Stress and Strain Oscillations in Syndiotactic Polypropylene and in Poly(Ethyleneterephthalate)

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ABSTRACT: Stress oscillations were produced and analyzed in partly-crystalline syndiotactic polypropylene (sPP) and in poly(ethyleneterephthalate) (PET) in cold drawing experiments. Strain oscillations, which always occur in connection with stress oscillations, were also investigated. The experiments were performed varying the parameters temperature, sample geometry and drawing velocity. This article gives first results of our investigations, which show discrepancies to the existing theories. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 813–817, 1999

Key words: stress oscillation; mechanical instability; syndiotactic polypropylene; poly(ethyleneterephthalate)

INTRODUCTION

Plastic deformation of many thermoplastic polymers results in the formation of a neck and its subsequent propagation. In general, the stress for elongation of the neck is constant. Under certain conditions, however, some polymers exhibit an unusual behavior in that this propagation becomes unstable and shows stress oscillations[1,2]; the moving zone at the shoulder between necked and non-necked material (the transformation zone) then does not propagate steadily. The neck shows a periodic change of its appearance in form of transparent/opaque streaks perpendicular to the tensile axis (Fig. 1). This phenomenon was first described in 1957 by Müller et al.[3] For technical and scientific reasons, there is a strong interest in understanding these stress oscillations. To date there has been no satisfactory explanation of this effect; all previous interpretations accept either heat production in the transformation zone,[1,4] or crystallization[2] as the cause of the oscillations.

Additionally, the literature on this effect[1–7] seems to be missing a systematic investigation of such important quantities as geometry of the specimen, length of the neck, and local strain rate. Therefore, here results from mechanical tests are presented that show that such parameters strongly influence the formation of stress oscillations. Through the investigation of two rather different polymers, poly(ethyleneterephthalate) (PET) and syndiotactic polypropylene (sPP), complementary details for the interpretation of stress oscillations can be found.

EXPERIMENTAL

PET was delivered in the amorphous state in form of a 130-μm-thick foil with a width of 30 cm (Kalle–Hoechst, Germany). Whether the specimen was taken from the lateral or the manufacturing direction had no influence on the results.

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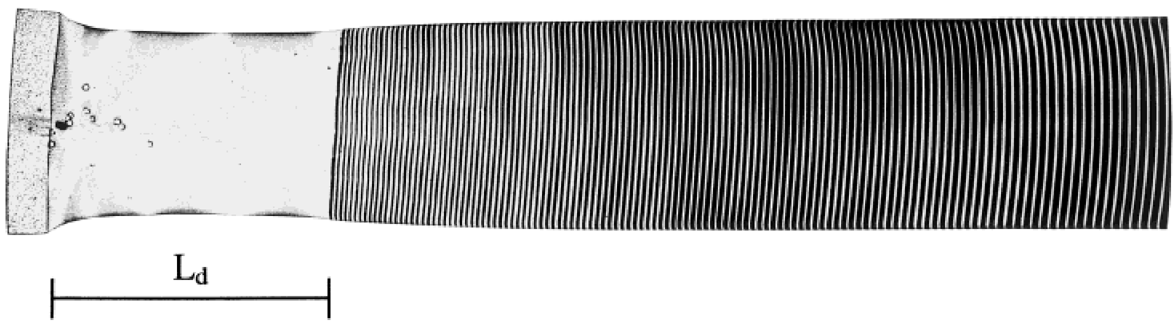

Figure 1 Test specimen with predeformed and oscillating areas (PET).

sPP was delivered as granules (Fina Oil & Chemical Co., Belgium). Rectangular plates ($5 \cdot 15$ cm^2, 2–4-mm thick) were prepared in heating presses.

The PET and sPP test samples were cut into strips of different lengths and widths. The width of these strips, ranging from 6 to 30 mm, had no influence on the results. By changing the original length L_0 (distance between the clamps in the tensile tester) and drawing rate v_t (velocity of the traverse), extension rates $\dot{\varepsilon}$ between $1 \cdot 10^{-5}$ and 1 s^{-1} were obtained. To measure local deformations, especially of the transformation zone, sensors were attached to the samples. Values for stress σ and strain ε are nominal. An Instron tensile tester (Type 1122) was used in all cases. The dynamics of stress oscillations was observed by either the integrated load cell or an external piezo load cell.

RESULTS AND DISCUSSION

Because PET samples fracture before necking when excessively high drawing rates are used, all samples were predeformed by drawing an appropriate piece of material at low rates (v_t = 1 mm/min) to form a stable neck. After v_t is increased in a step-like manner, the neck is extended, and stress oscillations can occur. Figure 2 is an example of a stress–strain curve (PET; original cross-section $A_0 = 0.1 \cdot 6$ mm^2, original length L_0 = 50 mm); the numbers in the diagram indicate the onset of the drawing rates v_t in mm/min. The diagram shows that in this sample the increase in v_t from 1 mm/min to 5 mm/min, marked by 5, results in a continuation of deformation at higher constant stress and that from 5 to 50 mm/min, marked by 50, results in stress oscillations at a lower average stress level.

The average stress levels and amplitudes of the oscillations decrease with increasing drawing rate.[2,4] According to Figure 3, stress oscillations are also influenced by the predeformed neck length L_d. The experimental conditions of the four curves in Figure 3 are all equal except for L_d. If L_d varies between 30 and 50 mm, then unstable oscillations occur. This means that a change in v_t from 5 to 50 mm/min creates a package of oscillations that subsequently decays to constant average stress. With further deformation and no change in the other parameters, the sample starts to oscillate again. The size of the sample between the decayed and resumed oscillations depends also on L_d: the longer L_d, the shorter this size. If L_d is long enough (in Fig. 3 at L_d = 60 mm), then the oscillations are stable from the beginning.

In addition, according to Figure 4, this effect also depends on the original sample length L_0. In

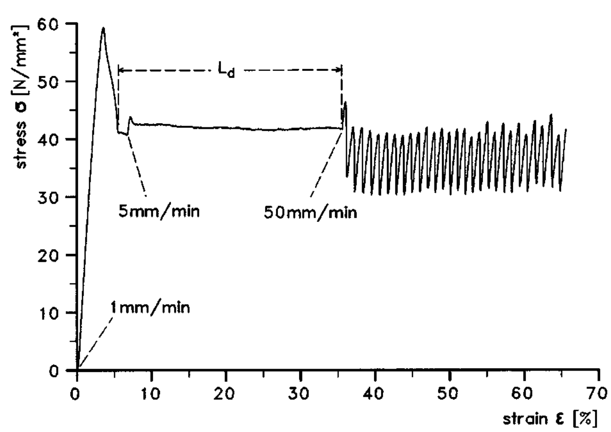

Figure 2 Stress (σ)/strain (ε) curve for PET at three different drawing rates: 1, 5, and 50 mm/min: L_d = length of predeformation.

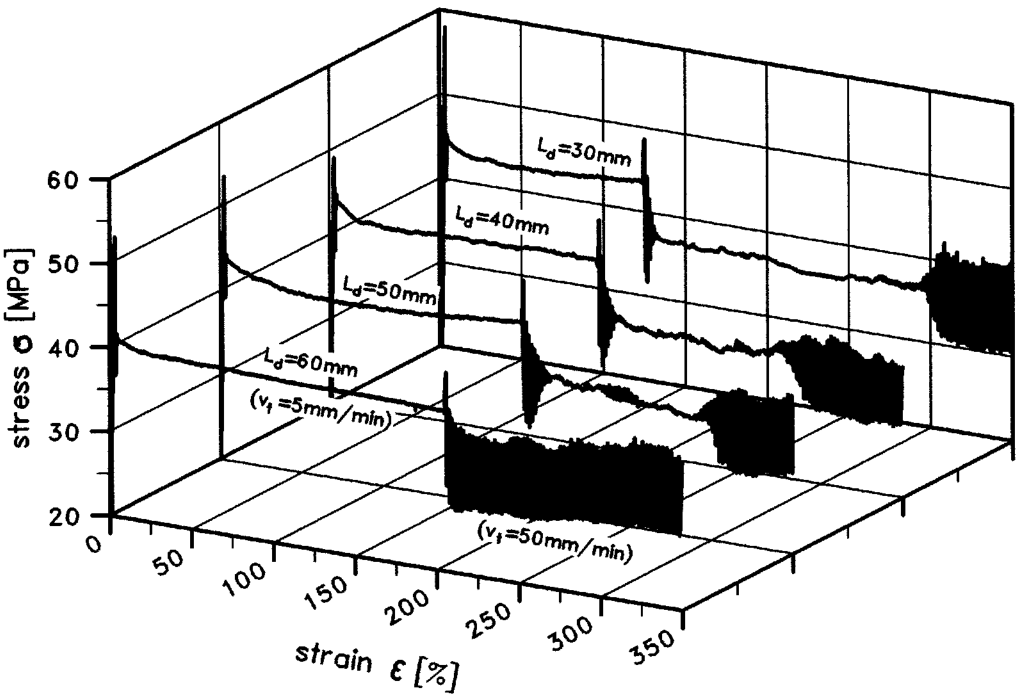

Figure 3 Stress (σ)/strain (ε) curves of different predeformation lengths L_d (PET): unstable oscillations at $L_d = 30, 40$, and 50 mm; stable oscillations at $L_d = 60$ mm.

this figure, the onset of oscillations is marked by the dotted line as depending on sample length L_0 and on the ratio of predeformation length L_d to sample length L_0. Samples that are long enough exhibit only stable oscillations. The limiting curve in Figure 4 depends also on v_t. With increasing v_t, the area of no oscillations is extended to larger sample lengths L_0.

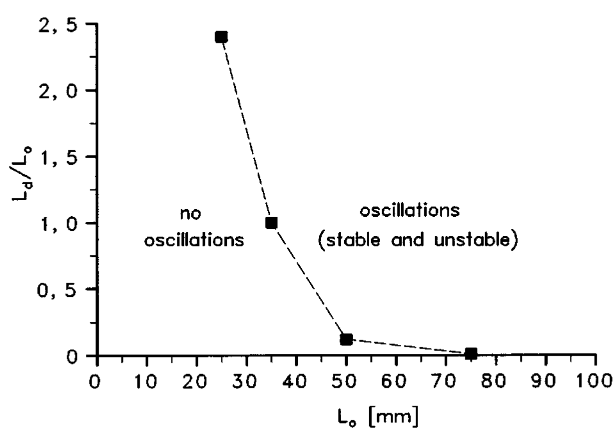

Figure 4 Dependence of the onset of (dotted line) unstable/stable oscillations in PET on sample length L_0 and the ratio of predeformation length L_d and sample length $L_0(v_t = 50$ mm/min.)

Stress oscillations are obviously strongly influenced by the mentioned geometrical different parts of the sample; that is, the undeformed part, the transformation zone, the part of the oscillations and the part of the neck. These factors have not been taken into account in existing theories to date.

Physical aging of the samples as well as deformation at elevated temperatures favors the unstable oscillation regions; if the temperature at which the samples are deformed is high enough, then the oscillations can be suppressed. On the other hand, however, with partially crystalline sPP samples, stress oscillations can occur even at drawing temperatures well above the glass transition temperature, T_g. This observation is of importance, because the molecular mechanisms within the neck (the transformation zone) may influence the occurrence of the stress oscillations, and conclusions about them may be drawn.[8] In our experiments, stress oscillations in PET occurred in amorphous samples or in samples with very low crystallinity only below T_g, whereas in sPP only partly crystallized samples and those deformed above T_g exhibited stress oscillations.

During stress oscillations, the neck of the sample experiences deformation "jumps"; that is, the

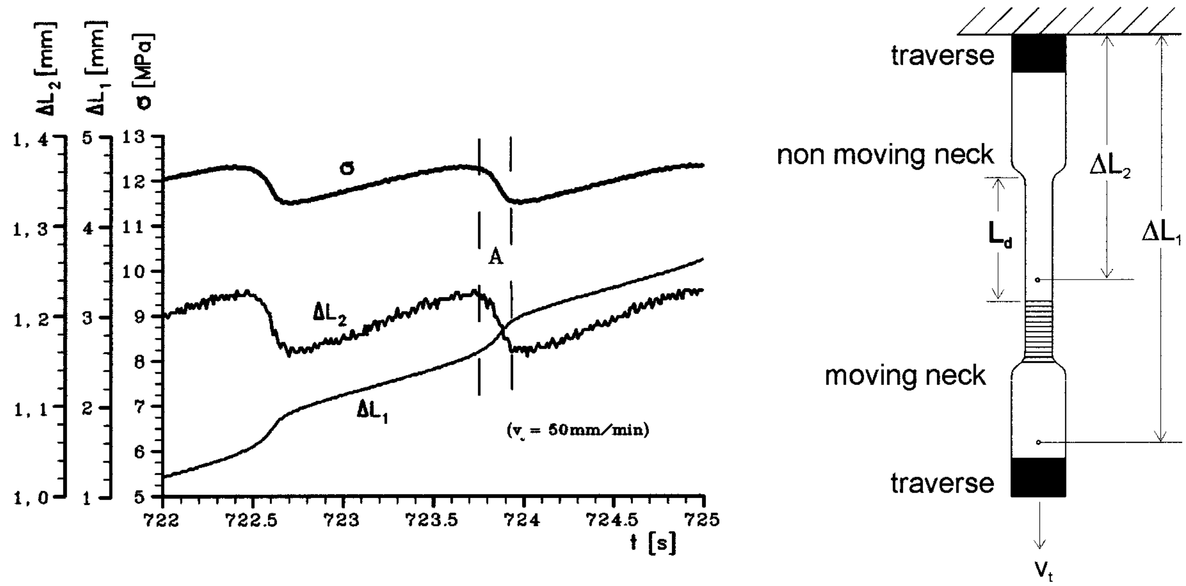

Figure 5 Dependence of the displacement of two sensors (ΔL_1, ΔL_2) and stress (σ) on time for two oscillations at v_t = 50 mm/min on sPP: ΔL_1, sensor displacement superimposed by traverse motion; ΔL_2, sensor displacement not influenced by traverse motion. Traverse and deformation zone (neck) moving in downward direction.

transformation zone does not move steadily. Related to the stress oscillations, strain oscillations occur. As an example of these on partially crystalline sPP, figure 5 shows the displacement of two sensors for two subsequent oscillations. The sensors do not displace steadily, but rather oscillate similar to the stress. The displacements are taken with respect to the machine's frame and depend on the sensor's location on the sample. Because the sample is drawn downward, displacement of the sensor underneath the transformation zone (ΔL_1) is superimposed on the motion of the traverse. On the other hand, the sensor situated above the transformation zone (ΔL_2) does not experience the traverse's motion. Therefore, it is necessary to separate the average velocity $\bar{v}_n$ of the neck and the locally variable neck velocity v_n. Here $\bar{v}_n$ is given with the natural draw ratio λ according to

$$\bar{v}_n = \frac{\lambda}{\lambda - 1} \cdot v_t \tag{1}$$

if the transformation zone and the traverse move in the same direction. Because λ is about 4.3 for sPP and for PET, $\bar{v}_n \approx 65$ mm/min if $v_t = 50$ mm/min. v_n can be much larger than $\bar{v}_n$. This can be seen in Figure 5; the derivative $d(\Delta L_1)/dt$ in (A) corresponds to v_n, superimposed by v_t. As $d(\Delta L_1)/dt$ is ~ 175 mm/min, v_n results in 125 mm/min. Much higher values for v_n were measured even in PET. The values of v_n refer to the measurements given by the sensors. Because the sensors have a certain distance to the transformation zone, their velocities are always smaller than the exact velocity of the transformation zone. Up to now, strain oscillations have been mentioned in the literature in connection with stress oscillations,[2] but have not been documented quantitatively and used in the framework of existing theories. Their occurrence and their times resolved values of stress and strain rates should be incorporated in the theoretical explanations of the oscillation effects.

The fact that sPP exhibits stress oscillations at room temperature does also not fit into the existing theories. The material is partially crystalline before deformation, and deformation occurs above T_g. However, in amorphous sPP deformed below T_g (−10°C), stress oscillations have not been observed in our investigations. Thus, the morphologies in the undeformed samples are also a major factor in the occurrence of the stress oscillations.

CONCLUSIONS

Drawing experiments were performed under different conditions, varying the drawing rate, the temperature, and the geometry of the samples. The drawing rate is an important parameter; the average stress levels and amplitudes of oscillations decrease with increasing drawing rate. Deforming at increased temperatures promotes the development of unstable oscillations; the oscillations disappear when deforming at even higher temperatures. The original sample length L_0 and the predeformed neck length L_d also influence the development of stable or unstable oscillations. Stress oscillations also occur if partially crystalline sPP is deformed above the glass transition temperature T_g.

The dependence of stress oscillations on sample geometry, sample crystallinity, and morphology and on the strain oscillations, which are directly correlated to the stress oscillations, are important experimental facts that may help in understanding the phenomenon of stress oscillations. Further experiments are being carried out to find a more general explanation for the occurrence of the stress and strain oscillations.

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