Component Redistribution in Extrusion
of Polyethylene Compounds*

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Synopsis

Calorimetrically determined integral heats of solution and swelling ratio measurements carried out on extrudates of low-density polyethylene blended with Surlyn ionomer and ethylene–ethyl acrylate copolymer provide independent evidence for the redistribution of components as a result of extrusion. Although this evidence for "migration" supports earlier data for extrusion-triggered molecular redistribution in polyethylene, the present data further suggest that the effect may be due at least in part to the tendency of crystallizable polydisperse polymers to form cohesively weak boundary layers upon cooling from the melt. Thus, molecular redistribution effects may be expected in the processing of polyethylene and related thermoplastics but would not be pronounced in the extrusion of amorphous, narrow molecular weight distribution polymers, e.g., polystyrene.

INTRODUCTION

Some years ago, Busse[1] observed that because of thermodynamic considerations molecular fractionation might be expected to occur across the radius of a capillary during the extrusion of polymeric fluids. The suggestion bears some resemblance to the documented[2-4] axial migration of particles suspended in sheared fluids and appeared to offer an attractive rationalization for the strong die–length dependence of postextrusion swelling in many thermoplastic melts.[5] Indeed, experiments reported by Schreiber and Storey[5] appeared to confirm the concept of molecular migration in the extrusion of polyethylenes. Subsequently, the kinetic theory of liquids was applied to this case,[6] and a crude model was thereby provided for the migration effect. Although the model accurately predicted the decrease of postextrusion swelling with increasing die length over a wide shear rate range, it also called for extrudate swelling to vary either with the inverse 3rd or 5th power of die radius, a prediction which is intuitively and experimentally untenable. Another problem is the conceptual difficulty of an effective transport of macromolecular chains through very viscous media in the short time span of an extrusion experiment. The recent work of Whitlock and Porter,[7] utilizing commercial polystyrene, further complicates the

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matter. These workers observed no significant molecular weight rearrange-
ments in the polymer following its capillary extrusion through a die with
$L/D = 66.7$, and over an appreciable range of shear rates and temperatures.

The present paper documents experiments carried out some time ago in
an effort to provide additional information on the suggested fractionation
phenomenon and to examine it by means other than complex and possibly
inaccurate molecular weight determinations. The results do not settle the
issue of whether or not molecular fractionation of the Busse kind occurs
during capillary extrusion of polymer melts. However, they introduce
calorimetric analyses into the extrudate evaluation sequence and thereby
broaden our view of the complex events occurring during and, ostensibly,
after extrusion. They are presented in the spirit of stimulating further
examination of important and as yet unresolved questions concerning the
processing behavior of polymers.

EXPERIMENTAL

Two series of experiments, each involving polyethylene (PE) and PE-
containing blends, are reported. One, referred to as the calorimetry series,
involved measurements of integral heats of solution on samples taken from
various radial positions of monofilament extrudates. In the second series,
swelling ratios of blend extrudates were measured as a function of die L/R.

Materials

Throughout this work, five polymer samples were used. Three of these
were low-density PE (LDPE), the others were a commercial sample of
ionomer (du Pont Surlyn A) and ethylene–ethylacrylate copolymer (EEA).
The PE's differed primarily in molecular weight: LDPE-1 (melt index[8] =
0.28) with $\bar{M}_w = 310,000$; and LDPE-2 (melt index = 2.1) and LDPE-3
(melt index = 19.3) with $\bar{M}_w$ values of 105,000 and 55,000, respectively.
The $\bar{M}_w$ values were obtained by light scattering in tetralin solutions of the
polymers at 140°C. Because of the large molecular weight differences,
combinations of these polymers might be expected to show appreciable
tendencies for migration in flow.

All polymer blending was performed at 190°C on a two-roll mill. Ther-
mal stability of the compounds was promoted by adding Santonox (trade
mark, Monsanto Chemical Co.) antioxidant to the molten mass (0.1% wt
of total polymer).

Calorimetry Series

Preliminary experiments using the isothermal solution calorimeter de-
scribed by Schreiber and Waldman[9] showed that tetralin was a solvent both
for LDPE and for the EEA copolymer. At 90°C, however, the integral
of the endotherm-versus-time trace, obtained when samples of these poly-
mers were immersed in the solvent, was very much greater for LDPE than
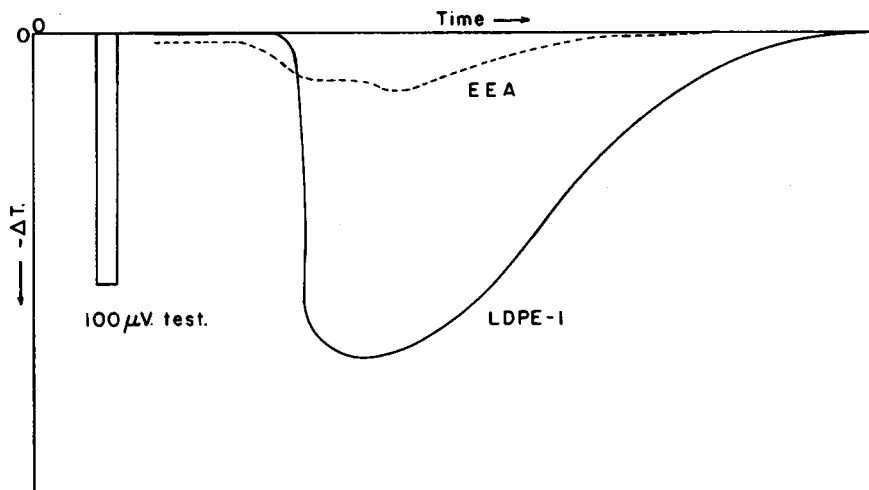for the copolymer. This was due, presumably, to a contribution to the

Fig. 1. Typical solution endotherms for PE and EEA in tetralin at 90°C.

endotherm of LDPE from residual crystallinity in that polymer at the moment of contact with the solvent. Typical endotherms are shown in Figure 1. Thus, determinations of the integral heat of solution for mixtures of the polymers could serve as a sensitive index of composition and therefore as a means of evaluating composition redistribution following extrusion.

All work in this series was based on LDPE-1, EEA, and a blend of these at the 95/5 (wt-%) composition. All materials were extruded at 100 sec^{-1} shear rate and 190°C from the familiar CIL viscometer,[10] fitted with a die having a radius of 0.100 cm and $L/R = 60.68$. Samples from various radial positions of the extruded monofilaments were obtained by the mechanical "skinning" method described in detail earlier.[5,6] The samples were placed in brittle glass bulbs, evacuated to a residual pressure of $<10^{-5}$ torr, and sealed under a pressure of about 10 mm He. The sealed bulbs were then placed in the isothermal calorimeter[9] and, following attainment of equilibrium (at 90°C), heats of solution were measured by methods described in the earlier publication. The endotherm generated by contact between the polymer and tetralin was followed until reestablishment of a baseline, a period of approximately 20 min. The area under the curve was integrated by planimeter, and heats of solution were calculated on the basis of moles of polymer repeating unit.

Swelling Ratio Series

Compounds of LDPE-1/Surlyn A, and LDPE-2/LDPE-3, each at a 95/5 wt-% composition, were extruded at 100 sec^{-1} shear rate and 190°C, through dies with a uniform radius of 0.100 (±005) cm and L/R in the range of 1–61 (see also refs. 5 and 6). Swelling ratios (filament diameter/die diameter = B) were determined from micrometer measurements of the

extrudate diameter and compared with B values for the individual resins in each composition.

RESULTS

Calorimetry Series

The integral heats of solution (ΔH_s) for LDPE-1, EEA, and the 95/5 blend are given in Table I. All values are averages of two determinations, with a mean error of ± 0.05 kcal/mole. The per cent cut designation in Table I indicates the per cent reduction of extrudate diameter caused by the sampling procedure. Thus, the 0–10% sample is the outer skin of the extrudate and represents a reduction of the extrudate diameter to 0.9 of its original value. Following this convention, the core, therefore, represents the central 20% of the monofilament's original diameter.

The observed ΔH_s for the blend is significantly lower than the value of 1.63 kcal/mole expected from simple combinatorial rules. The reduction may be attributed to reduced crystallinity at 90°C in the blend. Accepting the ΔH_s for unextruded compounds as the characteristic values of the materials, one can easily calculate effective concentrations of the blend components at various positions of the cross section from the experimental ΔH_s data.

Figure 2 shows the results of this procedure, by representing the effective EEA concentration as a function of radial position. Obviously, redistribution of composition has occurred as a result of extrusion, relative to the expected line of isotropic EEA content, which is also shown in Figure 2. The diagram suggests that in an annular region near the die wall, EEA copolymer is displaced by the polyethylene matrix; that an internal annulus, comprising about 60% of the overall cross section, contains almost all of the EEA; and that the core region ($\sim$10% of diameter) is nearly free of the additive. If this pattern of composition were assumed to be related

TABLE I
ΔH_s for Test Polymers as Function of Radial Position of Sample

Sample	ΔH_s, kcal/mole repeat unit		
	LDPE-1	EEA	95/5 Blend
Unextruded	1.69	0.46	1.20
Extrudate			
Full cross section	1.62	0.42	1.16
0–10% Cut[a]	1.58	0.50	1.76
10–20% Cut	1.62	—	1.40
20–30% Cut	—	0.43	1.03
30–40% Cut	1.98	—	1.03
40–60% Cut	1.70	0.47	0.73
60–80% Cut	1.53	—	1.35
Core	1.78	0.42	1.66

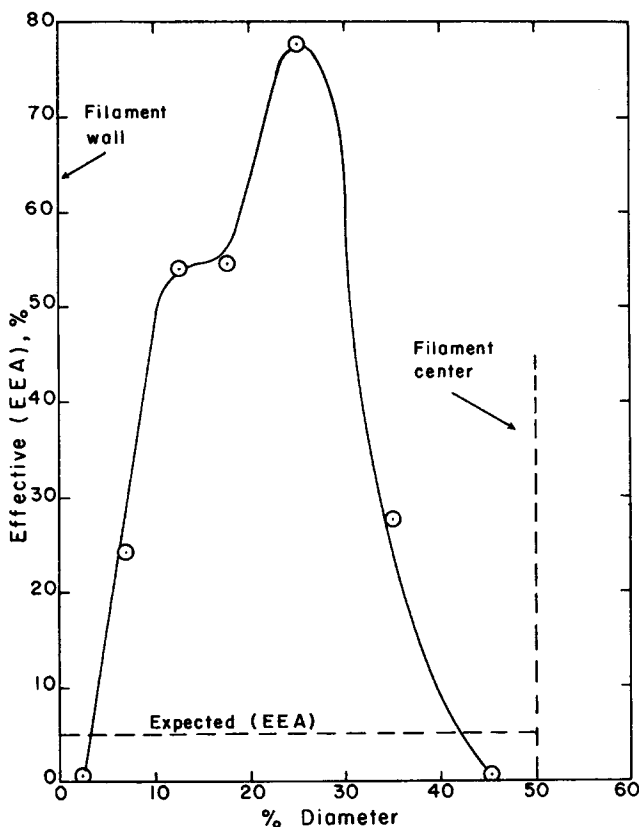[a] See text for explanation of cut designation.

Fig. 2. EEA concentration at various positions of extrudate.   Concentration calculated
from ΔH_s.

with velocity profiles in the extrusion die, as suggested in our earlier con-
siderations,[5,6] then the apparent velocity profile would be a blunted pa-
rabola with an annular region near the die wall with low velocity gradient.
Such profiles have been reported for the extrusion of polyolefin melts.[11]

Swelling Ratio Series

The variations of B with die L/R for LDPE-1/Surlyn A (95/5) and
LDPE-2/LDPE-3 (95/5) are shown in Figures 3A and 3B, respectively.
The swelling behavior of blend LDPE-2/LDPE-3 is striking in displaying
the characteristics of LDPE-2 for extrusion through short L/R dies, but
then shifting to the characteristics of LDPE-3 at high L/R values.   Con-
sidering that the two polymers differ primarily in molecular weight, it may
be concluded that the less elastic component becomes increasingly dominant
in determining B as L/R increases.   This finding is in qualitative agree-
ment with the hypothesis of shear-induced molecular migration.   The
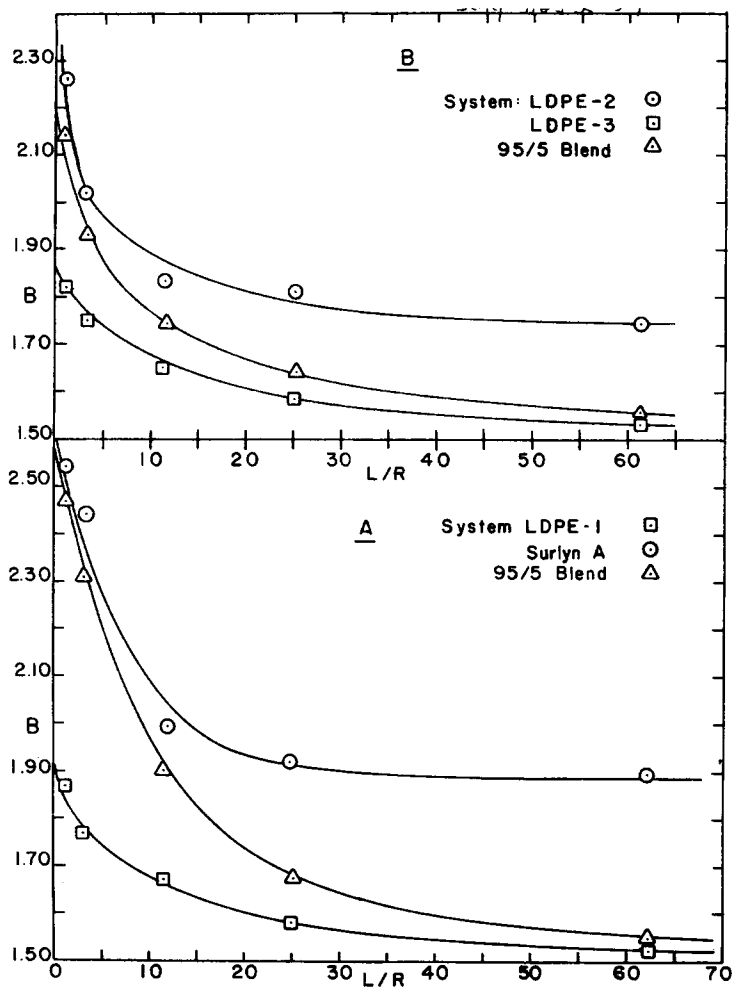same situation is observed in the system LDPE-1/Surlyn A.   If the higher

Fig. 3. A: Die length dependence of extrudate swelling for LDPE-1/Surlyn A. B: Die length dependence of extrudate swelling for LDPE-2/LDPE-3.

B value for the ionomer signifies that resin is more elastically deformable than the PE, then once again the less elastic component becomes dominant as die L/R increases.

DISCUSSION

The given results confirm the existence of component redistribution arising from melt extrusion. Since the calorimetric heats of solution are independent of the rheological and molecular weight parameters upon which earlier considerations of molecular fractionation were based,[5,6,7] it seems reasonable to conclude that a real effect is being observed for poly-

ethylene or PE-based compounds. The PE case is therefore quite distinct from polystyrene, the carefully obtained data of Whitlock and Porter[7] showing no similar effect with that material.

If, in view of very different behavior in two polymers, the thermodynamic origin for molecular fractionation must be questioned, it may be speculated, instead, that the molecular redistribution which we have observed is a feature of crystallizable polymers with very wide molecular weight distributions. These events may then be connected with the complex crystallization kinetics and with tendencies for weak boundary layer formation in such polymers. The experiments of Schonhorn and co-workers[12] and of Tordella[13] are to the point of this consideration. The former authors have shown clearly the presence of noncrystalline, cohesively weak boundary layers at surfaces of polyolefins. Logically, the materials constituting such layers would be low molecular weight, highly branched moieties in the distribution of a typical polyethylene.

Tordella's work[13] has shown that cooling rates (and therefore crystallization rates) in polyethylene extrudates can affect seriously the crystalline nature of the polymer surface, slower cooling rates leading to a more effective migration to the interface of noncrystallizable materials which form weak boundary layers. In our experiments, it seems entirely possible that the degree to which weak boundary layers form at a polymer surface is dependent upon polymer composition and die L/R. Accepting as probable the existence of a temperature gradient along the length of the (massive) capillary die, it follows that this gradient would increase with L/R, thus attenuating the annealing history of the extrudate, and favoring the accumulation of less readily crystallizable components at the die wall interface. On exit from the viscometer, an appreciable radial temperature gradient is set up, and the magnitude of this would be expected to vary inversely with die L/R. Thus, following Tordella's findings,[13] there would again be increased tendency for noncrystalline moieties to migrate to the extrudate surface following long-die extrusion.

If the observed effects in swelling behavior and heats of solution originate largely from the crystallization behavior of the polymer, then they do not arise in the extrusion die exclusively. Instead, their magnitude should change measurably (at least in the case of calorimetric determinations) with time after extrusion. This could represent a useful objective for further inquiry. Qualitatively, the hypothesis is consistent with experimental observations of lower molecular weight components being increasingly surface localized as die length increases (e.g., the LDPE-2/LDPE-3 blend), and with less elastic (higher degree of branching? lower molecular weight?) components becoming increasingly responsible for the swelling behavior at greater die L/R of LDPE/Surlyn. On the other hand, a more dramatic exudation of noncrystalline EEA might have been expected in the calorimetric experiment then was actually found. The hypothesis assuredly restricts observation of these redistribution events to crystallizable polymers, and particularly to those with a wide molecular weight, and branch

incidence distribution. On both counts, polyethylene represents a much more favorable medium for the effect than does polystyrene.

CONCLUSIONS

Extruded samples of polyethylene fluids once again demonstrate a redistribution of material components. The reality of molecular redistribution has been shown by calorimetric as well as by more conventional extrudate swelling experiments. It is proposed that component redistribution may occur partly in the extrusion die, partly following extrusion, and may be due to weak boundary layer formation in the crystallizing polymer. In terms of this hypothesis, the molecular redistribution effect must be limited to crystallizable polymers with large polydispersity. The reported experiments further attest to the subtlety of polymer processing behavior and should serve as an incentive to its further study.

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