

NOTES

Surface Melt Fracture in Polymer Extrusion

Two types of filament defect have been observed when polymer melts are extruded through a capillary. First, above a certain critical shear stress melt fracture¹ (elastic turbulence²) occurs in the interior of the melt at the die entry which results in gross filament defects.^{3,4} Second, a defect which appears to be a surface phenomenon is also observed.⁵ The purpose of this note is to describe a particularly striking example of this second (surface) defect observed during studies of the behavior of polyvinylidene fluoride (PVF 2) and to suggest that this second defect arises from a melt fracture process originating on the surface of the extrudate.

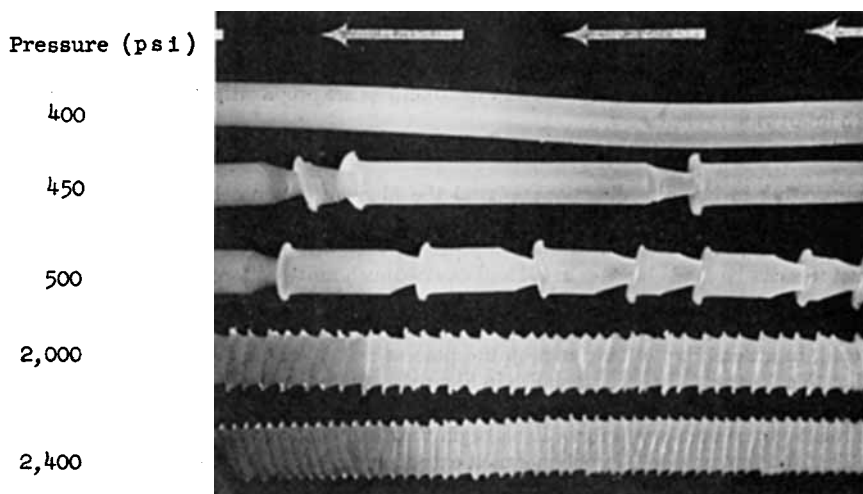


Fig. 1. Filaments of high molecular weight polyvinylidene fluoride extruded at 240°C. showing extreme matte. Extrusion is from right to left.

The resin, supplied by Pennsalt Chemicals Corp., was a commercial grade material, designated Grade 15, of estimated molecular weight greater than 1,000,000. The PVF 2 was extruded through a flat entry capillary of radius 0.1042 cm. and length to radius ratio 7.68, mounted in a viscometer previously described.⁶ The experiments were carried out at 240°C. and the quantitative results have been reported previously.⁷

The appearance of the extrudate is illustrated in Figure 1. At pressures of 400 psi and below, the extrudate is smooth and cylindrical in shape. At pressures of 2,000 psi and above the surface roughness (matte finish) previously observed during extrusion of high density polyethylene is obtained.⁵ At intermediate pressures this surface roughness becomes particularly striking. Examination of the filament suggests that at 400 and 450 psi a fracture of the melt has occurred at a specific point from which the fracture has propagated in two directions around the outside of the filament and radially inward at the same time. Because the filament is being continuously extruded the resultant fracture plane is not perpendicular to the direction of flow but forms an angle less than 90° with the extrudate axis. As the fracture plane propagates inward the highly oriented outer layers of the polymer melt peel back from the fracture surface. The two fracture planes,

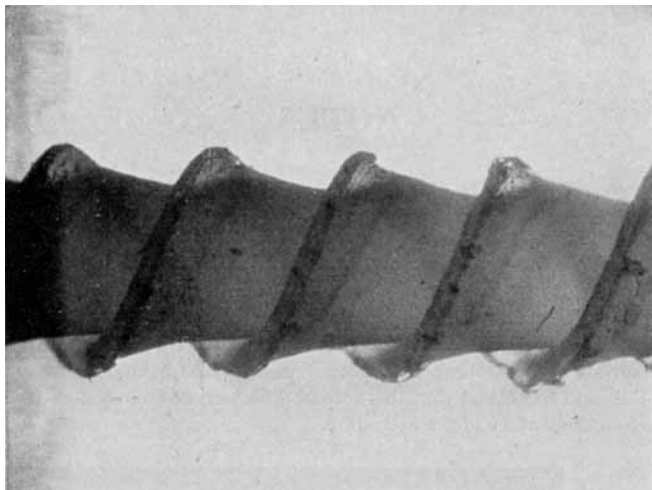


Fig. 2. Extrudate of polyvinylidene fluoride produced at 240°C. Surface fracture has occurred at two separate points and the fractures are propagating separately to form two intertwined spirals.

propagating in opposite directions around the filament, ultimately intersect and the propagation ceases. Subsequent extrudate then remains smooth until a surface fracture again occurs. By careful adjustment of pressures the "wavelength" or distance between fractures can be made large or small and can be much more uniform than shown in the Figure 1.

If the surface fracture propagates only in one direction around the filament there would, in general, be nothing to stop the process and a "screw thread" should result. That this does actually occur is shown in Figure 2. Here the line of surface fracture and the fracture plane are evident. (Note in this case the presence of two independent spirals.) Once such spiral formations begin they can continue indefinitely.

That fracture processes in polymer melt extrusion can occur at more than one location has been shown by Tordella⁸ and Benbow and Lamb.⁹ Using a birefringence technique they found^{8,9} that in addition to melt fracture in the die entry region a fracture process can occur within the capillary itself, possibly at the capillary wall. Such a process might be termed slip at the wall. Whether the melt fracture process considered in this note occurs at the capillary wall (i.e., is due to slip at the wall) or whether it represents still a third site of melt fracture is not, at the moment, known.

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References

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Solutions of Neutralized Poly-(acrylic acid) in Mixtures Water-Ethanol

It is well known that generally polyelectrolytes dissolve better when charged than in the uncharged state. The best known example for this is the minimum of the solubility of many proteins at the isoelectric point. The opposite was observed in solutions of poly-(acrylic acid) (PAA) in water-ethanol mixtures and is reported herewith.

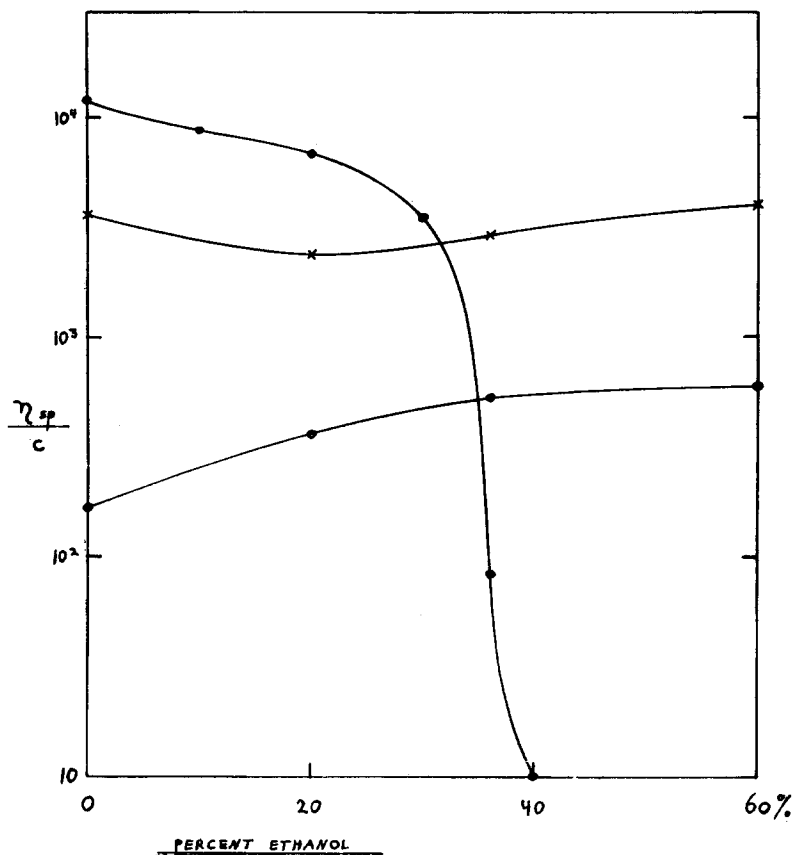


Fig. 1. The reduced specific viscosity of poly-(acrylic acid) ($c = 5.7 \times 10^{-4}$ g./cc.) in Water-ethanol mixtures (volume percentage) at 30°C.: O in 0.2N hydrochloric acid; X with no addend; ● fully neutralized with sodium hydroxide.