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The Formation of Translucent Cold-Drawn Polypropylene

C. LEE and D. R. UHLMANN, *Department of Metallurgy and Materials Science, Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

Synopsis

The behavior of quenched samples of polypropylene subjected to stress relax-reload cycles during cold drawing has been investigated as a function of quench severity and strain rate. Results obtained by cooling the propagating neck of a drawing sample are also discussed. A translucent cold-drawn form of the polymer, characterized by a small microvoid content, is observed when the propagating neck boundary is cooled or when stress relax-reload cycles are carried out at sufficiently high strain rates. A small mobility of the chains relative to the local strain rate is postulated as necessary for the formation of the translucent material.

INTRODUCTION

Considerable attention has been directed to elucidating the deformation mechanisms in semicrystalline polymers.[1,2] Most of this work has been concerned with cold drawing behavior at temperatures well above the glass transition temperature of the amorphous component.

In the present study, attention will be focused on the gross microstructural changes occurring in highly isotactic polypropylene (PP) as it is cold drawn at and below room temperature. Under these conditions, heat builds up in the vicinity of the propagating neck boundary. Such heat buildup is not unique to PP, but does appear to be more pronounced for this material than for other polymers.

When PP is cold drawn at or above room temperature, the drawn material is white-opaque, in contrast to the translucency of undrawn PP. This opacity is caused by the formation of microvoids in the drawn material and is also more pronounced in PP than in other common polymers.

It will be shown below that cold-drawn PP which is translucent and free of microvoids can be formed by cooling the propagating neck boundary or by use of stress relax-reload cycles at sufficiently high strain rates with quenched samples. A mechanism will be proposed to explain this phenomenon which considers the mobility of the amorphous regions to be of major importance. The results are compared with recent work on nylon 6-10[3,4] and polyethylene terephthalate[5] in which opaque drawn material is formed rather than the usual translucent or transparent forms of these materials.

EXPERIMENTAL

Commercial PP sheet, 0.06 in. thick, was cut into strips 1.5 in. $\times$ 6 in. These were clamped between two similar pieces of rolled aluminum and melted in a vacuum oven for 5 min at 220°C. After melting, samples were subjected to one of three quenching procedures: (1) cool in air with fan convection; (2) quench in water; or (3) quench in liquid nitrogen.

Following heat treatment, tensile specimens were cut from the sheet using a die. The resulting sample dimensions were: overall length, 5.125 in.; gauge length, 2.25 in.; grip width, 1 in.; gauge width, 0.24 in. at center; and thickness, 0.045 to 0.052 in. (varied from sample to sample).

Tensile specimens were drawn in an Instron mechanical testing machine at rates of 0.01 to 5 in./min ($\dot{\epsilon} = 7.4 \times 10^{-5}$ sec^{-1} to 3.7×10^{-2} sec^{-1}), with most runs being carried out at rates of 1, 2, or 5 in./min. After initial yielding had occurred and the neck was propagating smoothly, stress relax–reload cycle tests were carried out in some cases. These consisted of stopping the cross-head motion, holding the specimen at constant total strain while stress relaxation and cooling of the neck boundary occurred, then resuming cross-head motion at the same rate as before. In some cases, the propagating neck boundary of a drawing specimen was cooled by touching it with a finger, a piece of metal, or an ice cube, and the resulting behavior was noted.

The densities of the undrawn grip, the opaque cold-drawn, the translucent cold-drawn, and occasionally the undrawn grip material containing many deformation bands were measured by titration using an isopropanol–water system. A magnetic stirrer was used to ensure thorough mixing of the solution following each titration addition. The titration procedure was calibrated against results obtained with a density gradient column.

Differential scanning calorimetry (Perkin Elmer DSC-1B) was used to measure the crystallinity (heat content) of each of the different sample regions. Samples, typically 8 to 15 mg in size, were heated at 10°C/min. The area of the endotherm was measured using a planimeter and was calibrated using an indium standard. A value of 62 cal/g was taken for the heat of fusion of crystalline isotatic PP.[6]

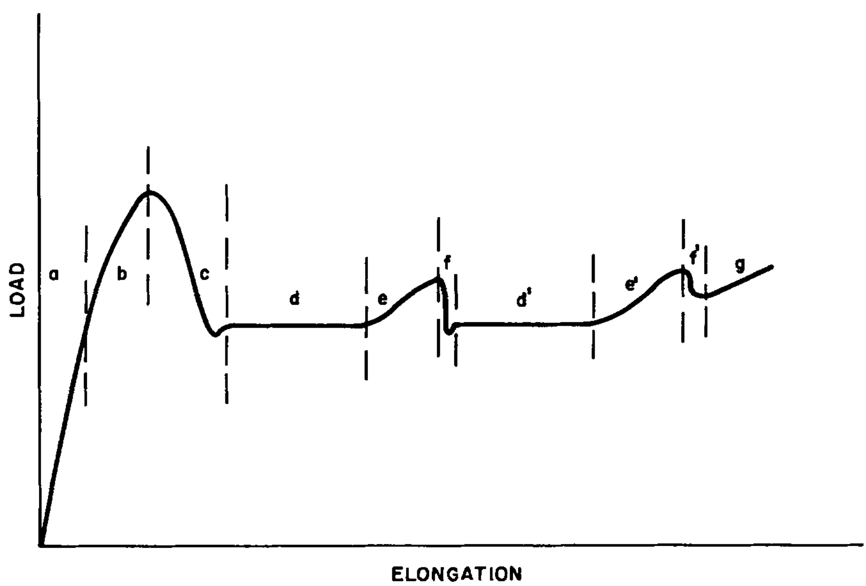
RESULTS

A typical load–elongation curve for a quenched sample of PP drawn at a moderate strain rate at room temperature is shown in Figure 1a, and the deformation of the sample is illustrated in Figure 1b. In region a (Fig. 1a), the curve is linear and the sample deforms homogeneously, remaining translucent throughout the gauge. The curve becomes nonlinear in region b, and shear deformation bands appear on the sample gauge as shown in diagram 1 of Figure 1b. These bands are usually concentrated in one or more regions of the gauge.

In region c, a neck becomes visible at the location of the most intense deformation bands on the gauge. This neck initially forms asymmetrically, starting on each side of the gauge at points where deformation bands intersect one another and the edge of the gauge, as shown in diagrams 2–5 of Figure 1b. The neck becomes symmetric and propagates over some length, with the edges remaining diffuse, in region c. At the end of region c, one boundary of the neck sharpens (see 6 of Fig. 1b); and in region d the neck propagates in the direction of the sharpened end, which is also the direction away from the most intense deformation bands (regardless of whether this is in the direction of the minimum cross section of the gauge). The groups of deformation bands are typically separated by 0.25 to 0.50 in. of gauge which shows no banding.

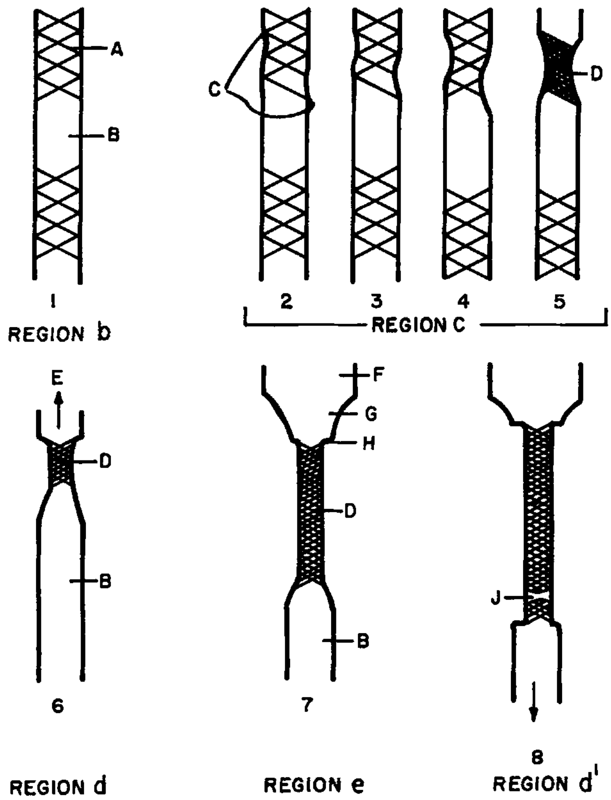
In region d, the neck propagates in only one direction until the shoulder of the gauge is approached. In region e, the neck propagates into the shoulder of the gauge; and in region f, yielding occurs at the other end of the neck with the neck boundary sharpening and some translucent cold-drawn material being formed as the load drops (provided the strain rate is high enough)—see 8 of Figure 1b. Propagation then continues in the other direction (region d′ of Fig. 1a) until the other shoulder is reached in region e′. In the final portion, either the first shoulder will yield and the direction reverse again or further drawing of the neck will occur.

For each given quench treatment there existed a strain rate above which samples would not draw the length of the machine without fracture. (Drawing the length of the machine corresponds to a strain of about 680%.) This strain rate, which shall be denoted as the "standard" strain



(a)

Fig. 1 (*continued*)



(b)

Fig. 1a. Load–elongation curve for PP: (a) uniform strain region; (b) deformation bands form; (c) neck forms; (d) neck propagates (cold draws) in one direction; (e) neck enters gauge shoulder; (f) propagation reverses direction; (d′) neck propagates in new direction; (f′) propagation direction again reverses; (g) further cold drawing into shoulder regions.

Fig. 1b. Necking and drawing of PP: (A) deformation bands; (B) undrawn gauge (translucent); (C) neck forming at loci of deformation bands; (D) opaque cold-drawn polymer; (E) propagation direction; (F) grip region; (G) shoulder region; (H) neck boundary; (I) translucent cold drawn material.

rate, was $\dot{\epsilon} = 0.0148\ \text{sec}^{-1}$ for air-cooled and water-quenched samples and $\dot{\epsilon} = 0.037\ \text{sec}^{-1}$ for liquid N_2-quenched samples.

Stress relax–reload cycles increased the probability of fracture at a given strain rate; and repeated cycles on a given sample further increased the likelihood of fracture. All stress relax–reload cycles were carried out while the sample was drawing smoothly, i.e., in region d or d′ of Figure 1a. The time of relaxation and the strain rate were varied for each type of quench.

When stress relaxation and reloading was done using the standard strain rate and a relaxation time greater than about 2 min (so that the load was

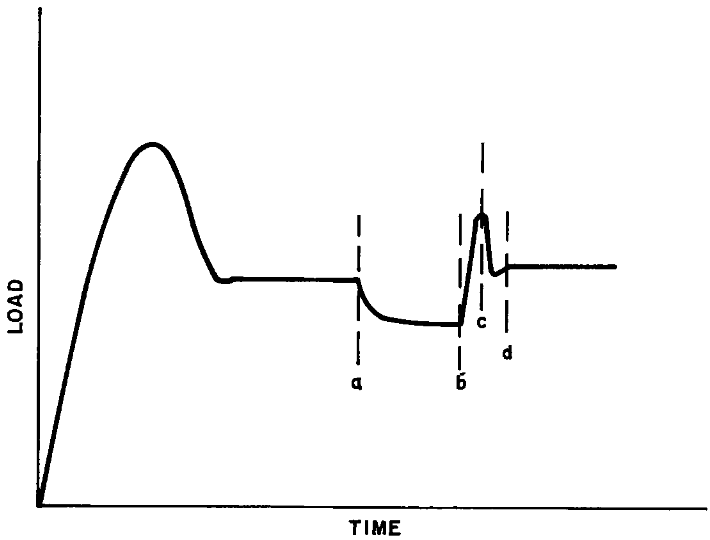


Fig. 2. Stress relax–reload cycle: (a) cross-head motion stopped; (b) cross-head motion restarted; (c) sample yields; (d) sample resumes normal cold drawing.

again approximately constant), the following sequence of events typically occurred: As the material is drawing, the boundary of the propagating neck is hot to the touch. As soon as the cross-head motion is interrupted, the material begins to cool and the load drops rapidly for about 30 sec (see region a–b of Fig. 2). The load continues to drop more slowly for about 2 min and then remains nearly constant for the rest of the stress relaxation period. During this interval, no visual changes are apparent in the sample.

As soon as cross-head motion is resumed, the load rises steeply to a value greater than the drawing stress, but less than the primary yield stress (b–c of Fig. 2). When the boundaries of the necked region are marked while cross-head motion is stopped, it is found that during this stress rise on reloading, the neck boundary does not propagate at either end provided the relax–reload cycle is carried out at or above the standard strain rate. For lower strain rates, however, some propagation of one or both neck boundaries is observed during the stress rise (prior to reyielding). At c, yield occurs in the material at one end of the neck, with the direction of propagation sometimes reversing in the process. This yielding is much more localized than that involved in the formation of the primary neck and involves only material in a small region at one boundary of the neck. The stress drops; and as it does, the neck propagates more rapidly for a fraction of a second than is observed for normal drawing at the given strain rate. The cold-drawn material formed in this brief period is translucent like the undrawn regions, not white and opaque like typical cold-drawn PP. The shape of this region is well defined and is illustrated in Figure 3. This

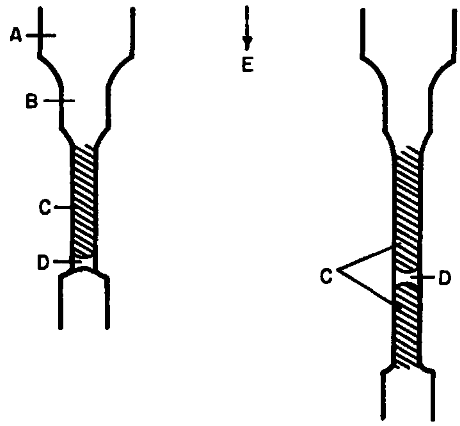


Fig. 3. Formation of single region of translucent cold-drawn PP: (A) sample grip; (B) undrawn gage; (C) opaque cold drawn PP; (D) translucent cold drawn PP; (E) neck propagation direction.

region is typically about 0.06 in. in length. As the load again reaches a plateau, normal cold drawing resumes and opaque PP is produced.

If the strain rate is increased to slightly greater than the standard strain rate, and the sample reaches the drawing stage without fracture, the following behavior is often observed in a stress relax–reload test: Relaxation takes place as described above. When the straining is resumed, the load rises up to yield point c as before, and again neck propagation is not observed. Again, the sample yields, and translucent cold-drawn material is formed at a high rate. Rather than resumption of normal cold-drawing, however, abrupt fracture occurs at the interface of the propagating neck.

If the strain rate is reduced to slightly less than the standard value, the same phenomena are observed as at the standard rate. Three differences, however, are apparent: (1) the yield point, c, is lower; (2) the material which is cold drawn in c–d is not as translucent as it was at the standard rate; and (3) the boundary between translucent and opaque cold-drawn material is not sharp as it was at the standard rate.

If the strain rate is reduced to much less than the standard rate, the yield point, c, decreases still further, although it never completely disappears over the range of strain rates covered by the present investigation. A strain rate of about one fourth the standard rate is, however, sufficiently low that no translucent cold-drawn material is formed and no material is observed to draw at a rate faster than the normal drawing rate for the given strain rate.

If the time allowed for stress relaxation is too brief (less than 2 to 3 min), so that the stress has not reached an apparent plateau, no translucent region is formed on reloading. The magnitude of the increase in load upon reloading is observed to increase with time of relaxation up to about 3 min, beyond which it is constant. In a large number of cases where relax–reload tests were performed on liquid N_2-quenched samples, the phenomena

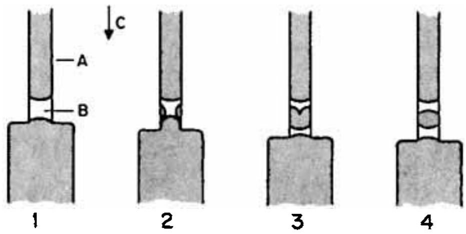


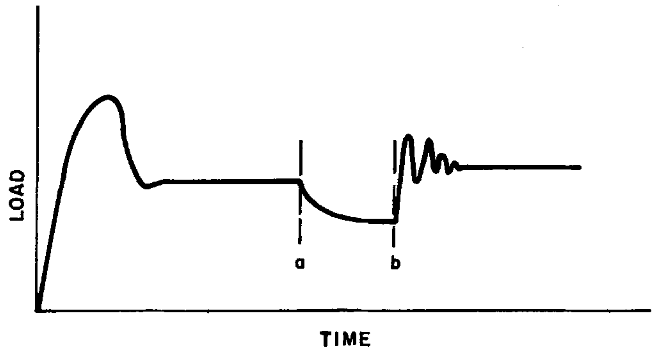
Fig. 4. Formation of two regions of translucent cold-drawn PP: (A) opaque cold-drawn PP; (B) translucent cold-drawn PP; (C) propagation direction.

on reloading were even more interesting. Rather than a single translucent cold-drawn region being formed, two such regions would appear and a double yield would be present on the stress–strain curve (see Fig. 4). The size of the translucent regions increases as the magnitude of the second yield increases.

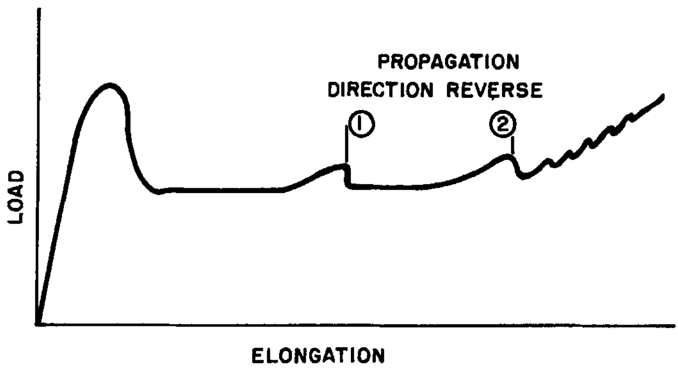
When two regions are formed, the behavior on reloading begins similarly to the case where only a single clear region is formed. When the crosshead motion is resumed, the neck does not propagate until the yield is reached. As before, during the initial portion of the stress drop after yielding, the neck propagates faster than in normal drawing at the given strain rate, and the cold-drawn material which forms is translucent. Then, instead of the stress leveling off with the resumption of normal drawing, some of the translucent region becomes opaque, with the opacity appearing to advance through it as shown in 2–4 of Figure 4. The stress again rises, and yielding again occurs with the formation of some new translucent cold-drawn material by rapid neck propagation. The stress then drops and levels off as normal cold-drawing resumes. The first normal cold-drawn material after this is frequently marked with three intense vertical striations about 0.25 in. in length. Sometimes these are actually slits going completely through the specimen, although they seldom cause fracture.

In all cases where translucent regions are formed, they remain translucent after removal of the stress for extended periods at room temperature. While the draw ratios (*DR* = initial cross section/final cross section) of these regions are approximately the same as those of the opaque cold-drawn material (*DR* 5–6), they are generally wider and thinner than the surrounding material. The difference (typically about 10 pct) is not nearly sufficient, however, to account for the observed difference in translucency.

In some cases, not one or two but three to ten translucent regions would form, one after another in quick succession, by a process similar to that described for the formation of two. This was often, but not always, observed under either of two conditions: (1) if a specimen was melted, liquid N_2 quenched, and subjected to a relax–reload cycle following prior storage after quenching of more than seven days at room temperature; or (2) if a specimen drew with a low cold-draw ratio (*DR* 5), so that the shoulder regions were reached well before the full extension of the Instron,



(a)



(b)

Fig. 5a. Stress relax–reload cycle, multiple yielding: (a) cross-head motion stopped; (b) cross-head motion resumed.
Fig. 5b. Multiple yielding in gauge shoulder.

and if the direction of neck propagation reversed after both boundaries were into the shoulder.

For each translucent region formed in either of these ways, a resolvable stress rise and yield drop were observed in the load–elongation curve. If the regions formed in a relax–reload cycle, each successive region was slightly smaller than the previous one. If they formed in the shoulder, the first clear region was larger than the others, which were all about equal in size. The magnitude of each yield was proportional to the size of the translucent region which formed. For a stress relax–reload cycle, the resulting stress–strain curve looked much like damped oscillations. When this happened, no more than five regions were ever formed, and three were most common. Typical load–elongation curves corresponding to the clear regions generated in those two ways are shown in Figures 5a and 5b. The appearance of a sample with multiple clear regions in the shoulder is shown in Figure 6.

Translucent regions can also be formed by cooling the neck boundary while the specimen is drawing. The colder the neck is maintained, the

TABLE I
Variation of Draw Ratio and Density with Strain Rate and Quench Employed

	Strain rate, sec^{-1}	Draw ratio	Density, g/cm^3
Liquid Nitrogen Quench			
Undrawn	0.037		0.881
Translucent	0.037	6.60	0.853
Opaque	0.037	6.55	<0.785
Undrawn	0.0148		0.881
Translucent	0.0148	5.40	0.830
Opaque	0.0148	5.38	0.805
Air Quench			
Undrawn	0.0148		0.880
Translucent	0.0148	5.25	0.862
Opaque	0.0148	5.31	0.815
Undrawn	0.0074		0.880
Translucent	0.0074	4.95	0.845
Opaque	0.0074	5.0	0.825

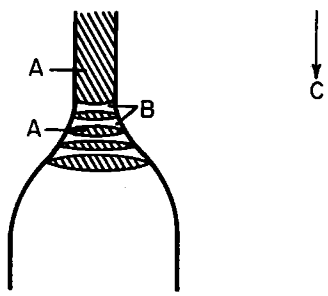


Fig. 6. Multiple translucent cold-drawn regions formed in gauge shoulder: (A) opaque cold-drawn PP; (B) translucent cold-drawn PP; (C) propagation direction.

clearer is the drawn material. This was verified by holding a finger, a piece of metal, an ice cube, and a piece of Dry Ice against the neck boundary as it propagated. Progressively clearer regions were formed. Accompanying the formation of the clear regions was a rise in load while the sample was kept cold. The colder it was maintained, the higher the stress rise; and in the case of Dry Ice cooling, fracture occurred almost immediately.

The cold-draw ratios and densities of the translucent and opaque regions produced at various strain rates for specimens given different quench treatments are shown in Table I. As shown there, the cold-draw ratios of the translucent material are in all cases similar to those of the corresponding opaque material, while the densities are intermediate between those of the opaque material and the undrawn samples. The densities of the opaque drawn regions decrease significantly with increasing strain rate. The densities of the translucent drawn regions appear to be higher for more translucent samples as well as for higher strain rates and more cooling of the propagating necks. Further, undrawn regions containing shear deformation bands have densities slightly less than those of undrawn regions not containing such bands.

DISCUSSION

The most striking feature of the present results is the formation of clear (translucent) regions of cold-drawn PP. The difference in opacity between these regions and the familiar opaque drawn material is associated with a difference in the extent of microvoid formation. This is indicated by the density measurements shown in Table I, where the undrawn material is seen to have the highest density, the translucent drawn material an intermediate density, and the opaque drawn material the lowest density. The density of the opaque drawn material is in all cases less than that of amorphous isotactic PP (0.85 g/cm^3), despite the fact that DSC measurements indicate a crystallinity in the opaque regions of about 20–30%. Consideration of these density data also indicates that the microvoids do not merely represent coalesced, smaller regions of lower density generated during the crystallization process, but must reflect the changes in topology and orientation which take place during drawing.

The conditions required for the formation of translucent cold-drawn PP suggest that strain rate and temperature are the two major determining factors. Since the formation of translucent material is favored by high strain rates on stress relax–reload cycles and by cooling the propagating necks, the single physical criterion appears to be the mobility of the chain segments in the neck region relative to the imposed strain rate (and the ability of the specimen to support the applied load without fracture). For the yield behavior being considered, the relevant mobility seems to be that in the amorphous regions, since it has been shown by others[7,8] that the structural integrity of the crystalline regions is maintained well beyond yielding.

In considering this behavior, a distinction must be made between the local strain rate and the overall strain rate. In the primary yield process as well as during drawing and stress relax–reload cycles at sufficiently low rates, the deformation process is not highly localized within a portion of the neck, and the local strain rates exceed the nominal strain rate by some given factor, α. During relax–reload cycles at high nominal strain rates, however, the straining becomes highly localized in one small region of the propagating neck. The ratio of the local strain rate to the nominal strain rate can then be much larger than the factor α.

The drawn material of high microvoid content would then be expected to form at strain rates which are sufficiently high that equilibrium with external surface sinks for void volume cannot be maintained, and sufficiently low that the mobility of chain segments permits the aggregation of the excess volume into discrete voids. These conditions are apparently fulfilled for the usual ranges of drawing rates and neck temperatures used and encountered with PP. In the range of high strain rates and low neck temperatures included in the present investigation, the mobility is apparently insufficient to permit void formation. Under these conditions, translucent drawn material can be formed.

It is recognized, of course, that the demarcation between opaque material and translucent material is not a sharp one. Rather, over a range of strain rates and temperatures in the neck regions, material of varying degrees of opacity will be formed. Evidence for such a variation was provided by the experiments in which the regions of propagating necks were cooled, where the translucency was observed to increase with increasing degree of cooling.

On stress relax–reload cycles, if the specimens are allowed to cool to ambient before reloading and deformation is resumed at high nominal strain rates, the strain is initially quite localized. (During the initial yielding, in contrast, the strain does not become localized until elongations of 10-15 pct. are reached. And when yielding occurs, the relative mobility in the neck region is below that required for the formation of a microvoid-rich structure, and the translucent material is formed. As drawing proceeds, however, heat builds up in the neck region and opaque drawn material is again observed. If the relax–reload cycles are carried out at low nominal strain rates, or if only a brief period is allowed for relaxation and heat dissipation prior to reloading, the mobility is sufficient for the opaque material to form immediately upon reloading or reyielding. The increasing translucency of the clear regions which form with increasing strain rates in relax–reload cycles is likely also associated with the smaller thicknesses and hence smaller thermal diffusion paths, which result at the higher rates.

The regions of initial neck formation in PP are slightly more translucent and narrower than the surrounding drawn material, and the original neck site can be located on a fully drawn sample by these characteristics. The somewhat greater clarity can be associated with the fact that the heat in the neck region has not built up to its steady-drawing value, and is reflected in the necks being rather diffuse during the initial yield.

The much greater opacity of the initial neck region relative to the translucent material formed on relax–reload cycles can be associated with the appreciably different heat flow conditions which are present in the two situations. Specifically, the initial neck forms in a region which is significantly thicker, and hence is characterized by a significantly longer thermal diffusion path, than the sharp neck region of a specimen subjected to a relax–reload cycle.

The presence of heat generated in flow has been suggested to lower the stress required for subsequent deformation.[9] The results of the present work are in accord with this suggestion. When the neck is cooled, the drawing stress rises in proportion to the severity of cooling. If the neck gets too cold, the stress rises steeply and brittle fracture occurs at the boundary of the propagating neck. When the neck is severely cooled at one end, stress rise and fracture occur at that end, rather than reversal of the propagation direction to the unchilled end of the neck region.

DSC studies of the undrawn, translucent drawn, and opaque drawn materials show no substantial differences in either per cent crystallinity or melting point for a given sample. This provides further indication that the difference between translucent and opaque drawn PP is a microstructural difference.

Phenomena similar to some of those described in the present work have previously been reported for nylon 6–10[3,4] and for amorphous poly(ethylene terephthalate).[5] When the nylon is subjected to sufficiently high strain rates during a stress relax–reload cycle or is left for sufficient stress-aging times during constant-load testing, it exhibits multiple yielding and corresponding regions of cold-drawn material different from normal-drawn material. In particular, while the normal-drawn nylon is translucent, the indicated treatments result in the formation of small opaque regions of high microvoid content. With the nylon, sustained oscillations (undamped multiple yielding) in the main gauge region could be achieved, whereas with PP they were noted only when the neck had propagated into the shoulder region. Further, the draw ratio of the opaque nylon is higher than that of the translucent material, while in the case of PP, the draw ratios of the two materials are approximately the same.

The formation of opaque drawn regions in nylon was attributed to thermal runaway.[3] It was suggested that a critical neck velocity exists for this material below which the runaway will not occur, and that temperature and stress are not critical for the formation of the unusual nylon. The opaque material was observed to form first in the central region (the hottest portion) of the neck and propagate to the surface regions. Just before formation of the opaque material, the diameter of the clear region was observed to decrease, providing a further indication of heating.

The importance of heat flow in the formation of sustained oscillations in the gauge length was also emphasized in a study of amorphous poly(ethylene terephthalate) (PET) films.[5] In this case, sustained oscillations—accompanied by the formation of opaque drawn material—were observed during steady drawing of the material (and not merely on relax–reload cycles). The drawn length of the sample was identified as another important factor affecting the formation of opaque material in sustained oscillations. Such a dependence was not investigated in the present study, where only a single specimen length was employed.

In contrast to nylon and amorphous PET, PP normally builds up enough heat in the course of drawing to form a microstructure with a high void content. Cooling the neck (either directly or during stress relaxation) dissipates this heat, and the subsequent drawn material is relatively free of such voids. Once heat again builds up in the neck region, the void-containing material will again be formed. If during the formation of such material the available heat is dissipated rapidly enough, a second translucent region will be formed, and multiple yielding can thus result.

The differences between the polymers in the heat buildup in the neck region seems likely to be associated with the significant difference in their thermal conductivities: 5.2×10^{-4}cal/cm-sec-°C for nylon 6–10 and 6.9×10^{-4}cal/cm-sec-°C for PET versus 2.8×10^{-4}cal/cm-sec-°C for PP.[10] The thermal conductivity of PP is lower than that of nearly all other crystallizable polymers, and the propensity of this material to form drawn regions of high microvoid content seems to be associated with the low conductivity and resulting large buildup of heat in the neck region.

Assuming the relation between heat buildup (local mobility) and microvoid formation is correct, it may be anticipated that other polymers with relatively small thermal conductivities would also form opaque cold-drawn material. An interesting candidate in this regard would be poly(vinylidene fluoride), which has a conductivity similar to that of polypropylene and can also be crystallized to a significant extent.

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