NOTATION

k = thermal conductivity, W./(m.)(°K.)
M = molecular weight
T = temperature, °K.
T_c = critical temperature, °K.
T_r = T/T_c, reduced temperature
V_c = critical molecular volume, cu.m./k.mole

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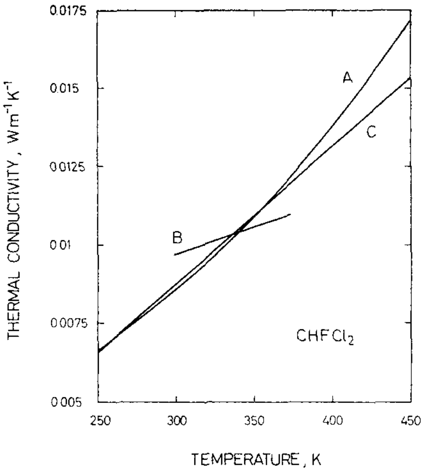

Fig. 2. Gas thermal conductivity of monofluorodichloromethane, CHFCl$_2$: (A) Touloukian et al. *(10)*, (B) Landolt-Börnstein *(5)*, (C) Equation (2).

Die Swell Behavior of Two-Phase Polymer Melts

CHANG DAE HAN and THOMAS C. YU
Department of Chemical Engineering
Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

It has long been believed that the increase in diameter that extrudate undergoes after leaving the die (hereafter called die swell) is characteristic of the elastic properties of visco-elastic fluids. In particular, there is abundant literature (*1* to *6*) concerning studies made on polymer melt die swell. This is because polymer melt die swell is closely associated with determining the most desirable operating conditions of various processing devices. Die swell measurements have often been used for designing dies for plastic extrusion and spinneretts for fiber spinning, etc.

However, most of the literature published to date has dealt with melt die swell behavior of homopolymer systems, but very little has dealt with incompatible two-phase systems. With respect to two-phase systems, it would be most desirable for practical purposes today to establish some kind of correlation between the die swell ratio and the composition ratio of individual components. Commercially important two-phase systems, for example, high-impact polystyrene and ABS resin, have different grades of the materials based on the amount of the rubbery component contained in each resin.

The purpose of this paper is to present some new experimental data on the polymer melt die swell behavior of two-phase systems. The two-phase systems chosen for study are blends of polystyrene and high density polyethylene.

EXPERIMENT

Materials

Blends were prepared from two polymers. These were: high density polyethylene (Union Carbide DMDJ 5140) which has a polydispersity ($\overline{Mw}/\overline{Mn}$) of about 8.4, and melt index of about 0.8, and general purpose polystyrene (Dow Chemicals STYRON® 686). The blending ratios and sample codes are given in Table 1.

Polymer blends were prepared by mixing the two polymers, in the form of pellets, in a tumbling operation. Fortunately, the pellet sizes of both polymers were almost identical (about 1/8 in.) and hence no particle segregation was observed when the blends were fed to an extruder.

Apparatus and Experimental Procedure

The description of the apparatus used in the present study has been given in a previous paper (*7*), and the detailed layout of the die design has been given in another recent paper by the authors (*8*) in which it was stated that the capillary diameter was 0.125 in. In the present study die swell measurements were taken with an L/D ratio of 4 at 200°C. The experimental procedure for the measurement of die swell is as follows:

1. Polymer melt flows vertically through a capillary device and into a chamber, about 15 in. long, maintained at a temperature the same as the capillary. The chamber is equipped with

TABLE 1. BLENDING RATIOS AND SAMPLE CODE OF TWO-PHASE SYSTEM

Sample code	Blending ratio
PS	100% polystyrene
PS/PE = 20/80	20% polystyrene and 80% polyethylene
PS/PE = 50/50	50% polystyrene and 50% polyethylene
PS/PE = 80/20	80% polystyrene and 20% polyethylene
PE	100% polyethylene

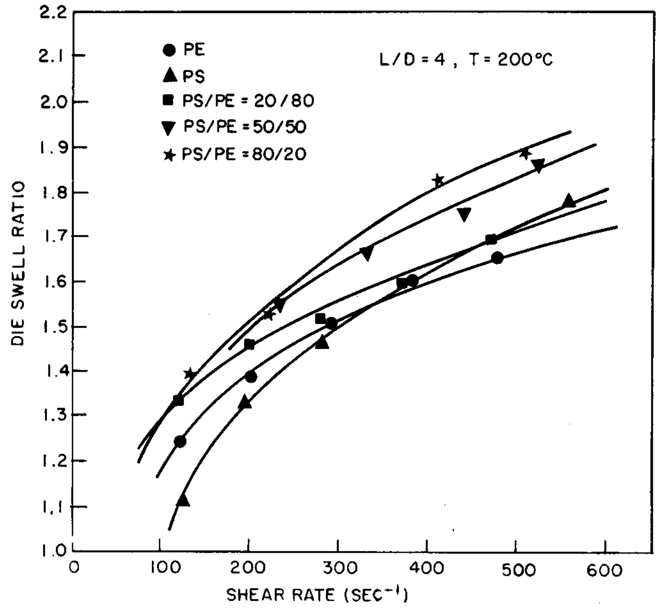

Fig. 1. Die swell ratio versus shear rate for polystyrene/polyethylene systems ($L/D = 4$, $T = 200°C$.).

a small pyrex window.

2. When a steady flow has been achieved, pictures are taken of the flowing polymer stream through the pyrex window at a distance of about 26 in. above the floor level. This distance has been kept constant throughout the whole experiment, so that pictures taken of all extrudate diameters might be approximately under the same gravity effect. Reasons for having determined the die swell ratio in this manner, instead of the experimental method recently suggested by Han and Charles (*5*), will be given below.

3. The melt diameter is then determined by comparison of the melt images to that of a standard.

RESULTS AND DISCUSSION

Figure 1 shows plots of die swell ratio versus shear rate for two pure components (PS and PE) and three two-phase blends using a die with an $L/D = 4$ at 200°C. One may notice from Figure 1 that the die swell ratios of polystyrene and polyethylene melts are relatively small compared to those reported in the literature (*1* to *6*). That is because the die swell data presented here has been taken under the influence of gravity as described above. The reasons why die swell measurements were taken in this way is as follows.

An attempt was first made to cut the flowing polymer stream at the die exit and to stop flow, in order to have a complete relaxation of stress which would yield a maximum die swell. However, the suspended melt stream underwent a tremendous recoil which shrunk its length from about 3 in. to less than 2 in. in less than 1 min. The length of recoil depends on the weight of the polymer stream hanging at the die exit. As a result of recoil, the swollen extrudate diameter was unusually large, which we felt was not due to the stress relaxation alone. Figure 2 shows a comparison of a recoiled extrudate sample with an extrudate sample collected under gravity for the PS/PE = 50/50 two-phase system. Furthermore, it was found that the final diameter of the recoiled extrudate sample was very sensitive to the relative position at which the flowing melt stream was initially cut. It was therefore felt that consistent die swell measurements for different blending ratios were not possible for the two-phase systems investigated by this method, which was recently suggested by Han and Charles (*5*).

Another attempt made was by an annealing procedure. This method did not work either, because polyethylene crystallizes out of the polystyrene/polyethylene mixture upon cooling and the result is a nonuniform extrudate diameter.

Therefore, it was finally decided that, under the circumstances described above, any method which would give consistent die swell measurements throughout the whole experimental program would be satisfactory, even if not the best, so long as a special care is given to impart the same gravity effect to all die swell measurements taken, and the die swell measurements are to be used for comparative purposes only.

Figure 3 shows plots of die swell ratio versus shear stress for two-phase systems with an $L/D = 4$ at 200°C. Recently, Han (*9*) suggested the use of such plots, instead of

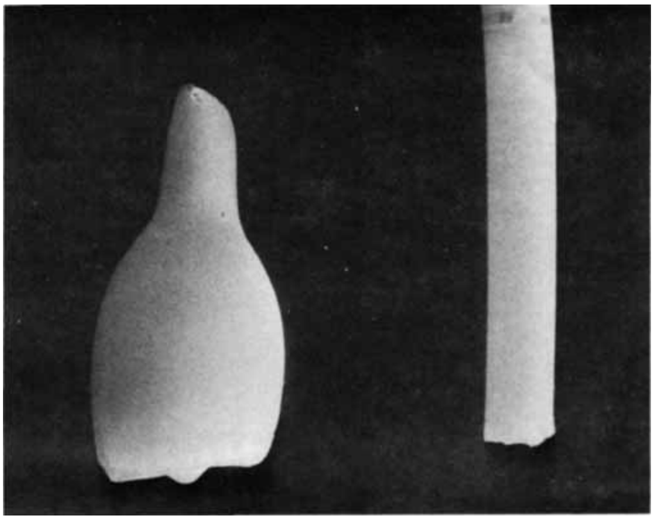

Fig. 2. Pictures taken of extrudate samples for $PS/PE = 50/50$ two-phase system; (a) Extrudate 2 min. after cut from flowing stream, (b) Extrudate collected under gravitational force ($L/D = 4$, $T = 200°C$.).

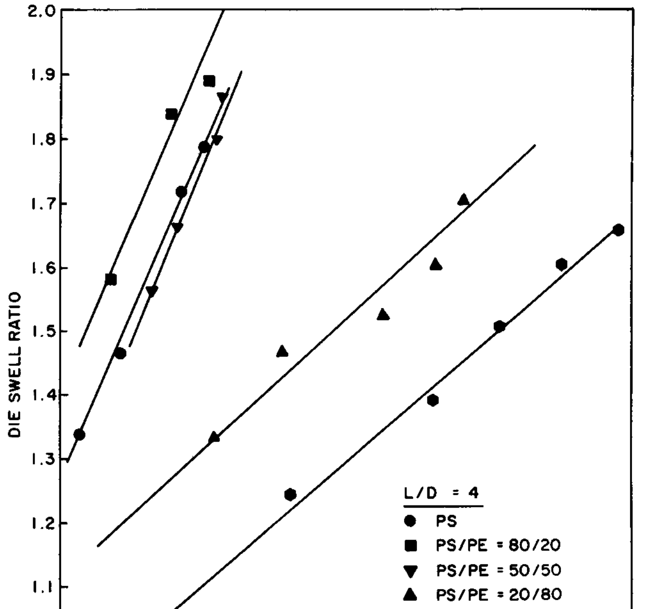

Fig. 3. Die swell ratio versus shear stress for polystyrene/polyethylene systems ($L/D = 4$, $T = 200°C$.).

plots of die swell ratio versus shear rate, in order to determine the relative elasticity of polymer melts. Note that the previous paper by Han et al. (*7*) has given a procedure for obtaining flow curves (plots of shear stress versus shear rate) from wall pressure measurements.

Cross plots of Figure 3 are shown in Figure 4, in which plots of die swell ratio versus blending ratio are given for fixed values of shear stress as parameter. It is very interesting to observe from Figure 4 that a maximum die swell ratio occurs at a blending ratio of about 20 wt. % of polyethylene. Note also that the authors (*10*) have recently reported a very similar phenomenon to that shown in Figure 4, by plotting exit pressure against blending ratio for fixed shear stress as parameter. At present there does not seem to be a theory available which can explain this rather interesting yet peculiar behavior.

Before closing we wish to point out clearly that the die swell ratios presented in this paper should not be taken as absolute quantities because of the procedure by which the measurements were taken. Hence, care should be taken by anyone who may attempt to use die swell data in the determination of other rheological properties. Such attempts would become meaningful only when the gravity effect on the die swell data presented here is properly taken into consideration.

Finally the authors wish to point out that the blends chosen for study form a two-phase system in the molten state which may be best seen in Figure 5. It is to be noted in Figure 5 that polystyrene forms the discrete phase (dark area) and polyethylene the continuous phase (white area) Note that these pictures were taken under 100× magnification. Details of the photographic procedure are given in a recent paper (*10*).

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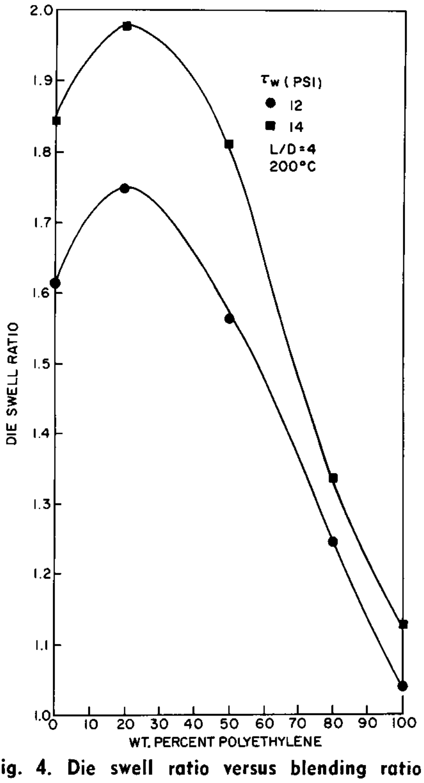

Fig. 4. Die swell ratio versus blending ratio for polystyrene/polyethylene systems (L/D = 4, T = 200°C.).

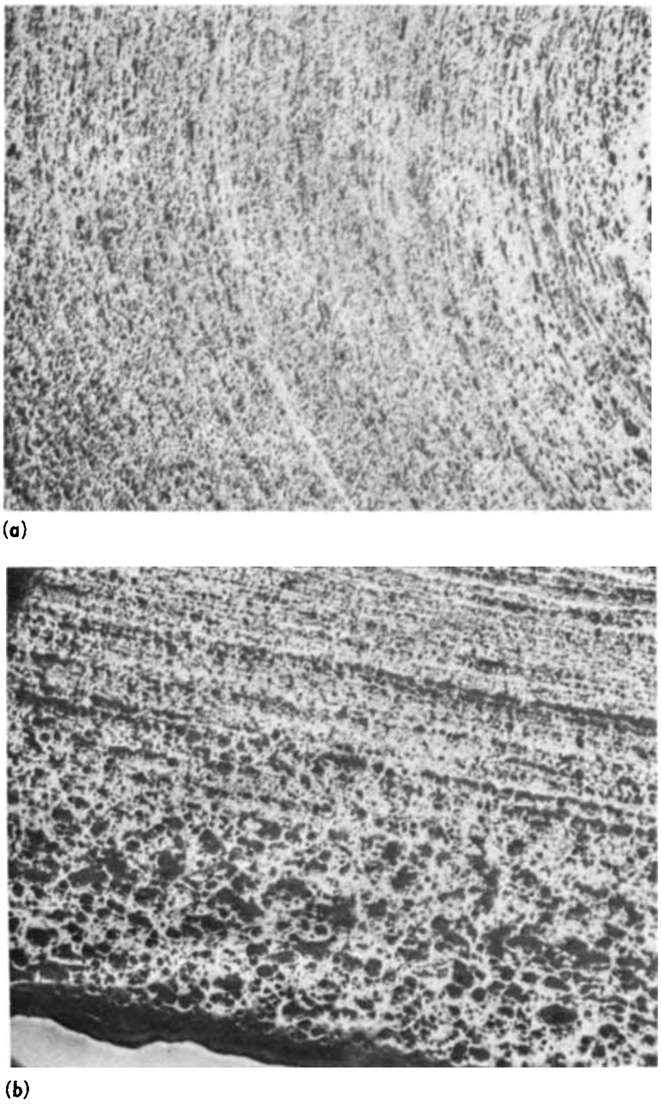

Fig. 5. Microphotographs (100×) of an extrudate sample for 20 wt-% polystyrene/80 wt-% polyethylene system; (a) center portion of the extrudate cross section, (b) edge portion in the longitudinal direction.

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