

Influence of Shearing History on the Properties of Polymer Melt. II.

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Synopsis

The flow pattern of molten polymer through capillaries was studied by using a tracing method. An incompatible polymer was added to polypropylene as a tracer, and the influence of shear in a capillary rheometer on the tracer particle size as well as on the distribution of the particles in the extrudate in relation to flow was studied. It was found that the particle size varied inversely with shear rate of extrusion, capillary aspect ratio, polymer viscosity, and extrusion temperature. The flow was found to be of the telescopic type, and the tracer particle size was independent of position along the radius of the cylindrical extrudate. It is assumed that the supermolecular structure of a polymer melt is of the cluster type suggested by Busse, and it is postulated that spherical clusters of molecules in the melt are modified by shear analogously to the spherical particles of the incompatible tracer polymer. The large spectrum of melt properties obtainable, by various shearing treatments, from a polymer of constant molecular structure suggests that a wide range of supermolecular structures must be possible in the polymer melt.

INTRODUCTION

In part I of this series,¹ an Instron capillary rheometer was used to investigate changes of shear stress at a given shear rate in relation to the previous shear history of samples of the same propylene polymer. It was found that both the shearing intensity in previous extrusions and the geometry of the entrance section to the capillary had substantial effects on the shear stress-shear rate relationship; apparent viscosity was changed by as much as one third and the slope of the viscosity versus shear rate curve was also affected. Similarly, as indicated by die swell studies, the normal stress in flow through capillaries varied with shearing history. It was postulated that change of melt supermolecular structure was the basis for these differences in the measured properties of polymer melts from essentially the same polymer.

Elucidation of the actual polymer supermolecular structure and the mechanisms of the changes in the polymer properties constitutes an extraordinarily interesting problem. An investigation of one aspect of this

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problem is reported here. Patterns of polymer flow were studied by observing the size as well as distribution of particles of an incompatible second polymer phase following extrusion through capillaries as used in part I of this work.¹

EXPERIMENTAL

Two polypropylenes of different molecular weight, coded A and B, were blended with ten parts per hundred of poly(ethylene-oxy-benzoate) of formula $[-\text{CH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{COO}-]_n$, subsequently designated PEB. Shear stress-versus-shear rate curves for the pure polymers and for the blends are given in Figure 1. The two polymers, polypropylene and PEB, are incompatible; the polyester was dispersed in the polypropylene as a separate phase of typically spherical globules. Their shape and size suggested that the interfacial tension between polymer phases was substantial. Polymer blends of A and B with ten parts per hundred of PEB were prepared in a screw extruder; they are designated as blend A and blend B.

The blends were extruded with the Instron rheometer using capillaries of 0.5-mm diameter and various lengths; the entrance angles were 180 and 20 degrees. Extrusions were carried out at 240°, 250°, and 260°C, and the extrudates were examined microscopically to observe the dispersion of the PEB phase.

In another experiment, conducted with melt spinning equipment, blend A was extruded, and the extrudate was subjected to axial extension while still in the molten state. The filaments obtained were subsequently neck-drawn and then examined microscopically.

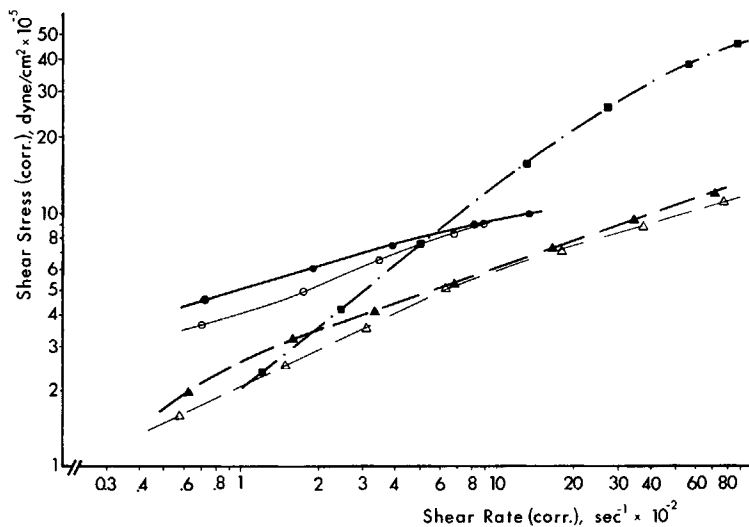


Fig. 1. Relation between corrected shear stress and shear rate at 240°C: (●) polymer A; (▲) polymer B; (■) poly(ethylene-oxy-benzoate) (PEB); (○) polymer A plus 10 pph PEB; (△) polymer B plus 10 pph PEB.

RESULTS

Figure 2 represents photomicrographs of cross sections of extrudates obtained in extrusion of blend A through a flat-entry capillary to aspect ratio 20, at shear rates of 50, 250, and 500 sec^{-1} . The approximately spherical shape and nonuniformity of size of the PEB globules are apparent, but it is also clear that the average globule size decreased markedly with increasing shear rate. Average PEB globule diameters were obtained from measurements on photomicrographs for all blend extrusions conducted. Average particle diameters are presented as function of shear rate in Figure 3 and of extrusion pressure in Figure 4, for extrusions of blends through flat entry capillaries of aspect ratio 3 and 20 and through a 20-degree conical entry capillary of aspect ratio 9. It will be noted that the average globule size, obtained with no extrudate stretching other than by the effect of gravity acting on a short length, decreased with increase of shear rate or extrusion pressure in every case. In the cases where the data were obtained at three shear rates, the decreases in particle size were not linear. The true relationships of average particle size to shear rate or to extrusion pressure appear to be representable by curves concave upward, perhaps asymptotic to some limiting value at high shear rate. Segments of straight lines have been drawn connecting the points in the figures for lack of sufficient data to permit drawing of curves with confidence.

Figure 5A is a low-magnification photomicrograph of the entire cross section of the extrudate. Figure 5B is a photomicrograph at higher magnification of a portion of a longitudinal section of the same extrudate. Both views show that the extrudate has a definitely laminar structure; the PEB globules appear to be concentrated along straight flow lines at constant radius, with relatively few particles in the space between the lines of concentration. Examination of these and other photomicrographs, irrespective of the shear rate of the specimen extrusion, revealed also that the

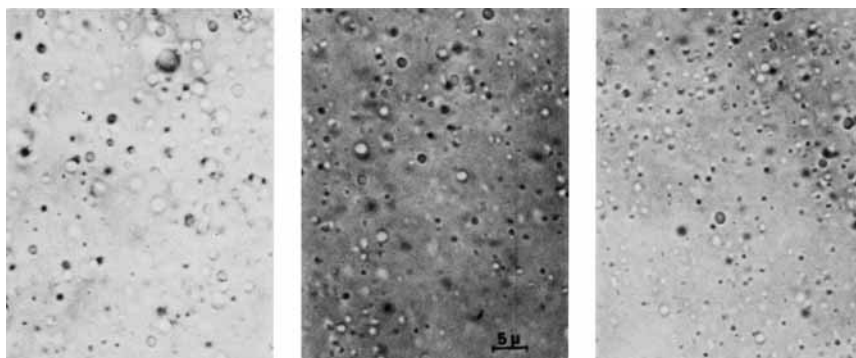


Fig. 2. Photomicrographs of the cross sections of polypropylene-poly(ethylene-oxybenzoate) blend. Extruded through a flat entry capillary at different shear rates: (A) 50 sec^{-1} , (B) 250 sec^{-1} ; (C) 500 sec^{-1} .

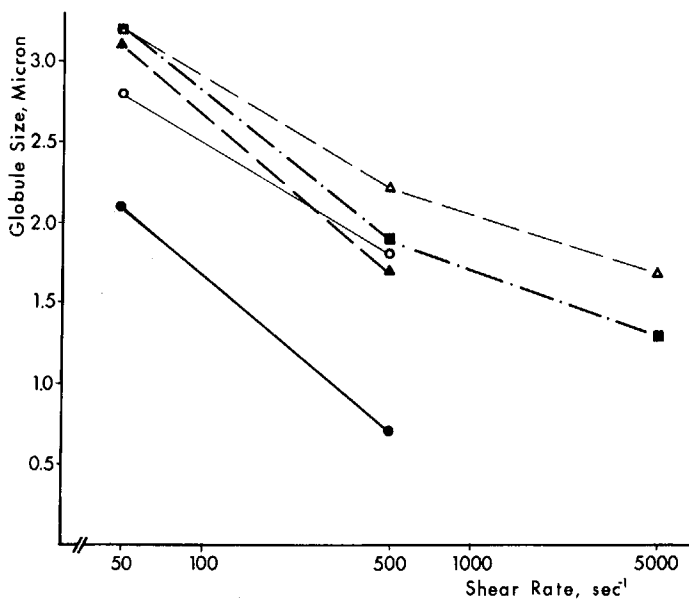


Fig. 3. Size of the poly(ethylene-oxy-benzoate) globules in relation to the apparent shear rate. Parameter: capillary type; (▲) entrance angle 180° , $L/D = 3$; (●) entrance angle 180° , $L/D = 20$; (■) entrance angle 20° , $L/D = 9$; black points, blend A; open points, blend B.

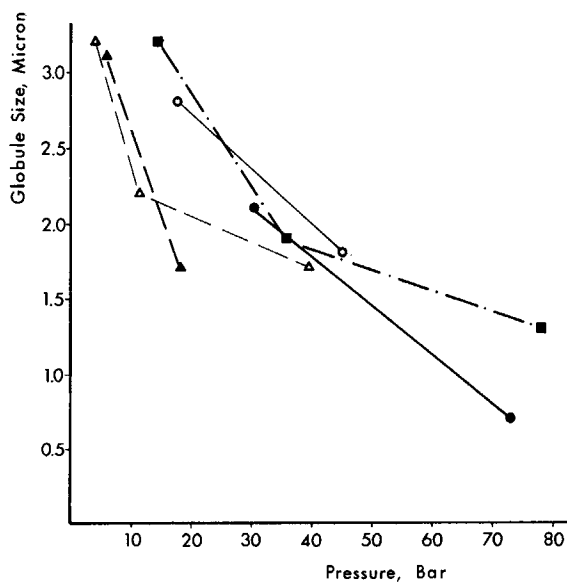
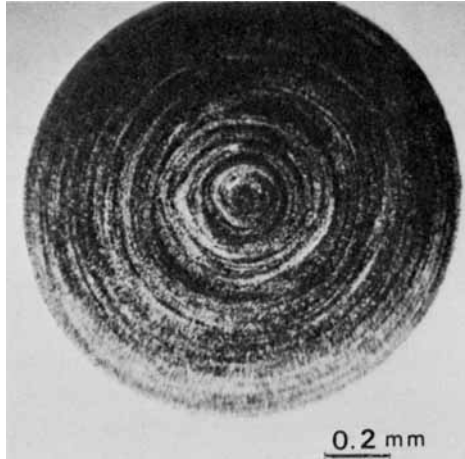
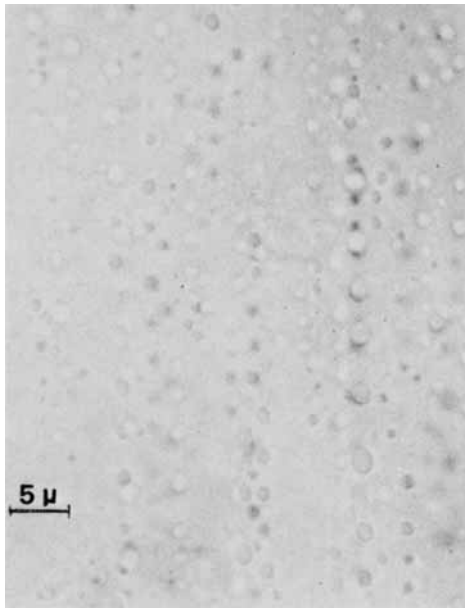


Fig. 4. Size of the PEB globules in relation to the extrusion pressure. Parameter: capillary type; (▲) entrance angle 180° , $L/D = 3$; (●) entrance angle 180° , $L/D = 20$; (■) entrance angle 20° , $L/D = 9$; black points, blend A; open points, blend B.

average particle size of PEB globules was constant for a given extrudate, independent of radial position. The flow pattern suggested by Figure 5A may be described as "telescopic," and this seems to have also a logical connection with the influence of capillary length on the globule size.



(a)



(b)

Fig. 5. Micrographs of the extrudate of polypropylene-poly(ethylene-oxy-benzoate) blend: (A) perpendicular cross section; (B) longitudinal cross section. The telescopic type of flow is clearly recognizable.

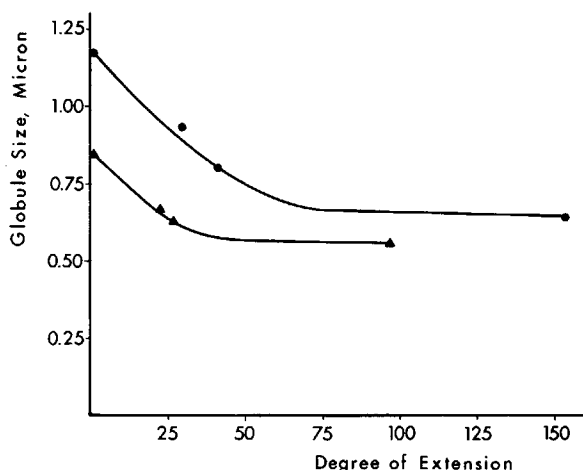


Fig. 6. Change of the size of the poly(ethylene-oxy-benzoate) particles with extension of the extrudate.

Figure 6 represents average globule size data obtained in experiments performed by extruding through two different capillaries mounted in the spinnerette position of a melt-spinning machine, and stretching the extrudate between the extrusion capillary and the take-up godet of the machine. The two capillaries were of different diameters and entrance angles selected so that, though at largely different shear rates, the extrudates had the same diameter. Samples were taken for microscopic observation by cutting sections of the extruded filament at different distances below the capillary. The extension ratios in Figure 6 are the ratios of local filament velocity, obtained from filament cross section, to the velocity calculated from the cross section at the die swell bulge where the velocity is at its minimum. The filament attenuation represented by the extension ratios in Figure 6 occurs with progressive decrease of filament temperature, and eventual solidification of the filaments.²⁻⁴ Figure 6 demonstrates that Trouton flow in the attenuation of a molten filament affects the globule size of a dispersed phase similarly to flow within a capillary.

Some of the filaments produced in the experiments represented in Figure 6 were subsequently drawn under conditions in which a localized neck was formed. Microscopic examination showed that the PEB globules, spherical in the undrawn filaments, were stretched out longitudinally in drawing, and their cross section diameters were reduced to the order of 0.1 micron, a size range in which measurements by optical microscopy are no longer possible.

DISCUSSION

It has been proposed that large molecules are subject to mechanical interaction, generally referred to as molecular entanglement.⁵ Many

properties of polymer solutions and melts would be unexplainable without accepting the possibility of such interaction. Similarly, the sensitivity of polymer behavior toward shearing history¹ seems to be explainable only with the help of some kind of entanglement theory. Although successful to some extent, the molecular entanglement theories published to date consider mainly interaction only between a few molecules, or segments of the same molecule.⁶⁻⁹ Experimental evidence recently published indicates that the molecules in a melt, or in a solid noncrystalline polymer, are aggregated into more or less spherical balls.¹⁰⁻¹³ Comparison between the reported dimensions of these molecular clusters and the macroscopic polymer density suggests that a cluster of polyethylene molecules may consist of from 4 to more than 100 individual molecules.

Mechanical perturbations of an assembly of coiled balls of molecules with some molecular interconnections may be expected to cause recombination and regrouping of the individual molecules, leading to changes of the average number of molecules per ball-like cluster. Although the dimensions are between one and two orders of magnitude larger, the volume change of the PEB tracer particles under shearing or traction may be considered to parallel the changes postulated to take place in the supermolecular structure of a sheared polymer melt. By analogy, one may expect that shearing, particularly intensive shearing, decreases cluster size. It is easy to visualize that the average size of molecular clusters as well as the size distribution would influence polymer melt properties, particularly flow.

In addition to the size of the balls of entangled molecules, the number, length, and type of interconnections existing between clusters should have a significant effect on the polymer properties. Some of the tie molecules may just penetrate a cluster, and some of them may loop around other molecules within it, creating very strong connections.

One may speculate also that the structure of the molecular clusters may vary; the molecules may be entangled to varying degrees. Such variations would create clusters with different ease of reorganization.

These three aspects of the postulated supermolecular morphology of a melt—average cluster size, interconnection of clusters, and degree of entanglement within clusters—would all be expected to contribute to variations in the detailed rheological responses of polymer melts identical with respect to molecular composition. While polymer molecular weight and weight distribution unquestionably remain primary determinants of melt rheological properties, the observations reported in the papers of this series indicate that substantial rheological variability can occur with no change in these molecular properties, as a result of a change of supermolecular structure produced by a prior history of shear. Considerations of molecular energy will certainly limit the range of supermolecular structures which can exist, and the molecular mobility in the melt, prior to extrusion, will limit the degree to which structural differences induced by previous shearing persist to affect observed extrusion behavior. The present work

is evidence that some differences in morphology do exist and persist sufficiently to be observed.

The microscopy involved in this study was the work of Mr. Paul J. Rau, whose assistance is gratefully acknowledged.

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Received June 21, 1972

Revised July 19, 1972