Crystalline Transitions and the Solid-State Extrusion of Polymers

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Synopsis

Extrusion experiments on eight polymers in our laboratory and eight additional polymers in other laboratories reveal that solid-state extrusion and malleability occur in semicrystalline polymers that have a reversible crystalline transition, T_c, and do not occur in crystalline polymers devoid of T_c. The solid-state extrusion takes place only in the temperature range of $T_c \leq T < T_m$. The transparency of the solid-state extrudates was shown to be largely due to void disappearance and may be due in part to the diminution in size of the scattering species. Increases in T_m were shown not to be correlatable with lamellar thickening or chain extension.

INTRODUCTION

The process conventionally termed solid-state extrusion has received increasing attention in recent years.[1-10] In this process the polymer entering the die is highly crystalline, and hence solid, and the polymer that emerges from the outlet orifice of the extrusion die is also solid. It is well known that the T_m increases under pressure. Therefore, one may solid-state extrude under pressure at temperatures above the T_m at atmospheric pressure. On the other hand, a minor component of some crystalline polymers may start flowing at the atmospheric T_m, or even below it, carrying with it the major crystalline components still in the solid state. A multiphase extrudate may be obtained which is under no means a solid-state extrudate.

It was stated in the literature (e.g., reference 10) that upon such treatment a significant measure of chain unfolding (also termed extension) in the extrusion direction takes place. In the case of semicrystalline polymers, this was seen through the increases in lamellar thicknesses, as observed by small-angle x-ray scattering (SAXS) (changes in peak position and decreased intensity) and through increases in the melting temperature T_m of the products relative to the T_m of the starting materials. A target of this work was to determine if a significant amount of chain unfolding results from the operation of solid-state extrusion and whether the observed increases in T_m are correlatable with such chain extension.

The process of solid-state extrusion for certain polymers proceeds below the melting point under the extrusion conditions. In the case of other polymers the process fails under the same temperature conditions. In both cases the amorphous component of the polymer is far above the glass transition point T_g and is in a fluid state. The difference in behavior between the two classes of polymers indicates that it is not the behavior of the amorphous part above or below T_g that controls the solid-state extrudability of the polymer. A second target of this study was hence an attempt to find a common denominator differentiating the solid-state extrudable polymers from those that fail to do so.

0021-8995/79/0023-0133$01.00

The criterion for success in our case was a solid-state extrusion at temperatures sufficiently lower than T_m yielding a smooth, clear, or transluscent extrudate of a reduction ratio larger than 14, with apparently no die swell.

EXPERIMENTAL

The polymers tested in this work were polyethylene (PE), Allied Chemical's PP-60-002, $M_n \cong 18,000$, $M_v = 96,000$; poly(4-methylpentene-1) (P4MP1), obtained from Aldrich Chemical Company, Cat. No. 19,099-3, melt index 20; poly(ethylene terephthalate) (PET), Allied Chemical, intrinsic viscosity = 0.54, $M_v \cong 38,000$; poly(butylene, terephthalate), (PBT), Goodyear's VFR 4716A, intrinsic viscosity = 0.76; poly(ethylene–tetrafluoroethylene) copolymer, du Pont's Tefzel 2008, Lot 344; poly(ethylene–chlorotrifluoroethylene) 1:1 co-polymer, Allied Chemical's Halar 500A, melt index 14 at 275°C under 2160 g load; poly(hexafluoroisobutylene–vinylidene fluoride) 1:1 copolymer (CM-1), melt index 9 at 345°C under 2160 g load; and isotactic poly-1-butene, medium molecular weight, Aldrich Chemical Co. Cat. No. 18,139-0.

For the extrusion experiments, a $\frac{3}{8}$-in.-diameter Instron rheometer was used. The dies were 0.100 in. or less in diameter, 1.00 in. long land, and with entrance angle of 45°–15°. The ratio of the cross-sectional area of the rheometer plunger to that of the die, termed the reduction, was hence 14 times or more. The polymer was loaded into the instrument and the rheometer sealed on both sides and evacuated. Then the plunger was lowered to exert pressure on the polymer, the temperature brought to the desired point, and the seal of the die removed. The pressure on the polymer was maintained throughout the heating cycle by slight movements of the plunger into the rheometer bore.

Successful solid-state extrusions did not require the full pressure of 45,000 psi the instrument is capable of delivering. In this case significantly lower pressures, of the order of 25,000 psi, were sufficient to solid-state extrude the polymer at rates averaging 1.5 in./min. In the cases of failure, even the full load of the instrument would not cause extrusion until right at the melting point range of the polymer, where the extrudate may squirt out with an almost complete loss of pressure. Sometimes this extrudate turned out to be a multiphase extrudate but exhibited no die swell. Otherwise, the extrudates obtained right above the T_m had rough surfaces brought about by fluctuations in the die swell.

It was found that when the solid-state extrusion was successful, the entrance angle of the die did not affect the extrudate; angles of 45° down to 15° gave the same results.

Melt extrusion was performed in the usual manner with the extrudate exhibiting die swell and turning opaque upon cooling (except for P4MP1).

Thermal analyses, microscopy, and x-ray studies were performed in the customary fashion.

RESULTS AND DISCUSSION

The results of our solid-state extrusion experiments are summarized in Table I. The criteria for successful solid-state extrusion are spelled out in the experimental section. From the table it is obvious that the solid-state extrusion succeeded only in the polymers that exhibit a reversible crystalline transition. The reversible crystalline transition is defined as a reversible transition from

TABLE I
Solid-State Extrusion Results

Polymer	Solid-State Extruded	Over temp. range, °C	Reversible crystalline transition temp., °C	Melting point T_m, °C[a]	Reference
PE	yes	138–145	(α') ~110	136	11
PET	no	—	none	258	
PBT	no	—	none[b]	223	12
P4MP1	yes	170–225	(β_c) 160	231	13
CM-1	no	—	none	326	
Tefzel	no	—	none	≤280	14
Halar	yes	170–228	(α) 130	236	15
Poly(1-butene)	no	—	none[c]	116	16

[a] Measured under atmospheric pressure.

[b] A reversible stress-induced transition exists at room temperature.

[c] An irreversible transition toward a stable modification occurs at about room temperature.

one crystal form at one temperature to a different crystal form at another temperature, without passing through a different phase. The temperature range over which the extrusion succeeded was, in our case, always in the temperature interval above the reversible crystalline transition T_c and below the melting point T_m. At temperatures lower than T_c, even when the full pressure of 45000 psi was applied, no extrusion took place. Above T_m, the extrusion occurred under extremely low pressures, in the order of 100 psi.

A literature search revealed that other polymers also show a transition at T_c from nonmalleable to malleable behavior or from unextrudable in the solid state to extrudable in the solid state. The observations are tabulated in Table II.

One may conclude, therefore, that a necessary requirement for a successful solid-state extrusion is the existence of a reversible crystalline transition below the temperature at which the extrusion takes place. The reversible crystalline transitions may result in either some conformational change or some change in intermolecular spacings. In either case some breakdown in intermolecular forces occurs[15] in going from one crystal state to the other. This breakdown in intermolecular forces manifests itself in a reduction in modulus at least in the cases of Halar,[15] P4MP1,[13] poly(tetrafluoroethylene),[23] and poly(organophosphazenes).[25] It is most likely that this reduction in modulus can allow shearing and thus extrusion in the solid state.

The claimed "extrusion" of nylon 6, nylon 66, and poly(oxymethylene) below T_m was under conditions of extremely small reduction (ratio of plunger area to die area) and, because this fact was omitted by the authors,[19,20] apparently yielded opaque extrudates and not clear or translucent ones. Such "extrusions" do not fit our definition of a successful solid-state extrusion and will not be discussed further. Extrusion of PE below T_c appears to proceed for very low molecular weight fractions, to be intermittant, and to be sensitive to the die angle.

X-Ray diffraction patterns obtained by the flat plate technique from the extrudates revealed that there was no significant orientation in the melt-extruded (high above T_m) samples and in the samples that failed to successfully solid-state extrude (closely above T_m), such as PET, PBT, CM-1, and poly(1-butene). In the solid-state extruded samples crystalline orientation did appear, the orien-

TABLE II
Literature Data Concerning Workability Below T_m

Polymer	Reversible crystalline transition temp., °C	Solid-state workability range, °C	Comments	Reference
Polypropylene	(α) ~100	yes, intermittant from 80	extrusion	11, 17
		70–150	extrusion at low reduction	18
Poly(vinylidene-fluoride)	~140 ~100	yes, intermittant from 120	extrusion at 80–160°C	11, 17, 24
Nylon 6	none[a]	no	Extrusion at 80–160°C under extremely small reduction	19
Nylon 66	none	no	extrusion at R.T. under extremely small reduction	20
Poly(oxymethylene)	none	no	extrusion at R.T. under extremely small reduction	20
Poly(p-hydroxybenzoic acid)	325–350	yes, >350	polymer becomes malleable	21
Poly(tetrafluoroethylene)	19, 30	yes, >20	polymer becomes malleable	11, 22
		20–30	sharp drop in strain modulus	23
Poly(organophosphazenes)	150–250 below T_m	yes, 150–250 below T_m	drop in modulus flowability	25

[a] An irreversible crystalline transition exists in this polymer.

tation fraction f_c approaching 0.95 for PE, about 0.8 for Halar, and 0.6–0.7 for P4MP1.

The above three materials, polyethylene, poly(ethylene chlorotrifluoroethylene), and poly(4-methylpentene-1), were transparent when solid-state extruded. Figure 1 is a typical example for Halar. When extruded in the melt and the extrudate cooled to room temperature, the PE and Halar extrudates became opaque while that of the P4MP1 remained clear. A possible explanation for this will be discussed later. The explanation will show that clarity is a poor criterion for successful solid-state extrusion.

The three solid-state extrudates tend to fracture with the formation of fibrils at the fracture zone. Upon sharp bending the bend region becomes opaque. Under the microscope it becomes apparent that this opacity results from large-scale, essentially longitudinal void formation between the fibrillar structures in the extrudate. No kink bands were noticed under the microscope.

It is of interest to note that the melt-extruded P4MP1 also turned opaque at the locus of sharp bending. Under the microscope this opacity appeared to be due to void formation. When strained the sample started necking from the opaque area, prior to failing.

As can be seen from Table III, several of our polymers exhibit multiple melting points (DTA and DSC scans at 10°C a minute) after being solid-state extruded. Such multiple melting points are known from the literature for PE,[26,27] PET,[28–31] and PBT.[32] The x-ray scans of the samples revealed neither dramatic increase in lamellar thickness to go hand-in-hand with the increase in T_m in the case of either PE, Halar, or P4MP1, nor a remarkably high level of crystalline orientation for the solid-state extrudates of the last two polymers. The increase in T_m of PET and PBT is again associated with neither crystal thickening nor crystalline
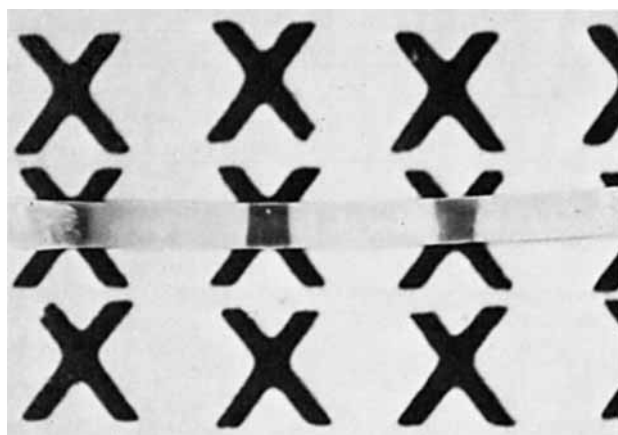
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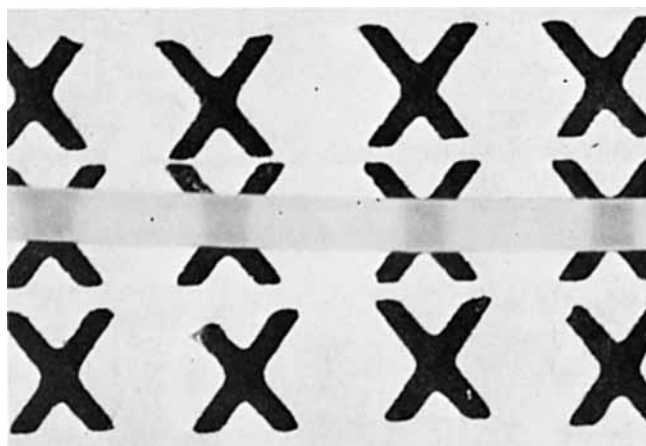
10X

Fig. 1. Top: Halar extruded at 170°C. Bottom: Halar extruded at 250°C. Both under 10× magnification.

orientation. Recall that during the extrusion the PET and PBT were under practically no pressure and that it is the application of pressure, with the resultant elevation of T_m, that is considered to encourage lamellar thickening and chain unfolding.

One must conclude, therefore, that the increases in melting points observed in the above polymers are not associated with increases in lamellar thickness or chain unfolding. Such increases are most probably connected with increased degrees of crystalline perfection. X-Ray data did in fact indicate a sharpening of the crystalline reflections, supporting the idea of increased crystalline perfection. It should be noted, however, that fully extended long polymer chains are not visible by means of the common SAXS equipment.

In the case of PE, it is of interest to note that while the solid-state extrudate exhibited three melting points, the material remaining in the rheometer barrel, i.e., exposed to the same pressure and thermal history but unextruded, showed only one T_m, similar to that of the starting material. It is obvious that the

Polymer	Treatment	T_m at atmospheric pressure, °C	X-ray observations
PE	starting material pressurized 10 min at 45000 psi in rheometer barrel at 142°C, not extruded	136	no orientation
	solid-state extruded at 135° to 145°C	$T_{m_1} = 140$	oriented, SAXS periods of 250 to 300 Å
		$T_{m_2} = 146$–147	
		$T_{m_3} = 149$–151	
	melt extruded at 152°C	136	no orientation
PBT	starting material	223.5	no orientation
	squirted at 220°C	$T_{m_1} = 225$–226	
		$T_{m_2} = 232$–233	
	melt extruded at 230°C	223.5	no orientation
P4MP1	starting material	231	no orientation
	solid-state extruded at 180°C	231	oriented $f_c \sim 0.6$–0.7
	melt extruded at 250°C	231	no orientation
CM-1	starting material	326	no orientation
	squirted at 311°C		no orientation
Halar	starting material	236	no orientation
	Solid-state extruded at 170°, 180°, 200°, 220°C	236	oriented $f_c \sim 0.8$ SAXS: meridional scattering ~125 Å absence of voids
	melt extruded at 250°C	239	no orientation
PET	starting material	258–259	no orientation
	squirted at 238°C	$T_{m_1} = 247$–253	no orientation
		$T_{m_2} = 263$–266	
		$T_{m_3} = 267$–271	
Poly(1-butene)	Starting material	116	modification II[16]
	squirted at 130°C	134	modification I[16]

shearing process during the extrusion is responsible for the appearance of the three melting points and for their displacement to higher temperatures. The SAXS periods of 250–300 Å, in the normal range for PE,[10] indicate that no significant lamellar thickening took place. Under the polarized light microscope one can see three distinguishable morphologies coexisting in the same solid-state extrudate of PE. One is very small spherulitic structures; another appears to be spherulites sheared in the flow direction; and the third, far less birefringent than the others, fills the space around the sheared and unsheared spherulites. It can be stated hence that in solid-state extruded PE the appearance of three melting points in thermal scans is correlated with the existence of three morphologies in the extrudates prior to the thermal scan.

In contradistinction to PE, both P4MP1 and Halar show only one melting point for their solid-state extrudates, and this T_m is exactly the same as that of the starting materials. Since these materials are oriented, one may not draw the conclusion that the orientation of PE alone may contribute to the elevation of its T_m and the appearance of multiple melting points. This conclusion is supported by the appearance of higher T_m and multiple melting points for the unoriented PET and PBT extrudates.

TABLE IV
Tensile Results and Density of Halar Extrudates

Extrusion temperature, °C	% Ultimate elongation	UTS, g/denier	TM, g/denier	Density, g/cm³	Residence time at temp., min
170	1.6	0.29	23.7	1.690	
180	1.8	0.45	34.4	1.690	
200	1.3	0.24	22.8	1.692	25–30
	2.0	0.29	19.5	1.692	37–41
220	1.4	0.22	19.7	1.693	35–40
	1.7	0.31	24.1	1.693	45–47
250	308	0.31	8.5	1.686	13–14
	237	0.22	5.7	1.686	16–18

The ultimate tensile strength (UTS) and tensile (Young) modulus (TM) of the solid-state Halar extrudates are significantly higher than those of the undrawn melt extrudate. The solid-state extrudates fail, in tensile tests, in a brittle manner without passing through a yield point. Attempts to draw the solid-state Halar extrudates over the temperature range of room temperature up to 220°C have all failed, the samples failing in a brittle fashion.

The results of the tensile tests of Halar extrudates, performed at 23°C and 50% relative humidity with a strain rate of 1.0 in./min, are presented in Table IV. In the table one can find also the densities of the extrudates. These extrudates were of about 0.030 in. in diameter (with denier values of about 6400–6600), except for the melt extrudates that showed die swell and, consequently, diameters approaching 0.040 in. (denier values of up to 8000).

Based on the disappearance of void scattering in the solid-state extrudates of Halar and on the absence of any other change discernible by x-ray techniques, one may draw the conclusion that, at least in the case of Halar, the attainment of transparent extrudate is merely a result of the elimination of all or most of the voids under the conditions of solid-state extrusion. In the case of PE, in addition to the elimination of voids, the shearing conditions may lead to the formation of sufficiently small crystalline entities that when embedded in an amorphous matrix will cause only a negligible amount of optical interference, leaving the sample transparent or very close to it.

The same reasoning holds also for P4MP1. Here, however, the clarity of the melt extruded material is of interest, since for the other polymers the melt extruded samples turned opaque upon cooling and crystallizing. We believe that the transparency of the melt-extruded P4MP1 is due to the fact that for this polymer the crystal density is lower than the amorphous density.[33,34] Therefore, when the polymer crystallizes from the melt, instead of shrinking and forming voids, largely at the crystal–amorphous interfaces, the P4MP1 tends to expand and by doing so eliminate all possibility for void formation.

One may also conclude that, as was shown above for PE, PET, and PBT, an elevation in T_m does not necessarily correlate with lamellar thickening or chain unfolding.

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