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THERMAL-MECHANICAL ANALYSIS OF DRAWN POLY(ETHYLENETEREPHTHALATE) AND POLY(AMIDE) FILMS

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ABSTRACT

Films of poly(ethyleneterephthalate) and poly(amide 6) drawn at different temperatures to various degrees of elongation are investigated by TMA. It is proved that for PET films the drawing temperature represents the decisive process parameter. Furthermore, the shrinkage starts within the region of the temperature at which the films have been stretched previously. For drawn PA films, the drawing temperature does not exert a great influence on shrinkage behaviour. In this case, the draw ratio fixes the nature of the shrinkage curves and the derived characteristic values. The results in hand demonstrate the great sensitivity of the chosen thermal-mechanical testing method, especially relative to the temperature of onset and maximum shrinkage as well as to the percentage of shrinkage.

INTRODUCTION

The morphological structure of polymeric materials can be altered within broad limits by drawing or annealing processes. By annealing at temperatures above the glass temperature, the existing structure of a mechanically and/or thermally pretreated specimen will be changed; crystallinity and molecular orientation do not remain constant and these changes cause a deformation of the polymeric solid. The deformation in extension (in most cases a shrinkage) can be observed using thermal-mechanical analysis equipment (TMA).

EXPERIMENTAL

TMA apparatus

A commercial apparatus, TMA 43 (DuPont), was used on which the deformation in extension of the specimen could be recorded as a function of temperature or time. Special clamps were constructed with a distance between clamps of 2 mm. A standard heating rate of 5 K min^{-1} was chosen.

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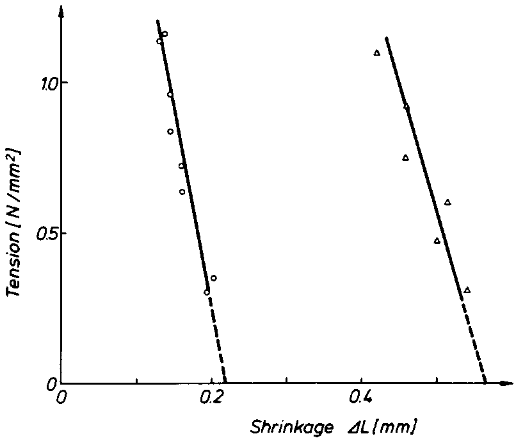

Fig. 1. Amount of maximum shrinkage of poly(ethyleneterephthalate) films as a function of applied tension during TMA measurement. O, PET film, $T_D = 140°C$, $\varepsilon = 205\%$; Δ, PET film, $T_D = 55°C$, $\varepsilon = 330\%$.

The cross-section of the samples was kept constant by cutting the appropriate specimens under a microscope. The amount of elongation (shrinkage) depends on the applied tension, therefore an extrapolation to tension zero was carried out (see Fig. 1). The chosen tension was of the order of 0.5 N mm^{-2}.

Birefringence

Birefringence was measured in a polarization microscope Ortholux II Pol-Mk (Leitz) using a Kipp compensator.

Materials

PET and PA 6 films were drawn in a glycerol bath at different temperatures and were subsequently quenched in ice water. The drawing conditions are listed in Table 1.

TABLE 1

Characterization of films

Material	Drawing temperature (°C)	Draw ratio, ε (%)	Density (g cm^{-3})
PET	55	300–440	1.360–1.365
PET	85	50–450	1.340–1.360
PET	140	6–200	1.380–1.389
PA 6	55	10–220	1.130–1.132
PA 6	85	20–210	1.135–1.143
PA 6	140	20–200	1.147–1.153

RESULTS AND DISCUSSION

Poly(ethyleneterephthalate)

Some characteristic TMA curves are reproduced in Fig. 2. As is evident, the nature of the curves is mainly influenced by the drawing temperature. Films drawn at 55°C, i.e. below the glass transition, shrink above a definite temperature continuously. A few degrees below the melting point, the specimens begin to lengthen until they break under the applied tension.

A different behaviour is observed with films drawn at 85°C, just above the glass temperature. These specimens show a considerable shrinkage over a small temperature interval between 85 and 115°C followed by an extension and, at higher temperatures, by a constancy of length.

Samples, drawn at 140°C do not vary their length up to their drawing temperature. At higher temperatures, they shrink moderately and then extend at about 30°C below the melting point.

The TMA curves can be analyzed quantitatively. Figure 3 defines, in a schematic way, the characteristic values: temperature of shrinkage onset, T_S,

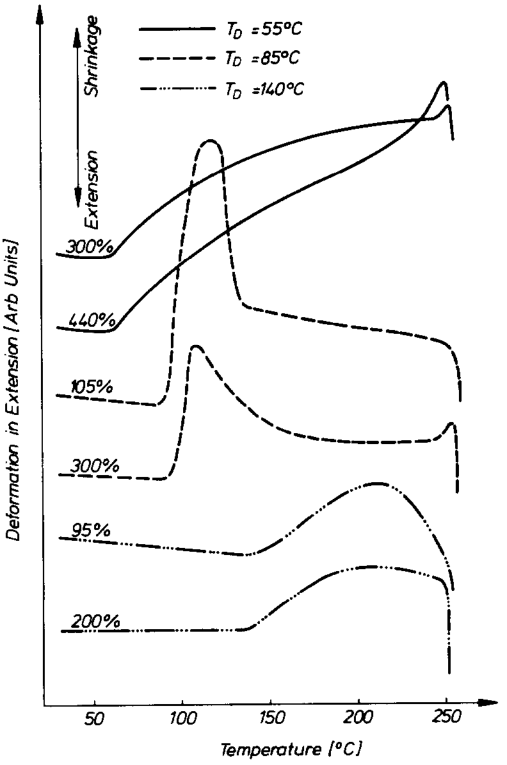

Fig. 2. Typical TMA curves of drawn poly(ethyleneterephthalate) films. The percentage represents the draw ratio.

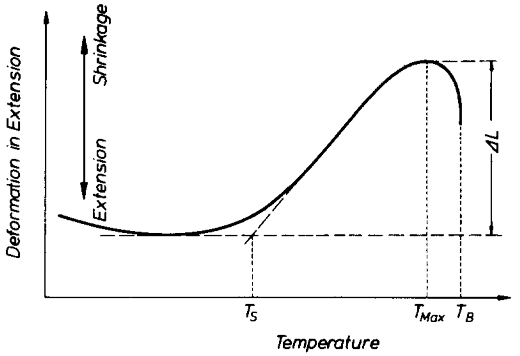

Fig. 3. Schematic TMA curve illustrating the characteristic measured values. T_S = temperature of onset of shrinkage; T_{Max} = temperature of shrinkage maximum; T_B = temperature of breakdown; ΔL = maximum contraction length (in percent).

temperature of maximum shrinkage, T_{Max}, temperature at break-down, T_B, and maximum contraction length, ΔL (in percent). Because the birefringence represents an excellent measure of the local molecular orientation, the characteristic quantities are plotted as a function of the respective values of birefringence.

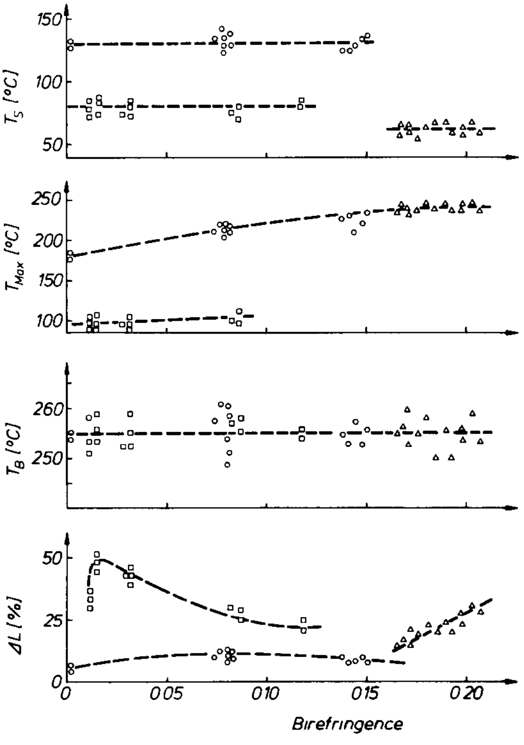

Fig. 4. Characteristic values of TMA measurements as a function of birefringence for drawn PET films. Δ, Drawing temperature 55°C; □, drawing temperature 85°C; ○, drawing temperature 140°C.

The results of our measurements are shown in Fig. 4. From these results and from the course of the TMA traces one can conclude that some of the characteristic values are strongly influenced by the molecular orientation (here represented by birefringence) and some of them depend only on the drawing temperature, but not on the degree of orientation.

In order to understand the results completely, it has to be mentioned that the specimens differ in their degree of crystallinity depending on drawing temperature. A low drawing temperature (55 and 85°C) produces nearly amorphous films [1], whereas the specimens drawn at 140°C are partially crystalline with a degree of crystallinity of about 20%. Moreover, the orientation of the samples drawn below the glass temperature looks very high compared with that of the others. Furthermore, it has to be taken into consideration that the oriented amorphous films crystallize by the increase of temperature during the TMA procedure [2].

The results in Fig. 4 prove that the onset of shrinkage is strictly related to the drawing temperature. Although the differences in molecular orientation are very high, the shrinkage of all specimens starts a few degrees above the drawing temperature. The temperature of maximum shrinkage is influenced as much by the drawing temperature as by the degree of molecular orientation. The specimens drawn at 85°C are surprising because of their considerable shrinkage in a small temperature interval between 90 and 120°C and the subsequent elongation at higher temperature. The difference of maximum temperature, T_{Max}, between the samples drawn at 55 and 140°C on the one hand and those drawn at 85°C on the other reaches 100°C and more.

The temperature of breakdown of all investigated samples seems to be constant within the limits of experimental error. With regard to the total amount of shrinkage, the films behave very differently; the shrinkage of the samples drawn at 140°C is very small (10%) whereas it reaches about 50% for specimens drawn at 55°C.

The reason for such different thermal-mechanical behaviour is given by the heterogenous morphological structures of the specimens. The films produced at 55°C are highly oriented and possess a density which is little, though significantly, higher than that of the undrawn original film. The increase in density is caused by small crystal nuclei consisting of highly oriented chain segments. These nuclei lower the onset of crystallization during the heating of the specimens to temperatures between 65 and 90°C, which are clearly below the onset temperature of crystallization for undrawn samples (110–120°C) [2]. Thus, the specimens drawn at 55°C crystallize and shrink simultaneously under the applied tension. With the films drawn at 85°C, the shrinkage starts by exceeding the drawing temperature without any crystallization. As a consequence, the high amount of shrinkage occurs. At higher temperatures (above 120°C), crystallization takes place leading to an extension of the sample. The samples drawn at 140°C are partially crystalline; the crystallites stabilize the sample dimensions and therefore the

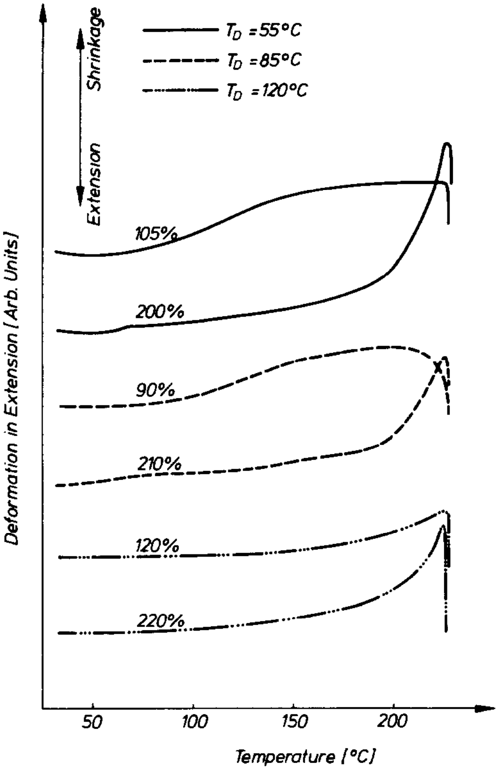

Fig. 5. Typical TMA curves of drawn poly(amide 6) films. The percentage represents the draw ratio.

changes of length during the thermal-mechanical test turn out to be comparatively small.

Poly(amide 6)

A selection of TMA curves of PA 6 films drawn at different temperatures is sketched in Fig. 5. As can clearly be seen from the course of the TMA traces, the differences between the various specimens are smaller than with the PET samples. The exact onset of shrinkage is very hard to evaluate; we are under the impression that this temperature increases with the drawing temperature. For most samples, the shrinkage velocity accelerates with increasing temperature.

Figure 6 represents a summary of the dependence of characteristic TMA values on the measured birefringence. In addition to the temperature of maximum shrinkage, the breakdown temperature and the maximum percentage of shrinkage increase more or less strongly with the degree of molecular orientation. The drawing temperature has only a slight influence on the measured values. In general, the amount of shrinkage is smaller for

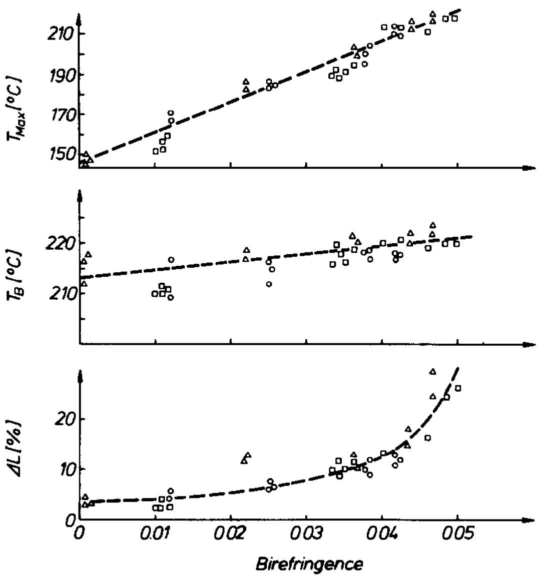

Fig. 6. Characteristic values of TMA measurements as a function of birefringence for drawn PA films. Δ, Drawing temperature 55°C; □, drawing temperature 85°C; O, drawing temperature 120°C.

PA films than for PET films, presumably due to the higher degree of crystallinity.

CONCLUSIONS

The TMA measurements allow an insight into the state of stress within the specimens. If the internal stresses are higher than the applied measuring tension, the samples respond by shrinking; if the contrary is true, the samples stretch. Using TMA investigations, the internal stresses can be recorded continuously with increasing temperature. This testing method has proved very useful in the literature in order to describe the dependence of the state of stress on temperature for poly(ethyleneterephthalate) fibers [3–5], for drawn poly(methylmethacrylate) [6], for drawn poly(carbonate) [7], and for drawn poly(styrene) [8]. The exact progress of deformation in extension is, of course, influenced by the amount of applied stress during the measurement.

In discussing the TMA curves, it must not be disregarded that the testing method is of a dynamical nature, i.e. the specimens are able to change their original structure (e.g. degree of crystallinity) and original molecular orientation. With respect to the samples investigated, this statement is particularly valid for PET films.

It can be seen from our measurements that the onset of shrinkage is determined by the drawing temperature. The temperature of maximum shrinkage increases with increasing molecular orientation; an exception is PET film drawn at 85°C. The temperature of breakdown is only slightly influenced both by drawing temperature and degree of orientation; with polyamide it increases slightly with orientation. The amount of maximum shrinkage depends decisively upon whether crystallization processes take place during the heating up or not. With the crystallized PA films, this quantity increases primarily with molecular orientation.

Further information about the shrinkage behaviour of drawn polymer films can be obtained from measurements of shrinkage stress, which will be reported elsewhere [9].

ACKNOWLEDGEMENT

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