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Tensile Drawing of Poly(Ethylene-Terephthalate)
Ultimate Properties

J.P. Cavrot, J.C. Engelaere and F. Rietsch

Laboratoire de Structure et Propriétés de l'Etat Solide, LA 234, Université des Sciences et Techniques de Lille, F-59655 Villeneuve d'Ascq Cedex, France

Summary

The limits of extensibility and orientation of poly (ethylene terephthalate) (PET) films are studied in drawing tests below and above the glass transition temperature. The behaviour of the polymer is compared with that of a stable network formed by the entanglements of chains, particularly concerning the limiting properties achieved in stretching. The influence of pre-deformation (hot and then cold drawing or inversely) on maximum extensibility is also reviewed.

Introduction

In previous papers (ALLISON et al, 1966, 1967; FOOT et al, 1975; RIETSCH et al, 1979; ENGELAERE et al,1980), the study of poly(ethylene terephthalate) (PET) fibers and films has conducted to think that the deformation of this polymer, just above the glass transition temperature, may be relatively well assimilated to that of a permanent network formed by the entanglements between the linear chains. Moreover, the natural draw ratio observed in cold drawing, has been related to the maximum extensibility of such a network structure.

However recent results (ENGELAERE et al, 1982;CAVROT et al) show that both pre-orientation and molecular weight affect the natural draw ratio, certainly due to a progressive desentanglement of the chains more easily as the molecular weight is lowered. So to test the validity of the concept of network structure we are concerned in the present paper with the limiting extensibility attainable by different drawing procedures, the associated birefringence in the plane of the films (which is a measure of the orientation of both amorphous and crystalline phases) and shrinkage force (assimilated to the entropic force due to the recovery of the amorphous phase orientation (RIETSCH et al, 1979; DE VRIES et al, 1977; PERENA et al, 1980).

Experimental

Drawing procedures

Dumb-bell shaped samples 5.15 mm in width and 20 mm

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in length were used from initially amorphous PET sheets of 200 µm in thickness. The films, kindly supplied by Rhône-Poulenc Industries laboratories, were characterized by different intrinsic viscosities, measured in solution in ortho-chlorophenol at 23°C, i.e. 0.61; 0.69; 0.75 and 0.78 $ml.g^{-1}$.

Each sample was marked along its centre line with a series of circular ink spots equispaced at a distance of 0.5 mm to permit strain measurements.

Different deformation processes have been performed in tension, up to the rupture of samples, at a constant crosshead speed (1 $mm.mn^{-1}$, i.e. an initial strain rate of 5.10^{-4} s^{-1}) low enough to approach isothermal drawing conditions :

(i) hot drawing at T = 80°C. The draw ratio is defined by $\lambda_H = L/L_O$ where L and L_O are the final and original length respectively

(ii) cold drawing at ambient temperature, the draw ratio is termed λ_C

(iii) homogeneous pre-orientation at 80°C up to the limiting draw ratio, followed by the residual neck propagation at 20°C

(iiii) cold drawing at T = 20°C, extended over the gauge length of the sample followed by an homogeneous drawing at 80°C.

For these two-stage processes, the final draw ratio can be write as :

$$\lambda_T = \lambda_H . \lambda_C$$

After hot drawing, the samples were always quickly cooled and the measurements of draw ratio and orientation (by means of the birefringence, Δn, in the plane of the films) made at ambient temperature. Reheating at constant length was also tested on all types of deformed samples. In this test a shrinkage force is generated in the vicinity of the glass transition temperature, which is generally attributed to the entropic force necessary to maintain the elastic deformation of the amorphous material, at least in a model of deformation of a rubber network (TRELOAR, 1958). In the tables, the results are reported as shrinkage stress, σ, i.e. shrinkage force per unit strained cross-section.

Results and discussion

For the four different series, the results (reported in Tables 1 to 4) represent average values from three samples, with a maximum dispersity of 5 %, to take account of the relative dispersion observed in the breaking phenomenon.

Hot drawing

The results collected in Table 1 show a marked influence of the molecular weight $\overline{M_V}$. As the chain length decreases (smaller values of $\overline{M_V}$), a significant desentanglement occurs - for the imposed temperature and strain-rate - and the final orientation is much lower than the maximum birefringence of the fully extended chains, $\Delta n_{max} = 0.235$ (FOOT et al, 1975).

TABLE 1

Ultimate properties for homogeneous drawn-samples, at T=80°C

viscosities $ml.g^{-1}$	0.61	0.69	0.75	0.78
molecular weight $\overline{M_v}$ g.	19200	22200	24600	25800
draw ratio λ_H	6.83	6.81	6.32	6.06
birefringence Δn	0.111	0.149	0.180	0.197
shrinkage stress σ 10^6 pascals	12.0	22.5	28.5	31.0

The non negligible disorientation of short chains leads to an increase in the extension ratio λ_H with relatively small values of the shrinkage stress, which proves a decrease in the number of active chains in the rubberlike deformation.

Cold drawing

Below the glass transition temperature, the effect of molecular weight is much more attenuated (Table 2).

TABLE 2

Ultimate properties for cold-drawn samples at T = 20°C

viscosities $ml.g^{-1}$	0.61	0.69	0.75	0.78
draw ratio λ_c	4.39	4.29	4.13	4.12
shrinkage stress σ 10^6 pascals	18.0	16.6	17.3	15.8
birefringence Δn	0.234	0.230	0.225	0.227

The natural draw ratio decreases slowly with increasing molecular weight; this result has been already mentioned (FOOT et al, 1975) these authors concluded that an increase in M_v is equivalent to an increase in effective points of entanglement. Moreover, the values observed for λ_c are comparable to the calculated limits of extensibility which can be deduced from the gaussian behaviour in hot drawing, in the hypothesis of a stable network structure (BHATT et al, 1976; CAVROT et al). This idea is reinforced by the high values of birefringence, although this measure also contains the orientation of the strain induced crystalline regions.

Two-stage deformation

This section relates the results of two series of two stage drawing. The first one corresponds to a pre-orientation by hot drawing up to the rupture limit followed by cold drawing (Table 3). The second inverts the order of the deformation stages (Table 4).

TABLE 3

Ultimate properties for two-stage deformation : hot drawing followed by cold drawing

viscosities $ml.g^{-1}$	0.61	0.69	0.75	0.78
homogeneous draw ratio λ_H	6.83	6.81	6.32	6.06
total draw-ratio λ_T	6.90	7.40	6.63	6.58
$\lambda_c = \lambda_T/\lambda_H$	1.01	1.09	1.05	1.09
total birefringence Δn	0.110	0.151	0.189	0.191
shrinkage stress σ 10^6 pascals	10.4	25.5	30.9	24.8

In the first procedure (Table 3) it can be seen that the cold drawing contribution has not a substantiate effect on final properties. This fact asserts the idea that, the maximum extensibility available by propagation of a neck is closely linked to the network structure existing previously in the polymer.

The table 4 shows a marked increase in birefringence and shrinkage stress. This reflects probably a larger number of effective entanglements, especially for the lower molecular weights, for which the slip of short molecular sequences could be trapped by the crystallisation induced by cold drawing. The corresponding results for the birefringence are significantly higher than the maximum values deduced from the aggregate model (FOOT et al, 1975; DE VRIES et al, 1977) ($\Delta n_{max} = 0.235$). However our results are more consistent with the value reports by DUMBLETON (1968) for the amorphous phase $\Delta n_{max} = 0.275$).

TABLE 4
Ultimate properties for two-stage deformation : cold drawing followed by hot drawing

viscosities ml.g^{-1}	0.61	0.69	0.75	0.78
cold drawing λ_C	4.39	4.29	4.13	4.12
total draw ratio λ_T	5.16	4.83	4.91	4.76
$\lambda_H = \lambda_T/\lambda_C$	1.18	1.13	1.19	1.16
total birefringence Δn	0.256	0.245	0.247	0.248
shrinkage stress σ 10^6 pascals	44.7	40.8	37.3	33.4

In conclusion for the all deformation processes studied, the limit of extensibility seems to be directly controlled by the network structure preexisting in the material. However above the glass transition temperature, and because the polymer is not chemically crosslinked, partial desentanglement can occur which is temperature and strain rate dependent. It will be interesting to confirm these observations by means of the analysis of the crystalline structure and degree of recoverable deformation which represents the state of orientation of the amorphous phase in the concept of the extension of a rubberlike network.

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