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Deformation of Polyethylene Oxide, Nylon-11 and Polyethylene Terephthalate by Rolling

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The tensile properties and structural changes in rolled polymers were studied for several systems, including: polyethylene oxide (PEO), nylon-11 and polyethylene terephthalate (PET). All showed tensile properties typical for rolled systems, i.e. increase in strength along the roll direction, and a corresponding decrease perpendicular to the roll direction. Wide angle X-ray diffraction showed that for PEO and PET the chains were aligned parallel to the roll direction. Molecular chains for nylon-11 are preferentially tilted from 20 to 25° to the roll direction at low deformation. This tilt decreased with increased rolling and the chains were aligned in the roll direction at high deformation. Nylon-11 and PET showed four-point patterns typical of such systems in the small angle X-ray region.

1. Introduction

Rolling of polymers has previously been shown to produce unique molecular and lamellar orientations [1-3], as well as an improvement in physical properties [4]. The dominant features of this orientation were molecular tilts of 0 to 35° to the roll direction [1, 2] and small angle X-ray diffraction four-point patterns observed with the beam along the transverse direction. The four-point patterns in rolled polyoxymethylene (POM) were shown to be caused by a system of tilted lamellae [1]. The present work is concerned with the orientation and tensile properties of rolled polyethylene oxide (PEO), nylon-11 and amorphous polyethylene (PET).

2. Experimental

The amorphous PET used for testing was provided by E.I. Du Pont De Nemours Inc. in the form of sheets 0.1 in. thick. PEO pellets (Polyox WSR-205*) were heated to 100°C in a compression moulding press and crystallised, by ambient cooling to room temperature, forming sheets 0.1 in. thick. Samples of nylon-11, provided by Belding Chemical Industry (No. 1157), were prepared in the same manner as PEO except that the pellets were heated to 210°C.

The samples for tensile tests and X-ray examination were uniaxially rolled, by the method described previously [1]. Wide angle X-ray diffraction (WAXD) and small angle X-ray diffraction (SAXD) photographs were obtained on Rigaku-Denki instruments using CuKα radiation.

Surfaces were prepared for electron microscopy by fracturing the rolled material in liquid nitrogen and platinum-carbon shadowing along the roll direction.

3. Results

The dimensional changes which occur during the rolling of PET and nylon-11 are presented in fig. 1. For comparison, previous results [1] for POM are also shown. The difference between POM and the others can be attributed to an increase in the width of rolled POM samples. No such increase occurs for PET or nylon-11. Thus, the increase in lateral dimension which has been reported for various other rolled polymer systems is not a general phenomenon, but depends on the polymer.

The results of tensile tests for rolled PEO, nylon-11 and PET for several values of L/L_0 (final thickness/initial thickness) and θ are shown in figs. 2, 3, and 4 respectively. (θ is the direction of the tensile specimen with respect to the roll

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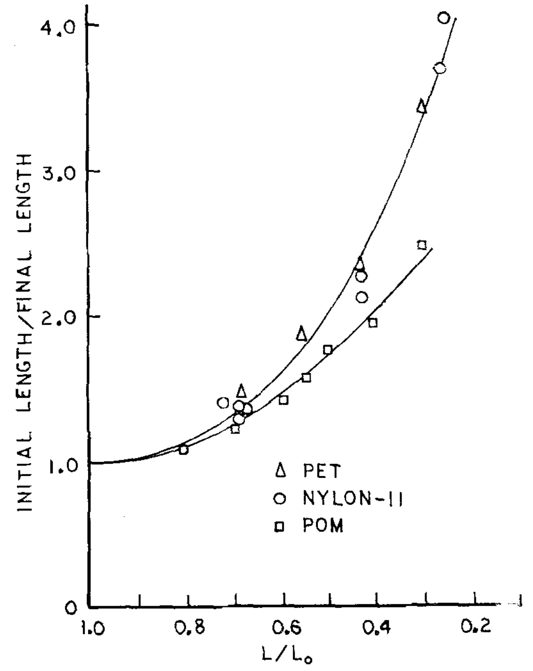

Figure 1 Dimensional changes of rolled PET and nylon-11. Results for POM [1] are shown as a comparison.

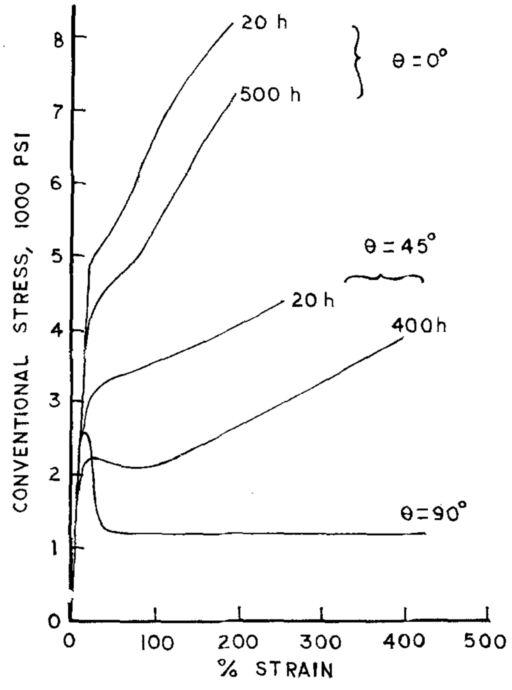

Figure 2 Stress versus strain for rolled PEO. Times shown are times elapsed between rolling and tensile tests. $L/L_0 = 0.3$

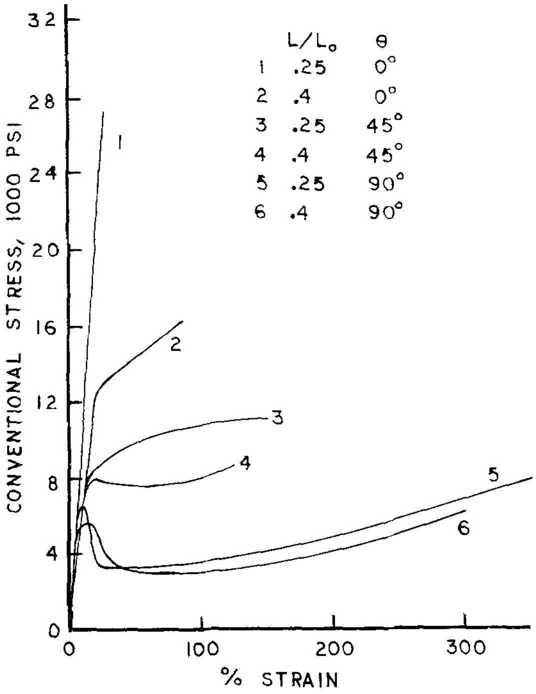

Figure 3 Stress versus strain for rolled nylon-11.

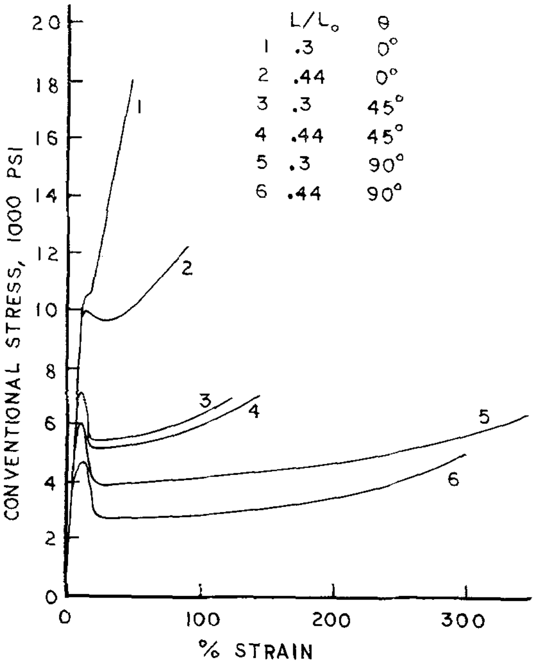

Figure 4 Stress versus strain for rolled PET.

direction.) Even though PET is considered to be amorphous, while PEO and nylon-11 are crystalline, the effects of rolling on the tensile properties were the same in all cases. The

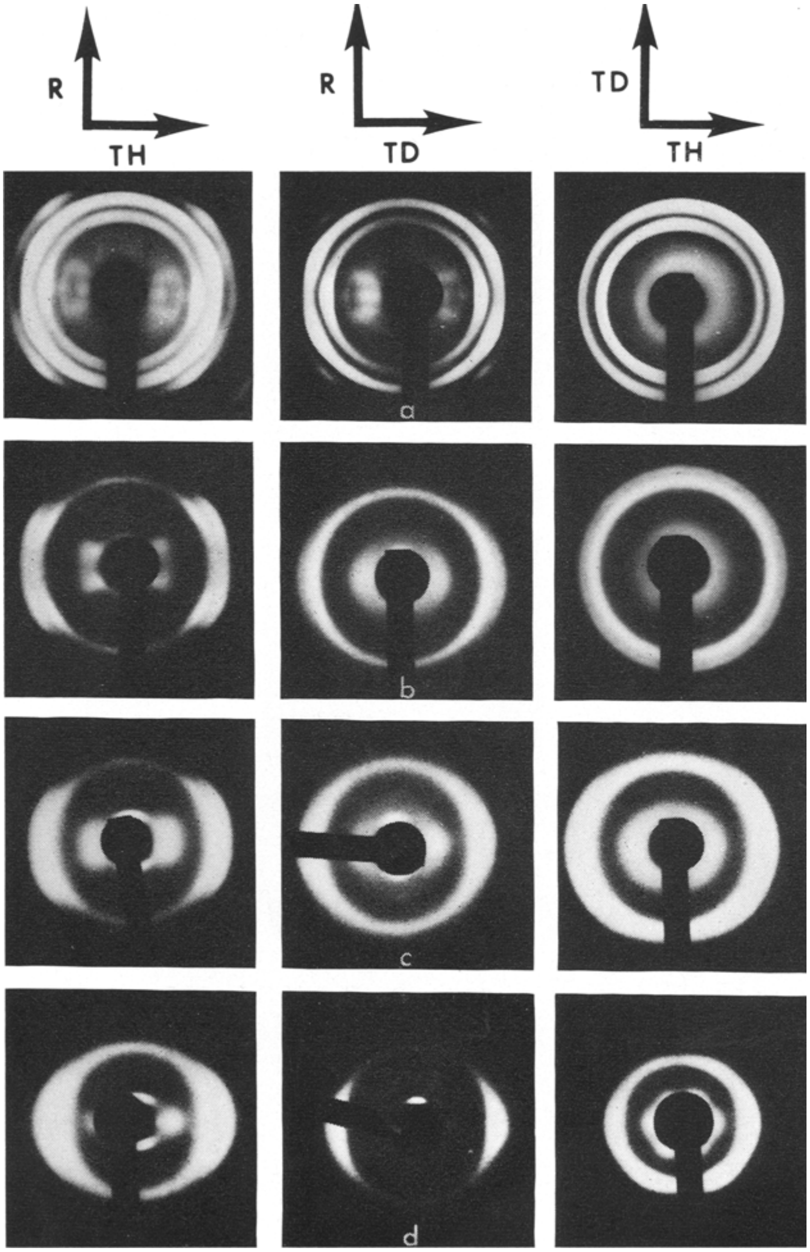

Figure 5 WAXD patterns for rolled PEO and nylon-11. (a) PEO, $L/L_0 = 0.3$. (b) nylon-11, $L/L_0 = 0.7$. (c) nylon-11, $L/L_0 = 0.4$. (d) nylon-11, $L/L_0 = 0.25$.

specimens were stronger along the roll direction and in most cases did not yield when tested in this direction. In contrast to rolled POM [1], the elongation to break in all of the above polymers increased as θ increased. This behaviour seems to be typical of most rolled polymers.

Results of the tensile tests of PEO (fig. 2) show that the stress-strain curves are dependent on the time after rolling; the samples tend to lose their strength with time. This effect is most apparent for values of θ less than 45°. Curves for tensile specimens cut perpendicular to the roll direction ($\theta = 90°$) are independent of time after rolling. Either molecular relaxation, or plasticisation due

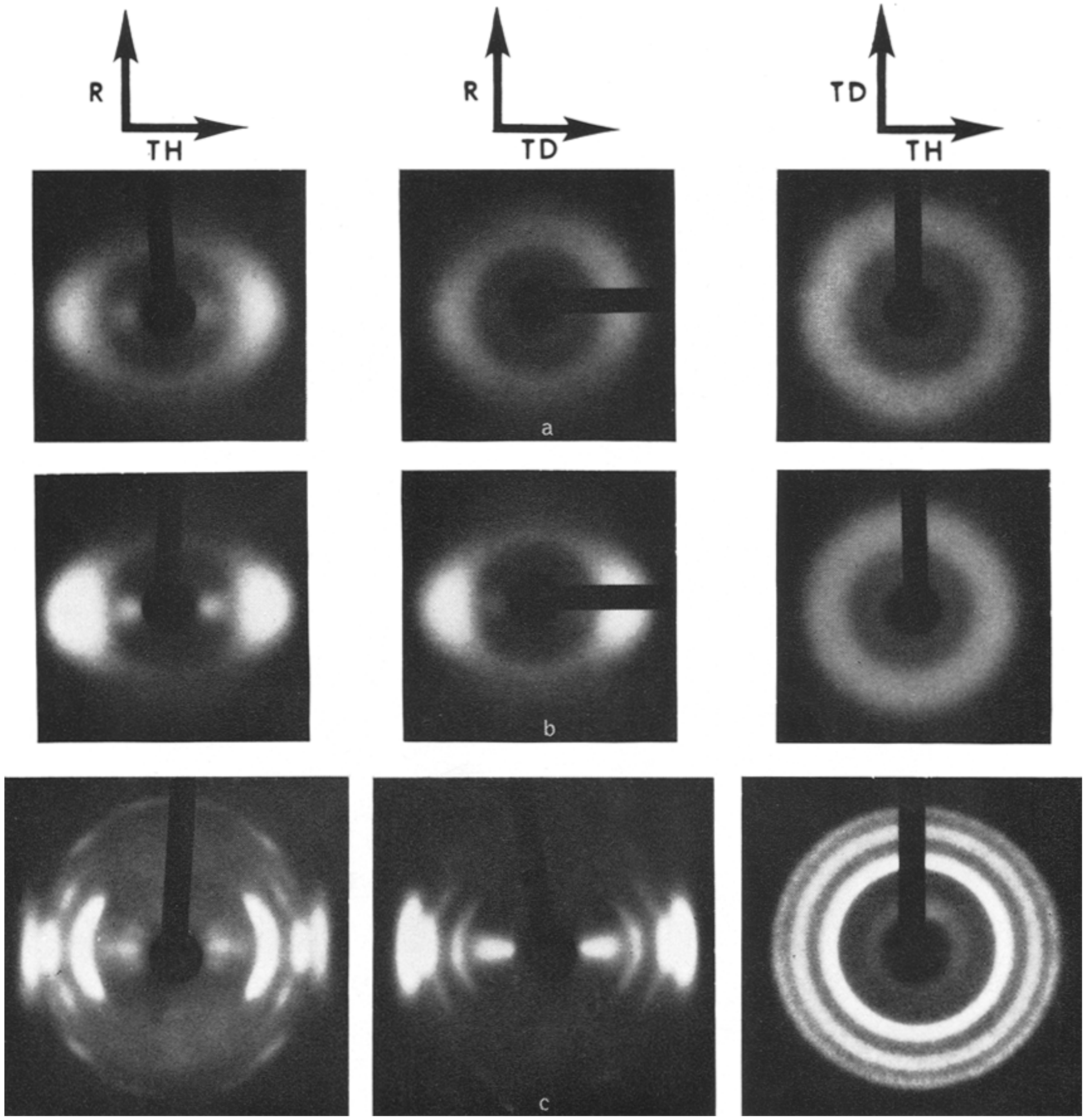

Figure 6 WAXD patterns of rolled, amorphous PET. (a) $L/L_0 = 0.5$. (b) $L/L_0 = 0.3$.

to water sorption, could be possible.

WAXD patterns of PEO rolled to $L/L_0 = 0.3$ are shown in fig. 5a. The patterns indicate that at high deformations the molecular chains are aligned in the roll direction. Because little or no orientation could be observed in the patterns for L/L_0 between 1.0 and 0.4 it was impossible to tell if the molecular chains were tilted with respect to the roll direction at low deformations.

Molecular tilt was observed, however, in rolled nylon-11 at low deformation. Figs. 5b, c and d show patterns obtained from nylon-11 with $L/L_0 = 0.7$, 0.4, and 0.25 respectively. The chains are preferentially tilted at 20 to 25° from the roll direction at $L/L_0 = 0.7$. Annealing these samples at 135°C sharpened the reflections, but did not change the degree of tilt. As the deformation increased this tilt decreased until $L/L_0 = 0.25$, where the chains were aligned in the roll direction. This change seems to be a gradual one, rather than the abrupt change in tilt observed at $L/L_0 = 0.4$ in uniaxially rolled POM [1]. Furthermore, the reflections are broadened during the rolling process which suggests a

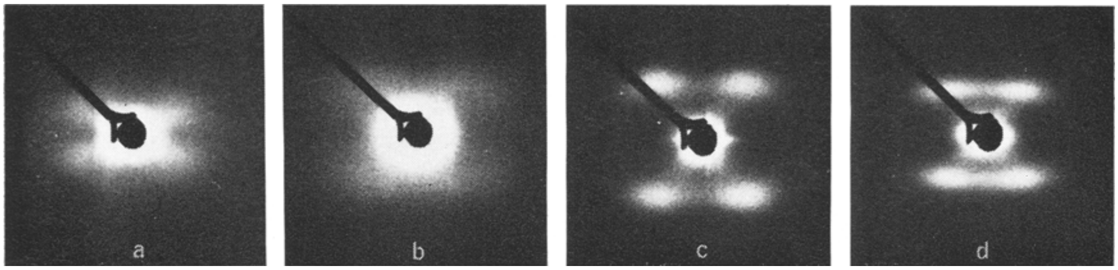

Figure 7 SAXD patterns. (a) nylon-11, $L/L_0 = 0.35$. (b) nylon-11, $L/L_0 = 0.25$. (c) nylon-11, $L/L_0 = 0.25$, annealed at 135°C. (d) PET, $L/L_0 = 0.3$, annealed at 180°C.

partial breakup of the crystallites.

WAXD patterns for rolled, amorphous PET are shown in figs. 6a ($L/L_0 = 0.5$) and 6b ($L/L_0 = 0.3$). Two strong but diffuse reflections are observed on the equator. Two weak, but relatively sharp meridional reflections ((001) and (003)) can be seen on the original negatives. These correspond to the chemical repeat distance of the molecule in the trans conformation (10.7 A) [5]. These patterns indicate an alignment of chains along the roll direction, but with the benzene rings not in register. This type of orientation has been described previously by Bonart [5] and Armeniades [6] for drawn PET.

If the sample of fig. 6b is annealed at 180°C, the result is fig. 6c. Again, the patterns are similar to those of drawn and annealed PET [5], indicating a triclinic unit cell with the *c*-axis along the roll direction.

The four-point SAXD patterns of the polymers discussed above were very weak and diffuse, especially at low deformations. In fact, patterns could not be obtained for rolled PEO or rolled, unannealed PET. Patterns obtained from rolled nylon-11 are shown in fig. 7a ($L/L_0 = 0.35$) and 7b ($L/L_0 = 0.25$). Upon annealing at 135°C, the patterns become stronger and sharper as shown in fig. 7c ($L/L_0 = 0.25$). Rolled PET annealed at 180°C gives a similar pattern, which is shown in fig. 7d.

Electron micrographs of fracture surfaces of rolled PEO ($L/L_0 = 0.6$) and nylon-11 ($L/L_0 = 0.6$) are shown in figs. 8a and b respectively. PEO gives an orientation similar to that obtained from rolled POM [1]: a banded zig-zag type of lamellar structure with the bands parallel to the roll direction. Nylon-11 however, shows lamellae aligned in two specific directions, but no indication of a banded structure.

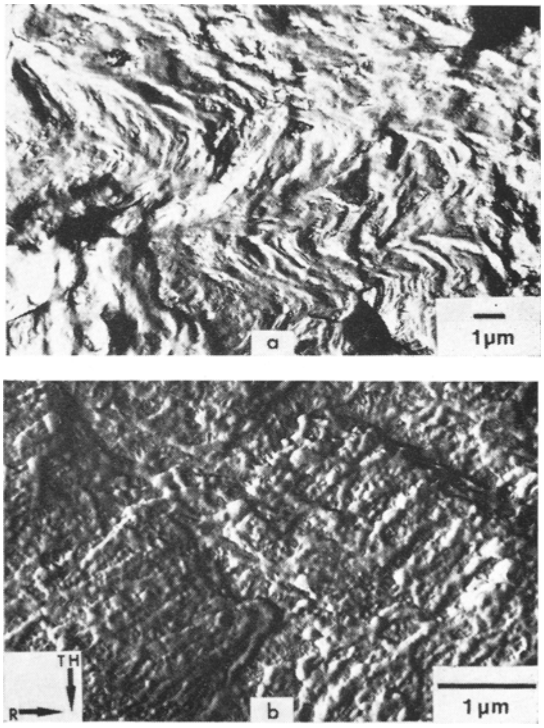

Figure 8 Electron micrographs of fracture surfaces. (a) rolled PEO, $L/L_0 = 0.6$. (b) rolled nylon-11, $L/L_0 = 0.6$.

4. Discussion

The effect of uniaxial rolling on the molecular orientation of PEO and PET is very similar to that of drawing; the chains are aligned in the roll direction. In PET, this alignment is not perfect but resembles a "liquid crystal" type of structure.

The supermolecular orientation, at least in rolled PEO, is somewhat different from that of the drawn material. SAXD fibre patterns [7] of drawn PEO reveal several orders of a meridional reflection indicating a periodicity of 240 Å. No SAXD pattern can be observed at all for rolled PEO, even at very high deformations. This presumably indicates that either the lamellar orientation is not strong or that the lamellae are "merged", or broken, in some fashion to nearly eliminate electron density differences. Also, PEO has a very low melting point (66° C) and some relaxation may be occurring during and after rolling. However, the latter would not account for the total disappearance of discrete small angle reflections. Electron microscopy (fig. 8a) reveals, however, that some lamellar orientation is present. SAXD diffraction is not observed in either drawn or rolled PET, which has not been annealed. Annealed, rolled PET, on the other hand, yields a four-point pattern similar to the drawn and annealed material [8]. This again points out the similarity between rolled and drawn PET.

The molecular orientation for rolled nylon-11 resembles that of rolled POM [1] and rolled polypropylene [2], where the chains are tilted with respect to the roll direction. Specifics regarding degree of tilt, and whether changes in tilt are sudden or gradual, seem to depend on the particular polymer in question. This tilting could also occur in PEO and PET, but the orientation may be too weak to be observed. (Even a pole figure analysis was not helpful in this respect as molecular orientation was below our level of detection.) The line broadening observed during rolling in nylon-11 indicates that two related events occur: the chains gradually tilt into the roll direction in relatively small units (probably on the order of 50 to 100 Å) causing a breakup of the larger crystallites. Thus, the state of the material at high deformations is many small crystallites with a high degree of orientation. Except for the time variation observed in PEO, tensile tests of these rolled materials provided nothing surprising nor inconsistent with the orientations observed. The increase in tensile strength is due to an alignment or near alignment of chains in the roll direction. No biaxial orientation (molecules aligned perpendicular to the roll direction), as has been found in POM [1], was observed in any of the polymers discussed here. Furthermore, no increase in width was observed for these samples. This confirms the contention that the width increase is responsible for the biaxial orientation in POM [1].

The results of this work have shown the effects of rolling to be somewhat general: rolled polymers show molecular tilts at small angles to the roll direction and lamellae arranged in two specific orientations giving rise to SAXD four-point patterns.

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