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The effect of cold and hot extrusion on the structure and mechanical properties of polypropylene

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The direct extrusion of isotactic polypropylene through a 90° die at 23, 65, 95 and 120°C has been studied. As a result of extrusion, the tensile strength and the elastic modulus of the material are considerably increased whereas the ductility is decreased. Owing to the deformation of the material occurring in the extrusion process, the *c*-axis of the monoclinic unit cell aligns itself parallel to the extrusion direction and the lamellar structure is orderly arranged. The tensile strength and the orientation of the material extruded at higher temperatures are much higher than those obtained by extrusion at room temperature. The changes in the density and the mechanical properties resulting from extrusion have been explained in terms of the structural changes occurring in the material. A method has been suggested for estimating the spring back of extruded material.

1. Introduction

The thermoplastics are conventionally formed by shaping the viscous molten polymer under pressure in a mould cavity. The factor limiting the rate of production in such forming processes is slow cooling of the part, because the thermal conductivity of polymeric materials is extremely low. The production rate could be speeded up considerably (limited only by the dynamics of the machine) if the cooling step required to solidify the part were eliminated. The difficulty also arises in the moulding of very high molecular weight materials because the flow characteristics of these materials in the molten state are very poor due to very high viscosity. Cold- and hot-forming are obviously the answer because in such processes the part can be ejected immediately after it is shaped. Furthermore, the viscosity of the molten material does not play any role. The only requirement for processing by these methods is a high ductility which most of the thermoplastics inherently possess. A description of such forming processes with respect to polymeric materials has been given by Coffman [1].

Of all the cold-forming processes, cold-rolling is the most studied process [2-13]. Most of these studies [2-11] are related with the effect of cold-rolling on mechanical properties. They all show that owing to cold-rolling, the yield and tensile strengths of the thermoplastic material are increased in the direction of rolling, the effect of necking and cold-drawing is reduced and the stress whitening observed in some polymers is eliminated [5]. The modulus of elasticity in some cases is found to increase and in others to decrease. The ductility of the polymer generally increases in the beginning with increasing amounts of cold-work due to rolling but finally decreases [10]. There are relatively few studies [12, 13] which examine the effect of cold-rolling on the structure and deformation behaviour of polymeric materials.

Next to the cold-rolling process, deep-drawing seems to have been most widely studied. The deep-drawing of polymers at room temperature and the test methods for judging drawability were reported by Ito [14], Gruenwald [15] and Warshavsky and Tokita [16]. The additional development work on this process has since been followed by a number of workers [5, 17-20]. Broutman and Kalpakjian [5] studied the drawability of high density polyethylene, polycarbonate and two types of ABS and compared their results with those of Smoluk and Klaus [21] on a similar process called hydroforming. They point out that for good deep-drawing ability the material should have a high value of the anisotropy ratio and the yield strength. Li *et al.* [20] studied the mechanics of the deep-drawing process and tried to correlate the maximum depth of draw with the basic properties such as the tensile strength and compressive yield strength of the sheet material. Evans [22] performed a theoretical analysis of the deep-drawing process using the classical plasticity theory and applied it successfully to a large number of thermoplastics. Wissbrun [23] studied the forces required in the forging of cups of high density polyethylenes with three different molecular weights and an acetal co-polymer both at ambient and elevated temperatures. There was a high degree of orientation observed in the forged material which produced a remarkable increase in the elastic modulus and tensile strength in the direction of orientation but with a sacrifice of toughness in the transverse direction. Werner and Krimm [24], studying the forging of high molecular weight polyethylene, found that the forged part had higher tensile strength and lower percent elongation than the injection-moulded part. There was virtually no change in the flexural modulus. The lower the forging temperature, the higher was the tensile strength with practically no change in strength in the high temperature range.

The studies on the solid phase extrusion of polymers are comparatively scarce. Buckley and Long [25] studied the feasibility of the extrusion of polymers and evaluated the mechanical properties of extrudates, obtained by extrusion under ambient conditions, as a function of the extrusion ratio. Lee *et al.* [26] compared the effect of cold-extrusion and cold-drawing on the tensile and compressive properties of high density polyethylene, nylon 6-6 and polycarbonate materials. They observed that due to extrusion the tensile true stress-true strain curve was raised but the comparable compressive curve was lowered. The elastic modulus of extruded or drawn polycarbonate was increased but for the other two materials it was decreased. The cold-worked material exhibited considerable directional effects in compressive loading.

In neither of the above two studies has the effect of solid phase extrusion at elevated temperatures on mechanical properties been investigated. In addition, these studies are not directed towards the investigation of the structural changes in the material produced as a result of extrusion. It was, therefore, intended in the present work to evaluate the effect of processing temperature on the properties of the end product. This was accomplished by extruding the cylindrical billets of polypropylene at various temperatures and measuring the properties of extrudates at room temperature. In order to study the structural changes resulting from extrusion, wide-angle X-ray diffraction patterns were obtained from the extruded and unextruded materials and the lamellar orientation was resolved by electron microscopy. The effect of processing on the mechanical properties is finally explained in the light of these structural studies.

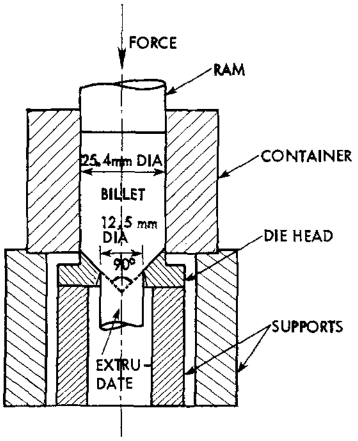

Figure 1 The schematic arrangement for extrusion set-up.

2. Experimental

An extrusion die set-up (Fig. 1) was used for the direct extrusion of polypropylene cylindrical billets. The container and the die head were machined from hot-rolled AISI 4340 steel, and were then austenitized, oil quenched and stress relieved. The surfaces encountering the sliding of polymeric material during extrusion were ground. Both parts of the die rested on rigid supports during the extrusion process. In the preliminary stages, 180° die was tried. Since it did not provide satisfactory extrudates at any temperature, a 90° die was finally used. The extrusion force was provided through a ram by a Baldwin Tate-Emery universal testing machine. The cylindrical surface of the container and the conical surface of the die head were lubricated thoroughly with Molykote lubricant 505 supplied by the Alpha-Molykote Corporation. It served as an effective lubricant under the temperature conditions used and the high pressures involved in the extrusion process.

Polypropylene used for experimental work was obtained from Cadillac Plastic and Chemical Co as a regular commercial material in the form of 32 mm diameter extruded rods. All the test specimens were machined from the same rod so as to avoid any variation in the processing conditions of the extruded rod.

The extrusion billets were machined in the form of cylinders about 25 mm diameter and 51 mm long. The extrusion was performed both under the cold (ambient) and hot conditions. For the latter case, the billets, the container and the die head were kept in the furnace at 65, 95 and 120° C for 2 h. The billet diameter for each case was computed from the coefficient of thermal expansion of material and the test temperature so as to provide a sliding fit between the heated billet and the die container. In order to minimize the heat loss from the die during the extrusion test, the latter was made much bulkier as compared to the size of the extrusion billet. It was further anticipated that the minor loss in heat would be compensated by the dissipation of mechanical energy during the extrusion process.

The nominal reduction of area in the extrusion process was 75% and this was obtained in a single pass at any temperature. Each test produced an extrudate in the form of a rod about 14 mm diameter and 180 mm long. Round tensile specimens, 5 mm diameter and 25 mm gauge length, were machined from the extrudates as well as the unextruded rod. They were tested in an Instron testing machine using a cross-head speed of 5.08 mm min^{-1}. Owing to the cold-drawing phenomenon exhibited by all the samples when pulled in tension, the instantaneous load and diameter needed to provide the true stress–true strain behaviour were considered unnecessary. As such only the load–elongation plots were obtained.

The density measurements on the extruded as well as the unextruded material were carried out using the ASTM D-792-64T method. The samples, about 1 mm thick, were cut from the longitudinal and transverse directions of the material in each condition. The X-ray diffraction patterns were obtained using the flat plate camera and Ni-filtered Cu$K\alpha$ radiation. For the investigation of the lamellar arrangement resulting from extrusion, the extrudate corresponding to 120° C was brittle fractured in liquid nitrogen. The two-stage replica of the fractured surface was made by shadowing with Pt–C at 30° and using the polyacrylic acid detachment technique.

3. Results and discussion

3.1. Extrusion at different temperatures

The results obtained from the extrusion of polypropylene cylindrical billets at different temperatures are shown in Fig. 2 in terms of the extrusion pressure and ram travel. The early part of the ram travel corresponds to the elastic deformation of the billet in the container. The pressure in all the cases reaches a maximum and then drops suddenly indicating the onset of material flow or extrusion. In the period the material is extruding, the pressure remains more or less constant which signifies the presence of very low frictional resistance on the sliding surfaces. As would be expected, the higher the extrusion temperature, the lower the pressure required to extrude the material. Furthermore, the higher the temperature, the smaller the ram travel at which the material starts extruding.

3.2. Tensile behaviour

The engineering stress–engineering strain diagrams (Fig. 3) were made from the load–elongation data obtained from tension tests performed at room temperature on the unextruded and extruded materials. Table I lists the important tensile properties for comparison. It is obvious that due to extrusion the mechanical properties of the material are improved substantially in the direction of extrusion. Even the extrusion at room temperature almost triples the ultimate strength while the extrusion at higher temperatures results in still higher values. Similarly, the elastic modulus of the material extruded at room temperature is more than doubled, but the extrusion at higher temperatures somewhat reduces it, the value being still higher than that for the unextruded case. The ductility of the material decreases considerably due to extrusion. It is the lowest in the case of 95° C extrusion for which the ultimate strength is the highest. The above findings are in agreement with those of Buckley and Long [25] who measured the properties of the material extruded only under the ambient conditions.

The material in the unextruded condition exhibited the typical cold-drawing and stress-whitening behaviour. In the case of the extruded materials the cold-drawing was less pronounced.

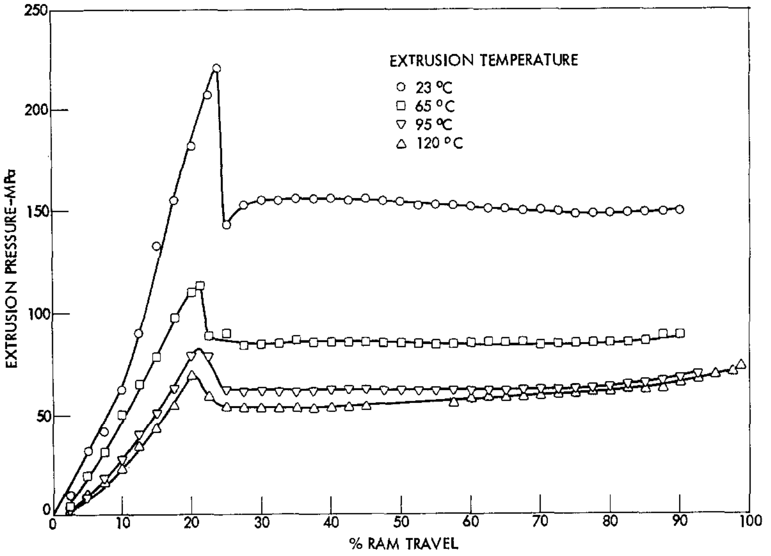

Figure 2 Extrusion pressure versus ram travel for extrusion at different temperatures.

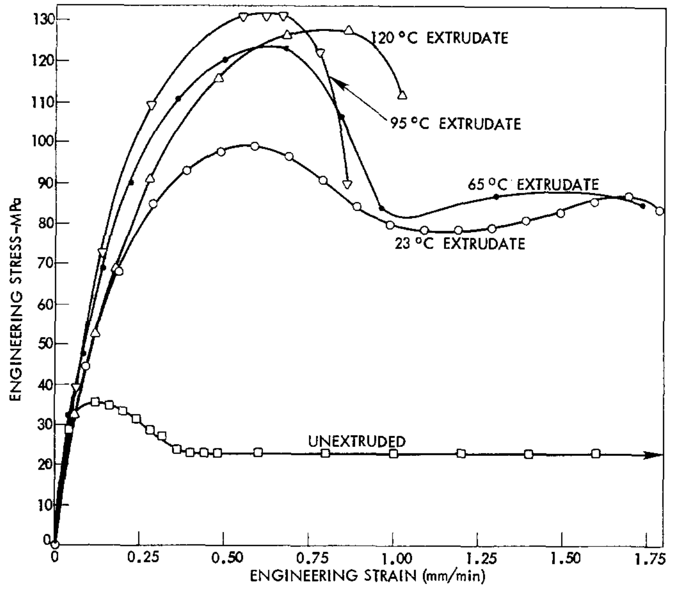

Figure 3 Engineering stress versus engineering strain behaviour of unextruded and extruded material, the latter corresponding to extrusions at different temperatures; gauge length 25 mm, cross-head speed 5.08 mm min^{-1}.

It in effect decreased with the increase in extrusion temperature, as may be seen from the natural draw ratio values given in Table I. There was virtually no cold-drawing observed during the stretching of sample extruded at 120° C. The fracture of extruded samples was fibrous.

3.3. X-ray diffraction

In order to investigate the changes in molecular orientation resulting from extrusion, X-ray diffraction patterns were obtained from the longitudinal and transverse directions for each extrusion condition. Since the extruded material was in the form of a rod which possesses symmetry about its axis, two diffraction patterns were obtained for each case, one with the X-ray beam perpendicular to a longitudinal plane parallel to this axis and the other with the X-ray beam perpendicular to a transverse plane normal to this axis. The former is designated as the longitudinal pattern (L) and the latter the transverse pattern (T). These diffraction patterns

TABLE I Tensile properties of polypropylene, as-received and extruded at different temperatures

Condition	Elastic modulus (kPa)	Ultimate strength (kPa)	Natural draw ratio*	% Elongation
As-received	7.36×10^5	35 337	5.17	560
Extruded at 23°C	16.35×10^5	98 874	2.9	178
Extruded at 65°C	11.20×10^5	123 613	3.07	174
Extruded at 95°C	13.28×10^5	131 453	1.45	87
Extruded at 120°C	11.79×10^5	128 109	1.38	104

*Ratio of the cross-sectional areas before and after drawing.

are given in Fig. 4. It was concluded that the material is in the monoclinic form because the diffraction peak with a *d*-spacing of 5.494 Å which is characteristic of the hexagonal form is not present.

The diffraction patterns obtained from the unextruded material (Fig. 4a), show hardly any significant orientation in the axial direction (if there is any, it is from the manufacturing process of the rod material) and none in the transverse direction. The extrusion orients the material considerably in the axial direction of the rod. The degree of orientation and the crystal perfection increase initially with an increase in the extrusion temperature, but in the high temperature range there is no significant difference. The indexing of the patterns showed that the sharp diffraction rings with increasing diameters correspond to the planes (1 1 0), (0 4 0), (1 3 0) and (1 1 1)-(0 4 1) doublet. A somewhat weak diffraction is also found from the (1 5 0) and (2 0 0) planes. The (1 1 1)-(0 4 1) doublet consists of four intense arcs separated by 90°. From the spacing of the first layer line, the period in the axial direction is found to be 6.5 Å which is the polypropylene monoclinic unit cell length in the *c*-direction. The material is, therefore, uniaxially oriented after extrusion in the axial direction. The shape of the arcs shows that the crystallites are imperfectly aligned. It is also noted that the extruded material has no orientation in the transverse direction.

The *c*-axis orientation is also obtained in the cold-drawing of polypropylene [27]. On the other hand, in the cold-rolling of polypropylene the *c*-axis orientation is in two preferred directions which make equal angles with the rolling direction [3]. Thus the orientation in the extrusion of polypropylene is analogous to that obtained in the cold-drawing process. The same was found to be true by Buckley and Long [25] in the extrusion of low- and high-density polyethylene and nylon 6-6. The same workers observed selective orientation in the room temperature extrusion of polypropylene for extrusion ratios up to 3. They observed a good *c*-axis orientation at an extrusion ratio of 3.8, but the orientation severely diminished and became selective again at an extrusion ratio of 5.4.

3.4. Electron microscopy

The transmission electron micrograph of a surface parallel to the extrusion direction, obtained by brittle-fracturing in liquid nitrogen a sample of polypropylene extruded at 120°C, is shown in Fig. 5. The extrusion direction is marked by the arrow. It may be seen that, owing to the flow of material in the extrusion process, the lamellae have rearranged themselves in a more or less parallel fashion. The fold planes of these lamellae are normal to the extrusion direction. The lamellae are about 200 to 300 Å thick and the long period is about 500 to 600 Å. It should be noted that an unextruded material would not have any such orderly lamellar arrangement. Such a material would merely comprise of the spherulites having lamellae arranged in a random fashion.

3.5. Density

The density measurements on the material in the unextruded and extruded conditions were made to provide an indication of the gross molecular and lamellar readjustments in the material. The measured density values are given in Table II. It is noted that the extrusion reduces the density of the material which is similar to that of cold-rolling [4, 10, 28]. A decrease in density for a crystalline material implies a decrease in crystallinity and *vice versa*. Thus it is seen from Table II that due to the extrusion under ambient conditions the density (and so also the crystallinity) decreases, but with the increase in extru-

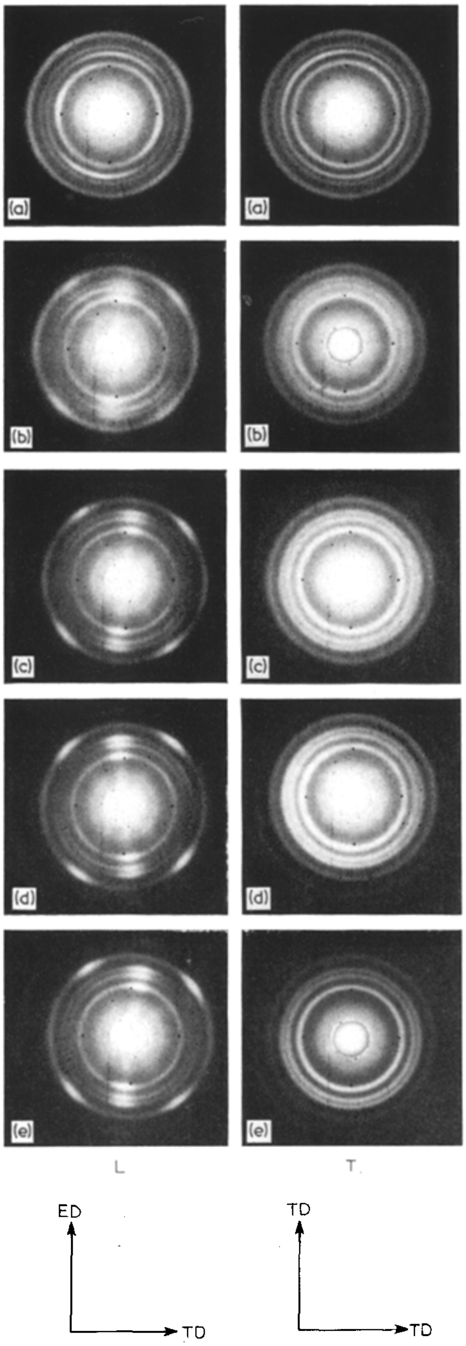

Figure 4 Wide-angle X-ray diffraction patterns for the extruded and unextruded materials: (a) as-received; (b) extruded at room temperature; (c) extruded at 65° C; (d) extruded at 95° C; (e) extruded at 120° C. ED – extrusion direction; TD – transverse direction.

TABLE II Density of extruded and unextruded materials

Condition	Density (g cm^{-3})
Unextruded	0.9147
Extruded under ambient conditions	0.9011
Extruded at 65° C	0.9017
Extruded at 95° C	0.9031
Extruded at 120° C	0.9071

sion temperature it increases. Since the processing reduces the density, the increase in density with increasing extrusion temperature over that of the material extruded at room temperature must be due to the heating of the billet prior to extrusion. It is supported by Schotland's work [29] on the annealing of polypropylene in which the density and the crystallinity of the material were found to increase and the line width of the (1 1 0) diffraction peak to decrease with increasing annealing temperature. The decrease in line width has been explained by Schotland owing to the increase in crystal perfection and/or crystallite size. The detailed investigations by Morosoff *et al.* [30] on the crystallite size of annealed polypropylene have confirmed the above explanation.

TABLE III Spring-back on extrusion. Diameter of extrusion die = 12.598 mm

Extrusion temperature (° C)	Extrudate diameter (mm)	Spring-back* (%)
23	13.970	10.89
65	13.868	10.08
95	13.843	9.88
120	14.275	13.31

*% Spring-back =

$$\left(\frac{\text{diameter of extrudate} - \text{diameter of die}}{\text{diameter of die}}\right) 100 .$$

3.6. Spring-back

A serious limitation of the cold-forming operations often cited is the large spring-back suffered by the formed polymeric part. It poses problems of dimensional control. Table III provides an idea of the magnitude of spring-back that was involved in the extrusion of polypropylene at various temperatures. Here the extrudate diameter was measured about 4 months after the extrusion process so as to allow the recovery at room temperature to take place completely. The spring-back for 120° C extrusion is the highest whereas for the other three temperatures it is more or less equal.

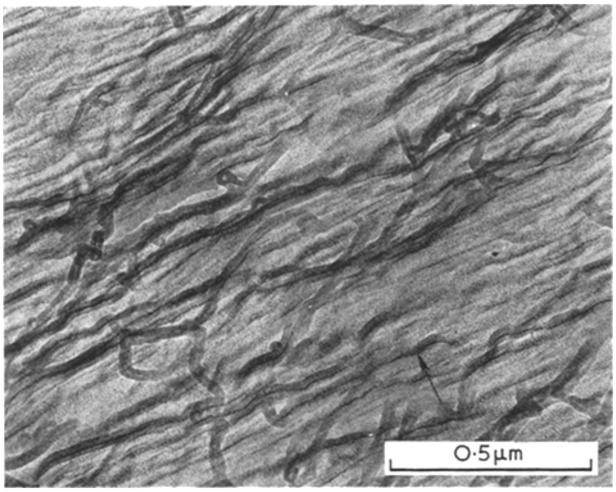

Figure 5 Electron micrograph of the fracture surface, parallel to the extrusion direction, of polypropylene extruded at 120° C. Arrow shows the extrusion direction.

The spring-back was estimated theoretically using the extrusion expression [31] derived from the free body equilibrium approach using von Mises' yield criterion and assuming spherical velocity fields. For the case of 90° die and extrusion ratio of 4 (as used in our experiments), while neglecting friction, the expression reduces to

$$\sigma_0 = -\frac{\sigma_{xb}}{2.872}$$

where σ_0 is the flow stress and σ_{xb} the extrusion pressure. From the extrusion pressure of 150 MPa determined from the data corresponding to the extrusion under ambient conditions (Fig. 2), the normal pressure, p, against the die container walls was calculated, using the von Mises' yield criterion, as 97.772 MPa. Considering the spring-back due to elastic recovery, the relaxed extrudate diameter (d) may be estimated from the following equation

$$\frac{d}{D} = 1 + \frac{p}{E}$$

where D is the diameter of extrusion die and E the modulus of elasticity of extrudate at the temperature of extrusion. Using $E = 16.35 \times 10^5$ kPa for the material extruded under ambient conditions (Table I), the extrudate diameter was calculated as 13.360 mm. This value is somewhat lower than the measured value (Table III), because the value of the elastic modulus used in calculation is somewhat higher. The actual value would be lower due to the temperature rise occurring in the extrusion process, as reported in the literature [26, 32]. In the absence of the elastic modulus values of the extruded material at the high extrusion temperatures used, similar estimates could not be made for the other cases.

Buckley and Long [25] report that the repeat experiments show a constant relaxation for a given material under constant conditions. Thus an extrudate of predetermined dimensions can be produced easily after a small trial. The spring-back should, therefore, not be considered as a serious limitation for cold forming processes.

3.7. Structure and property relationship

The X-ray diffraction studies showed that the extrusion process produced orientation of the material where the c-axis aligned with the axis of the round extrudate. The electron micrograph indicated the orderly arrangement of the lamellar structure in the extrusion direction. Owing to the orientation of the molecules and the ordering of the supermolecular structure, the ultimate strength of the extruded material in the extrusion direction is much higher than that of the unextruded material (Table I). Since at higher temperatures the molecular and lamellar adjustments are easier due to the increased mobility of molecules, the material extruded at 65, 95 and 120° C has higher orientation. The heating of the material at these temperatures prior to extrusion increases its crystallinity. Both these effects are responsible for the ultimate strength of the material extruded at above room temperatures being higher than that corresponding to the room temperature extrusion. There is not much difference noticeable in the orientation of the material extruded at higher temperatures as a result of which the ultimate strength of the extrudates corresponding to 65, 95 and 120° C is more or less the same.

It is noted from Table I that the higher the ultimate strength of the material, the smaller is its ductility. Thus the extrusion has the effect of reducing the ductility. This agrees with the observations of Pae *et al.* [33] in the high pressure deformation of polypropylene which is relevant because the deformation of material in the extrusion process is constrained. Thus similar morphological changes during the deformation process may be expected. Reference to Table II shows that there is a sudden drop in the density (and so also in the crystallinity) of material as a result of the extrusion at room temperature. The decrease in density is suggested owing to the break-up of the lamellar structure into clumps due to intralamellar shear occurring in the lamellae located with their fold planes perpendicular to the extrusion direction. These mosaic blocks rearrange themselves one above the other in an oriented pattern so that no loss in orientation is caused by this process. Owing to this rearrangement, the ductility of the material decreases whereas the stiffness (elastic modulus) and the tensile strength increase considerably. Heating of the billet at high temperatures prior to extrusion results in the increase of long period and the thickness (or extent) of mosaic blocks parallel to the *c*-axis [30]. These factors which contribute to increased density together with the higher orientation at elevated temperatures account for the increase in tensile strength and the decrease in percentage elongation for high temperature extrusions. The decrease in elastic modulus for the material extruded at higher temperatures seems difficult to explain at this stage.

4. Conclusions

(1) Isotactic polypropylene can be extruded satisfactorily in the solid phase using 90° dies. The use of 180° die does not provide satisfactory extrusions.

(2) As a result of extrusion, the molecular and lamellar orientation of the material takes place. The extrusion at higher temperatures provides better orientation than at room temperature.

(3) Owing to extrusion, the tensile strength and the elastic modulus of the material are increased but the ductility is lowered. The tensile strength of the material extruded at higher temperatures is higher than that extruded at room temperature.

(4) The density of the extruded material is lower than that of the unextruded material.

(5) The spring-back of the extruded material can be estimated to a reasonable extent.

(6) The effect of extrusion on the mechanical properties can be explained in terms of the changes occurring in the material at the molecular and lamellar levels.

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