Effect of cold extrusion and heat treatment on the mechanical properties of polypropylene

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Polypropylene rods are cold extruded through a die with three nominal area reductions of 18, 40 and 64 %. These extrudates are subject to subsequent heat treatments at 100°, 120° and 140 °C for two hours after which this is followed by either air cooling or water quenching. The effect of cold extrusion increases the tensile strength, the elastic moduli in tension and compression as well as the specific impact energy absorption. The 0.2 % offset yield strength in tension decreases slightly for the 18 and 40 % extrudates but increases ~~above the value of the as-received polymer at 64 % cold work. However, cold extrusion~~ decreases the compressive yield strength and the density which is a measure of crystallinity of the cold worked polymer. Cold extrusion followed by heat treatment reduces the elastic moduli but raises the yield strengths of the extrudates. The impact energy absorption shows a sharp increase with annealing temperature and the fracture surfaces display increasing orientation effect with increasing amounts of cold work. Air-cooled and quenched samples do not have any significant differences in these macroscopic mechanical properties. It is apparent that heat treatment increases the density and hence the crystallinity of the cold worked polymer. The improvement is marginally larger for the air-cooled than for the quenched samples. The results of this investigation suggest that it is possible to obtain a combination of mechanical properties of polypropylene by a suitable extrusion-heat treatment process.

1. INTRODUCTION

There has been considerable interest in applying metalworking processes to solid phase polymers in order to study the influence on subsequent mechanical properties. Cold rolling [1-9] is the most widely studied process for a wide range of amorphous and crystalline polymers. Improvements of both yield and tensile strengths, suppression of stress whitening, and postponement of necking and cold drawing have been reported. Another advantage not available in cold-worked metals is that cold-rolled polymers have a large increase of ductility [1, 5] if the cold work imparted is not excessive. This desirable effect has enhanced the drawability of cold-rolled polymers [2, 10, 11]. The effect on the modulus of elasticity is, however, less clear as in some polymers increases are obtained [2-5] but in others reductions are reported [1].

Fewer investigations have been conducted on solid phase extrusion of polymers [12]. While there is general agreement that cold extrusion increases the tensile strength and true strain at maximum load there is again no definite effect on the elastic modulus. For example, cold extruded amorphous polymers such as polycarbonate [13, 14] and a crystalline polymer, polypropylene [15], have higher elastic moduli compared to the as-received material. But for some other crystalline polymers such as polyethylene and nylon [13] cold extrusion decreases the elastic moduli. Hot extrusion of polypropylene produces even higher tensile strengths but lower elastic moduli than the cold extrudates [15].

Other metalworking processes that have been applied to polymers have been summarised by Broutman and Kalpakjian [2]. The list given is however not exhaustive and it does not include the more recent work related to cold drawing [13, 16] and upsetting processes [17, 18]. Metalworking followed by appropriate heat treatment

(¹) The 1981 Robert L'Hermite Prize and Medal was granted to Dr. Mai who wrote the above paper on this opportunity.

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are commonly adopted in the metals industry to provide a combination of mechanical properties to metals and alloys. This is a relatively unexplored method for polymers although a few investigations have been carried out previously on the effect of heat treatment on mechanical properties [7, 14, 20] and microstructures [21, 22] of cold-worked polymers. For amorphous polymers it is important that the heat treatment temperature does not exceed the glass transition temperature. Otherwise, all cold-work effects induced in the polymers are erased [3, 7, 14]. Lee *et al.* [14] have shown that heat treatment of polycarbonate raises the yield strength of the cold extrudates without a noticeable decrease in tensile strength. However, heat treatment tends to lower the elastic modulus, the true fracture stress [14] and the impact energy absorption [7] of the cold-worked polycarbonate samples. For crystalline polymers the annealing temperature is usually above the glass transition temperature but below that for melting. Annealing at sufficiently high temperature usually encompasses partial melting which is followed by recrystallisation. This gives an increase of density for the cold-worked polymer and results in lamellar thickening [21, 22]. For cold-drawn polypropylene fibres which are subsequently annealed at 140 °C Nadella *et al.* [20] have demonstrated that compared to the as-spun fibres both the elastic modulus and tensile strength are increased but the percentage elongation to break is decreased. In another crystalline polymer, polyoxymethylene, Bahadur [19] has studied the effect of annealing over a range of temperatures on the anisotropic mechanical properties of the cold-rolled polymer. Cold rolling increases the tensile strength and the ductility in the rolling direction. These increases however become less as the angle from the rolling direction is increased and there is almost no effect in the transverse direction. Annealing at 70 °C increases the ductility of the cold-rolled polymer in the rolling direction but decreases the yield and tensile strengths as well as the elastic modulus. At higher annealing temperatures of 120° and 170 °C the cold-rolled material has approximately the same yield and tensile strengths in the longitudinal direction and the percentage elongation to break is smaller at the higher temperature. In the transverse direction all the mechanical properties are either inferior or at most approximately equal to the cold-rolled polymer. These results indicate therefore that it is possible to alter the mechanical properties of the polymer, as in metals, by cold-working and subsequent heat treatment. Much future research work should be carried out in this direction.

The present paper reports the results of an exploratory experimental investigation to study the effect of cold extrusion and subsequent heat treatment on the mechanical properties of a typical engineering polymer, polypropylene (PP). There does not seem to be any such work reported previously in the literature on this polymeric material. This work is confined mainly to mechanical properties and not microstructures of the polymer as affected by extrusion and heat treatment.

2. EXPERIMENTAL WORK

The polypropylene used for the experiments was obtained from Cadillac Plastics (Australia) Pty. Ltd as a regular commercial material in the form of 16-mm diameter extruded rods. To avoid any variation in the processing conditions of the extruded rods all subsequent test specimens were machined from rods of the same batch. Solid cylindrical billets of 12.7 mm diameter and 110 m long were prepared for cold extrusion in the experimental setup shown in figure 1. By using three dies of varying outlet diameters three "nominal" area reductions — 18, 40 and 64 % — were available. All extrusion experiments were performed in a single pass at room temperature using an Instron testing machine with a crosshead speed of 10 mm per minute. For lubrication between contacting surfaces petroleum jelly was used.

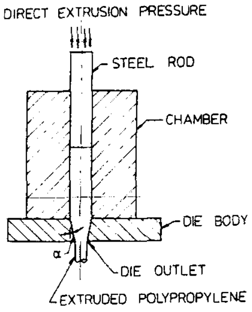

Fig. 1. – Experimental setup for extrusion operation.

For subsequent tensile and compressive testing a total of 35 standard round specimens was prepared for each reduction. These specimens were tested in the following conditions : (1) as extruded; (2) as extruded and subsequently heat treated for two hours at 100°, 120° and 140 °C respectively, followed by either air cooling or water quenching. True stress ($\bar{\sigma}$)-true strain ($\bar{\varepsilon}$) curves were obtained from the load-diameter records using the standard definitions : $\bar{\sigma} = 4\,F/\pi D^2$ and $\bar{\varepsilon} = 2 \ln (D_o/D)$, where F is the applied load, D and D_o are the instantaneous and original diameters of the test specimens. The tensile and compressive tests were not carried to fracture due to the very large deformations that could be sustained by the polymer.

Charpy impact tests were also conducted on the various heat treated samples containing notches according to the ISO Recommendation R179 but these were not successful as many testpieces did not break during impact and slipped out of the supports. To increase the bending stiffness non-standard round specimens (12.20, 11.50 and 10 mm diameter for the 18, 40 and 64 % reductions respectively) with segmental cuts to depths of approximately 2 mm were eventually used in the impact experiments.

Diametrical measurements were made for the as-extruded and heat treated specimens to determine the dimensional recovery or "spring-back" over a 48-hour period. Finally, to determine crystallinity changes of the polymer after extrusion and heat treatment density measurements were made on small off-cuts using the ASTM D-792-64 T method.

As a basis for comparison all the above experiments were repeated for the as-received polypropylene.

3. RESULTS AND DISCUSSIONS

3.1. Dimensional Changes

The significant elastic recovery or "spring-back" suffered by a cold-formed polymeric part has often been suggested as the major limitation of cold forming operations since this presents problems of dimensional control. However, if dimensions of cold-formed parts can be accurately predetermined given constant forming conditions, as have been shown from previous experiments [12, 18], "spring-back" should not be considered as a serious obstacle to the use of cold-formed plastics. Figure 2 shows the magnitude of elastic recovery for the polypropylene specimens after being subjected to various mechanical-thermal treatments. The percentage spring-back is calculated from the ratio of the diameter difference of the extrudate and die to the diameter of the die. For a given heat treatment temperature, the larger the cold work the larger is the dimensional change. For the 40 and 64 % cold-worked polymer the heat treatment temperature has a considerable effect on the spring-back. There is no obvious difference between either air-cooling or water quenching on the spring-back. It may be noted that these elastic recoveries are much larger than those obtained for polycarbonate with similar mechanical-thermal treatments [14]. This may be partly due to the different glass transition temperature of these two polymers which influences dissimilarly the relaxation behaviour.

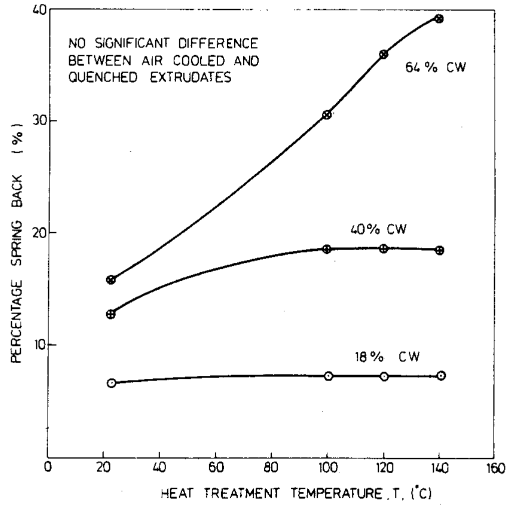

Fig. 2. – Variation of spring-back with heat treatment temperature for the three nominal reductions : 18, 40 and 64 %.

It has been suggested that the spring-back is directly related to the relative proportion of the crystalline region to the amorphous domain of the spherulite [18]. The crystalline part takes up the plastic deformation and the amorphous part which is rubber-like influences the spring-back. This hypothesis provides an acceptable qualitative explanation for the results of the plain extrudates given in figure 2 (since as discussed in section 3.2 the crystallinity of the polymer decreases with cold work). It seems that there is no rigorous theoretical analysis to date that can be used to predict the spring-back or elastic recovery of cold formed parts. The difficulties of modelling this phenomenon have been highlighted in [18]. For any successful analysis structural parameters must be built in the model to account for changes due to various mechanical-thermal treatments.

3.2. Density Changes

Density measurements give an indication of the gross molecular readjustments of the polypropylene samples. An increase in density for a crystalline material implies an increase in crystallinity and vice versa. Table I gives the density values of the as-received and various mechanical-thermal treated polypropylenes. It may be seen that increasing amounts of cold-work progressi~~vely reduce the crystallinity and hence the density of the~~ polymer. Annealing tends to increase the density (and crystallinity) and the improvement is higher the higher the annealing temperature. These results are in agreement with those reported in [15, 21] for the same polymer. An additional information, not previously studied, is that quenched samples have consistently slightly lower density (and crystallinity) than air-cooled samples at the same heat treatment temperature.

3.3 Mechanical Properties of Non-Heat Treated Extrudates

A summary of the mechanical properties of the non-heat treated extrudates is given in Table I. Note that the yield strength is calculated based on the 0.2 % offset method and the tensile strength is determined from the maximum load sustained by the testpiece. Figure 3 shows the true stress-true strain curves for the various cold worked extrudates and the as-received polymer. As noted in Table I small amounts of cold working (18 and 40 %) reduce slightly the 0.2 % yield strength but at the maximum level of cold work (64 %) the yield strength is fully recovered to the value of the as-received polymer. It is however more remarkable that cold working improves both the tensile elastic modulus and the tensile strength. These results are in agreement with those reported by other investigators [15, 20].

It is initially thought that the cold worked polymer can be regarded as the as-received material with an imparted equivalent prestrain ($\bar{\varepsilon}_o$) being determined by the degree of cold work. By matching the true stress-strain curves to that of the as-received polymer as

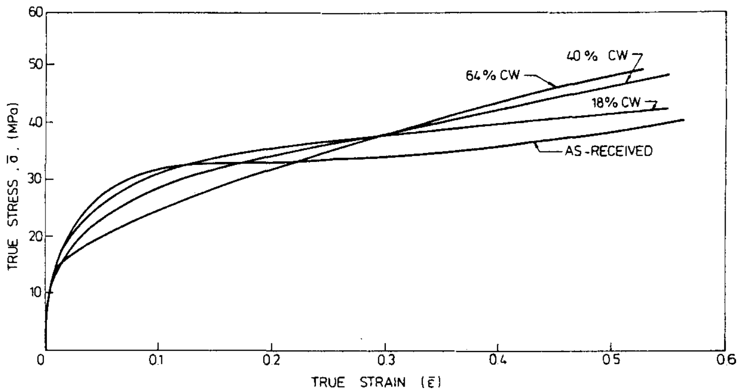

Fig. 3. — **Tensile true stress-true strain curves for the as-received and cold worked polypropylene.**

TABLE I

MECHANICAL PROPERTIES OF POLYPROPYLENE AFTER VARIOUS EXTRUSION-HEAT TREATMENT PROCESSES

Nominal % reduction in area	Heat treatment*	Elastic modulus Tension (MPa)	Elastic modulus Compression (MPa)	0.2 % offset yield stress Tension (MPa)	0.2 % offset yield stress Compression (MPa)	Engineering tensile strength** (MPa)	Specific impact energy absorption*** (kJ/m²)	Density (gm/cm³)
As-received	None	1150	710	13.5	14.0	29	4.02	0.9189
18	None	1210	1190	12.5	10.0	33	5.65	0.9006
	100 °C A	1160	952	13.2	10.5		7.05	0.9040
	100 °C Q	1150	940	13.15	10.5		6.60	0.9010
	120 °C A	1128	788	13.20	11.5		15.88	0.9058
	120 °C Q	1120	770	13.25	11.6		12.20	0.9029
	140 °C A	1050	730	13.40	13.25		37.90	0.9090
	140 °C Q	1050	725	13.40	12.50		24.73	0.9032
40	None	1329	1210	12.90	11.0	35	14.05	0.8868
	100 °C A	1270	993	13.20	12.5		20.15	0.8988
	100 °C Q	1250	985	13.20	13.0		18.0	0.8910
	120 °C A	1200	861	13.40	13.25		34.0	0.9052
	120 °C Q	1205	845	13.45	13.0		33.0	0.9008
	140 °C A	1130	771	13.70	14.0		58.0	0.9138
	140 °C Q	1120	771	13.80	13.5		56.0	0.9104
64	None	1400	1480	14.0	11.5	43	>60	0.8676
	100 °C A	1223	903	14.20	10.75			0.9090
	100 °C Q	1220	885	14.15	10.80			0.9060
	120 °C A	1148	755	14.30	12.0			0.9130
	120 °C Q	1144	775	14.20	12.2			0.9101
	140 °C A	1019	720	14.50	13.0			0.9158
	140 °C Q	1025	715	14.50	13.0			0.9107

* Heat treatments were at indicated temperature for 2 hours. A implies air cooling and Q is for quenching in water.

** Calculated from maximum load divided by original cross-sectional area.

*** Calculated from energy absorbed divided by nominal ligament area of notched cylindrical specimens. For 40 % C.W. specimens fracture plane is not flat. None of the 64 % C.W. specimen breaks by the available impact energy.

N.B. All values shown in the above table are average of at least three measurements.

shown in figure 4 it is clear that ϵ_o is not identical to the cold work induced prestrain. This implies that the structural changes (i.e. crystallinity transformation, molecular chain orientation, etc.) caused by cold extrusion are not the same as by simple tensile pre-straining. The same finding has also been observed for an amorphous polycarbonate polymer [3].

To examine the effect of drawing on tensile strength specimens that were extruded with nominal 18 and 40 % cold work were further drawn at room temperature with an Instron testing machine to a maximum draw ratio of 2. Standard tensile tests performed on these drawn samples showed that enormous improvements could be obtained for tensile strength as given in figure 5.

In figure 6 and Table I the compressive true stress-true strain curves are given. It is seen that cold working decreases the 0.2 % offset yield and the compressive strengths but it increases significantly the elastic modulus. The stress-strain curves for the extrudates are lower than the as-received polymer. Shayota and Babcock [17] have observed the same behaviour for polypropylene cold worked by upsetting and specimens cut along the billet axial direction. They explained the reduction of compressive strength in terms of the competing processes between molecular chain orientation which for the particular load/specimen configuration increases the strength and the breaking of backbone chains by upsetting which decreases the strength. Due to the lack of equipment we have not conducted any x-ray diffrac-

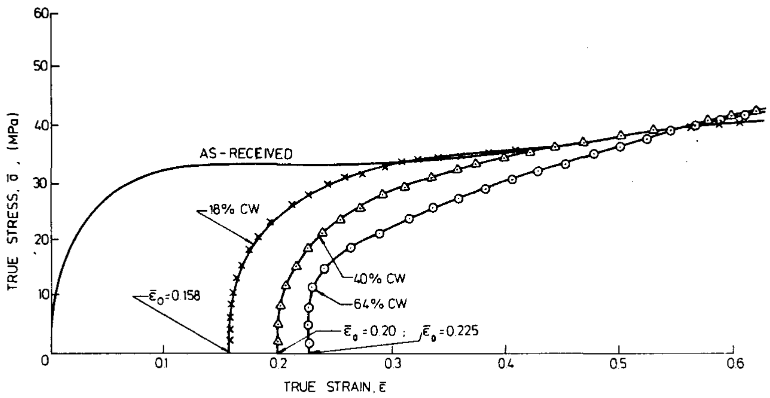

Fig. 4. – **Matching of the true stress-true strain curves of the extrudates to that of the as-received polymer.**

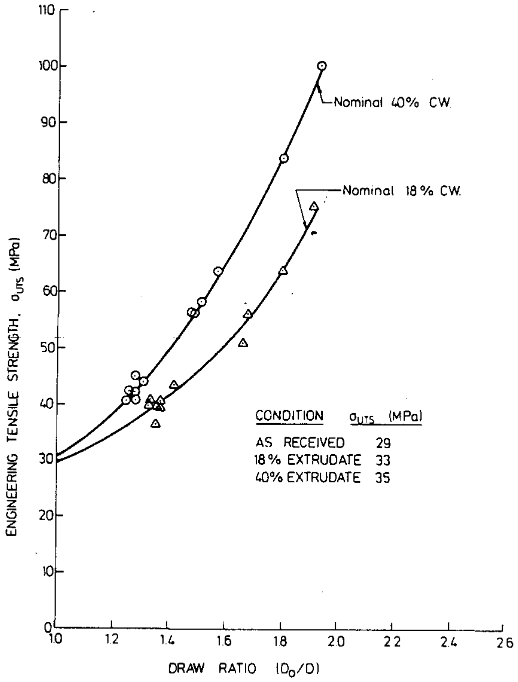

Fig. 5. – **Variation of tensile strength with draw ratio for the 18 and 40 % extrudates.**

tion and gel permeation chromatograph studies to investigate the molecular orientation and molecular weight change of the extrudates. There is ample evidence that extrusion tends to orientate the c-axis in the direction of extrusion and that the orientation increases with increasing cold work and temperature [15]. Little information is however known about molecular chain breakage (i.e. molecular weight reduction) due to extrusion. We cannot therefore conclude whether the unfavourable chain orientation and/or the chain breakage mechanisms are responsible for the reductions in compressive strength.

The impact resistances of the as-received and cold worked polymers are given in Table I. There is a considerable improvement in the Charpy value as the amount of cold work is increased. At 64 % cold work the potential energy available in the impact tester is unable to cause complete fracture of the notched samples (i.e. C.V. > 60 kJ/m²). It is further noted that the orientation effect becomes increasingly dominant as the cold work increases. The fracture plane is at an angle to the longitudinal axis of the sample at above 40 % cold work and its surface roughness also increases with cold working (*fig. 7*). Impact resistances enhanced by cold working should widen the use of the polymer in engi-

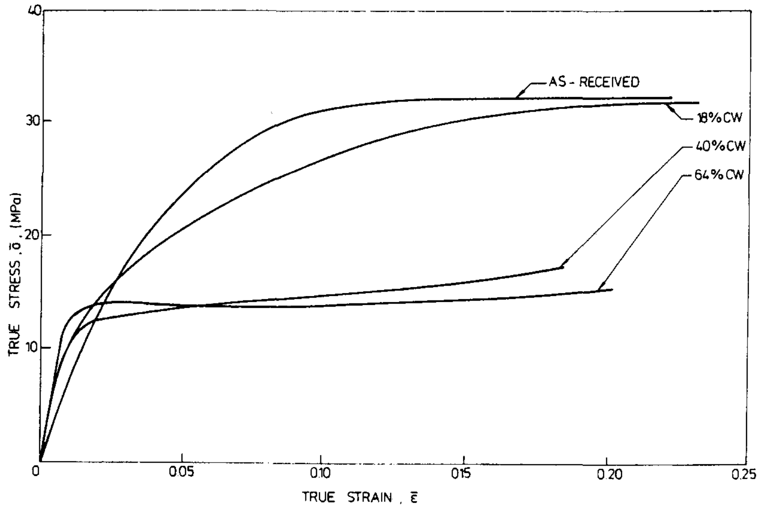

Fig. 6. – **Compressive true stress-true strain curves for the as-received and cold worked polypropylene.**

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