

Capillary Extrudate Puff-Up of PVC and Other Structural Melts

The extrudate swell or puff-up (the Barus effect) of commercial poly(vinyl chloride) (PVC) at extrusion temperatures is unusual. For amorphous polymers, such as polystyrene above the glass transition temperatures or polyethylene (PE) in the liquid state, the capillary extrudate swell is usually large and has an inverse dependence on temperature at constant rates of shear. For PVC, however, it is found that puff-up increases with increasing temperatures and that the levels of puff-up are quite small. The explanation of the anomalous behavior of PVC is felt to lie in the fact that PVC is still crystalline at the processing temperatures and that this crystallinity leads to structural units in PVC melts. (Various estimates indicate that $T_m \sim 200^\circ\text{C}$. for PVC.)

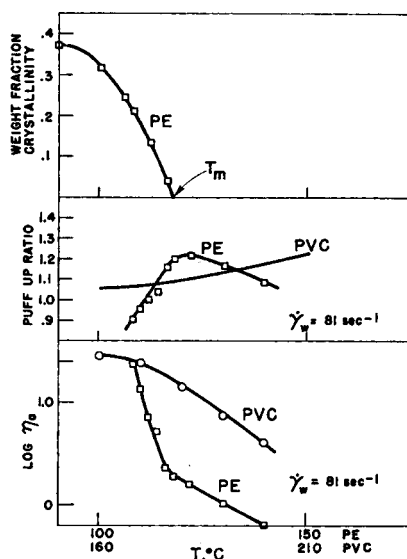


Figure 1.

If one starts with a suspension or emulsion PVC resin, then one has a particulate structure consisting of partially interfused large deformable particles. (Subsequent to this writing Berens¹ has advanced evidence that indicates PVC melts consist of large flow units. Ballman also has suggested that such flow units exit in PVC melts² and, Mooney³ has claimed that even amorphous melts consist of deformable flow units.) As the crystallinity decreases, the deformability of the particle increases. At the lowest temperatures one might imagine that in the extrusion process one is mainly shifting around rigid spheres.⁴ Thus a high viscosity and low puff-up are expected. As the deformability of the particles increases (by decreasing crystallinity with increasing temperature) the particles become elongated and partially fused in the extrusion process. The puff-up should thus increase and the viscosity decrease as the melting point is approached.

To lend support to the above argument, capillary extrusion rheometer measurements on a PE system consisting of 25- μ diameter particles (Microthene, U.S. Industries) were obtained at temperatures below but near T_m and also above T_m . Figure 1 shows apparent viscosity and puff-up, at a constant shear rate, over a range of temperatures for the polyethylene system. Superimposed are data for a commercial PVC (Opalon 630, Monsanto Co.). In obtaining these data the rheometer was refilled with new material at each test temperature. Dilatometric estimates of crystallinity (courtesy of J. R. Taylor, Monsanto Co., Springfield, Mass.) on the polyethylene system are also shown.

As is observed from Figure 1, the puff-up for the PE indeed increases until the melting point is reached, at which point the puff-up begins to decrease with increasing temperature. Since this PE system is clearly crystalline (temperature rise in the capillary was estimated to be a negligible value), then it ought to retain some of its initially particulate nature in the extrusion process below T_m . Note, however, that the slopes of the curves for PE and PVC differ considerably. This may be expected if the melting ranges differ for the two materials, as is probably the case.

It is thus felt that the explanation advanced for the puff-up behavior of PVC has merit. It is hoped in the near future to treat the puff-up behavior of polymer melts consisting of deformable particles or flow units.

References

1. A. R. Berens and V. L. Folt, paper presented at the Society of Rheology Meeting, Santa Barbara, Calif., February, 1967.
2. R. L. Ballman, private communication, 1965.
3. M. Mooney. *J. Appl. Phys.*, **27**, 691 (1956).
4. N. E. Aubrey, private communication, 1960.

STEPHEN STRELLA

Hydrocarbons and Polymers Division
Monsanto Company
Springfield, Massachusetts 01101

Received June 2, 1967

Revised July 31, 1967