LETTERS TO THE EDITORS

Cold Working of Polyethylene

Traditional methods for fabrication of thermoplastic high polymers involve the heat-plasticizing of the material to a temperature above its melting point and the forcing of the material into the desired shape by the application of pressure to the melt. Some interest has developed recently in the application of cold-working techniques[1,2] to the fabrication of these materials. It is the purpose of this letter to describe some preliminary results of an investigation of the effect of cold working on the properties of polycrystalline polymers and to present an interpretation of these results.

For our purposes, cold work may be defined as the ductile deforming of polymeric materials into finished shapes by the application of mechanical strain at a temperature above the glass transition temperature (T_g) but below the crystalline melting point (T_m). The cold-working characteristics of polyethylene were investigated both by cold rolling and by compression forming in a closed mold as a function of cold-working temperature and degree of crystallinity.

Experimental Details

Injection-molded blanks, 1 in. by 1 in. by 0.030 in. in thickness, were prepared under various molding pressure–temperature cycles to produce different degrees of crystallinity.[3] These blanks were then cold-worked by rolling in a small two-roll mill at controlled temperatures below the polymer melting point. Both single- and multiple-pass rolling operations were used, but all passes were in the same direction so that uniaxially oriented strips were produced. After rolling, tensile specimens were cut from the strips both in the direction of rolling and perpendicular to this direction. Stress–strain curves were then obtained at a straining rate of 0.05 in./min. at room temperature.

Results

Figure 1 displays typical stress–strain curves for linear polyethylene cold-rolled to a 50% reduction of thickness and tested parallel and perpendicular to the direction of rolling. The curve for an unrolled specimen of the same material is included for comparison. As a result of cold rolling the tensile strength in the direction of rolling is markedly increased and the knee in the curve at the yield point usually associated with the onset of orientation of crystallites has disappeared. The elongation at break has decreased only slightly from that exhibited by the unrolled material. Perhaps the more interesting result is exhibited by the stress–strain curve for the direction perpendicular to the cold rolling. Since the process of rolling produces an elongation in the direction of rolling and no increase in the width of the specimen in the direction perpendicular to rolling, it would be expected that a uniaxially-oriented structure would result. Uniaxial orientation produced by the hot stretching of film results in a reduction in strength and elimination of ductility in the direction perpendicular to the orientation. In the cold-rolled material the maximum stress exhibited in the stress–strain curve perpendicular to the direction of cold rolling is less than that of the unworked material but the ductility in this direction is increased as indicated by the higher elongation at break.

TABLE I
Mechanical Properties of Cold-Rolled Polyethylene

Type of material	Mold temp., °F.	Mold pressure, psi	Rolling temp., °F.	Thickness reduction, %	Max. stress, psi	Ultimate elongation, %
Ziegler	150	5,000	—	0	4100	340
	150	5,000	150	10	4300 (‖)	370 (‖)
	150	5,000	150	50	8000 (‖)	266 (‖)
	200	10,000	—	0	4600 (yield)	140
	200	10,000	100	50	5200 (‖)	306 (‖)
	200	10,000	150	50	5300 (‖)	260 (‖)
Phillips	70	15,000	—	0	4000	>660
	70	15,000	70	50	6400 (‖)	470 (‖)
	−50	15,000	—	0	4000	>660
	−50	15,000	70	50	7300 (‖)	445 (‖)
Ziegler	70	15,000	—	0	3800	530
	70	15,000	70	50	6600 (‖)	400 (‖)
	70	15,000	70	50	2500 (⊥)	>660 (⊥)
Phillips	70	15,000	—	0	4000	>660
	70	15,000	70	50	6500 (‖)	480 (‖)
	70	15,000	70	50	3000 (⊥)	>660 (⊥)
Branched	70	15,000	—	0	2900	100
	70	15,000	70	50	4100 (‖)	80 (‖)
	70	15,000	70	50	2000 (⊥)	360 (⊥)

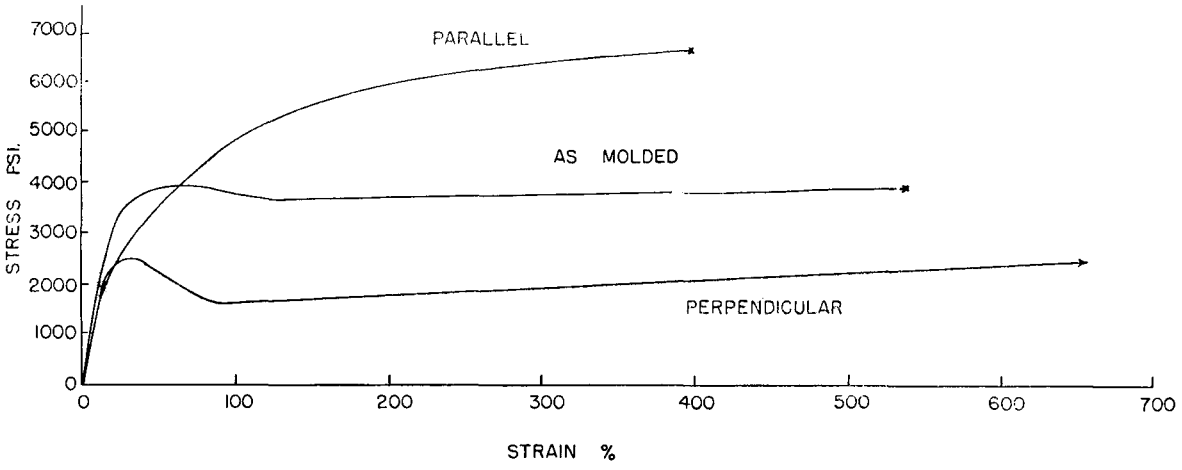

Fig. 1. Stress vs. strain for polyethylene reduced 50% in thickness by cold rolling and tested parallel and perpendicular to direction of rolling.

It was found possible to cold-work polyethylene by multiple passes to 2% of original thickness thereby achieving a 50-fold increase in length. The effects of magnitude of thickness reduction, rolling temperature, and molding conditions are given in Table I. No tests were performed on specimens reduced more than 50% in thickness, due to limitations in the sensitivity of the stress-strain apparatus.

The following general conclusions may be drawn. Cold rolling increases the tensile strength and slightly decreases the ultimate elongation in the direction parallel to the cold rolling. Maximum strength perpendicular to the direction of rolling is reduced but the ultimate elongation is increased in all cases. Quenching during the molding operation prior to cold rolling increases the ductility of the cold-worked material but decreases the maximum strength. This can be attributed to the reduction in degree of crystallinity caused by the quench. The properties of branched polyethylene were not improved by cold work to the same degree as were those of the more linear materials.

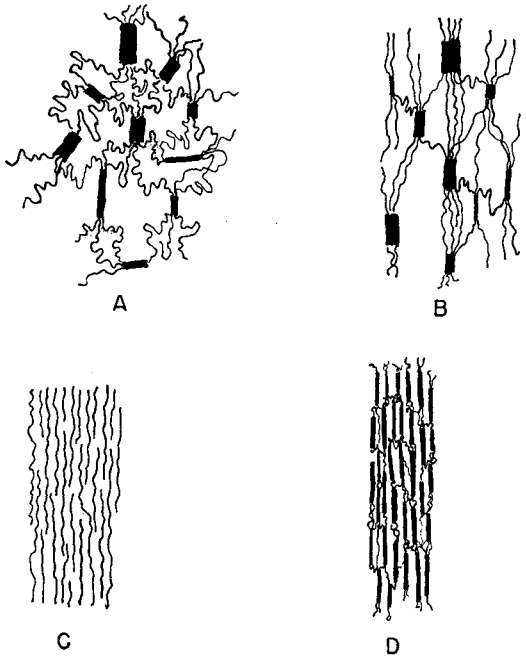

Fig. 2. Schematic representation of structure of polyethylene (*A*) as molded, (*B*) cold-rolled, (*C*) hot-oriented, (*D*) crystallized after hot orientation.

Discussion

Density measurements before and after rolling indicate that a 0.1% to 0.2% decrease in density takes place with cold working. Such small density changes suggest that the cold working operation results only in orientation of the structure and does not produce any appreciable change in the crystalline content. Figure 2 illustrates schematically a possible structural interpretation of the results observed. If a polymer melt is cooled in the absence of orientation, a structure containing randomly oriented crystallites connected by amorphous regions of coiled chains results (Fig 2*a*). If this structure is cold-worked, the crystallites will be oriented in the direction of cold rolling and the amorphous chains will be uncoiled and oriented in the same direction (Fig. 2*b*). Upon application of a tensile stress in the direction of rolling to this structure no yield point would be expected since the structure is already oriented. A high tensile strength would be expected in this direction, due to the orientation. If a tensile stress is applied to this structure in the direction perpendicular to the cold rolling, the presence of long amorphous chains between crystallites permits the reorientation of the structure, thus producing a ductile deformation of large magnitude.

If we contrast this with hot orientation followed by crystallization while the material is oriented (Figs. 2*c* and 2*d*), we see the reason for the lack of ductility in the perpendicular direction for uniaxially hot-stretched sheet: The stretching above T'_m produces an oriented structure which when cooled will form oriented crystallites with little "slack" in amorphous regions between crystallites and low strength and lack of ductility in the direction perpendicular to orientation will result, since amorphous chains of long length are not present to permit reorientation of the crystallites.

The above demonstrates that tough, ductile structures of polyethylene can be formed by cold rolling. In order to

demonstrate that similar results can be obtained by other cold-working techniques, quenched cylinders of linear polyethylene, 0.25 in. in diameter by 0.5 in. long, were placed in a steel cavity 0.25 in. in internal diameter and 1.5 in. long. A steel rod 0.23 in. in diameter was then pushed into the cold blank in order to extrude a cold-formed sleeve of polyethylene back up around the rod. It was found easy to form tubes of 0.01 in. wall thickness and over 6:1 length/diameter ratio by this method.

References

1. Gruenwald, G., *Modern Plastics*, **38,** 137 (1960).
2. Rothschild, P. H. and B. Maxwell, Princeton University Plastics Laboratory Technical Report No. 59C, October 1960.
3. Matsuoka, S., and B. Maxwell, *J. Polymer Sci.*, **32,** 131 (1958).

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An Improved Microscope Hot Stage

The recent discovery of a large number of crystalline polymers with well-defined melting points[1] has resulted in the increased use of melting point determinations of polymeric materials, mainly for identification, but also for structural elucidation.[2] As many crystals of polymers exhibit birefringence, the measurements are generally performed on a heated microscope stage, under crossed Nicol prisms or Polaroids, the melting point being taken as the temperature at which the birefringence entirely disappears. A number of suitable microscope hot stages have been described in the literature,[3] and several are commercially available,[4] the Kofler stage being most commonly used. This model consists of an electrically heated block on which the sample is placed, being protected from air currents by means of a glass baffle and cover plate. Temperatures are measured with a thermometer, inserted through a well in the block, which is so marked that readings coincide with melting points of standards measured with the equipment.

Satisfactory results are obtained with this stage when a precision of about 1°C. is required. For better measurements, however, certain modifications are necessary because sample and block temperatures differ considerably and cannot always be precisely related. For this purpose a second electrically heated block was constructed to be placed over the original one (Fig. 1). It was provided with a small indentation (I) in the center for accommodating the sample, a lip (L) for seating, and a cover glass (G) in a small circular indentation at the top, held in place by a circular clip (C), which sealed the center hole (H) to air currents. In other respects it was similar to the parent block and in operation could be simply lifted for the introduction

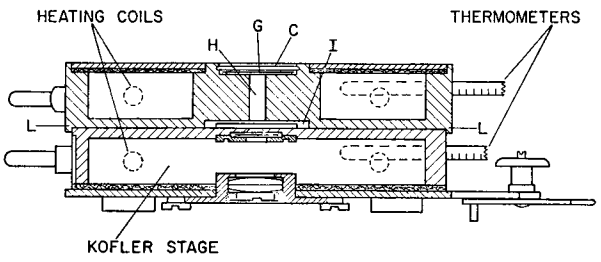

Fig. 1. Schematic diagram of modified stage.

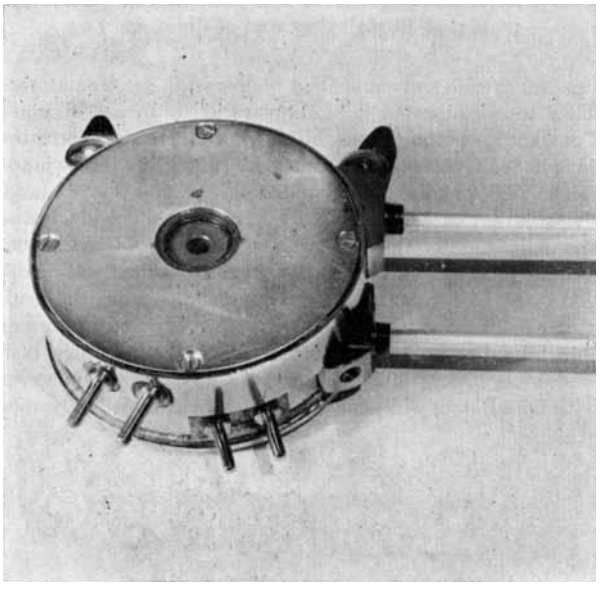

Fig. 2. Photograph of modified stage.

or removal of the sample. The joining faces of both blocks were polished and chrome-plated to reduce temperature gradients between them. A photograph of the modified stage is shown in Figure 2.

TABLE I
The Apparent Melting Point of Phenacetin as a Function of Sample Distance from Heat Source[a]

Stage	Observed m.p., °C.	Distance, mm.	Remarks
Kofler	139.4	2.8	Sample on two microscope slides (each 1.4 mm. thick) and covered by 0.14 mm. thick cover glass[b]
Kofler	137.2	0.14	Sample between two cover glasses (0.14 mm)[b]
Modified	135.5	0	Sample between two cover glasses (0.14 mm.)

[a] U.S.P. grade phenacetin, recrystallized three times from a 50/50 (vol.) mixture of $CHCl_3$ and *n*-hexane.
[b] The usual baffle and top glass cover was also used.

Two matched thermometers with 0.1°C. divisions covering a 20-degree range and equipped with reading lenses were