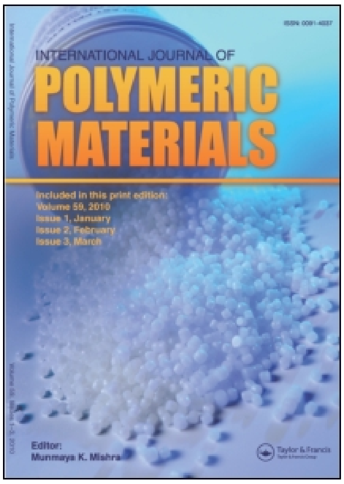

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INFLUENCE OF THICKNESS OF HOMOPHASE AND HETEROPHASE POLYMER FILMS ON THEIR MECHANICAL PROPERTIES

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INFLUENCE OF THICKNESS OF HOMOPHASE AND HETEROPHASE POLYMER FILMS ON THEIR MECHANICAL PROPERTIES

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Effect of thickness on mechanical properties ("scale factor") of polymer films with different structures was studied. Polymer films with different structures include: isotropic homophase films prepared by melt extrusion (PC, PP, PET) or solution-cast (PC, polyimide), also foamed films and polyblend films (made of incompatible polymers such as PET, PP, HIPS). Classical manifestation of this scale factor was observed mainly for homophase extruded films (including foamed ones). This effect is masked by residual stresses in solution-cast films or by specific heterophase structure in polyblend films. Influence of orientational drawing on scale factor was also established for various types of polymer films.

Keywords: polymer films, orientational drawing, strength, scale factor

NOMENCLATURE

PP	polypropylene
PET	polyethylene terephthalate
PC	polycarbonate
PI	polyimide
HIPS	high-impact polystyrene
PMMA	polymethylmethacrilate
Δn	experimental value of birefringence
Δn_{max}	the ultimate value of birefringence for ultradrawn polymer

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δ_o	undrawn film/wall thickness
δ_{ot}	threshold thickness
δ	drawn film thickness
σ_t	tensile strength
σ_{ft}	tensile strength of foamed film
ε_t	elongation at break
λ	draw ratio
λ_{max}	limiting (prebreak) draw ratio
N	number of monomer units in chain segment between joints
D	average gas bubble diameter
ϕ_m	limiting gas volume part
P	porosity
d_f	the average particle diameter

INTRODUCTION

It is well known that the strength of any material is a complex function of its bulk structure and surface quality. These are two factors that determine the structure, size, and danger of sample defects and therefore have decisive influence on strength level. Griffith's theory was the first taking into consideration defects' influence on strength. It suggested the existence of minor weak site (flaw, crack) in the material body that provokes macroscopic breakdown, when stress, during loading, reaches some critical level at this site.

For polymer films and fibers, strength distribution function was recently characterized by polymodal curves, which suggest the existence of discrete strength levels controlled by a set of defects such as microcracks of different size in the bulk and on the surface of the sample [1].

The character of defects location leads to manifestation of the scale factor—dependence of strength on sample size. Naturally, the thinner the film sample is, the less its surface and thus the less the quantity of surface defects, which are, as a rule, the most dangerous ones. The decrease of number of surface defects naturally leads to the growth of strength with decrease of film thickness.

It should be emphasized that polymer films are characterized by some specific features: processing-induced orientation of macromolecules; residual stresses; nonuniform or even heterophase structure and as a consequence by a variety of bulk defects, which could be particularly important in thin polymer films.

In this study the aims to demonstrate the effects of the scale factor, using as the objects homophase polymer films (melt extruded or solution-cast), foamed films, or polyblend films made of incompatible polymers with various degrees of macromolecular orientation in the matrix.

EXPERIMENTAL

The polymer films used in these experiments were obtained either by extrusion of the melt (PP, PET, PC) or by casting polymer solution onto substrate (PC, PI when PI films were prepared by thermal imidization of Poly(amic acid)). PP foamed films were prepared by extrusion of the melt, containing chemical blowing agent (azodicarbonamid). PET films, containing various amounts of the second polymeric component (HIPS, PP, PMMA), were obtained by melt extrusion.

Uniaxial drawing of the films was carried out at optimum temperatures, the strain rate and draw ratio ($\lambda = l/l_o$) provided proper degree of polymer chain orientation, which was characterized by $\Delta n/\Delta n_{max}$ value (Δn—experimental value of birefringence, Δn_{max}—taken from literatures, the ultimate value of birefringence for ultra-drawn polymer).

Tensile properties of polymer films were determined on an Instron testing machine at room temperature using standard dumbbell samples. The strength value was calculated for the initial cross section of the film.

RESULTS AND DISCUSSION

Effect of Undrawn Film Thickness on Its Properties

Figure 1 shows the tensile strength of different undrawn polymer films (PI (1), PC (2, 3), PET (4), PP (5)) as a function of their thickness, δ_σ. One can see that solution-cast films (1,3) show a clear trend of decreasing σ_t with decreasing δ_o below threshold value $\sigma_{ot} = 20-40$ μm. By contrast, extruded films show a trend of increasing σ_t with decreasing δ_o below the same value ($\delta_{ot} = 20-40$ μm). These differences in behavior can probably be attributed to the differences in films structures (cast or extruded).

The solvent removal from solution-cast films during their preparation is likely to induce a distribution of residual stresses throughout the cross section of the final film. One can assume that the residual stress relaxation is suppressed in thin films on substrate, thus giving rise to higher concentration of structural defects, which prevails over usual decrease in defect concentration of films when their thickness decreases. For unconstrained, extruded films the situation is opposite. Thin films seem to be less defective compared to

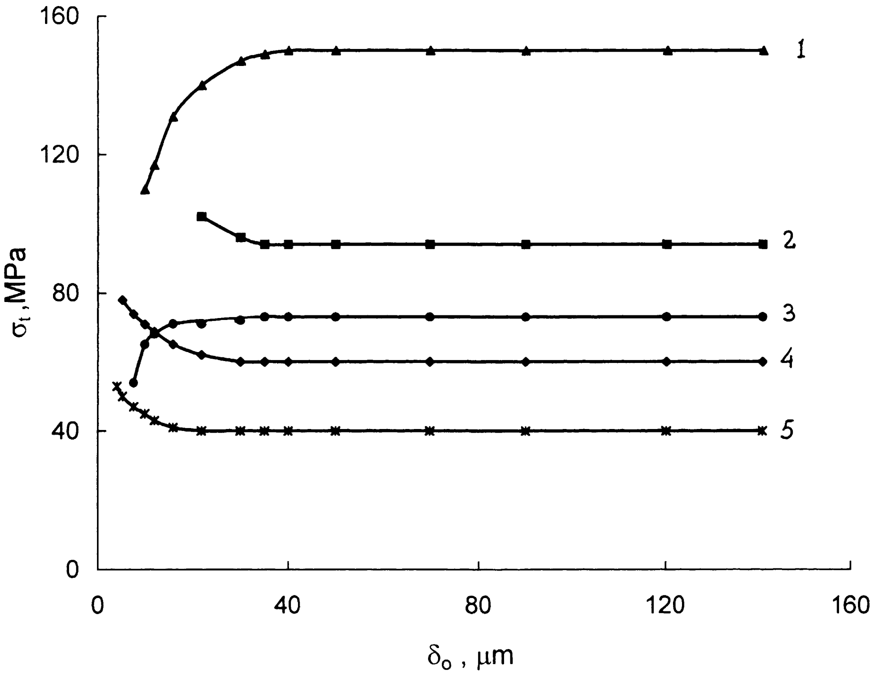

FIGURE 1 Tensile strength (σ_t) as a function of film thickness (δ_o) for undrawn solution-cast PI (1), PC (3), and extruded PC (2), PET (4), PP (5) films.

solution-cast: their strength increases in the region of thin films ($\delta_o < \delta_{ot}$).

The variation of δ_o affects also the elongation at break (ε_t) of films. The (ε_t) value, which is almost constant for thick films, decreases sharply when the film thickness decreases below δ_{ot}. This behavior was observed for both solution-cast and extruded films. One can assume that the lower deformability (as well as strength) of thin solution-cast films is a consequence of their higher imperfection (compared to thicker ones). As to extruded films the reason for their decrease is deformability (ε_t) will be discussed in the next section.

One may conclude that "classic" dependence of strength on film thickness is observed only for melt extruded films, whereas for solution-cast films "inversion" of scale factor is more usual.

Influence of Thickness on Tensile Properties of Drawn Films

In order to obtain polymer films with the structure of oriented macromolecules one should deform them at optimum temperature and strain rate [2–4]. Under optimum stretching conditions the highest elastic deformation and then the highest orientation of chain molecules can be achieved.

Maximum (prebreak) draw ratio (λ_{max}) was shown to be affected by the initial film thickness δ_o (Figure 2). Tensile strength σ_t and degree of orientation $\Delta n/\Delta n_{max}$ of drawn PP (extruded), PC (solution-cast) films decreases with the increase in drawn film thickness δ ($\delta \approx \delta_o/\lambda$) (Figure 3). A good correlation was observed between σ_t and $\Delta n/\Delta n_{max}$ for PP films, whereas there is only a small increase in σ_t as δ decreases for solution-cast PC films. It is believed that this effect is due to the low strength of initial (undrawn) thin PC films (Figure 1). Therefore, the effect of drawing of the film only slightly compensates for the imperfection of initial films. Nevertheless, the strength–thickness dependence (scale factor) after orientational drawing resumes its "natural" appearance for solution-cast PC films.

More thorough investigation of the initial structure of polymer films and its change during orientational drawing can be performed considering polymer deformation as deformation of entanglement network, consisting of chain segments, tied by fluctuating joints. In case

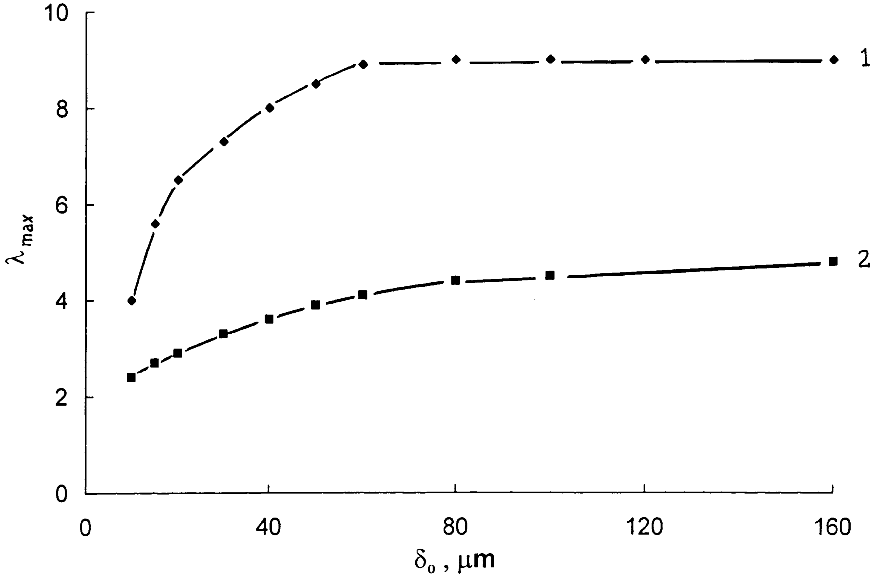

FIGURE 2 Limiting draw ratio (λ_{max}) vs. initial thickness (δ_o) of extruded PP (1) and solution-cast PC (2) films. Films were drawn under optimum conditions.

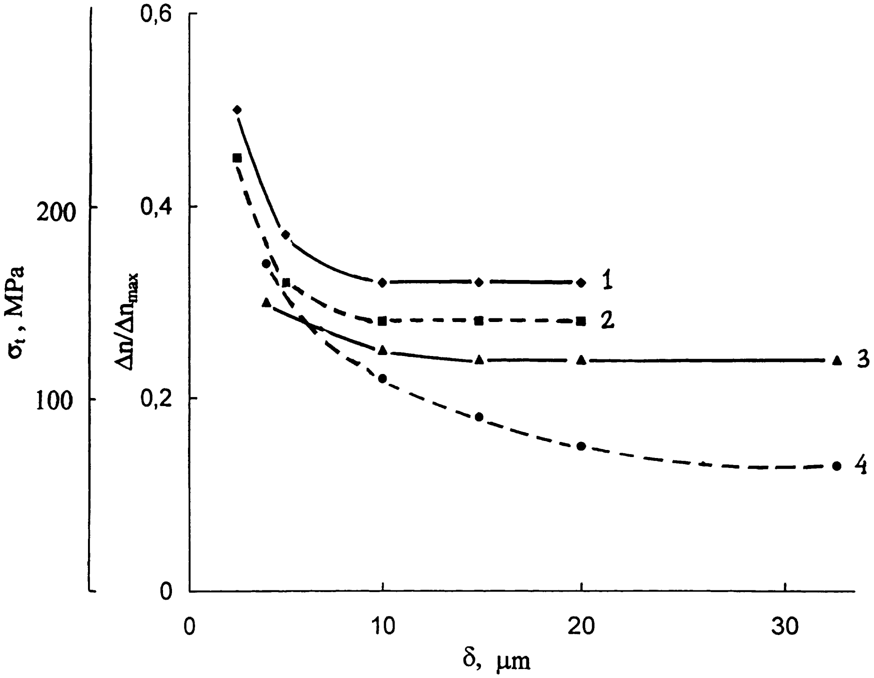

FIGURE 3 Tensile strength (σ_t) (1,3) and relative degree of macromolecules orientation ($\Delta n/\Delta n_{max}$) (2,4) vs. film thickness after drawing (δ). 1,2- PP films, extruded and then drawn up to $\lambda = 4$; 3,4- PC films, solution-cast and then drawn up to $\lambda = 2.5$.

of polymer deformation, orientation should be provided by transfer of these segments, when the number of fluctuating joints is unchanged up to certain deformation degree. It makes possible to use the simplified Roy-Kriegbaum equation [5]:

$$\Delta n/\Delta n_{max} = (1/5N)(\lambda^2 - 1/\lambda) \qquad (1)$$

where N is the number of monomer units in each chain segment, indicating network density (as N decreases, the network becomes more dense).

Linear dependence of $\Delta n/\Delta n_{max}$ on (λ^2 $- 1/\lambda$) shown for solution-cast PC films in Figure 4 proves that the model is valid to describe polymer deformation. This conclusion allows an estimation of N for

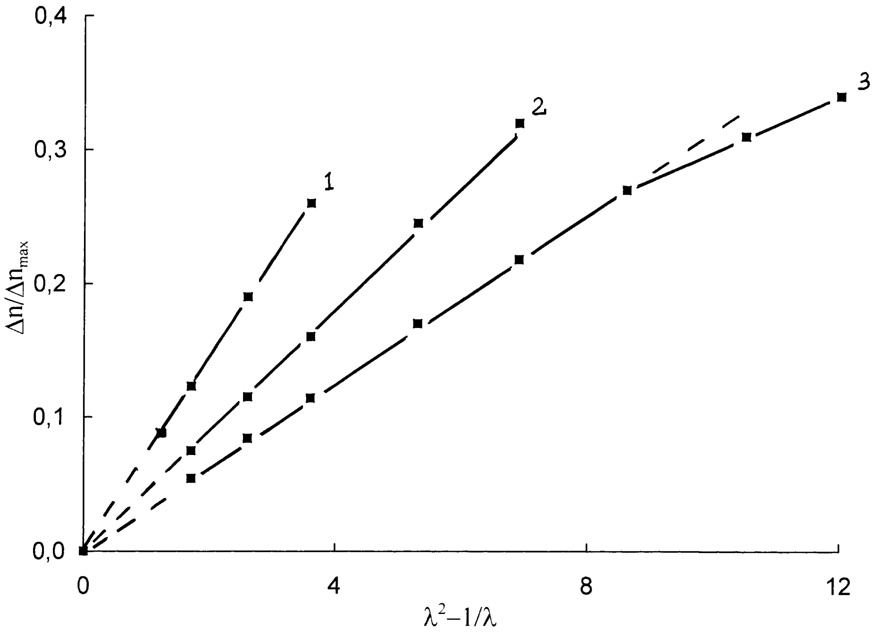

FIGURE 4 Relative degree of orientation ($\Delta n/\Delta n_{max}$) vs. ($\lambda^2 - 1/\lambda$) for solution-cast and subsequently drawn PC films. Initial film thickness: 10 μm (1), 50 μm (2), 80 μm (3).

films of different thickness. Calculated N value is 2.5, 4.3, 6.0, for 10 μm, 50 μm, 80 μm PC films, respectively. It means that network density is higher in thin films compared to thick ones.

The arrangement of lines 1–3 in Figure 4 suggests that, in the case of orientational drawing of thin films, the same degree of orientation and therefore the same film strength is achieved at lower λ than in the case of thicker films with lower network density. In other words, thin polymer films reveal more pronounced growth of orientation of macromolecules and thus higher growth of strength than thick films in the process of orientational drawing up to the same draw ratio λ.

At high values of λ, in the case of thicker films, the dependence of $\Delta n/\Delta n_{max}$ on draw ratio shows a well-pronounced deviation from the straight line (Figure 5, curve 3). This implies that at high λ the value of N increases. This allows one to conclude that, at certain values of λ, disruption of the weakest joints of physical network takes place, longer chain fragments are involved in orientation, and the rate of increase in $\Delta n/\Delta n_{max}$ slows down.

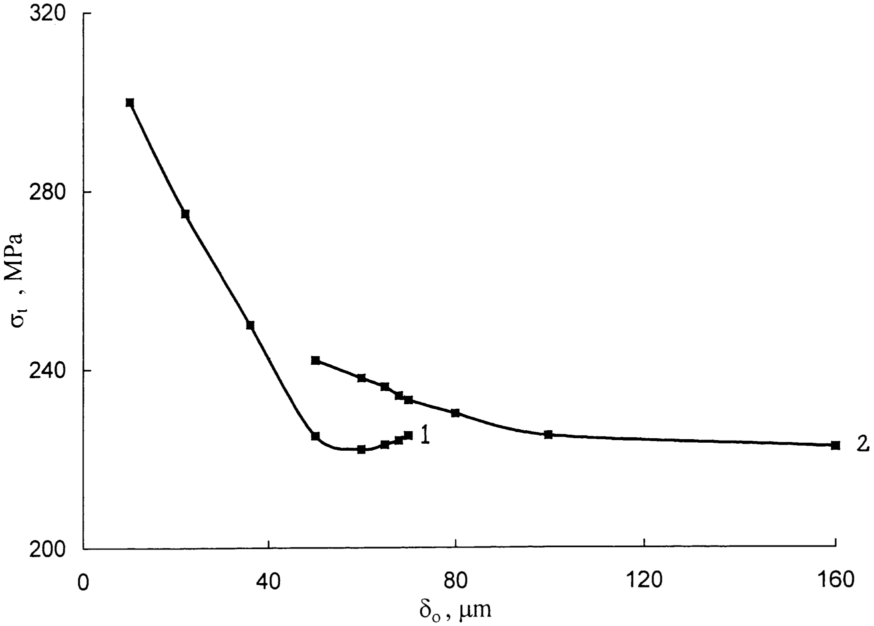

FIGURE 5 Comparison of tensile strength values (σ_t) for drawn foam walls (1) and drawn unfoamed PP films (2). 1-data calculated on Eq. 3 as a strength of walls in foamed films after drawing it up to $\lambda = 8$. Initial (before drawing) wall thickness (δ_o) was calculated according to Eq. 2. 2–tensile strength of monolithic PP film drawn up to $\lambda = 8$ and represented vs. initial film thickness (λ_o).

A similar trend—an increase in network density with decrease in film thickness—was observed also for extruded (PP, PET, PC) films. On the basis of the data obtained one can assume that it is higher network density that ensures higher degree of macromolecular orientation during drawing in thin films compared to thick ones (Figure 3, curves 2, 4).

Returning now to the effect of thickness on properties of undrawn films, one can assume that a higher network density in thin extruded films may be considered as a reason for their low deformability.

Thus, it can be concluded that orientational drawing of both thick and thin polymer films ensures increase in their mechanical properties. Thin polymer films reveal more pronounced growth of strength due to drawing because of higher degree of induced, macromolecular orientation and as a sequence "classic" manifestation of scale factor is observed for drawn films of different origin (extruded, solution-cast).

Influence of Film Thickness on Properties of Foamed Polymer Films

Preparation of thin polymer films ($\delta_o < 20\ \mu m$) in a process of extrusion is a rather complicated process. In order to investigate thin polymer film properties one can use foamed films. In this case the matrix polymer actually appears as a great number of thin films, or walls between gas bubbles [6].

If D is the average gas bubble diameter, ϕ_m—limiting gas volume part, P—ϕ_m; P porosity, the average thickness of polymer walls can be defined as [6]:

$$\delta_o = D(\phi_m/P - 1)^{1/3} \qquad (2)$$

The strength of this polymer film layer (σ_t) is related to the strength of foamed film (σ_{ft}) by the following equation [7]:

$$\sigma_t = \sigma_{tf}/(1 - P) \qquad (3)$$

The calculated values of σ_t for PP layers in oriented foamed films are shown versus initial layer thickness (δ_o) in Figure 5 (curve 1), where curve 2 represents experimental values of σ_t of monolith (unfoamed) oriented PP films versus initial films thickness (δ_o). As seen, curve 1 and curve 2 are close in some δ_o region and curve 1 may be considered an “extention” of curve 2 in a low thickness range. It can be clearly noted that there is a trend of increasing σ_t with decreasing thickness of PP monolith films as well as PP layers in foamed films, particularly in the low thickness region. The highest level of strength ($\sigma_t = 300$ MPa) is observed for very thin films ($\delta = 1\text{–}1.5\ \mu m$).

Increase in the degree of polymer orientation in thin polymer layers, surrounding gas bubbles in foamed films, during drawing leads to a remarkable growth of strength of polymer layers as well as foamed films with decreasing thickness, thus revealing the clearest manifestation of the scale factor.

Influence of Thickness of Heterophase Polyblend Films on Their Tensile Properties

Mechanical properties of polymer blends are usually studied using relatively thick specimen whose thickness is much greater than the size of particles of dispersed phase [8,9]. In the case of thin polyblend films, the size of the particles may become comparable with the film thickness and consequently the particles of dispersed phase may behave as macroscopic defects, whose influence on the properties of the film would be much more significant.

To demonstrate the effect of polyblend film thickness on its properties, PET films containing various amounts of HIPS, PP or PMMA were chosen. The dispersed phase in these films consisted of spherical particles, the average particle diameter was about 1, 3, 5 μm for PMMA, HIPS, and PP, respectively.

Typical $\sigma_t - \delta_o$ curves for undrawn extruded films are shown in Figure 6. As seen, the strength of the films, which is constant for thick films, decreases when film thickness decreases below δ_{ot}.

From experimental strength values of different films the authors found a correlation between δ_{ot} and the average particle diameter d_f:

$$\delta_{ot} = nd_f \tag{4}$$

when n is the coefficient, independent on the nature of the dispersed polymer, but affected by dispersed phase concentration. It was found that increase in concentration from 5 to 20% gives rise to increase in n from 7 to 9.

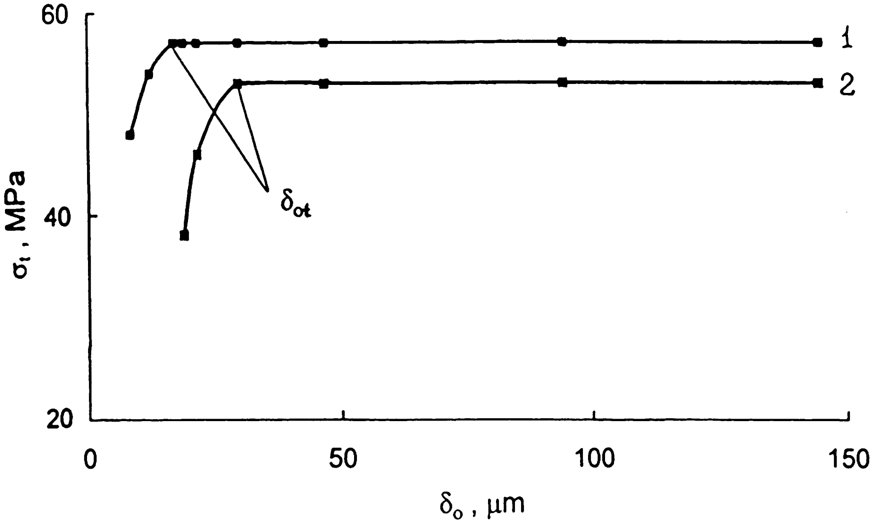

FIGURE 6 Tensile strength (σ_t) of extruded PET films, containing 5% HIPS (1) and 5% PP (2) vs. initial film thickness (δ_o).

The differences between thick and thin heterophase films are especially pronounced in the process of their orientational drawing. The value of λ_{max}, which is almost constant for thick films, falls sharply when the film thickness decreases, the position of the inflection point on the curve again gives the threshold thickness δ_{ot}.

Detailed investigation of samples structure at different draw ratios revealed, that almost all particles of the dispersed phase are deformed when thick films are drawn ($\delta_o > \delta_{ot}$). As the film thickness decreases below δ_{ot} only a small fraction of the dispersed particles is deformed; and this fraction decreases with a decrease in film thickness. Particles that are not deformed during the drawing do not contribute to the overall deformation of the system and, what is more important, perform as additional stress concentrators, thus limiting λ_{max} values and the strength of drawn polyblend film. The strength of PET films, containing 10% HIPS (initial thickness ($\delta_o = 30-200$ µm) after orientational drawing ($\lambda = 4$) is 180−200 MPa in the draw direction, whereas the strength of thin drawn films is only 130−150 MPa. Nevertheless, this value significantly exceeds the strength of undrawn films of HIPS/PET blend with the same thickness.

Thus, one observes that the main features of heterophase polyblend films is a very pronounced manifestation of the scale factor: thin films ($\delta_o \leq (7-9)\ d_f$) are characterized by sharply reduced strength and deformtpdel
ability compared to thicker ones.

CONCLUSIONS

On the basis of the data obtained, it can be concluded that mechanical characteristics of polymer films are in fact dependent on the thickness of the films. Extruded films show a trend of increase in σ_t with lowering δ_o below a "threshold" thickness $\delta_{ot} = 20-40$ µm. In other words, "natural" scale factor influence is observed in this case. By contrast, thin ($\delta_o \leq \delta_{ot}$) solution-cast films have low strength, presumably due to higher level of residual stress.

Orientational drawing of both extruded and solution-cast films leads to a significant increase in strength, which is higher when thin films are drawn. As a result, the "inversion" of scale factor is no more observed for solution-cast films. Orientational drawing of foamed films allows one to investigate the manifestation of the scale factor in the low polymer film thickness region (1−3 µm).

In was found, that thin heterophase polyblend films, when δ_o is less than 7−9 particle diameters, are characterized by reduced strength and deformability compared to thicker ones.

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