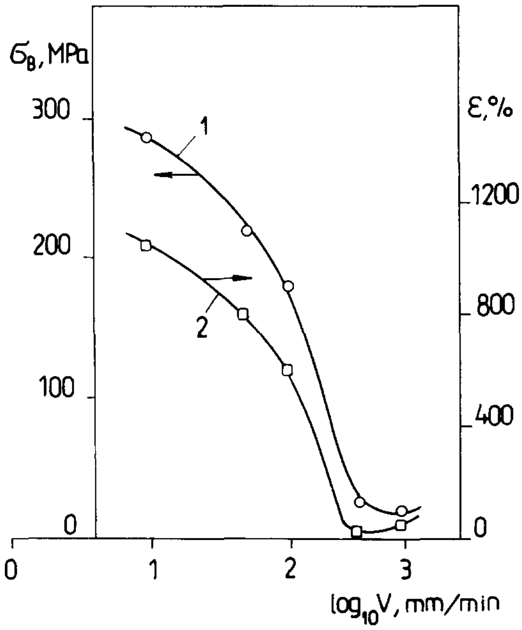

Figure 1 Dependence of the real strain at break (1) and the elongation at break (2) on the stretching rate for non-oriented iPP film samples

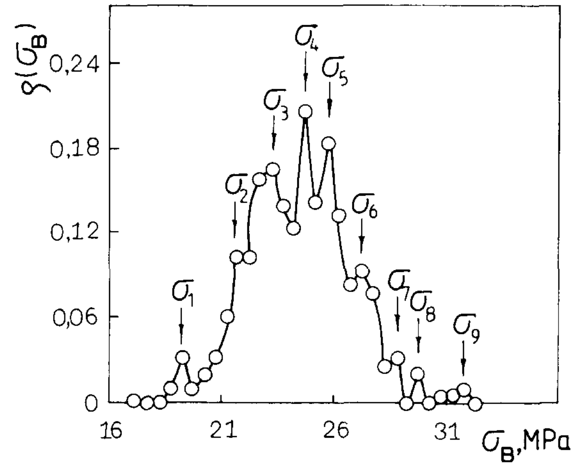

Figure 2 Distribution of the strain at break of non-oriented iPP film at 293 K

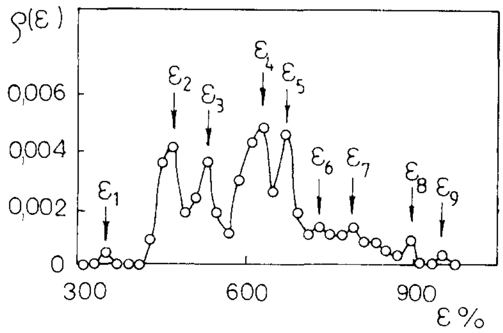

Figure 3 Distribution of the elongation at break of non-oriented iPP film at 293 K

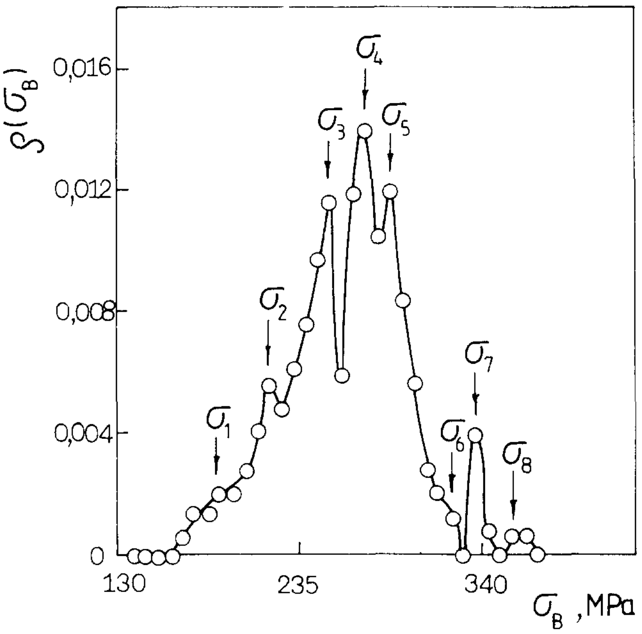

Figure 4 Distribution of the strain at break of oriented iPP film at 293 K

The dependence of the differential curve of the strength distribution $\rho(\sigma_B)$ on the nominal tensile stress at failure σ_B can be obtained from:

$$\rho(\sigma_B) = \frac{1}{n}\frac{\Delta n}{\Delta \sigma_B} \tag{1}$$

where $\Delta\sigma_B$ is the range of the breaking strengths from σ_B to $\sigma_B + \Delta\sigma_B$; Δn is the number of samples with strengths

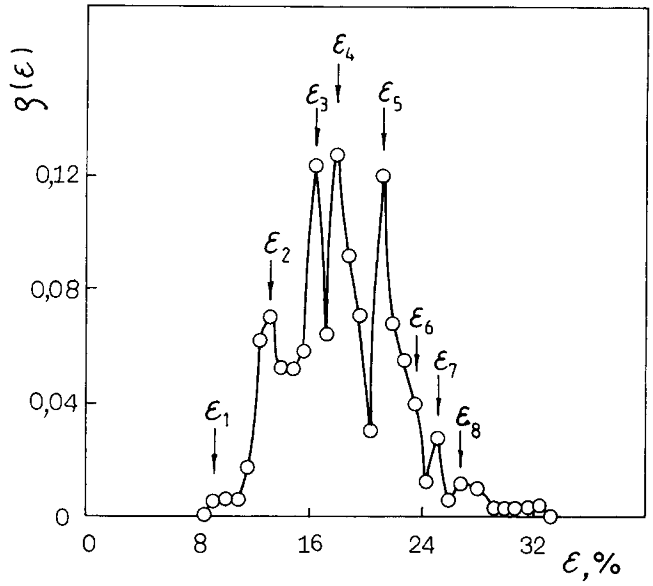

Figure 5 Distribution of the elongation at break of oriented iPP film at 293 K

within this range; and n is the total number of tested samples, in this case $n \geqslant 200$.

For elongations at break ε_B, similarly:

$$\rho(\varepsilon_B) = \frac{1}{n}\frac{\Delta n}{\Delta \varepsilon_B} \qquad (2)$$

There is a correlation between σ_B and ε_B, i.e. every discrete level of σ_B corresponds to a discrete level of ε_B.

The real stress at break σ_B^ϕ was calculated by using the dependence:

$$\sigma_B^\phi = \sigma_B(1+\varepsilon)^{2\mu} \qquad (3)$$

where σ_B and ε_B are related to every maximum of the differential curve; and μ is Poisson's ratio, known to be 0.46 for oriented PP.

Because of the structural changes taking place during the stretching of the non-oriented samples of PP films, the equation:

$$\sigma_B^\phi = \sigma_B(1+\varepsilon_B) \qquad (4)$$

was used. The values calculated by equation (4) are close to those obtained by equation (3) because 2μ for PP is close to unity.

Tables 1 and *2* show the numerical values of all discrete strength levels from *Figures 2–5*.

The average values of the stress at break $\bar{\sigma}_B$ and the elongation at break $\bar{\varepsilon}_B$ for all samples are: $\bar{\sigma}_B = 24.6$ MPa and $\bar{\varepsilon}_B = 607\%$ for non-oriented films, $\bar{\sigma}_B = 261$ MPa and $\bar{\varepsilon}_B = 18.5\%$ for oriented films. The average real stress at break $\bar{\sigma}_B^\phi$ according to equation (4) was 149 MPa for the non-oriented and 306 MPa for the oriented films (equation (3)).

The results obtained show that at least nine strength levels were found to exist (*Figure 2*) for non-oriented films and eight for oriented ones (*Figure 4*). Some authors[10–16] suggested that the discrete strength levels correspond to discrete defects within the polymer — submicrocrazes, microcrazes and macrocrazes — with characteristic length l_0. Conventionally, the defects are called submicrocrazes for $l_0 < 100$ nm, microcrazes for $100 < l_0 < 1000$ nm and macrocrazes for $l_0 > 1000$ nm. The crazes are accepted to be circular and to lie in the plane of the sample at right angles to the direction of loading and l_0 is the craze diameter. According to ref. 16, when the sample is in the form of a plate, l_0 can be calculated by the formula:

$$l_0 = 4\lambda^*(\beta-1)^2 \qquad (5)$$

where β is the coefficient of stress concentration at the craze ends; and λ^* is the characteristic linear dimension of the material microstructure, with $\lambda^* = \lambda_0 = 0.42$ nm for oriented polymer and $\lambda^* = 3\lambda_0 = 1.26$ nm for non-oriented, where λ_0 is the intermolecular distance.

The coefficient of stress concentration β can be calculated for each strength level via the formula:

$$\beta = \sigma_g/\sigma_i^\phi \qquad (6)$$

where σ_i^ϕ is the true stress at break from *Tables 1* and *2* for each strength level and σ_g is the theoretical limit strength of the material.

According to ref. 1:

$$\sigma_g = \frac{U_0}{\gamma_T} - \frac{2.3kT}{\gamma_T}\log\left(\frac{\tau}{\tau_0}\right) \qquad (7)$$

where $U_0 = 236\ \mathrm{kJ\,mol^{-1}}$ is the potential barrier for bond destruction; $\tau = 10^{-13}$ s is the period of atom vibration; $k = 1.38 \times 10^{-23}\ \mathrm{J\,K^{-1}}$ is Boltzmann's constant; $T = 293$ K; γ_T is the structure coefficient; and τ is the polymer durability.

The theoretical limit strength σ_g is the strength of a defectless material being unevenly stressed owing to its heterogeneous structure throughout its volume. For oriented material $\gamma_T = 3V_A^T$, where V_A^T is the fluctuation volume of the elementary act of destruction for an oriented polymer. It is commonly accepted that destruction takes place when the overstress in the microcrazes reaches its theoretical value $\sigma_T = E_D/V_A^T$, where E_D is the chemical bond dissociation energy. For

Table 1 Tensile properties of non-oriented PP films at a stretching rate of 50 mm min^{-1} and 25°C

No.	σ_{Bi} (MPa)	ε_B (%)	σ_i^ϕ (MPa)	β_i	l_{0i} (nm)	Comment
1	19.3	350	87	31.0	4536	
2	21.8	470	124	21.8	2180	Macrocrazes
3	23.8	530	150	18.0	1457	
4	24.8	630	181	14.9	974	
5	25.8	670	199	13.6	800	
6	27.3	730	227	11.9	599	Microcrazes
7	28.8	790	256	10.5	460	
8	29.8	890	295	9.2	339	
9	31.0	950	326	8.3	269	

Table 2 Tensile properties of oriented PP films at a stretching rate of 50 mm min^{-1} and 25°C

No.	σ_{Bi} (MPa)	ε_B (%)	σ_i^ϕ (MPa)	β_i	l_{0i} (nm)	Comment
1	180	9.5	205	13.2	250	
2	218	13.2	245	11.0	168	Microcrazes
3	255	16.4	290	9.3	116	
4	274	18.0	318	8.5	95	
5	288	21.2	343	7.9	80	
6	323	23.6	393	6.9	58	Submicrocrazes
7	337	25.2	414	6.5	50	
8	354	26.8	440	6.1	44	

PP, $E_D = 345\,\mathrm{kJ\,mol^{-1}}$ (ref. 22) and the theoretical strength $\sigma_T = 11\,000$–$12\,500$ MPa (ref. 23). Taking into account these considerations, V_A^T was calculated to be $(4.6\text{–}5.2) \times 10^{-29}\,\mathrm{m^3}$ and $\gamma_T = (13.8\text{–}15.6) \times 10^{-29}\,\mathrm{m^3}$. An average value of $\gamma_T = 14.7 \times 10^{-29}$ was adopted for further calculations.

According to ref. 9, the durability at constant stretching rate can be calculated by:

$$\tau = 1/\alpha\omega \qquad (8)$$

where $\alpha = \gamma_T/kT = 0.036$ MPa; and $\omega = E\,\mathrm{d}\varepsilon/\mathrm{d}t$. For our experiments $\mathrm{d}\varepsilon/\mathrm{d}t = 0.0416$ s, the elasticity modulus $E = 1940$ MPa and, therefore, $\omega = 80.8\,\mathrm{MPa\,s^{-1}}$.

By formula (8) the durability τ was calculated to be approximately 0.4 s. According to (7) the theoretical limit strength of oriented PP films was calculated to be $\sigma_g = 2667$ MPa; an approximate value of 2700 MPa was adopted in this case. Other authors[23] reported $\sigma_g = 2000$–4000 MPa for oriented PP films.

For non-oriented polymer $\gamma_T = V_A$, where V_A is the fluctuation volume, and γ_T is three times larger than that of the non-oriented, i.e. $\gamma_T = 3V_A$. By using formula (8) for non-oriented films it was calculated that $\tau = 1.2$ s, and according to (7) $\sigma_g = 2667$ MPa. It could be accepted, therefore, that $\sigma_g = 2700$ MPa for both series. Henceforth, the value of β was calculated by (6), and l_0 by (5). The calculated values are shown in *Tables 1* and *2* for both materials.

The cross-sectional dimension of a microfibril was reported to be 33 nm (ref. 19). It was calculated for the highest strength levels σ_8, σ_7 and σ_6 of oriented PP films that l_0 is 44, 50 and 58 nm, respectively, which indicates the existence of submicrocrazes with diameters corresponding to the cross-sectional dimensions of two microfibrils. At the lower levels σ_5 and σ_4 the submicrocraze diameters correspond to the cross-sectional dimensions of three microfibrils, at levels σ_3 to four microfibrils, at σ_2 to five microfibrils, and at σ_1 to eight microfibrils. The results obtained for oriented PP films showed that the discrete strength levels correspond to a discrete spectrum of submicrocrazes and microcrazes (*Table 2*).

The analysis of the results obtained for non-oriented PP films (*Table 1*) showed that the discrete strength levels correspond to a discrete spectrum of micro- and macrocrazes. If the diameter of a microfibril, 33 nm, is assumed to be the basic dimension, then the microcraze diameters correspond to cross-sectional dimensions of eight, 10, 14, 18 and 29 microfibrils. If the cross-sectional dimension of a single fibril is 1200 nm, then the macrocraze dimensions correspond to one and three fibrils. It was established that at a stretching rate of $50\,\mathrm{mm\,min^{-1}}$ (*Figure 1*) the non-oriented PP possesses comparatively high real strength owing to the transformation of the spherulite structure into one consisting of oriented fibrils. It could be suggested that submicro-, micro- and macrocrazes formed in the amorphous domains of the fibrillar structure during stretching and breaking of the material are the result of merging of developing defects. Furthermore, σ_4 is the highest level, which means that most of the samples were grouped around it. For non-oriented films $\sigma_4 = 181$ MPa, which coincides with the average strength $\bar{\sigma}_B^{\phi} = 174$ MPa; for oriented film $\sigma_4 = 318$ MPa, which is very close to $\bar{\sigma}_B^{\phi} = 306$ MPa. Therefore, the average strength changed mainly due to a redistribution of the samples over the different strength levels. It was smaller for non-oriented film because it was stipulated by lower strength levels corresponding to micro- and macrocrazes. Oriented films had no groups of defects and higher strength levels, corresponding to a spectrum of submicrocrazes.

CONCLUSION

The existence of a certain number of defects in the molecular structure of a non-oriented polymer determines its smaller strength. If higher discrete strength levels corresponding to submicrocrazes are observed in the film studied, then the film possesses higher strength, which is a proof that it was obtained by optimum technology. The nature of the defects of a polymer film prepared under various technological conditions might be assessed by the discrete spectrum of strength levels and the optimum conditions might be selected.

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