

Mechanical properties–morphology of rolltruded propylene–ethylene block copolymers

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Commercially available propylene–ethylene (P/E) block copolymers have been processed by the rolltrusion technique. Properties such as tensile modulus, tensile strength and sample clarity are significantly enhanced compared to the original commercial material. The latter is found to be comprised of ethylene globules distributed uniformly or heterogeneously throughout the P/E copolymer, depending upon the manufacturing process. In the rolltruded copolymer, the mechanical and morphological properties depend upon the processing temperature and deformation ratio experienced by the workpiece. The chemical composition of the P/E copolymers also plays a significant part in the improvements in properties induced via rolltrusion that may be carried out below or above the melting temperature of the ethylene component of the copolymers. Differential scanning calorimetry thermograms are very useful in assessing transitional behaviour in this respect and may be used to distinguish between different copolymers (processed and original samples). Correlations among some properties and processing conditions are presented and discussed in relation to polymer composition–processing conditions–morphology–property relationships.

1. Introduction

Oriented polymers have been investigated for many decades. In order to improve mechanical properties, including stiffness, solid-state deformation processes have received much attention in recent years [1–7]. One of the most recently developed processing techniques is called rolltrusion, which enhances simultaneously the mechanical properties (tensile strength and tensile modulus) significantly in the machine and transverse directions in the workpiece that is undergoing processing at some pre-selected temperature and deformation ratio [6–11]. A simplified schematic representation of the process is shown in Fig. 1, where the original polymer is passed under a high compressive load between two rollers (usually heated) and it is simultaneously drawn under a high “take-off” tension just insufficient to cause failure. This deformation procedure induces a triaxial stress field in the workpiece when it is in the nip area of the roller, so creating a unique morphology wherein the crystallites are formed and aligned in a uniplanar, unidirectional manner (i.e. triaxially oriented) and they become interconnected or bridged by tie molecules in the three mutually perpendicular directions X , Y , Z of the processed workpiece. The width of the processed poly-

mer corresponds closely ($< 10\%$) with the original material.

Rolltrusion and the two-roll-mill operation commonly used in metallurgy and often employed in plastics rolling operations are not synonymous. In rolltrusion there is considerable take-off tension employed and this, coupled with the high compressive load experienced by the workpiece in the roller nip region induces a triaxial texture in the material in a single step operation. The processed workpiece is transparent because it is free of voids and crystalline/amorphous inhomogeneities that are ascribed to scatter light and create opacity in the polymer specimen. This morphological distinction with rolling has not been appreciated by several polymer processors.

The strengthening of the workpiece through processing greatly improves its properties over those recorded for the original specimen. In this paper, rolltrusion is used to toughen the P/E copolymers and to enhance their strength and impact behaviour. Until now, compositional modification of the P/E copolymers has been made mainly to improve the poor impact strength of polypropylene homopolymer, especially at low test or use temperatures. There have been pronounced improvements in properties demon-

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strated in the P/E composition and catalytic activity. Consequently, there has been a considerable growth in commercial applications for these copolymers.

It is now well established that P/E block copolymers are comprised of crystalline, as well as non-crystalline, E/P random copolymers (EPR), i.e. contains EPR phases [8, 12–17]. Through morphological investigations it has been determined that the globular particles dispersed within the polypropylene matrix of the P/E copolymer vary in size distribution and in their dispersion throughout the copolymer. The dispersed state of the globules is strongly influenced by the commercial catalyst system and polymerization conditions used in the chemical reactor. The concentration and dispersion of the ethylene globules contribute significantly to the overall mechanical behaviour of the P/E copolymers [7, 10, 13, 16]. This well-established fact has received attention recently in the literature [7]. However, the influence of rolltrusion processing on properties and the morphological features of the P/E copolymers induced by this double-orientation procedure (rolltrusion) has only been reported briefly at a recent polymer processing meeting [7]. It is the purpose of this paper to elaborate somewhat upon this presentation and to document processing–morphology–mechanical properties correlations in several P/E copolymers of commercial interest.

2. Experimental procedure

2.1. Material

Commercially available propylene–ethylene block copolymers with characteristics listed in Table I were employed in this work. Samples were processed by rolltrusion, a unique solid-state deformation process that is now well established for producing strong high-quality transparent polymers in a single operation (see Fig. 1) [6–11]. The copolymers in question were processed from 1/2 in. (1.27 cm) thick billets. Processing temperatures, T_p , in the range 110–150 °C, were employed. Samples with deformation ratios, DR, between $\times 1$ and $\times 21$ were prepared.

TABLE I Propylene–ethylene block copolymers used in this study (commercially open data)

Physical property	Copolymer		
	A	B	PP
GPC			
M_n ($\times 10^5$)	0.44	0.44	0.92
M_w ($\times 10^5$)	2.85	3.05	3.78
M_z ($\times 10^5$)	11.1	13.3	13.1
M_w/M_n	6.43	6.99	4.12
Ethylene content (total %)	12	15	—
DSC			
T_m (°C)	122, 161	122, 162	162
ΔH_{Tm} (J g ⁻¹)	100	91	90
Tensile strength (MPa)	25.5	26.8	34.3
Elongation at break (%)	> 200	> 400	> 200
Flexural modulus (GPa)	0.98	1.06	1.18
Izod impact strength at 23 °C (notched) (J cm ⁻¹)	17.6	18.2	6.9

2.2. Mechanical testing

Tensile tests were carried out at 25 °C using the tensile testing machine (Model MTS 800) according to the ASTM D-638 procedure.

2.3. Thermal measurements

A Perkin–Elmer DSC2 calorimeter with a scanning auto zero and computer integration accessories was used to measure the thermal properties of the rolltruded copolymer samples induced by processing conditions. Measurements were usually made in the heating and cooling modes at a rate of 10 K min⁻¹ for comparison purposes. Baseline corrections were made.

2.4. X-ray diffraction measurements

Wide-angle X-ray diffraction (XRD) measurements were made with an X-RD5 GE diffractometer and a Laue-type film camera. CuK α radiation of 35 kV was employed.

2.5. Sample preparation for electron microscopy

The rolltruded copolymers were fractured in liquid nitrogen along the draw direction. The fracture surface was etched chemically by an etchant and procedure described by Olley and co-workers [18, 19]. The texture of the etched rolltruded samples, on the lamellar scale, was enhanced by (i) direct shadowing with Au/Pd (60/40) alloy, or (ii) after replication of the surface by the cellulose-acetate film. The replicated samples were examined with a Jeol JEM 200 CX electron microscope at 200 kV. The fracture surfaces of rolltruded samples were ion-bombarded in a Jeol JFC-1100 ion sputtering instrument at 500 V (AC) and 3–4 mA in air at a chamber pressure of 27 Pa for times ranging from 30–60 min. Afterwards the samples were coated with Au/Pd alloy and then examined with a Jeol JSM-300 scanning microscope at 15 kV.

3. Results and discussion

Differential scanning calorimetry (DSC) measurements indicate that P/E block copolymer (Type A) exhibits more than one melting temperature. Fig. 2a shows an endotherm about 121 °C (T_m)_E, arising from the PE component and two other peaks occur about 149 and 163 °C, corresponding to the β -form and α -form of polypropylene, respectively, in this copolymer. Type B copolymer also shows (Fig. 2b (i)) a polyethylene melting region, but only one broad polypropylene endotherm centred about 163 °C. However, there is an important difference observed in that rolltruded copolymer B shows two isotherms of equal intensity peaking at 163 and 169 °C, respectively. In this way, even the DSC is capable of distinguishing between two types of P/E copolymer made by two different manufacturing processes.

Although DSC thermograms may be used to distinguish between copolymers A and B in their processed and unprocessed states, there is some experimental evidence that is conflicting in this comparison.

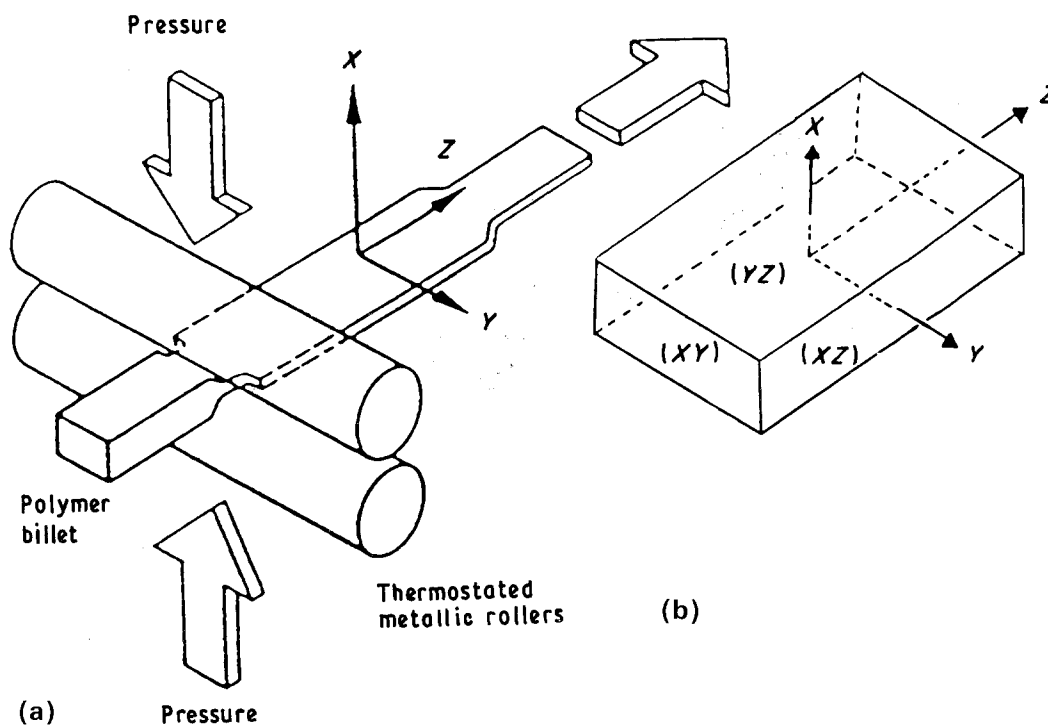


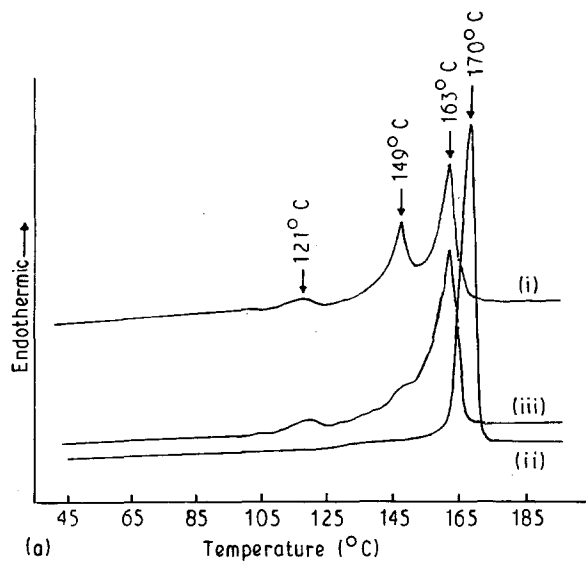
Figure 1 (a) Schematic illustration of the rolltrusion apparatus for double orientation. (b) The triaxial dimensionality of the processed workpiece.

For example, a broad but small endotherm corresponding to each copolymer exhibits an ethylene component and this peak is not present in the rolltruded polymer. However, this feature does reappear in endotherms Fig. 2A(iii) and b(iii) after each rolltruded copolymer has been melted and recrystallized. One interpretation of the behaviour is that rolltrusion processing produces extended chain polyethylene, of higher melting temperature (corresponding in a sense to a transformation into a hexagonal polyethylene phase). However, there is no X-ray evidence to support this suggestion, because X-ray results only support an orthorhombic phase. For the present, this issue must remain unresolved, although we would suggest that the polyethylene component, because of its suggested extended state, is better distributed throughout the processed copolymer so that it melts at the same time and range as the polypropylene matrix. Interestingly, morphological properties associated with processing conditions are anticipated based upon the rolltrusion temperature employed. In order to investigate these features, processing temperatures, T_p , between 110 and 150°C were employed using different draw ratios and draw speeds. Several morphology-property correlations will be discussed for some selected processing conditions, but there are general features that are expected, particularly when surface melting is observed $T_p > 140^\circ\text{C}$. Stress-whitening in the copolymer may occur below $T_p \approx 125^\circ\text{C}$. This crazing phenomenon also depends upon the speed of deformation.

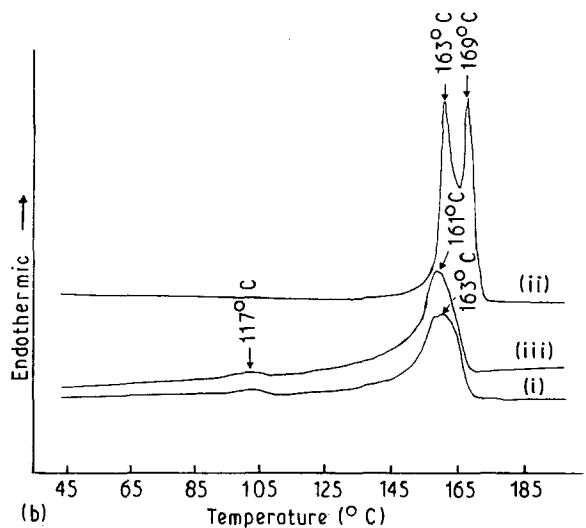
During rolltrusion it is thought that PE components when they are melted, seem to function as plasticizers and modify the interfaces between PE and PP regions in the copolymers. There is older documentation to this effect in the literature [12] for

several polymer systems. This process improves material toughness. Ethylene/propylene random copolymer (EPR) material is located in the globular-matrix interfaces of the commercial P/E block copolymers [14, 15]. The dispersion of globules, as well as their size, have a significant influence on physical properties. While it has been demonstrated that tensile strength can be enhanced significantly by rolltrusion, the basic limiting factor is the sequence distributions in the copolymers as manufactured. Polymer-chain chemistry dictates the fundamental distribution of P/E and E moieties throughout the polymer as manufactured. The processing scenario illustrated in Fig. 3 brings together the key factors responsible for basic property correlation as it relates to technology and applications. The distribution of inhomogeneities has such a strong influence on behaviour that it is less desirable in a material than homogeneously dispersed particles of uniform size in the manufactured product, as illustrated below.

The mechanical properties of two different copolymers A and B measured along the Z and Y directions in the processed sample are illustrated in Fig. 4a-d as a function of rolltrusion deformation ratio. Results are also tabulated in Table II and III. In general, there is a significant increase in tensile strength, Fig. 4a, and in tensile modulus, Fig. 4b, whenever deformation conditions are in-line with reported results for polypropylene [10]. Specifically, in these illustrations, the modulus enhancement noted in the "take-off" direction, Z, is about $\times 16$ - $\times 18$ for copolymers A and B, respectively, over the corresponding starting copolymer that has been rolltruded up to about $\times 24$ DR approximately. However, the improvements in the tensile strength are less clear over the same processing conditions, but the properties of copolymer B are generally



(a)



(b)

Figure 2 (a) DSC melting curves for the copolymer A: (i) original workpiece, (ii) specimen rolltruded at 150°C (DR = 21), (iii) after heating specimen to 200°C followed by cooling to room temperature. (b) DSC melting curves for the copolymer B: (i) original workpiece, (ii) specimen rolltruded at 150°C (DR = 17), (iii) after heating specimen to 200°C followed by cooling to room temperature.

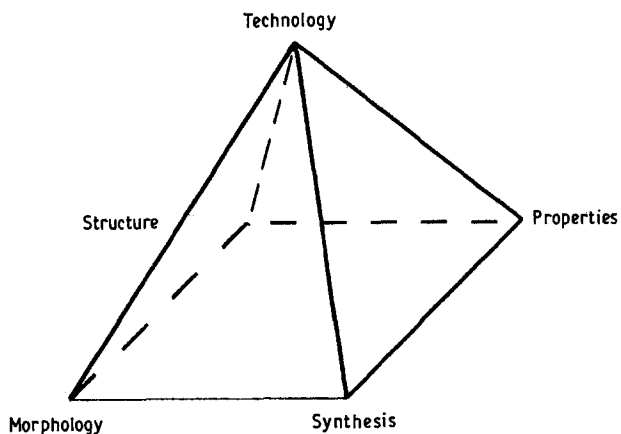
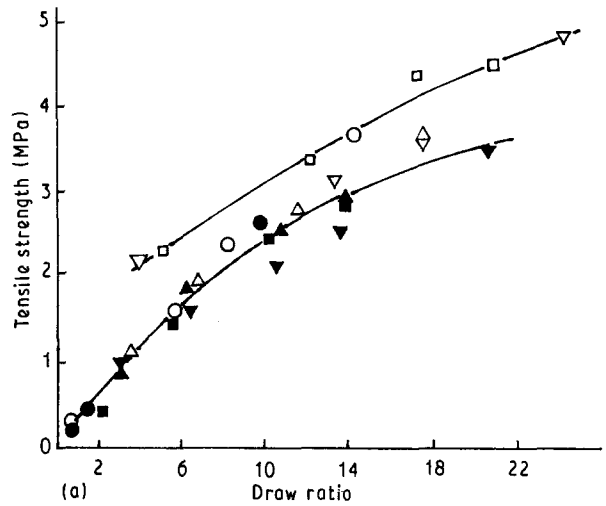
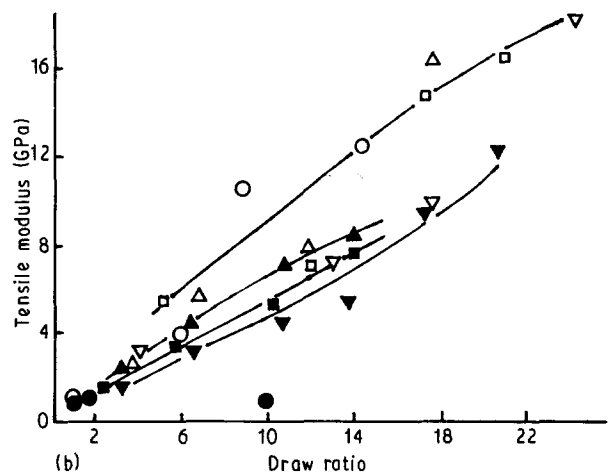


Figure 3 Scenario for polymer processing.

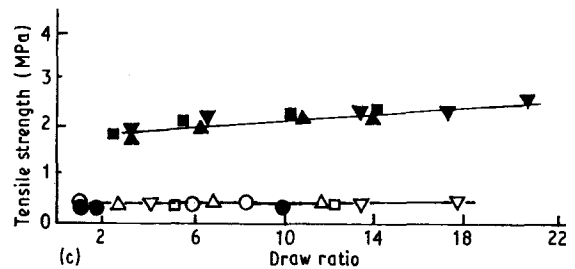
superior to copolymer A overall. These are distinguishing morphological features that seem to account for this behavior. An increase in the rolltrusion processing temperature improves the strength more than the modulus, for morphological reasons. (The texture



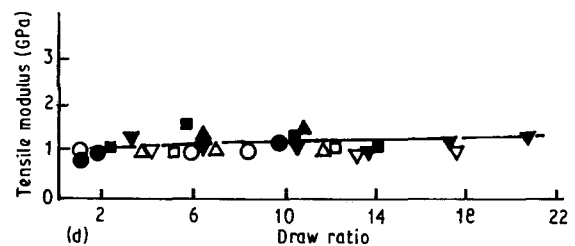
(a)



(b)



(c)



(d)

Figure 4 (a) Tensile modulus, (b) tensile strength, in the Z direction, (c) strength and, (d) modulus in the Y direction as a function of draw ratio for the P/E block copolymers rolltruded at indicated temperatures. Solid symbols, copolymer A, open symbols, copolymer B: T_p (°C) = (●, ○) 110, (▲, △) 125, (■, □) 140, (▼, ▽) 150.

of a processed material is known in general to influence tensile strength considerably more than tensile modulus when measured under comparable conditions; as, for example, in steels, where the latter may remain invariant.)

A case in point is illustrated for the two different copolymers studied here. For $T_p = 140^\circ\text{C}$ i.e. $> (T_m)_E$

TABLE II Rolltruded P/E block copolymers: tensile properties, Z

T_p (°C)	A				B			
	DR	DS (cm min ⁻¹)	Modulus (GPa)	Strength (MPa)	DR	DS* (cm min ⁻¹)	Modulus (GPa)	Strength (MPa)
110 (○)	1		0.76	18	1		0.97	23
	1.7		1.03	46				
	9.8		0.83	262				
125 (△)	3.2		2.41	87	5.9	0.26	3.93	159
	6.4		4.28	183	8.4	0.26	10.62	234
	10.8		7.10	250	14.4	1.44	12.55	366
	14.0		8.41	283	3.7	0.52	2.28	111
					6.9	0.52	5.79	191
140 (□)	2.4		1.52	43	11.7	0.52	7.86	277
	5.6		3.38	145	17.6	2.28	16.41	363
	10.2		5.38	241	5.1	1.86	5.52	228
	14.0		7.59	276	12.2	0.52	7.03	338
150 (▽)					17.4	1.44	14.83	434
	3.2		1.52	91	21.0	2.28	16.62	448
	6.5		3.10	158	4.0	0.26	3.17	214
	10.6		4.35	207	4.8	0.52		
	13.7		5.31	241	13.4	0.90	7.24	310
	17.3		9.52	303	17.6	0.90	9.24	352
	20.7		12.28	345				
					24.3	1.86	18.21	476

*no preheater used.

TABLE III Rolltruded P/E block copolymers tensile properties, Y

T_p (°C)	A				B			
	DR	DS (cm min ⁻¹)	Modulus (GPa)	Strength (MPa)	DR	DS* (cm min ⁻¹)	Modulus (GPa)	Strength (MPa)
110	1		0.76	18	1		0.97	23
	1.7		0.93	17				
	9.8		1.17	21				
125	3.2		0.94	172	5.9	0.26	0.99	24
	6.4		1.32	200	8.4	0.26	0.99	28
	10.8		1.47	220	14.4	1.44	—	—
	14.0		0.90	228	3.7	0.52	0.98	26
					6.9	0.52	0.98	26
140	2.4		1.03	179	11.7	0.52	0.97	30
	5.6		1.59	213	17.6	2.28	—	—
	10.2		1.31	234	5.1	1.86	0.96	26
	14.0		1.03	237	12.2	0.52	0.99	31
150					17.4	1.44	—	—
	3.2		1.25	182	21.0	2.28	—	—
	6.5		1.03	213	4.0	0.26	0.97	28
	10.6		1.03	225				
	13.7		0.97	234	13.4	0.90	0.98	31
	17.3		1.17	241	17.6	0.90	0.96	35
	20.7		1.24	262				
					24.3	1.86	—	—

*no preheater used.

a linear increase in the strength of copolymer B (reaches about 90% of rolltruded polypropylene itself) is noted in the Z direction, whereas in copolymer A the change is much less impressive, reaching only 60%–70% of this tensile strength. In this case, the distribution of globules is less well-dispersed than in copolymer B. Transverse to the Z direction, the tensile strength in copolymer B is again found to be superior

to copolymer A for almost all of the same deformation (processing) range. Note, however, that the differences in tensile modulus are less marked, with copolymer B just exhibiting noticeably higher results over copolymer A, a fact that is generally displayed by many materials, whatever their type.

Some understanding of the difference in properties may be obtained from DSC scans of rolltruded and

original copolymers. For example, in Fig. 2a, the distinction between copolymer A rolltruded at 150 °C, DR ~ 21 (ii) and the original workpiece (i) is striking. Only a single peak is observed at 170 °C in the rolltruded copolymer A compared to the original sample. Whenever the rolltruded material is then recrystallized, its thermograms mimic the features displayed in the starting material. These significant and distinguishable enthalpy features between Fig. 2a(i) and (ii) can only be ascribed to morphological differences induced by the rolltrusion processing itself. The fact that Fig. 2a(iii) and b(iii), compare favourably with Fig. 2a(i) and b(i), in phase characteristics signifies that the original features or morphological state of the sample are regained after the rolltruded copolymer is melted and recrystallized. Rolltrusion tends to “redistribute” or internally homogenize the sample, consequently improving its overall physical properties (i.e. induces increased mechanical properties and transparency). However, the original chemical and physical state of the polymer as manufactured, is the overall determining factor. In copolymer B the distribution of globules is found to be more homogeneous than it is in copolymer A which is claimed to be made by a different catalyst and manufacturing procedure. The manufacturing procedures are not public knowledge.

Morphological evidence from fractured rolltruded samples supports this distinction. An electron micrograph obtained in the initial deformation stages of the rolltruded copolymer A at $T_p = 110\text{ }^\circ\text{C}$, DR = 1.7, depicts the presence of plate-like crystals located in arrays that are more or less lying in the deformation direction, with irregularly dispersed PE globules located on the XZ fracture surface (Fig. 5). In the specimen processed at higher draw ratio (e.g. DR = 10.8, $T_p = 140\text{ }^\circ\text{C}$), there is alignment of fibrous crystals in the machine direction, Z, of the workpiece (see Fig. 6). The deformed PE globules (arrowed) tend to be distributed randomly amongst the fibrillar PP crystals in the sample. Fine structure is noted perpendicular to the fibrillar textures and this probably corresponds to the remnants of deformed lamellar crystals. The spacing of the striations in Fig. 6 are estimated to be about 20 nm apart, and that is close to

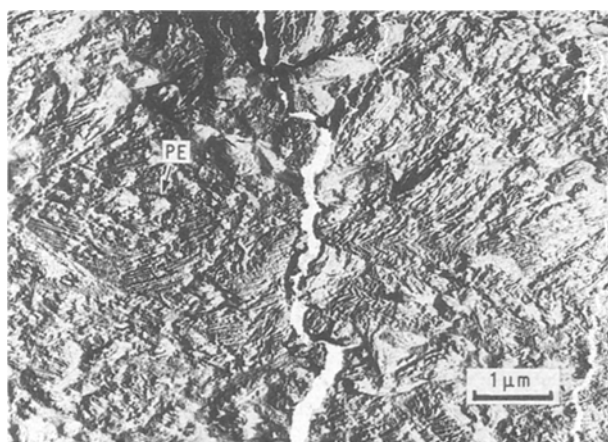


Figure 5 Electron micrograph of fractured and chemically etched XZ plane of the rolltruded copolymer A processed at $T_p = 110\text{ }^\circ\text{C}$, DR = 1.7.

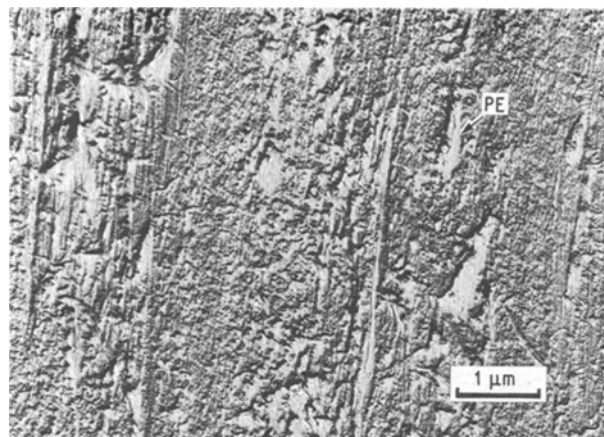


Figure 6 Electron micrograph of fractured and chemically etched YZ plane of the rolltruded copolymer A corresponding to $T_p = 140\text{ }^\circ\text{C}$, DR = 10.8.

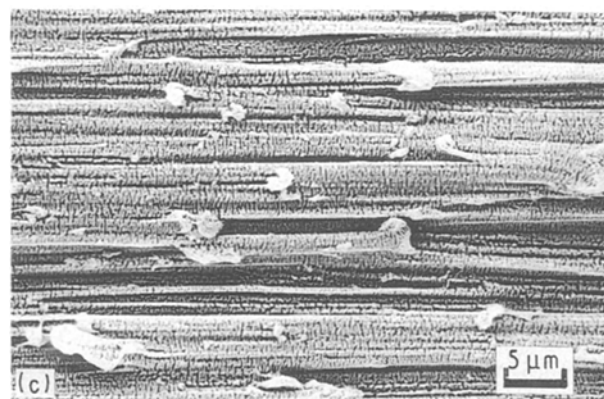
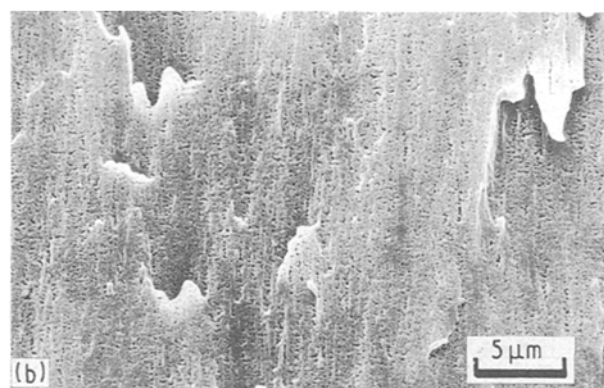
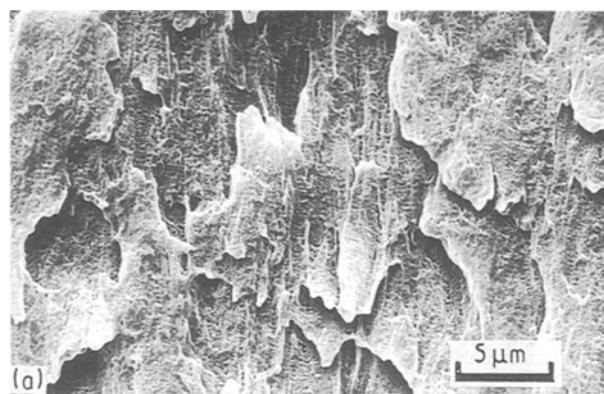


Figure 7 Scanning electron micrograph of ion-bombarded fracture surfaces XZ of the rolltruded copolymer A at $T_p = 150\text{ }^\circ\text{C}$ and DR = (a) 3.3, (b) 6.4, (c) 20.3.

the long-period spacing measured by small-angle X-ray scattering measurements for the same samples.

Scanning electron microscopy of the fracture surface in the XZ plane of the rolltruded PP specimens exhibits a uniform layer texture that gradually improves with increasing the draw ratio [6–8]. The layer separation originates from cracks that propagate in these moderate molecular weight polymers, parallel to the machine direction. With increasing draw ratio, the planar (0k0) orientation improves. These trends are also noted in P/E block copolymers, where less layer uniformity is observed because of the distribution of ethylene components. The layer texture found for the rolltruded copolymer A of different draw ratio at $T_p = 150^\circ\text{C}$ is shown in Fig. 7. Unlike polypropylene, where the fracture surface is relatively smooth, there is less surface uniformity in the copolymers and well-developed layers are found only for specimens of higher draw ratio where the deformed PE globules are distributed between the layers. Fig. 8 is an electron micrograph of the chemically etched fracture surface (XZ plane) of the processed copolymer A at $T_p = 150^\circ\text{C}$, DR = 3.3. Compared with Fig. 7a, which is an ion-bombarded fracture surface of the same material, fine striations are observed perpendicular to the machine direction and these are visible at 20 nm intervals, but in contrast, the overall surface exhibits textured irregularities when the ethylene components are present. No distinct textural layering is recognized for low DR specimens. Rolltrusion improves the (0k0) planar orientation with increasing DR, as well as an enhancement in the mechanical properties [6].

Fig. 9 illustrates some XRD patterns of the copolymer A rolltruded with $T_p = 150^\circ\text{C}$ and at different DR values PP is used for comparison. Fig. 10



Figure 8 Fracture surface morphology of the XZ plane of the rolltruded copolymer A for $T_p = 150^\circ\text{C}$, DR = 3.3.

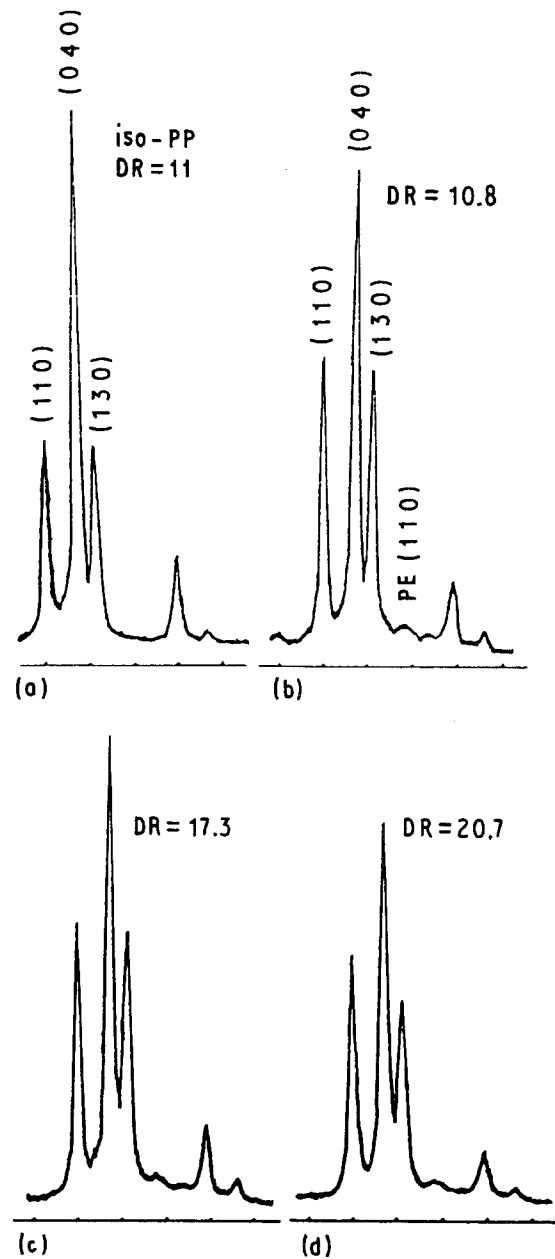


Figure 9 X-ray diffraction patterns of the rolltruded copolymer A, $T_p = 150^\circ\text{C}$ and for various DR values.

shows the intensity ratio of (040) and (110) reflections produced with increasing the DR. The rolltruded PP shows better defined (0k0) planar orientation than copolymers processed under comparable conditions (e.g. compare Fig. 9a and b).

Fig. 11 shows scanning electron micrographs of the XZ fracture surface of copolymer B where the texture is more uniform than it is in copolymer A. These distinct differences observed in morphological features are responsible for the improved mechanical properties of copolymer B over copolymer A when these copolymers are rolltruded.

4. Conclusions

1. Rolltrusion processing induces a triaxial orientation in P/E copolymers which improves the mechanical properties parallel and transverse to the draw, Z,

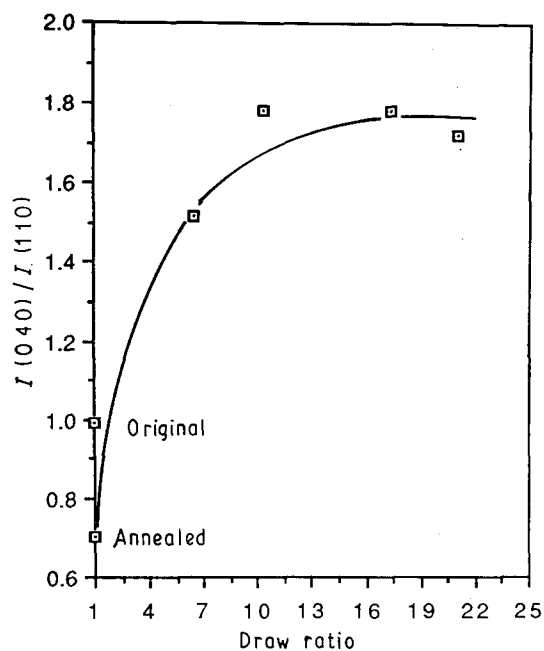


Figure 10 The intensity ratio of (040) and (110) reflections versus DR for P/E copolymer.

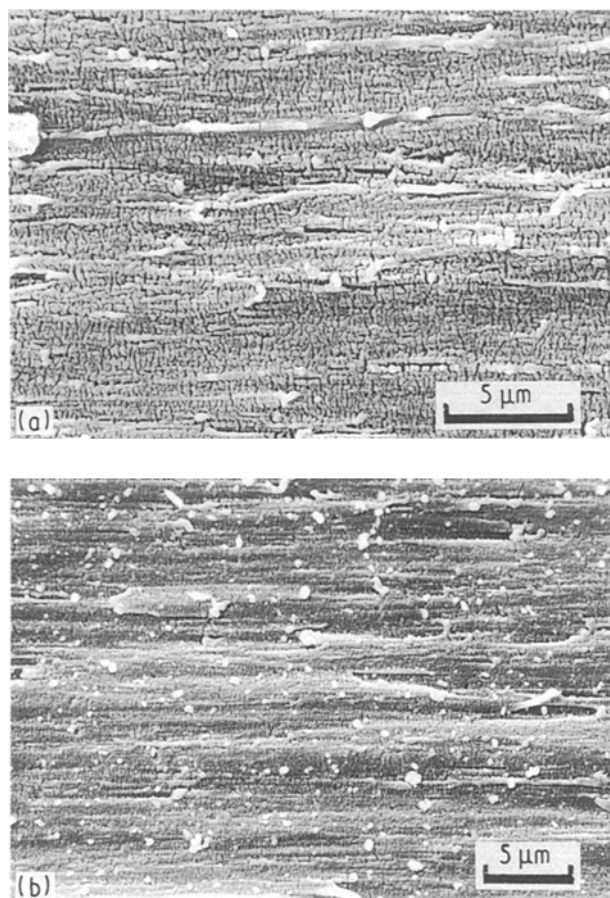


Figure 11 Scanning electron micrographs of an ion-bombarded fracture surface XZ of the rolltruded copolymer B: made at (a) $T_p = 125^\circ\text{C}$, DR = 7 and (b) $T_p = 150^\circ\text{C}$, DR = 18.

direction. The three-dimensional sample orientation is supported by X-ray diffraction evidence.

2. Rolltrusion induces transparency in otherwise opaque copolymers when the proper processing conditions are used.

3. DSC thermograms exhibit features that allow one to distinguish between copolymers manufactured by different polymerization methods. Distinct characteristics are also evident in rolltruded copolymers.

4. P/E copolymers exhibit globular features that arise due to a segregated polyethylene phase that may be redistributed via rolltrusion processing in order to improve copolymer properties.

5. Ion etching and permanganic etching techniques enable textural features to be highlighted and molecular orientation to be determined via TEM, SEM and electron diffraction techniques.

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