

# Cold Drawing of Polyethylene Terephthalate / Polyethylene Films

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## Synopsis

Films made from a 77/23 weight percent polyethylene terephthalate/polyethylene blend were stretched using an Instron apparatus. The structures of the samples were examined by methods which included ion beam etching and electron microscopy. The drawn samples exhibited a metallic luster and highly reflective surface up to a draw temperature,  $T_R$ , of 70°C and a draw ratio of about 5. Under certain conditions the change in structure caused by the stretching resulted in the formation of a highly uniform fibril-void structure. The voids are up to 3  $\mu\text{m}$  in width and 160  $\mu\text{m}$  in length and are formed primarily as a result of aggregation and then separation of the microfibrils of the individual polymer components.

## INTRODUCTION

The phase separation behavior and the structure-property relationships of polymer blends have been studied extensively. Thermodynamically incompatible polymers form heterogeneous polymer dispersions upon blending. The phase structure of such blends depends on the properties of the components, the blend composition, the mixing conditions, and the thermal history. Such blends may have properties which are not observed in the pure polymers with similar histories. For example, under specific conditions of stretching, the structure of a polymer blend can change to such an extent that its transparency is drastically reduced and a previously opaque sample may take on a metallic luster. This phenomenon is probably due to a specific structural rearrangement. The detection of structural changes during the cold-drawing of specific polymer blend films is the subject of this paper.

The occurrence of changes in transparency accompanying structural rearrangements during the drawing process has been observed with several polymers and polymer blends. For example, an opaque to translucent sample has been reported when polyethylene was drawn at low temperatures.<sup>1-3</sup> The stretching of pure polyethylene terephthalate (PET) also resulted in a structural change which influenced the light transmission of the sample. During the cold drawing of pure polyethylene terephthalate and of a pure polyamide, silvery striations were frequently obtained perpendicular to the direction of draw.<sup>4-8,10</sup> A uniformly lustrous sample of polyethylene terephthalate has been produced at very high drawing speeds.<sup>7-9</sup> In the present case, the

addition of small amounts of polyethylene to polyethylene terephthalate increased the silvery luster so that this "metallic effect" could be observed even at a low rate of stretching.<sup>9</sup>

Wenig and Hammel<sup>9</sup> investigated films made from a 70/30 wt% polyethylene terephthalate/polyethylene blend and suggested that the change in transparency on cold drawing can be explained by the formation of microvoids. The transparency change may occur at the formation stage of fibrils created during the deformation; the size of the fibril-void structure formed then determines the degree of change in transparency.

The structural changes brought about by stretching polymer blend samples are strongly influenced by the degree of mobility of the molecular chains and by the intensities of interactions between different polymer components.<sup>11,12</sup>

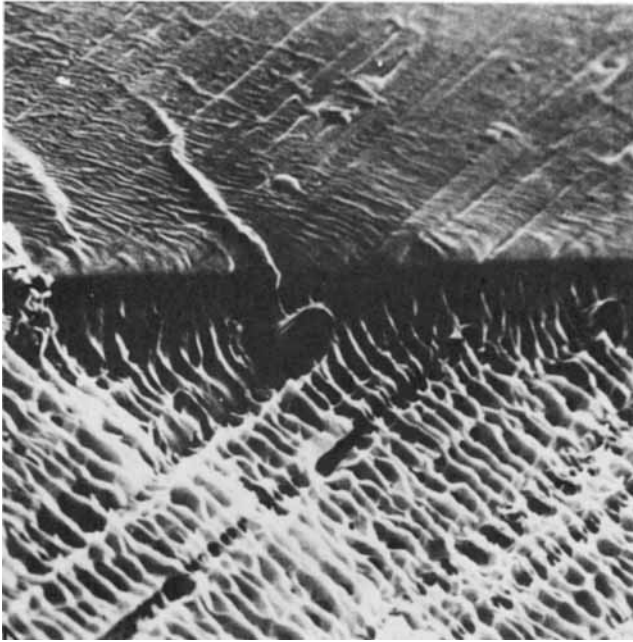
### EXPERIMENTAL

A series of films of different blend compositions was produced by extrusion of pellet mixtures. A one screw mixing extruder with a set die was used. The extrusion temperature was 290–300°C. The film obtained was drawn off from the die by a take-up device with a velocity of 0.2 cm/s and cooled to room temperature. The following polymer compounds were used: polyethylene terephthalate produced by VEB Chemiefasorkombinat "Wilhelm Pieck" Schwarza, with an intrinsic viscosity of 0.68 (measured in phenol/tetrachloroethane at 25°C); low density polyethylene produced by VEB Leuna-Werke "Walter Ulbricht" with a melt index of 7 g/10 min and a density of 0.975 g/cm<sup>3</sup>; polyamide-6 produced by VEB Chemiefasorkombinat "Wilhelm Pieck" Schwarza, with an intrinsic viscosity of 0.9 (measured in *m*-cresol at 25°C).

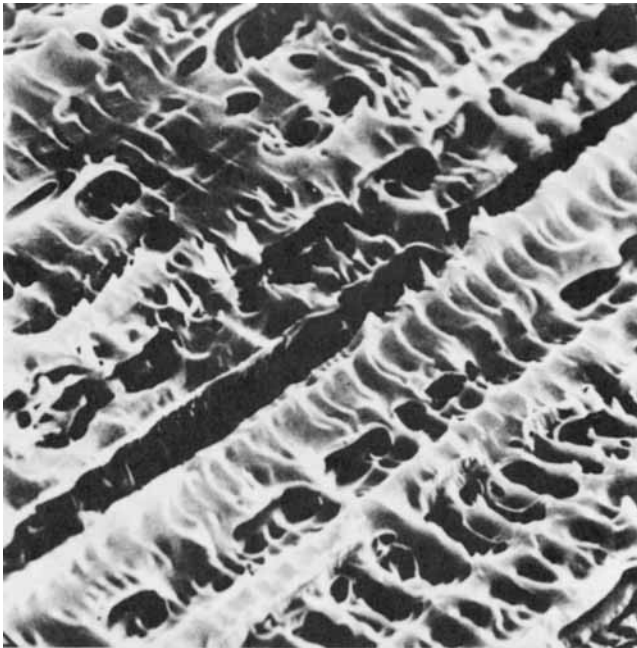
The polyethylene terephthalate and the polyamide-6 pellets were dried before extrusion in a vacuum oven at 100°C to reduce the water content to 0.005% for polyethylene terephthalate and to 0.05% for polyamide-6.

Films initially 84 μm thick were drawn using an Instron apparatus. The following parameters were varied: (1) the rate of extension ( $q$ ) from 8 %/min to 1200 %/min; (2) the draw temperature,  $T_R$ , from 22°C to 100°C; and (3) the draw ratio,  $RV$ , from 2 to breakage. The draw ratio was calculated from the change in length  $\Delta l$  relative to the initial length  $l_0$ . Stress-strain curves were recorded during the stretching.

The morphology of the film was examined by electron microscopy. Images of the film surfaces (upper part of Fig. 1a and Fig. 3) were obtained after gold evaporation coating using a scanning electron microscope (JEOL JSM 1). The approximate sizes of the fibrils could be determined in microtomed samples (Fig. 2) but no definite conclusions could be drawn about the internal structures of the films because of the disturbances created by the microtoming process. For this reason ion beam etching, which produced an undisturbed surface cut by the gradual removal of material, was tested. In this procedure, which has been described previously,<sup>13</sup> part of the sample was covered by a screen (BL) as shown in Figure 5 and the area A was exposed by ion beam sputtering. A cut through the material, slope B, was generated between the exposed and covered regions. The angle and location of this cut surface could be predetermined with a high degree of accuracy and controlled by the scanning electron microscope.



(a)



(b)

Fig. 1. Scanning electron micrographs of (a) partially and (b) completely etched drawn polyethylene terephthalate/polyethylene film ( $T_R = 40^\circ\text{C}$ ;  $q = 40\%$  stretch/min,  $RV = 3$ ) (a) 255-fold enlargement, (b) 2550-fold enlargement.

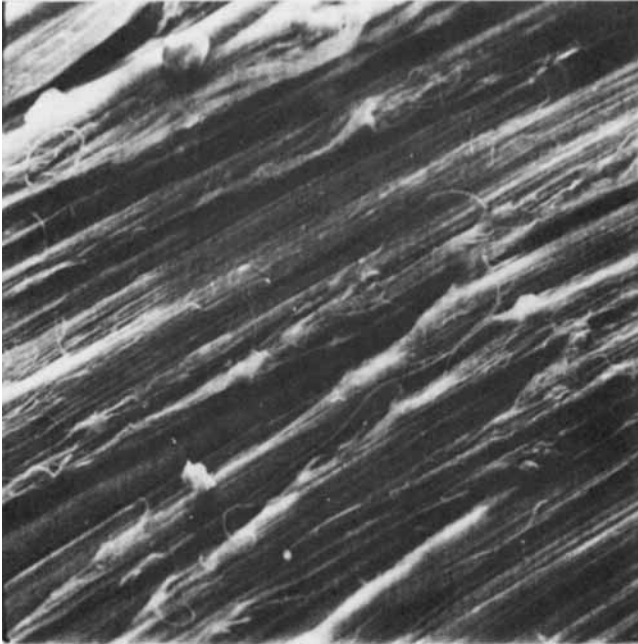


Fig. 2. Scanning electron micrograph of a drawn and subsequently sliced polyethylene terephthalate/polyethylene film ( $T_R = 30^\circ\text{C}$ ;  $q = 800\%$  stretch/min,  $RV = 4.5$ ), 255-fold enlargement.

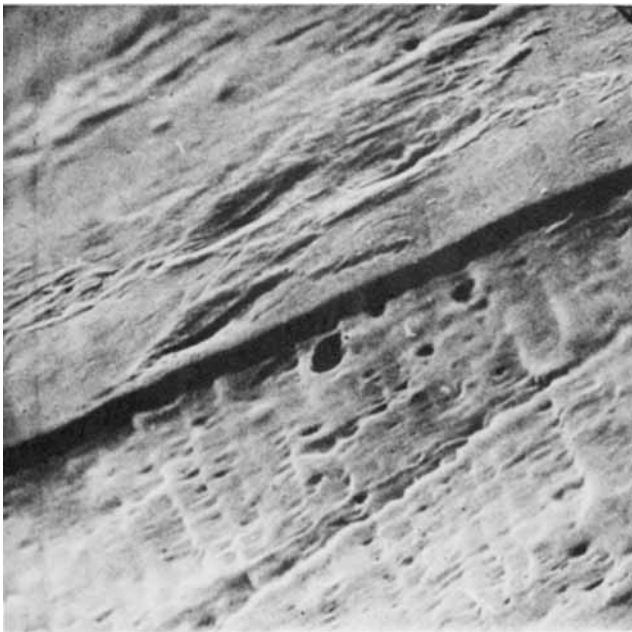


Fig. 3. Scanning electron micrograph of an undrawn partially etched polyethylene terephthalate/polyethylene film, 2550-fold enlargement.

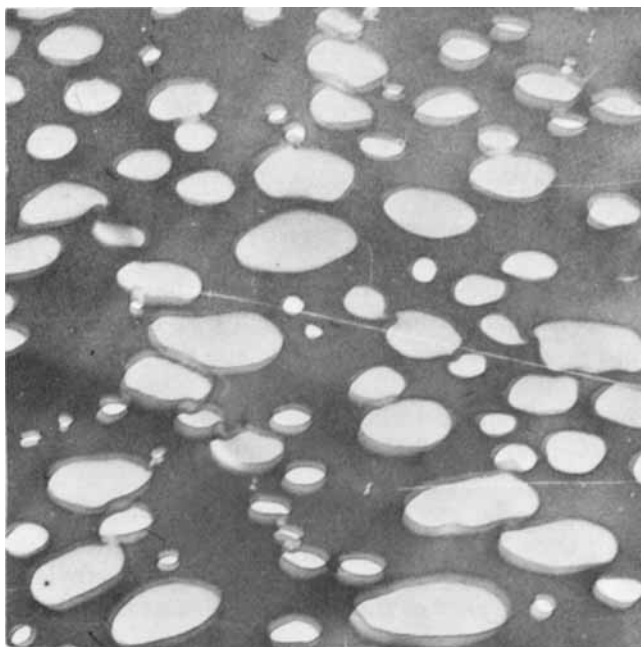


Fig. 4. Transmission electron micrograph of a stretched polyethylene terephthalate/polyethylene film ( $T_R = 40^\circ\text{C}$ ;  $q = 800\ \%/min$ ,  $RV = 4.5$ ), 3400-fold enlargement.

A disadvantage of this method was that the exposed surface A could be roughened to an extent depending on the ion beam parameters, thus resulting in artifacts of preparation. However, using this method of sample treatment, information could be obtained about the size, distribution, shape (cross section, internal surface), and position of the voids in the polymer material (cf. Figs. 1 and 3).

Thin sections of polymer films were examined by electron microscopy (SEM 3-2, Werk für Fernsehelektronik Berlin) in order to study the distribution of the disperse phase (polyethylene) in the polyethylene terephthalate matrix. However, as for scanning electron microscopy, the sample treatment, in this case microtome cuts, was assumed to affect the results.

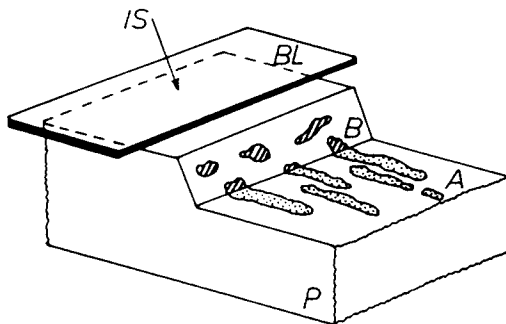


Fig. 5. Removal of the surface of polymer blend films by ion beam sputtering. P-polymer blend film; BL-screen; IS-ion beam direction; A-exposed surface; B-cut surface.

The volume and the volume distribution for voids of radii ranging from 4 to 6500 nm were determined using a mercury high pressure porosimeter, model 225 (Erma Carlo Erba Strumentazione). The data obtained were evaluated using a computer program.<sup>14</sup> The degree of crystallinity of the films was determined by measuring the heat of melting by scanning calorimetry (Perkin-Elmer DSC-1B).

## RESULTS

Preliminary examination of the occurrence of the metallic effect and the light transmission differences due to stretching were made for a series of films of different blend composition: (1) polyethylene terephthalate/polyethylene films with a polyethylene terephthalate content of 40–93 wt%; (2) polyethylene terephthalate/polyamide-6 films with a polyethylene terephthalate content of 80–90 wt%; (3) polyethylene/polyamide-6 films with a polyamide-6 content of 80–90 wt%.

It was found that the metallic effect was observed only with samples containing more than 50 wt% polyethylene terephthalate. The film of the 77/23 weight percent polyethylene terephthalate/polyethylene blend was used in detailed examinations of the structural change brought about by cold drawing.

### Influence of the Stretching Conditions

The stretch experiments performed on the polyethylene terephthalate/polyethylene film showed that the following conditions were optimal for the occurrence of the metallic effect: (1) The temperature of draw should not exceed 70°C. (2) The rate of draw ( $q$ ) must be at least 40 %/min. (3) The draw ratio ( $RV$ ) must not exceed a critical value. The draw process must be terminated after the neck has passed through the sample. For the film examined the value of  $RV$  was between 4 and 5. It is important to emphasize that stretching reduced the light transmittance of the metallically lustrous films by 96% and decreased the thickness of the films from 84  $\mu\text{m}$  to 23  $\mu\text{m}$ .

### Stress–Strain Behavior

The stress–strain behavior of the polymer blends depends on the stretching parameters. The stress–strain curves exhibit a shape typical of a cold-drawing process with neck formation up to a draw temperature ( $T_R$ ) of 70°C and draw rates ( $q$ ) of 40% stretch/min (Fig. 6). The initial maximum (close to 0.1  $RV$  in Fig. 6) is characteristic of stress-strain behavior of polymers at low draw temperatures and is caused by irreversible flow processes during neck initiation. The neck propagates along the sample and will reach the clamps of the measuring apparatus at a draw ratio of about 3–5. Small defects in the samples caused by these clamps may be the reason for the anomalous slight depression of stress observed in the stress-strain plots for  $3 < RV < 5$  and  $T_R$  below 70°C. At draw temperatures above 70°C the initial maximum in the stress-strain diagram of the polyethylene terephthalate/polyethylene film disappears. The mobility of the molecular chains increases with temperature and results in lower forces than are necessary at low temperatures.

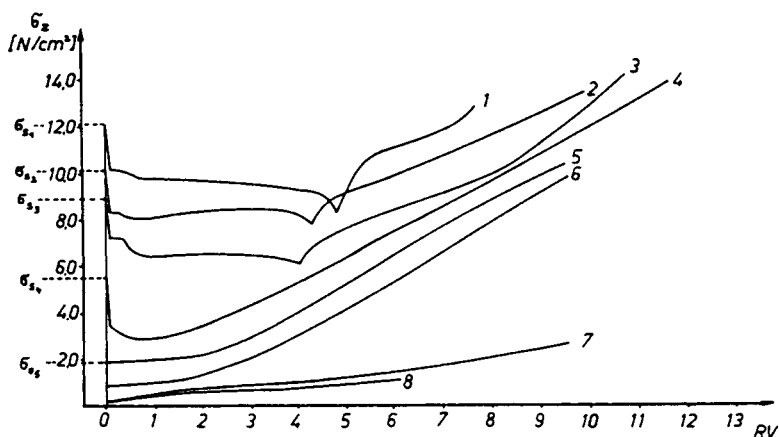


Fig. 6. Stress ( $\sigma_z$ ) vs. draw ratio at different draw temperatures ( $T_R$ ) (polyethylene terephthalate/polyethylene = 77/33 wt%, rate of draw  $q = 40\%$  stretch/min).  $q = 40$  pc. stretch/min. (1)  $T_R = 22^\circ\text{C}$ ; (2)  $T_R = 40^\circ\text{C}$ ; (3)  $T_R = 50^\circ\text{C}$ ; (4)  $T_R = 70^\circ\text{C}$ ; (5)  $T_R = 75^\circ\text{C}$ ; (6)  $T_R = 80^\circ\text{C}$ ; (7)  $T_R = 90^\circ\text{C}$ ; (8)  $T_R = 100^\circ\text{C}$ .

It can be concluded from the stress-strain behavior of the blend samples that at draw temperatures below  $75^\circ\text{C}$ , the formation of voids proceeds preferentially during the deformation. Macromolecules oriented in the direction of the stress aggregate to form fibrils resulting in the formation of voids.

The relaxation of the molecular chains is greatly limited below  $75^\circ\text{C}$  especially for the matrix polymers, polyethylene terephthalate. The change in drawing behavior observed at this temperature can be related to the glass transition temperature of polyethylene terephthalate (measured by differential scanning calorimetry:  $70.6^\circ\text{C}$ ). Above this temperature the chain flexibility increases and the influence of flow relaxation becomes more important.

## Structural Studies

### *Electron Microscopy*

Using scanning electron microscopy (SEM) it was shown that a very uniform fibril structure with elongated voids is formed during the stretching of polyethylene terephthalate/polyethylene films under certain conditions ( $T_R = 75^\circ\text{C}$ ;  $q \geq 40\%$ /min). In the micrographs the voids (Fig. 1) and the fibrils (Fig. 2) are distinctly visible.

By comparison, only random individual holes are recognizable in the unstretched samples (Fig. 3). The voids seen in Figure 1 are up to  $3\ \mu\text{m}$  in width and  $160\ \mu\text{m}$  in length and are characteristic of samples showing a metallic luster. The voids observed by Wenig and Hammel<sup>9</sup> in the cold-drawn 70/30 wt% polyethylene terephthalate/polyethylene blends were much smaller,  $1\ \mu\text{m}$  in width and  $25\ \mu\text{m}$  in length and the fibrils are much narrower than the intervening voids with diameters of approximately  $0.4\ \mu\text{m}$ . A more detailed comparison of these values with those presented in this study is not possible because of insufficient detail concerning stretch conditions in reference.<sup>9</sup>

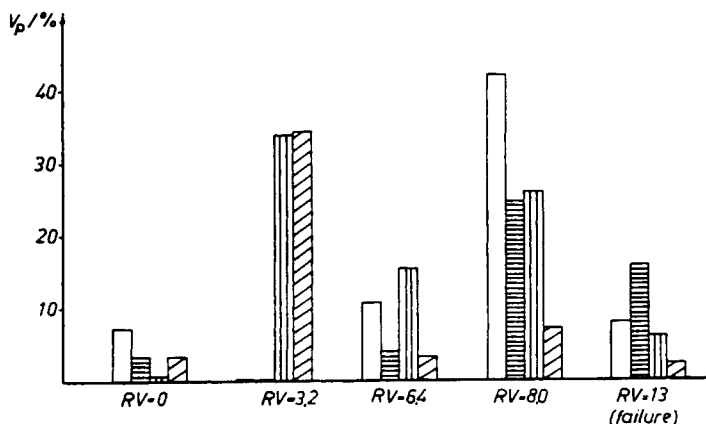


Fig. 7. Pore volume distributions during the drawing process of polyethylene terephthalate/polyethylene films ( $T_R = 22^\circ\text{C}$ ;  $q = 1000\%$  stretch/min). Pore radii ranges: (□) 4–10 nm; (▨) 10–100 nm; (▧) 100–1000 nm; (▩) 1000–6500 nm.  $T_R = 22^\circ\text{C}$ ;  $q = 1000\%$  /min.

In transmission electron micrographs (Fig. 4) of cross sections of stretched films it was observed that polyethylene is uniformly distributed throughout the film, but the diameters of the polyethylene domains exhibit a large range (0.1–0.8  $\mu\text{m}$ ). The particle size of the polyethylene phase corresponds approximately to the size of previously measured fibrils. A uniform distribution of the disperse phase in polyethylene terephthalate/high density polyethylene blends has also been found by Dietrich and Versaumer.<sup>15</sup>

#### Measurements of Porosity

The measurements of porosity yielded results on the size distribution of voids in the polyethylene terephthalate/polyethylene films. Figure 7 shows how the size distribution of the voids varies as a function of draw ratio. The unstretched film mainly contains small voids with widths below 10 nm, but pores with relatively large diameters are also present. However, these voids are not elongated but can be seen in electron micrographs as roughly circular holes (Fig. 3). Large, elongated voids with widths greater than 0.5  $\mu\text{m}$  are found almost exclusively in stretched, metallically lustrous films (Fig. 7 at  $RV = 3.2$ , and Fig. 1). A polyethylene terephthalate/polyethylene film which is uniformly metallically lustrous throughout the sample can be obtained at a draw ratio of 4–5, or when the neck characteristic of cold drawing has reached both ends of the sample. During further stretching the volume fraction and shape of the voids change further and the metallic luster decreases. The large voids become narrower and microcracks occur more frequently and the proportion of smaller voids again increases (Fig. 7).

The measurements of porosity generally yielded somewhat larger values for the void diameters than electron microscopy. The reason is that the use of the mercury high pressure porosimeter results in a slight expansion of the pores.

#### DISCUSSION

In this section a theory which explains the metallic effect is presented which uses the polymer deformation model of Glenz and Peterlin.<sup>16</sup>



The film examined was a dispersion of one polymer in another in which the polyethylene and polyethylene terephthalate components differ in the following properties: (1) flexibility of the macromolecular chains: polyethylene terephthalate is more rigid than polyethylene, (2) crystallinity: polyethylene terephthalate crystallizes primarily during the process of orientation. (It is noted that the degree of crystallization of the polyethylene terephthalate component was found to be about 13% for the unstretched film produced by the cooling conditions during film preparation). The crystallinity of the polyethylene terephthalate in the blend increases to about 35% for the samples stretched up to  $RV = 3 - 5$ , and (3) elasticity; polyethylene terephthalate, the continuous phase controlling the course of stretching, is a polymer of low elasticity.

The action of mechanical forces on the polyethylene terephthalate/polyethylene film results in a purely elastic extension at the beginning of the draw process. The strong forces of interaction in polyethylene terephthalate cause a steep slope in the stress-strain curve (Fig. 6). As the stretching continues the strain in the system increases and concentrates upon the weakest point of the film to such an extent that plastic deformation of the initial structure sets in. This phase is chiefly characterized by glide and shear processes and by the formation of crystalline and amorphous regions within the films. Macroscopically, this start of the local orientation process is recognizable by the formation of the plastic zone (neck formation). The formation of the neck region is comparable to the mechanism of formation of crazes in semicrystalline polymers.

As the deformation proceeds the initial structures are rearranged. The intermolecular stresses lead to strong orientation of crystallites and of the macromolecules in the amorphous layers in the spherulites, which are caused by glide and shear processes. The molecular chains are particularly drawn out of crystalline aggregates. A higher mobility of macromolecular chains in the oriented regions will be reached by the temperature increase in the neck during the cold drawing. During that process neighboring structural regions approach so that the interaction forces will come into operation and fibrils will be formed which will be separated by elongated voids (Figs. 1 and 2).

The structure created is relatively stable because of the low flexibility of the polyethylene terephthalate chains, the strong interaction forces between the benzene rings of the polyethylene terephthalate molecule in the crystallites, and the crystallization process during orientation.

Due to the differences in stress on the macromolecular components, it is possible that single molecules in the matrix can break, resulting in the formation of small voids. Because of steric hindrances between the macromolecules, the formation of voids is increased by the presence of a second component; the disperse phase disturbs the aggregation of the microfibrils of the continuous phase. There are almost negligible forces of interaction between polyethylene terephthalate and polyethylene [which is also the reason that the films can be readily microtomed (Fig. 2)]. The interfacial energies between the different polymer components and the electrostatic forces of repulsion cause a distinct separation of the fibrils and thus an expansion of the voids between the fibrils. The formation of voids is enhanced by different deformation behaviors of the two phases. The increasing stresses during the course of the stretching and the inhomogeneities within the fibrils caused for

## KINDS OF VOIDS IN COLD-DRAWN MICROHETEROGENEOUS POLYMER BLENDS

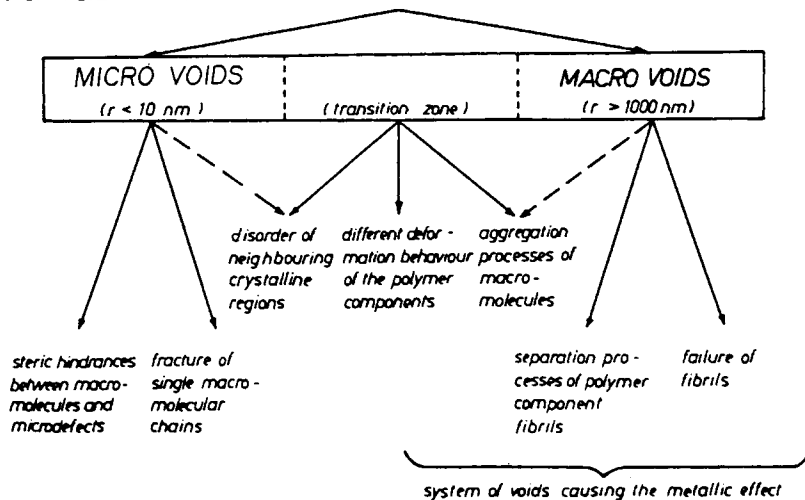


Fig. 8. Overall scheme of void formation in the cold drawing of thermodynamically incompatible polymer blends.

example by irregular deformation result in their failure. Macroscopically this process is not recognizable but it makes a contribution to the formation of voids. Which of these processes plays the predominant role in the formation of a very distinct void system depends primarily on the stretch conditions. The very uniform fibril-void structure in the metallically lustrous samples is assumed to be brought about mainly by strong aggregation of the macromolecules within the film and by separation of the fibrils of different polymer components and only to a small extent by fracture.

In Figure 8 the most probable mechanisms of void formation are summarized. The fibril-void structure has developed completely when the plastic deformation zone has passed the entire sample. When the maximum extensibility of the fibrils is reached, the sample begins to tear.

### CONCLUSIONS

It was found that a highly metallic appearance occurs in stretched polyethylene terephthalate/polyethylene films as a consequence of the formation of a very uniform fibril-void structure. The development of the metallic luster depends not only upon the properties of the materials but also the deformation parameters. The following points are important for the occurrence of the metallic effect: (1) the presence of an excess of polyethylene terephthalate in the blend; (2) the draw temperature; (3) the draw rate.

The voids can be formed in different ways and to different extents during cold drawing. The voids optimal for a metallic luster exhibit a width of about  $3 \mu\text{m}$  and a length of more than  $160 \mu\text{m}$ . These large voids are brought about by aggregation of the oriented crystalline and amorphous regions within one polymer component during the deformation followed by separation of the fibrils of the different polymer components. In addition fracture and different deformation behavior may lead to the development of voids.

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