NOTES

Notes on the Cold-Drawing of Polyethylene

The deformation possible to amorphous unoriented polymers at temperatures below their glass temperature $(T<T_g)$ is of low magnitude. Under certain conditions, however, cold-drawing can occur with resultant (rubberlike) deformations of several hundred per cent. In this situation, extension occurs more readily in a shoulder because of the temperature rise occurring in this region.[1] Local heating produces a thermal wave front as a consequence of the mechanical work done on the polymer and the conduction of heat along the sample. The existence of a mechanical loss maximum above the nominal temperature of the stress-strain experiment offers a convenient explanation for the temperature at the neck.[2] At temperatures above T_g, cold-drawing ceases and homogeneous strain of the sample is observed.

For semi-crystalline polymers, e.g., polyethylene (PE), polycaprolactam (PCL), and crystallizable polypropylene (CPP), cold-drawing may again be observed when the T_g of the amorphous phase is approximately equal to or less than the test temperature. However, an alternate explanation for the process must be sought to the one given above.

Frequently, cold-drawing may be avoided by slow straining as with PCL or low density PE. In this instance, one might argue by analogy with amorphous polymers, that the heated zone becomes diffuse and the shoulder less pronounced so that at sufficiently low speeds of drawing, a neck disappears entirely. For high density PE, however, it does not appear possible to stretch slowly enough to produce uniform deformation. In fact, a yield point and neck still develop if stretching is carried out in a number of small discrete steps with waiting periods long enough between steps for thermal equilibrium to be established with room temperature. (See Fig. 1.)

Further light on the cold-drawing process is obtained from the strain distribution in a sample of Marlex 50 during a tensile test. The sample, as mentioned previously, exhibits a non-uniform strain due to the fact that it cold draws. The resulting load-extension curve which shows a maximum
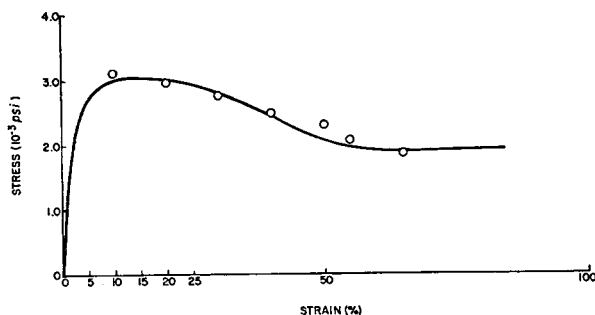

STRAIN (%)

Fig. 1. Stress vs. strain for continuous and discontinuous extension of high density polyethylene. Stress calculated from original cross-sectional area. Strain based on jaw extension. Extension rate (nominal) 1%/min. ⊙ Interrupted extension; (———) continuous extension.

represents a composite behavior of different parts of the specimen. By photographing grid lines on the sample during a stress-strain curve, it is possible to measure actual local strain by the increase in length and decrease in width. With this data, the stress-strain curve based on the minimum cross-sectional area in the yield region was calculated and is shown in Figure 2.

For comparison, a stress-strain curve of a low-density polyethylene was obtained at very low strain rates (1%/min.). This sample undergoes homogeneous strain under the conditions mentioned; the strains as measured from the cross-sectional area and from the jaw separation of the tester were in close agreement and it was a relatively simple matter to calculate a stress-strain curve based on actual dimensions. Comparison of the resulting curves shows that they possess the same overall characteristics except that the more dense polymer has a higher modulus, yield stress, and requires more energy to deform. Part of this is due to the fact that the strain rate while nominally 1%/min. may actually be 15%/min., but the major difference is due to the higher resistance or "internal viscosity" to the orientation and reorganization process taking place in the more crystalline polymer.

In the nonyielding region of the Marlex 50 sample, a maximum strain of ∼30% is reached; and, while cold-drawing occurs elsewhere, stress-relaxation and even strain recovery may take place in the sample as a consequence of a diminished load.

When the straining is interrupted and the sample allowed to cool, point A of Curve 1, a stress relaxation occurs accompanied by an increase in extension in the drawn zone. On re-straining, the stress builds up to the level at point A and the curve continues as if no interruption had occurred.

When the elongation is stopped at point A and the sample held for a short period of time to cool, then redrawing continued, only a small amount of additional energy is required to continue the process. This would be far from enough to produce an appreciable temperature rise in any but microscopic volume elements.

These findings may be rationalized by assuming that flow occurs more readily in the region of the neck because of the state of orientation in this region.[3] Richard and Gaube[4] have found that if a drawn sample of polyethylene is redrawn at various angles to the original draw direction, deformation occurs more readily at an angle of 60°. Deformation occurs more easily in this direction than it does for the original unoriented sample or the completely drawn sample. Similarly, in our laboratory it has been found that polyethylene (Marlex 50) possessing a preferred direction of the crystallite unit cell a-axis when tested at fast rates (100%/min.), cold-draws readily parallel to the a-axis, but fractures ductilely when tested perpendicular to the a-axis.

Furthermore, it is found that in the neck the crystals are in a state of partial orientation[3] so that it is reasonable that deformation should continue here more readily than in the region before the neck, where there is no orientation, or after it where there is complete orientation.

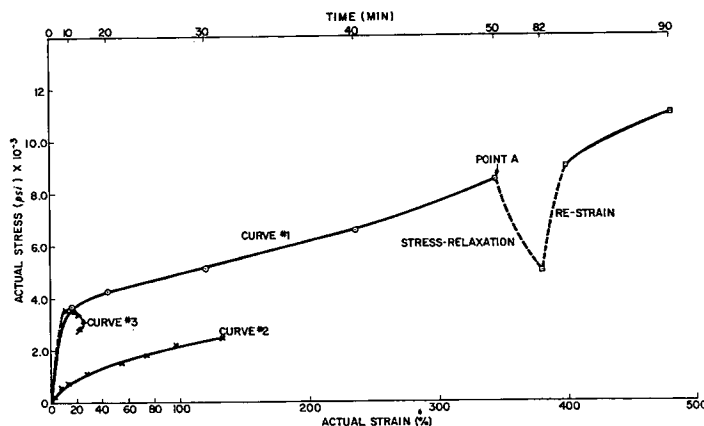The greater yield force exhibited under conditions of

Fig. 2. True stress-strain curves of high and low density polyethylene. Curves *1* and *3* refer to the yielding and nonyielding regions of a sample of high density polyethylene, annealed. Curve *2* refers to an annealed sample of a low density polyethylene. Jaw rate (nominal) = 1%/min.

biaxial orientation versus uniaxial tension in low density polyethylene is probably related to the difficulty in the former of producing a state or orientation in which biaxial flow can occur.

It would seem, therefore, that the purely thermal approach[1,2] to cold-drawing in a material such as Marlex 50, in which one would postulate elevation of the temperature to that approximating the loss peak at the melting point, is not a completely tenable explanation, and that the dependence of drawability on crystallite orientation is the more important factor.

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References

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Migration of Copper Through High Purity Poly(methyl Methacrylate)*

Migration of copper from a metal surface into solid poly(methyl methacrylate) in contact with it has been observed

when the purity of the monomer is high, with especial emphasis on low water content.

The monomer was purified so that the water content was below 0.04% (by the Karl Fischer reagent method), the inhibitor having been removed to well below 1 p.p.m., and other impurities having been similarly reduced. The purified monomer was transferred and partially polymerized in a lamp-grade nitrogen atmosphere at 70°C. and poured onto the prepared metal surfaces, either in an atmosphere of nitrogen or with less than 15 seconds exposure to air. The polymer completely filled the constant thickness gap between the metal plates. Copper metal surfaces were prepared to yield a clean surface free from a thick oxide layer by grinding with Al_2O_3 under reagent grade toluene. Assembling was accomplished rapidly by a technique which had previously been shown to yield the same adhesional strength and electrical pattern[1] on adhesional break as when the entire operation was carried out in lamp-grade nitrogen. The assembled samples were polymerized at 40°C. and cured at 100°C.

After breaking, it was observed that the polymer layer was colored green for some distance (at least 3×10^{-3} cm.) into the polymer. The region gave a positive spot test for copper by the o-toluidine test which detects down to 0.003×10^{-6} g.; the sample taken from the interior of the polymer in each case was several milligram, so that the concentration of copper was at least of the order or 1 in 10^6.

No copper migration was observed with an identical procedure if the water content of the original monomer had been reduced only to 0.10%.

If traces of acrylic, methacrylic, or other acid had been present because of degradation during polymerization, a copper salt or soap could be responsible for the migration. The mobility of the product would be favored by removal of H_2O. In view of the low temperatures used during preparation, a different process appears more likely.

Water is known to bond to polyacrylic acid molecules by an H-type bond, and differences are observed when the water is displaced by other molecules. The absence of the nonmigrant water would leave volume for the copper migration. Cu(II) complexes with polyacrylic and poly-