

Ultradrawing of "springy" polypropylene films

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SUMMARY

It is demonstrated that in the process of ultradrawing of semi-crystalline polypropylene the morphology of the initial material plays major role. Extremely high draw ratios are obtained ($\lambda_{\max} \approx 50$) when drawing "hard elastic" polypropylene films perpendicular to their initial molecular orientation. This behaviour is explained by the molecular processes of plastic deformation.

INTRODUCTION

Ultradrawing of semi-crystalline polymers has been performed by many investigators (1-6). The resulting material exhibits outstanding mechanical properties (7-11). Several methods were used to obtain very high draw ratios (1-4) and it was established that the Young's modulus, E , is a linear function of the extension ratio (12). But not much work is done on the dependence of the ultimate extension on the initial morphology. Recently, the deformation of mats of solution grown single crystals has been very successful in obtaining high draw ratios and ultra high moduli (13, 14). It is evident that the molecular mechanism of plastic deformation is the key in understanding the ultra-drawing process. It has been demonstrated that unfolding of molecules out of the single crystals is the main molecular mechanism to highly extend polymer single crystals (15,16). The unfolding occurs over the distance of the molecule's re-entry and has the spacing of near neighbour molecules when having adjacent re-entry. From this point of view, high drawing ratios are always expected when deforming a stacked lamellar arrangement perpendicular to the initial molecular direction within the lamellae. The number of tie-molecules between the lamellae should be small and the fold surface should approach the adjacent re-entry conformation. "Springy" (hard elastic) films are approaching these requirements closely (17, 18). It is the purpose of this paper to compare the ultra-drawing of spherulitic and "springy" polypropylene (PP) materials, and discuss the results in terms of the deformation mechanisms in semi-crystalline polymers.

EXPERIMENTAL

The polypropylene used for the experiments was Novolen 1300E (BASF AG) and microporous Celgard 2400 (Celanese). The Novolen 1300E was extruded at $T=200^{\circ}\text{C}$ and the Celgard film was deformed as delivered. The deformation was carried out in a tensile testing machine (Zwick 1445) equipped with a heating chamber. The deformation direction for the Celgard films was perpendicular to molecular orientation direction of the original films. The gauge length of all the samples were 30 mm and the deformation velocities 50 mm/min. The drawing was performed in a one step process at

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various temperatures, but highest deformation ratios were obtained at 135°C for all the samples. All samples were deformed via neck formation and propagation. In all cases highest deformation ratio λ was obtained, when only a single neck was created and expanded over the whole sample. The Young's modulus, E , and fracture stress, σ_F , of the deformed material were measured in the same tensile testing machine at room temperature.

RESULTS AND DISCUSSION

In Fig. 1, the Young's moduli of the deformed samples are plotted against the deformation ratios, λ .

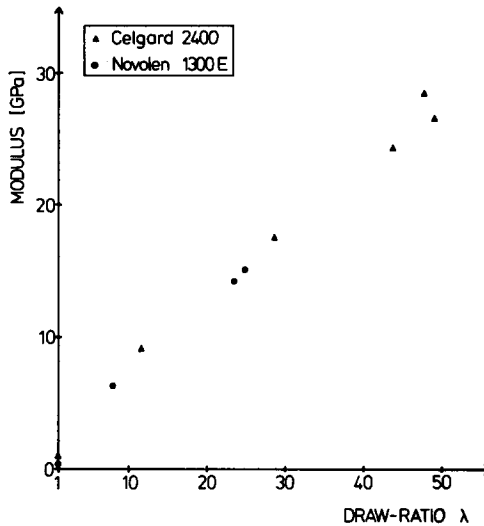


Figure 1: Draw ratios λ and Young's modulus E of spherulitic ● and "hard elastic" ▲ polypropylene

It should be noted, that the maximum deformation ratios at one single temperature can scatter by about a factor of two. The corresponding Young's moduli depend more on deformation ratios than on deformation temperature. For both kinds of samples, the Celgard microporous films and the spherulitic materials, a linear dependence of the Young's moduli on deformation ratios are obtained. The maximum draw ratios were $\lambda=25$ for the spherulitic material and $\lambda=48$ for the Celgard films, respectively. Table 1 summarizes the mechanical data for the materials. The extremely high values of λ_{max} and E of the material obtained by stretching the Celgard film perpendicular to the original molecular orientation are remarkable. From Table 1 it is evident that the morphology of the undrawn material has an important influence onto the ultra-drawing process.

Material	Ultimate draw ratio, $[\frac{l}{l_0}]$	Young's modulus, E [GPa]	Fracture stress, σ_F [MPa]	Fracture strain, ϵ_F [%]
Novolen 1300E	25	15	500	6
Celgard 2400 stretched perpendicular to molecular orientation	48	28,4	750	5
Celgard 2400 stretched parallel to molecular orientation	1,3	2,6	40	4

Table 1: Mechanical data of the drawn materials

The influence may be understood from the molecular and supermolecular structure as well as from the mechanisms of plastic deformation. In semi-crystalline polymers, the plastic deformation occurs mainly by three molecular processes (19, 20), Fig. 2a-c:

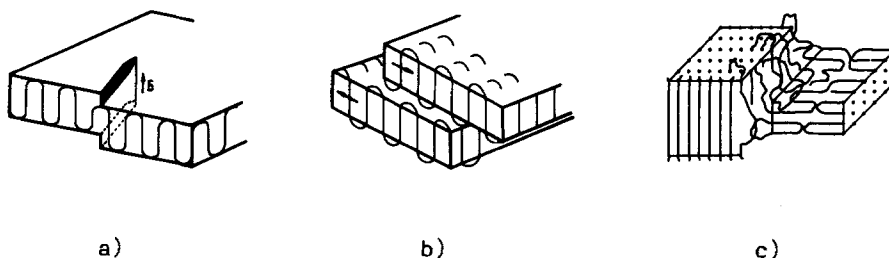


Figure 2: Molecular mechanisms of plastic deformation in semi-crystalline polymers

- a) chain slip within the crystal
- b) lamellar slip
- c) pulling the molecules out of the crystals and orienting them into draw direction

The last process plays the major role during the neck formation. After necking, at very high deformation ratios, disentanglement of the oriented molecules may also occur. The pulling process, transforming a lamellar superstructure into a fibrillar superstructure, has been investigated by different authors (21, 22, 15). Peterlin describes it as breaking off the lamellae into small blocks, which arrange into a fibrillar conformation, Kobayashi assumes peeling off single molecules out of the lamellar crystals and Petermann et al (16) considers it as an inhomogeneous transformation, occurring in a disordered zone which has the width of the fold length. They calculate the draw ratio, λ , of polymer single crystals to $\lambda = \frac{D}{d}$, where D is the crystal thickness and d is the distance between the exit and entrance of a single molecule from the crystal (assuming, that no interlamellar slip occurs). In a multi-lamellar arrangement, the dis-

tance d can be expanded by entanglements of different molecules in the amorphous intercrystalline zones. Consequently, the draw ratios of mats of single crystals of high molecular weight polymers is expected to be higher before annealing than after annealing because interweaving of the molecules takes place during annealing (23, 24). Similar aspects can be considered deforming the "springy films" perpendicular to chain direction. In Fig. 3, a schematic picture of the molecular arrangements of the lamellae is presented.

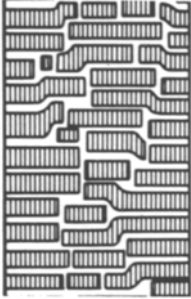


Figure 3: Schematic model of the morphology of "springy films"

The number of tie molecules between the lamellae is supposed to be small, which reduces the entanglements of molecules within the amorphous layers. The microporous Celgard 2400 films exhibit two further advantages for the drawing process (Fig. 4):

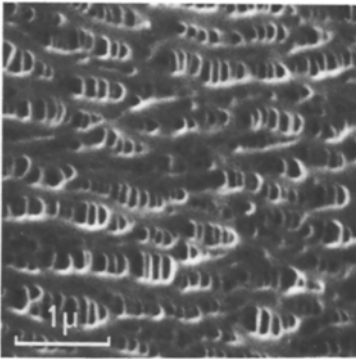


Figure 4: SEM micrograph of a microporous Celgard "springy film"

- (i) Many lamellae are separated and behave as non interwoven single crystals.
- (ii) The microvoids are bridged by fibrils. Those fibrils are obstacles for crack propagation in molecular direction (Fig. 5a,b) and reduce brittleness.

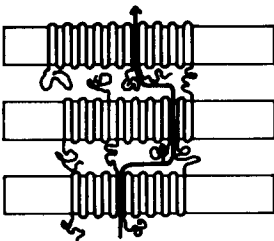


Figure 5a: Crack growth in virgin springy films

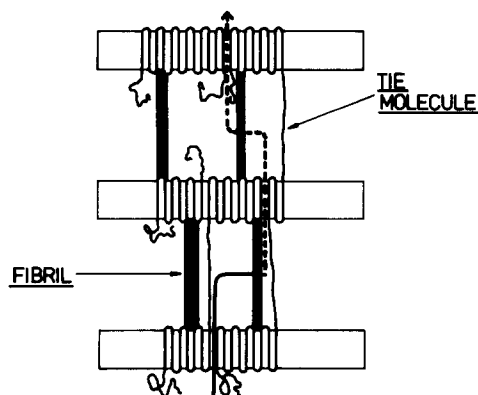


Figure 5b: Crack growth in microporous springy films

Geometric considerations let suppose that in drawing the springy films perpendicular to chain direction, the pulling deformation process dominates the plastic deformation while the deformation of spherulitic materials involves the other two mechanisms to a great part, too, which may lead to deformation induced entanglements within the neck and consequently to smaller draw ratios. Highest draw ratios and Young's moduli from ultra drawn spherulitic polypropylene reported in the literature are well below our results (8, 11). Further investigations using scanning and transmission electron microscopy to study the structure of the deformation zone are in progress.

REFERENCES

1. G. Capaccio and I.M. Ward, *Polymer* 15, 233 (1974).
2. T. Kunugi, A. Suzuki, I. Akiyama and M. Hashimoto, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* 20, 778 (1979).
3. J.H. Southern and R.S. Porter, *J. Macrom. Sci., Phys.* 4, 541 (1970).
4. T.K. Kwei, T.T. Wang and H.E. Boir, *J. Polym. Sci. C* 31, 87 (1970).
5. P. Smith and P. J. Lemstra, *J. Mat. Sci.* 15, 505 (1980).
6. P.J. Barham, A. Keller, *J. Mat. Sci.* 20, 2281 (1985).
7. T. Williams, *J. Mat. Sci.* 8, 59 (1973).
8. D.L. M. Cansfield, G. Capaccio, and I.M. Ward, *Polym. Eng. Sci.* 16, 721 (1976).
9. W.N. Taylor and E.S. Clark, *Polym. Eng. Sci.* 18, 518 (1978).
10. P.D. Coates and I.M. Ward, *Polymer* 20, 1553 (1979).
11. T. Kunugi, T. Ito, M. Hashimoto and M. Ooishi, *J. Appl. Polym. Sci.* 28, 179 (1983).
12. G. Capaccio, T.A. Crompton, I.M. Ward, *J. Polym. Sci., Polym. Phys. Ed.* 14, 1641 (1976).
13. T. Kanamoto, E.S. Sherman and R.S. Porter, *Polymer Journal* 11, 497 (1979).
14. T. Kanamoto, A. Tsurata, K. Tanaka, M. Takeda and R.S. Porter, *Polymer Journal* 15, 327 (1983).
15. J. Petermann, W. Kluge and H. Gleiter, *J. Polym. Sci.: Polym. Phys. Ed.* 17, 1043 (1979).
16. H. Krug, A. Karbach and J. Petermann, *Polymer* 25, 1687 (1984).
17. B.S. Sprague, *J. Macrom. Sci.-Phys.* 8(1-2), 157 (1973).
18. H.D. Noether and W. Whitney, *Kolloid-Z.Z. Polym.* 251, 991 (1973).

19. I.L. Hay and A. Keller, *Kolloid-Z.Z. Polym.* 204, 43 (1965).
20. W.W. Adams, D.Jang, E.L. Thomas, *J. Mat. Sci.* 21, 2239 (1986).
21. A. Peterlin, *Kolloid-Z.Z. Polym.* 233, 857 (1969).
22. K. Kobayashi, cited in Geil, P.H., *Polymer Single Crystals, Inter-science*, New York, 465 (1964).
23. P.J. Lemstra and R. Kirschbaum, *Polymer* 26, 1372 (1985).
24. P.J. Lemstra, N.A. J.M. van Aerle and C.W.M. Bastiaansen; *Polymer Journal* 19, 85 (1987).

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