

Flow Properties of Molten Ethylene-Vinyl Acetate Copolymer and Melt Fracture

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Synopsis

In an investigation of the behavior and formation mechanism of melt fracture the flow properties of molten ethylene-vinyl acetate (EVA) copolymer in the region of high shear rate were measured with a capillary-type rheometer. EVA copolymer differs slightly in flow curve from low-density polyethylene (LDPE); it seems, however, that the difference is due to the difference in molecular weight distribution (MWD) rather than to the materials themselves. The fluidity of molten EVA copolymer having a narrow MWD is equivalent to that of LDPE having a broad MWD and, generally, EVA copolymer has a higher fluidity than LDPE. It is expected that the fluidity increases with incorporation of vinyl acetate at the same MWD and the same \bar{M}_w . The critical shear rate increases with melt index and temperature. It cannot be found that the materials themselves and the MWD directly influence the critical point of melt fracture formation when the melt index is taken as a parameter. The critical viscosity (η_c) at which melt fracture forms decreases in an almost straight line with an increase of melt index. It was found from the studies of end correction and behavior of melt fracture formation that melt fracture occurs at the inlet of the die, and it is supposed that the melt fracture formation is caused by the elastic turbulence in the flow pattern due to a failure of recoverable shear strain at the die inlet.

INTRODUCTION

Flow properties of molten ethylene-vinyl acetate (EVA) copolymer in the region of comparatively high shear rate were measured by means of a capillary-type rheometer in an investigation of mechanism of melt fracture formation. The studies of the flow properties of EVA copolymer melt are very important from the viewpoint of resin-processing, such as extrusion and molding, since, notwithstanding that the physical properties of EVA copolymer bear resemblance to those of gum,¹ EVA can be treated by the same method as polyethylene or plasticized poly(vinyl chloride) in its processing. It has been generally said, however, that melt fracture is more apt to form in EVA copolymer than in low-density polyethylene on account of its elastic behavior.

The object of this work was, first, to investigate the flow properties of the molten EVA copolymer as compared with those of low-density poly-

ethylene, giving special attention to the behavior of melt fracture, and, second, to consider the mechanism of melt fracture formation.

EXPERIMENTAL

Materials

The materials used in this work are listed in Table I. To investigate the effect of molecular weight distribution on the flow properties of EVA copolymer and low-density polyethylene melts, their molecular weight distributions were measured by means of gel permeation chromatography (GPC). Standard polystyrenes (prepared by Waters Associates, Inc.) were used for the calibration of fraction numbers for calculating \bar{M}_w and \bar{M}_n from the GPC pattern. It must be noted that the numbers do not always coincide with those by means of light-scattering and osmotic-pressure methods.² The measurements of all samples were carried out in the same run.

Procedure

In this work the capillary-type rheometer Koka Flow Tester³ was used with flat dies of length-to-radius ratios, L/D 10, 20, 30, and 36, $L/D = 0$ being a sharp-rimmed orifice. The reservoir temperature was controlled to within $\pm 1^\circ\text{C}$. at any desired temperature by means of a resistance heater and the thermistor-sensing element with appropriate electronic circuit. The force was applied to the polymer melt at any desired pressure in increments of 5, 10, or 20 kg./cm.² by a suitable combination of weights through a plunger by means of a lever arrangement. Especially in the neighborhood of the critical point at which the melt fracture forms the pressure was applied in increments of 2 or 5 kg./cm.².

The volumetric flow rate Q in cubic centimeters per second was exactly determined from the autorecorded curve which shows the relationship between downward displacement of the plunger (the cross-sectional area of the plunger is 1 cm.²) and the extrusion time. The end correction n was obtained by Baglay's method.⁴ The effective shear stress τ_{ew} and the actual shear rate $\dot{\gamma}$ at the wall of the capillary can be calculated by the following well-known equation, with the terms of the flow rate Q , the end correction n , the applied pressure P , and the dimension of die used (nozzle length L and radius R),

$$\tau_{ew} = PR/2(L + nR) \quad (1)$$

and Rabinowitsch's equation,⁵

$$\dot{\gamma} = (\dot{\gamma}_a/4)[3 + (d \ln Q / d \ln \tau_{ew})] \quad (2)$$

where $\dot{\gamma}_a$ is the apparent shear rate at the wall of the capillary and is defined by

$$\dot{\gamma}_a = 4Q/\pi R^3 \quad (3)$$

TABLE I
Materials Used in the Investigation

Material no.	Density	Melt index	VAC incorp., % ^a	Degree of branching (CH ₃ per 1000 C)	\bar{M}_w^b	\bar{M}_n^b	\bar{M}_w/\bar{M}_n
EVA copolymer							
A	—	1.18	14.8	—	71,800	21,200	3.4
B	—	1.33	19.0	—	63,000	21,100	3.0
C	—	7.01	14.3	—	57,100	14,900	3.8
D	—	2.90	28.2	—	44,300	17,400	2.5
E	—	9.31	8.3	—	—	—	—
Low-density PE							
F	0.917	0.40	—	—	129,600	19,400	6.7
G	0.917	1.18	—	—	100,000	17,000	5.9
H	0.916	8.03	—	—	—	—	—
I	0.924	20.6	—	—	—	—	—
J	0.923	2.32	—	34.0	48,000	11,300	4.2
K	0.924	2.10	—	29.3	47,600	11,900	4.0
L	0.920	1.15	—	37.0	52,500	12,600	4.2

^a Determined by infrared method; VAC = vinyl acetate.

^b Calculated from gel permeation chromatograph (GPC) pattern.

Then the actual melt viscosity η of EVA can be calculated by the definition of viscosity from the following equation:

$$\eta = \frac{\tau_{ew}}{(\dot{\gamma}_a/4)[3 + (d \ln Q/d \ln \tau_{ew})]} \quad (4)$$

The critical shear rate and shear stress where the melt fracture occurs were defined by the minimum values of the critical shear rates and shear stresses observed in each die.

RESULTS AND DISCUSSION

Flow Properties

Figure 1 shows the relationship between the actual melt viscosity and the actual shear rate of EVA copolymer A, and low-density polyethylene G; the melt indices of both resins are all the same, and those of EVA copolymer B are close to them. One can see from the figure that the relationship between $\log \dot{\gamma}$ and $\log \eta$ is described by two lines whose slopes are different.

Their intersecting point corresponds to the critical shear rate found on the curves of $\log P$ versus $\log \dot{\gamma}_a$ shown in Figures 2 and 3. An inclination of this kind has already been found in the case of low-density polyethylene⁶ and polypropylene,⁷ and it seems to be a special feature in cases in which a capillary-type viscometer is used. In this experiment the slope of the

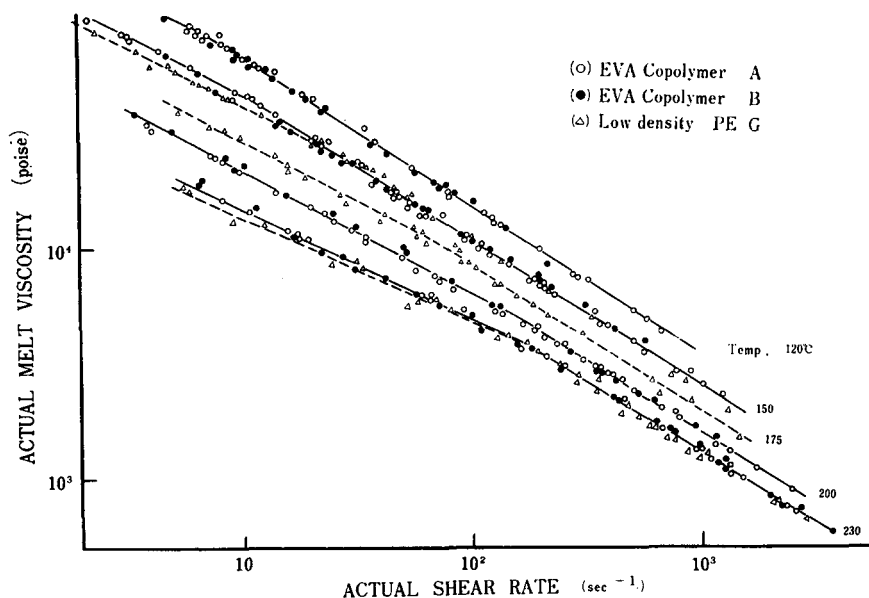


Fig. 1. Relations between actual melt viscosity and actual shear rate for three kinds of polymer.

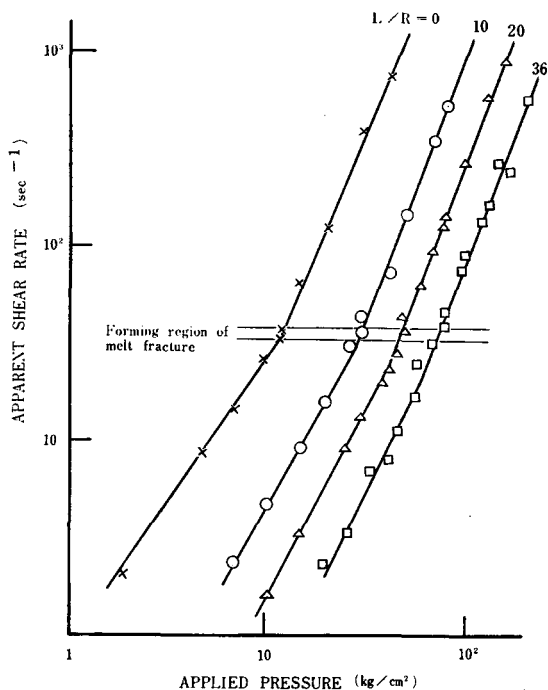


Fig. 2. Relations between applied pressure and apparent shear rate at 150°C. for EVA copolymer A.

straight line in the region of shear rate above the critical point was about -0.64 , having relation neither to the kind of resin nor to the temperature. However, in cases in which the shear rate is lower than the critical point the slope depends upon the kind of resin and temperature; that is, the slope of $\log \dot{\gamma}$ versus $\log \eta$ for low-density polyethylene G is lower than that of EVA copolymer A or B, and generally they decrease with increase of temperature as shown in Figure 1.

As is well known, the flow properties of polymer melt depend, not only upon the molecular weight and structure of the polymer and the temperature, but also upon the molecular weight distribution.⁸ Generally, melt viscosity of a polymer with broad molecular weight distribution exhibits greater reduction in its melt viscosity with increase of shear rate than does one with narrow molecular weight distribution.⁹

If the difference in shear rate dependence on melt viscosity between EVA copolymer and low-density polyethylene results from molecular weight distribution, it must be expected that a reduction in the melt viscosity of low-density polyethylene would be greater than that of EVA copolymer, since low-density polyethylene G has a broader molecular weight distribution than does EVA copolymer A or G, as seen in Table I. However, experimental data indicate that the shear rate sensitivity to melt viscosity is slightly greater in EVA copolymer with narrow molecular weight distri-

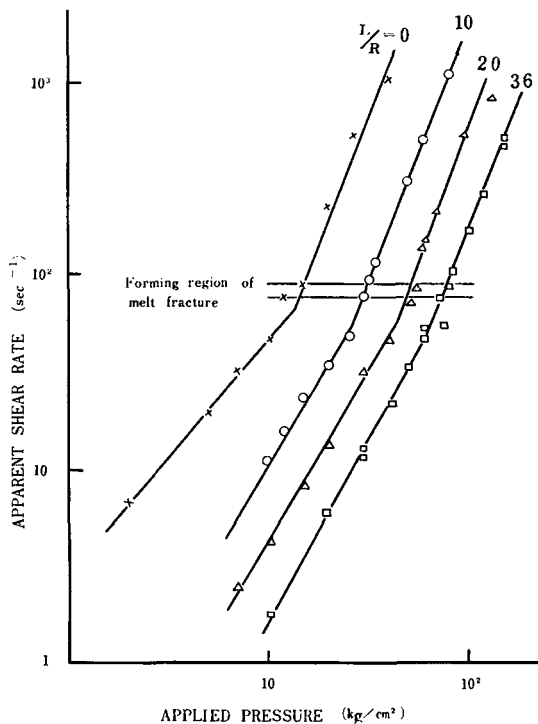


Fig. 3. Relations between applied pressure and apparent shear rate at 175°C. for low-density polyethylene G.

bution than in low-density polyethylene and also that the flow properties of molten EVA copolymer are like those of molten low-density polyethylene with broader molecular weight distribution.

This is illustrated by Figure 4, which shows the relationship between the melt index and weight-average molecular weight of low-density polyethylene and EVA copolymer. Generally, the broader the molecular weight distribution of the polymer, the higher its melt index, if the degree of branching is the same.¹⁰ One can see from the figure that the fluidity of EVA copolymer having a ratio \bar{M}_w/\bar{M}_n of about 3 may be equivalent to that of low-density polyethylene having a ratio \bar{M}_w/\bar{M}_n of 4 to 7; further, it is expected that, if the measure of the dispersity and the shape of the molecular weight distribution and weight-average molecular weight of EVA copolymer are similar to those of low-density polyethylene, then EVA copolymer may have the higher melt fluidity, and that, the higher its vinyl acetate content, the better its fluidity.

Figure 5 shows the relationship, at 150 and 190°C., between melt index and actual melt velocity at 5 and 50 sec.⁻¹ of the actual shear rate, respectively. This figure indicates that the melt viscosity of EVA copolymer is slightly higher than that of low-density polyethylene at low shear rates, such as 5 sec.⁻¹ of the actual shear rate, in the same melt index. How-

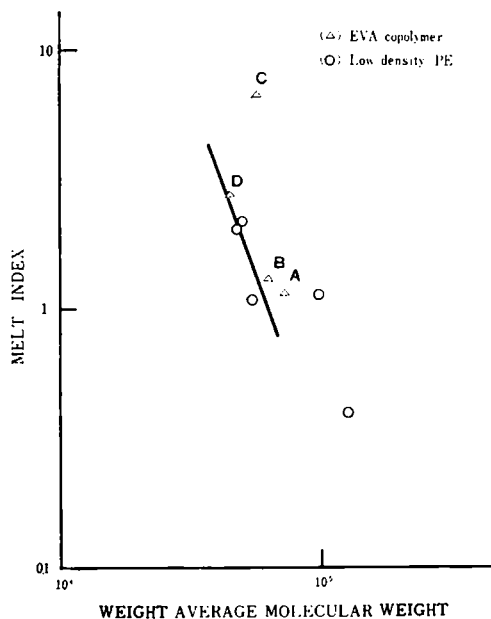


Fig. 4. Relations between melt index and weight-average molecular weight for low-density polyethylene and EVA copolymer. Solid line shows relation between melt index and \bar{M}_w for low-density polyethylene chosen within the limitation of 4 for the ratio \bar{M}_w/\bar{M}_m and also smooth shape of the molecular weight distribution curve.

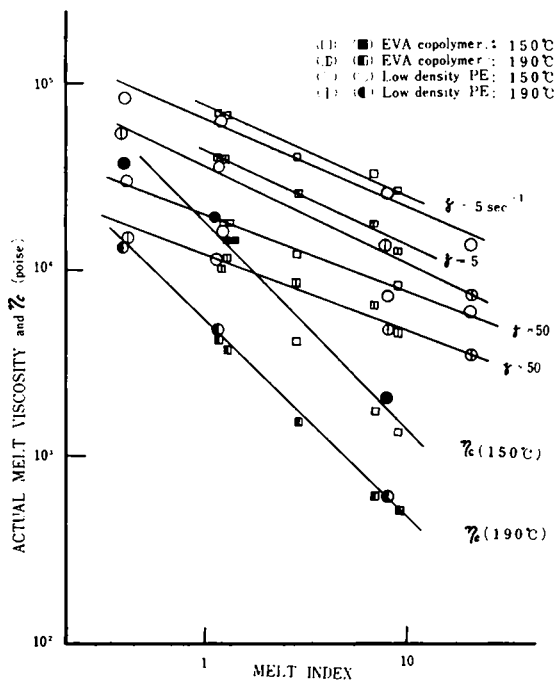


Fig. 5. Relations between melt index and actual melt viscosity at 150 and 190°C. η_c is defined as the ratio of the critical shear stress to the critical shear rate.

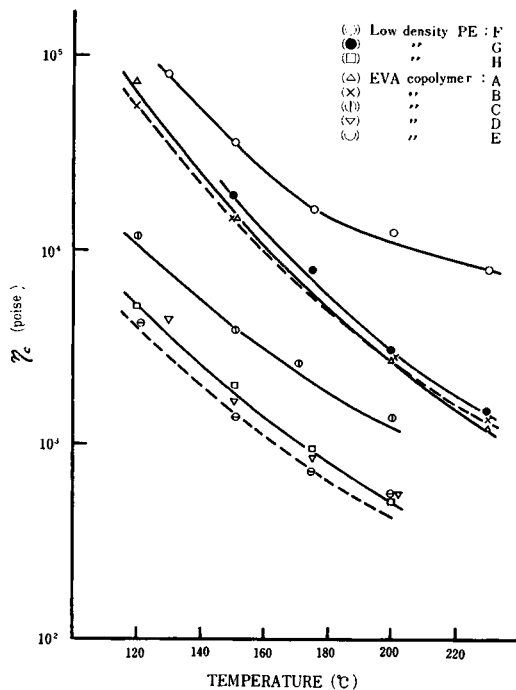


Fig. 6. Relations between temperature and η_c .

ever, in the case of such a high shear rate as 50 sec.^{-1} the difference due to the kind of polymer disappears with respect to melt viscosity. The difference in melt viscosity between EVA copolymer and low-density polyethylene may be due largely to the difference in molecular weight distribution rather than to the materials themselves. The reason why the influence of the incorporation of vinyl acetate on the melt viscosity is not found in Figure 5 is that the melt index is taken as a parameter.

As is well known, the critical shear rate at which melt fracture begins to form generally increases with temperature.¹¹ Figure 6 shows the temperature dependence, for EVA copolymer and low-density polyethylene, of the critical ratio of critical shear stress τ_{e0c} to critical shear rate $\dot{\gamma}_c$, that is, the critical melt viscosity η_c at which melt fracture occurs. The temperature dependence of η_c is greater than that of the melt viscosity ($\dot{\gamma} = \text{const.}$) and decreases rapidly with elevation of temperature. However, the effect of temperature on the formation of melt fracture becomes small at temperatures greater than about 180°C .

The relationship between η_c and melt index at 150 and 190°C . is described by a straight line having no relation to the kind of polymer, as shown in Figure 5.

Mechanism of Melt Fracture Formation

The mechanism of melt fracture formation has been studied by many investigators.¹²⁻¹⁶ Their chief recent studies indicate that melt fracture

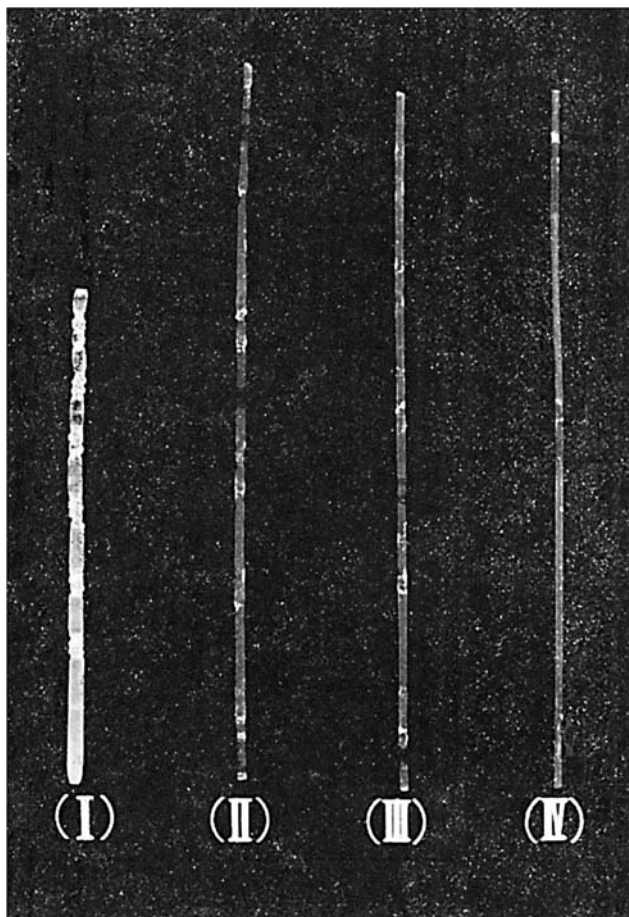


Fig. 7. Fractured extrudates extruded at 150°C. through dies 0, 5, 10, and 18 mm. in length within the limitation of an apparent shear rate of about 50 sec.⁻¹. Material is EVA copolymer A. Die lengths and apparent shear rates: (I) 1 ϕ \times 0 mm., 44.8 sec.⁻¹; (II) 1 ϕ \times 5 mm., 49.3 sec.⁻¹; (III) 1 ϕ \times 10 mm., 50.0 sec.⁻¹; (IV) 1 ϕ \times 18 mm., 47.1 sec.⁻¹ (ϕ is diameter of die in millimeters).

is caused by either elastic failure of the viscoelastic melts at the die inlet or the slip-stick effect at the wall of the capillary and also that these depend upon the materials.¹² In our work we investigated these factors on the basis of the results of our experiments.

In Figures 2 and 3 the relationship between $\log p$ and $\log \dot{\gamma}_a$ illustrates that melt fracture occurs at a constant value of apparent shear rate within the experimental errors having no relation to the L/R of the die. Even in the case of zero-length capillary no exception is found. At the critical point, however, the greater the length of the die becomes, the less becomes the instability of the extrudates, as shown in Figure 7. This is due to the relaxation phenomenon of polymer melt and means that melt fracture

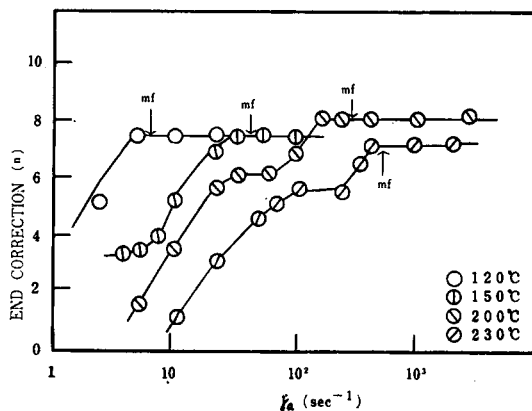


Fig. 8. Relations between end correction and apparent shear rate for EVA copolymer A; "mf" signifies melt fracture.

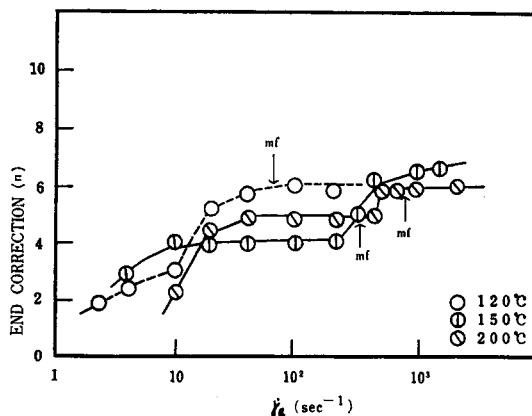


Fig. 9. Relations between end correction and apparent shear rate for EVA copolymer D.

occurs at the die inlet, because, if the formation of melt fracture is caused by slip-stick effects at the wall of the capillary, the degree of instability of the extrudate must be independent of the length of the capillary. Such a phenomenon may be found in the case of low-density polyethylene melts.

The relationship between the end effect of the capillary and the inflow pressure loss also has been studied by many investigators.¹⁷⁻¹⁹

In general, the end correction n should be divided into two parts, an elastic part and a viscous part, called the term of the Couette correction. Philippoff and Gaskins¹⁸ have reported a Couette correction of 0.57 in their study; Arai and Aoyama,¹⁷ 0.77. However, in the case of polymer melts the viscous term of total end correction may be lower than the elastic term.

Polymer melts may stagnate in the reservoir on account of an elastic behavior of the polymer melt, and in such case the "dead space" in the reser-

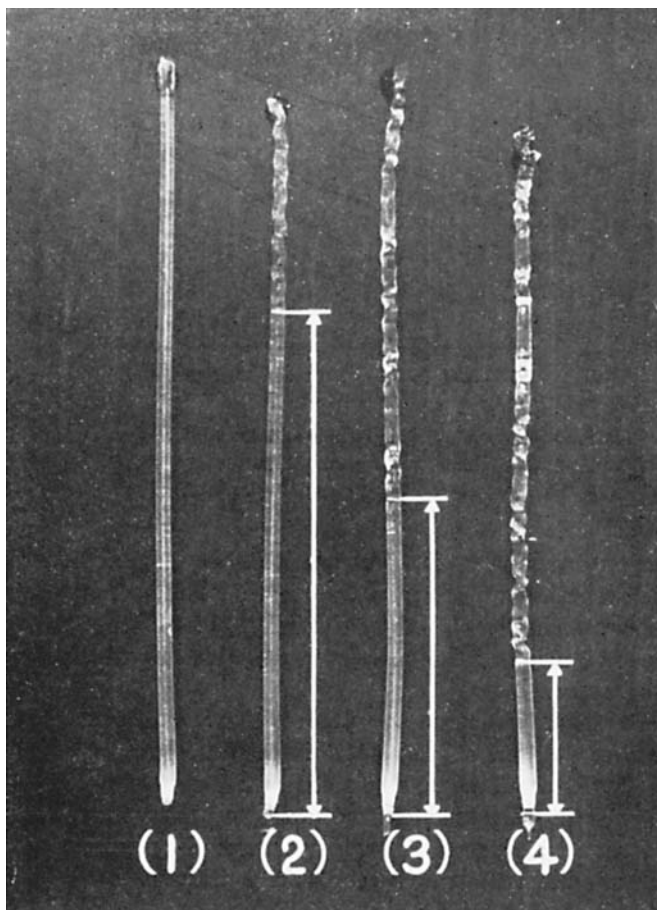


Fig. 10. Retardation effect of shear strain of polymer melt. The experimental conditions of the four extrudates are shown in Figure 11.

voir produces the effect of a lengthened capillary. Figures 8 and 9, which show the relationship between the end correction and the apparent shear rate, illustrate that in the case of either low temperature or low melt index of resin the end correction increases with apparent shear rate until melt fracture forms, after which it becomes constant; on the other hand, in the case of either high temperature or high melt index of resin two broad plateaus appear in the curve of end correction versus apparent shear rate. In the latter a melt roughness appears on the surface of the extrudate, but the point of formation of this roughness is obscure. Equation (1) expresses formally that this phenomenon is due to an increase of the inflow pressure drop resulting from growth of dead space and that the dimension of the dead space remains constant after melt fracture forms.

Baglay and Birks,¹⁶ however, have pointed out that in their visual observation the size and shape of the dead space is not affected by pressure to any

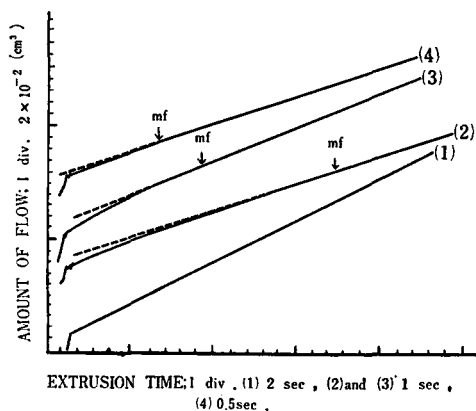


Fig. 11. Relations between extrusion time and amount of flow at 120°C. for EVA copolymer D. Apparent shear rates (sec.^{-1}) at steady state: (1) 67.9; (2) 92.6; (3) 122; (4) 190. Die diameter, 1 mm.; length, 0.5 mm.

marked extent, as long as the pressure is below that required to produce a distorted extrudate. It is expected from such facts that the great part of the inflow pressure loss is due to elastic behavior of both the dead space, which is expanding, and the polymer melt, which flows into the capillary over the dead space.

Baglay²⁰ has studied, moreover, the relation between melt fracture and end correction, and has pointed out that melt fracture occurs after the recoverable shear strain reaches a certain critical value and that the end correction is constant after the melt fracture forms. Our experimental results almost coincide with those of Baglay, though they are slightly different in detail and indicate that melt fracture formation is caused by the failure of the recoverable shear strain of the polymer melt.

Figure 10 shows four extrudates. Smooth extrudate 1 was extruded below the critical pressure; extrudates 2, 3, and 4, above the critical pressure. Melt fracture disappears in the initial part of the extrudates 2, 3, and 4.

The nonlinear part of the autorecorded curves shows the relation of the extrusion time versus the amount of flow (Fig. 11) and corresponds to the smooth part of the extrudates (arrows in Fig. 10) in each case. As seen in Figure 11, the apparent shear rate at which the smooth part of the extrudates is produced is greater than the melt fracture part in each case.

It seems that this phenomenon is due to a change of shear stress in the dead space that results in an increase of shear strain and that the time required for flow rate to become steady corresponds to the retardation time of the polymer melt.²¹

From the phenomenon described above it is seen that the mechanisms of melt fracture formation in EVA copolymer and in low-density polyethylene are basically the same and that their type of melt fracture is "inlet melt fracture," so named by Tordella.¹² It is also seen that these

melt fractures are the result of elastic turbulence in the flow pattern, due to a failure of recoverable shear strain of the polymer melt at the die inlet.

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References

1. R. Yamamoto, *Rubber Dig.*, **14**, No. 8, 66 (1961).
2. T. Takagi, T. Hashimoto, and S. Kido, *Sci. Rept. Toyo Soda Mfg. Co., Ltd.*, **11**, 8 (1967).
3. T. Arai, *A Guide to the Testing of Rheological Properties with Koka Flow Tester*, Maruzen, Tokyo, 1958.
4. E. B. Baglay, *J. Appl. Phys.*, **28**, 624 (1957).
5. B. Rabinowitsch, *Z. Phys. Chem.*, **A145**, 1 (1929).
6. J. P. Tordella, *J. Appl. Phys.*, **27**, 454 (1956).
7. K. Kamide, Y. Inamoto, and K. Ohno, *Kobunshi Kagaku*, **22**, 529 (1965).
8. H. V. Boening, *Polyolefins*, Elsevier, Amsterdam, 1966, p. 270.
9. J. E. Pritchard, *Modern Plastics Encyclopedia*, **44**, 237 (1967).
10. B. Tamamushi, *Rheology Handbook*, Maruzen, Tokyo, 1965, p. 25.
11. J. P. Tordella, *SPE J.* **36** (1959).
12. J. P. Tordella, *J. Appl. Polymer Sci.*, **7**, 215 (1963).
13. O. Bartos, *J. Polymer Sci. B*, **3**, 1025 (1965).
14. J. J. Benbow and S. Lamb, *SPE Trans.*, **B3**, 7 (1963).
15. J. P. Tordella, *Trans. Soc. Rheol.*, **1**, 203 (1957).
16. E. B. Baglay and A. M. Birks, *J. Appl. Phys.*, **31**, 556 (1960).
17. T. Arai and H. Aoyama, *Trans. Soc. Rheol.*, **7**, 333 (1963).
18. W. Philippoff and F. H. Gaskins, *Trans. Soc. Rheol.*, **2**, 263 (1958).
19. M. Ishimaru, et al., paper presented at the Annual Symposium on Polymer Chemistry, Nagoya, Nov. 4, 1963.
20. E. B. Baglay, *J. Appl. Phys.*, **31**, 1126 (1960).
21. T. Arai, *Measuring Methods of Rheology*, Kyoritsu, Tokyo, 1965, p. 102.

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