

Foam Extrusion Characteristics of Thermoplastic Resin with Fluorocarbon Blowing Agent. I. Low-Density Polyethylene Foam Extrusion

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Synopsis

An experimental study was conducted to investigate the foam extrusion characteristics of low-density polyethylene resin. For the study, we used dichlorotetrafluoroethane and dichlorodifluoromethane as blowing agent and talc as nucleating agent. In the study, we investigated the effects of processing and material variables on the foam extrusion characteristics, namely extrudate swell behavior, foam density, and cell morphology. It was found that an inverse relationship exists between the extrudate swell ratio and the foam density. Also investigated was the effect of die geometry (the L/D ratio, D_R/D ratio, and entrance angle) on the foam extrusion characteristics of low-density polyethylene resin. Suggestions are made on the experimental technique that may be useful in selecting resins for foam extrusion operation. Also suggested are guidelines for selecting an optimum die geometry that would produce good quality foams of low-density polyethylene.

INTRODUCTION

In recent years the use of fluorocarbon blowing agents for producing thermoplastic foams has grown considerably. Among many thermoplastic resins, low-density polyethylene and polystyrene most enjoy the commercial success of producing low-density cellular products. Because of the difference in their molecular structures, low-density polyethylene and polystyrene yield plastic foams having different mechanical properties, and consequently have different end-use applications.

For a given chemical structure of resin, a successful production of plastic foam products depends, among many things, on the following factors: (1) the chemical structure and concentration of blowing agent; (2) the extrusion melt temperature; (3) the extrusion pressure (hence extrusion rate or apparent shear rate in the die); (4) the type and concentration of nucleating agent; (5) the geometry of the extrusion die.^{1,2} In controlling the quality of low-density cellular products, the following three variables are considered most important: (a) density; (b) cell size and open cell fraction; (c) the expansion ratio of extrudate.

As may be surmised, the control of foam quality in the extrusion process requires an understanding of the thermodynamic and transport properties of mixtures of molten polymer and blowing agent, the phenomena of bubble nucleation and bubble growth, and the mass and heat transfer operations involving gas-liquid and gas-solid systems. Indeed, the problem at hand is very complex. No wonder that little fundamental information is available in the literature, dealing with the effects of material and processing variables upon the foaming

characteristics of thermoplastic resins containing gases, or volatile organic liquids, as blowing agent.

As part of our continuing efforts towards enhancing our understanding of foam processing operations, we very recently conducted a comprehensive experimental investigation on the extrusion characteristics of thermoplastic resins containing fluorocarbon blowing agent. More specifically, we investigated the effects of the following variables on the foaming characteristics of low-density polyethylene and polystyrene resins. They are: (1) the molecular parameters (hence rheological properties) of the resins; (2) the type and concentration of fluorocarbon blowing agent; (3) the type and concentration of nucleating agent; (4) the processing variables (i.e., extrusion melt temperature and extrusion rate); (5) the geometry of the cylindrical extrusion die (i.e., the reservoir-to-capillary diameter ratio, die entrance angle, and capillary length-to-diameter ratio).

In this paper we shall report the highlights of our findings on the foam extrusion characteristics of the three low-density polyethylene resins employed, and in a subsequent paper we shall present our results on the foam extrusion characteristics of the polystyrene resins employed.

EXPERIMENTAL

Materials

Three different grades of high-pressure, branched, low-density polyethylene, Rexene PE143, Dow PE510, and Norchem PE952, were used. The molecular characteristics and rheological properties of these resins are given in our earlier paper.³ We also used a low-pressure, linear, low-density polyethylene (Dow Chemical, Dowlex 2035) blended with Rexene PE143. The molecular characteristics and rheological properties of Dowlex 2035 are given elsewhere.⁴

As blowing agent, dichlorodifluoromethane (FC-12) and dichlorotetrafluoroethane (FC-114) were used. As nucleating agent, talc was used.

Apparatus

The apparatus employed is essentially the same as that described in one of our previous publications,³ except for the extrusion die. A schematic layout of the process line is shown in Figure 1. The motionless mixers, shown in Figure 1, are placed between the extruder and the extrusion die, in order to cool the mixture of molten polymer and blowing agent and to achieve a uniform melt temperature. In order to control the melt temperature in the static mixers, two hot-oil heat exchangers (Berg Industrial Co., Model BTU 10T-610-GO) were employed, one for each static mixer. The heat exchangers can cool, as well as heat, and are equipped with a proportional temperature controller.

For the purpose of investigating the effect of die geometry on the foaming characteristics, we used several capillary dies differing in the entrance angle (α), the reservoir-to-capillary diameter (D_R/D) ratio, and the capillary length-to-diameter (L/D) ratio. The capillary diameter (D) was kept constant (3.175 mm) in all the dies employed. Figure 2 describes the die geometries employed.

During extrusion it is essential to maintain a constant flow rate of blowing

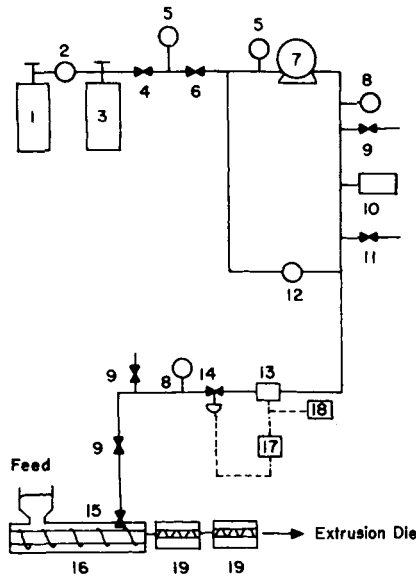
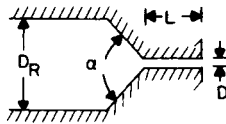


Fig. 1. Schematic of the process line: (1) nitrogen tank; (2) pressure regulator; (3) volatile liquid tank; (4) ball valve; (5) pressure gauge; (6) filter; (7) diaphragm pump; (8) pressure gauge; (9) bleed valve; (10) accumulator; (11) adjustable relief valve; (12) back pressure regulator; (13) flow meter; (14) control valve; (15) check valve; (16) screw extruder; (17) pneumatic controller; (18) pneumatic recorder; (19) static mixer with hot oil temperature control unit. (—) Fluid; (---) pneumatic line.

agent. For this, we used a flow control loop that monitors the flow rate of blowing agent and compares it to a set value. Any deviation sends a signal to a flow control valve that controls the flow at the set value. The accumulator in the system dampens any surge from the pump. The system maintains a constant flow rate regardless of suction pressure, pump and extruder pulsations, or back pressure.

The performance of the process was checked by continuously recording the die pressure, and the flow rate of blowing agent. The injection pressure of the blowing agent (1,000–2,000 psi) was also recorded and provided an indication of how uniform the feed of the extruder was.



| | |
|----------|---------------|
| α | 15°, 30°, 60° |
| D_R/D | 2, 8 |
| L/D | 0, 2, 4, 8 |

Fig. 2. Schematic describing the geometry of the extrusion die employed.

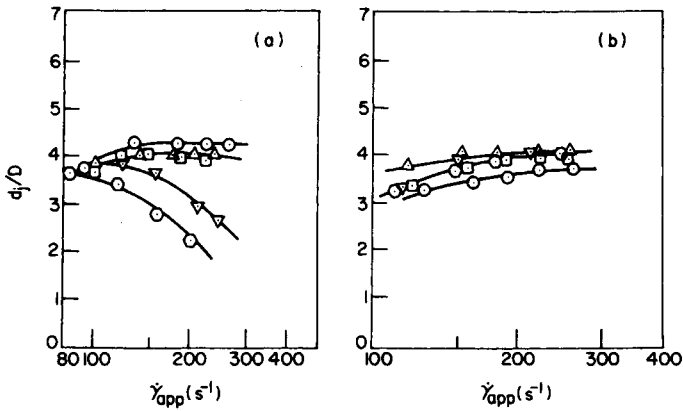


Fig. 3. Extrudate swell ratio vs. apparent shear rate for the Rexene 143/FC-114 (15 wt %) system, with various talc concentrations (wt %): (○) 0.0; (△) 0.25; (□) 0.50; (▽) 0.75; (◇) 1.00. (a) Die temperature at 110°C; (b) die temperature at 100°C. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^\circ$.

Experimental Procedure

Both the extruder (for resin) and pump (for blowing agent) were calibrated for each material before mixtures of resin and blowing agent were fed into the extrusion die. As the extruder speed was increased, the flow rate of blowing agent had to be increased accordingly in order to maintain the blowing agent concentration at its preset value.

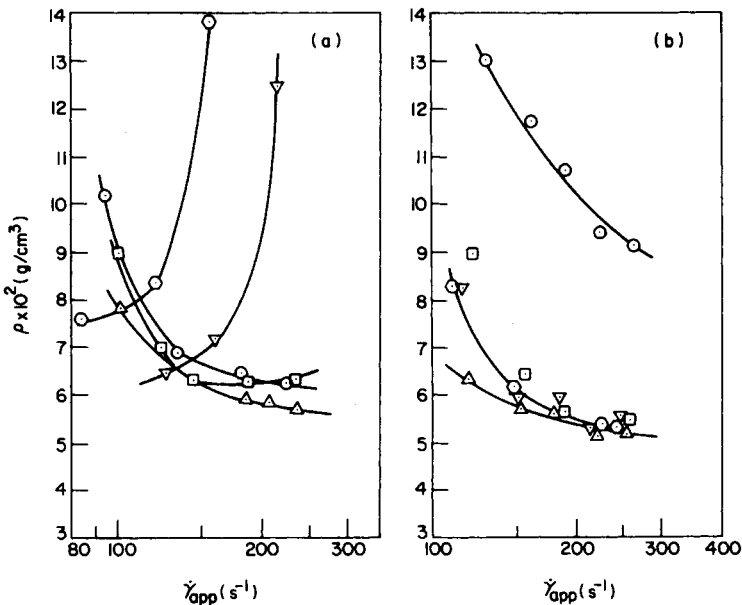


Fig. 4. Foam density vs. apparent shear rate for the Rexene 143/FC-114 (15 wt %) system, with various talc concentrations. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^\circ$. (a) Die temperature at 110°C; (b) die temperature at 100°C. Symbols are the same as in Figure 3.

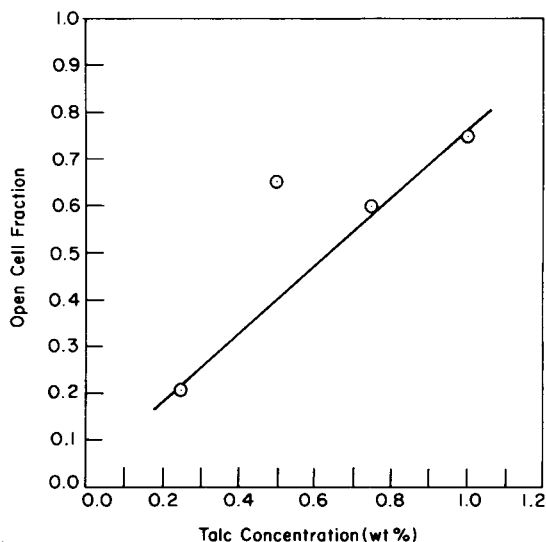


Fig. 5. Open cell fraction vs. talc concentration for the Rexene 143/FC-114 (15 wt %) system. The extrusion conditions employed are: die temperature at 100°C and apparent shear rate at 210 s^{-1} . The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^{\circ}$.

Using a drum tumbler, nucleating agent (talc powder in the present case) was blended with the plastic pellets, which had previously been wet with mineral oil. In this way, a small amount of talc powder was uniformly distributed to the plastic pellets. The blend was then fed to the hopper of the extruder, where mixing of the ingredients was continued and the material was brought to a homogeneous melt at a pressure of about 2,000 psi and a temperature of about 340°F .

During the experiment, we varied the extrusion rate, melt temperature,

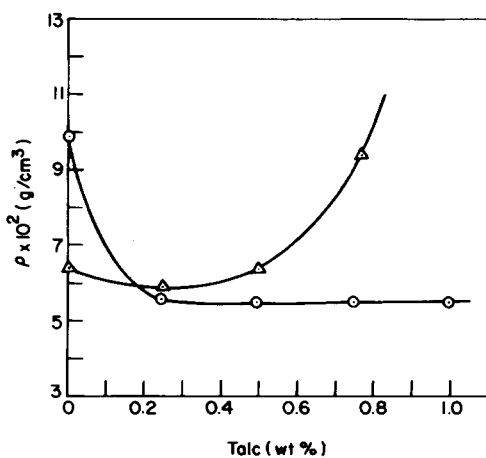


Fig. 6. Effect of talc concentration on foam density for the Rexene 143/FC-114 (15 wt %) system at $\dot{\gamma}_{\text{app}} = 200\text{ s}^{-1}$. (○) $T = 100^{\circ}\text{C}$; (△) $T = 110^{\circ}\text{C}$. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^{\circ}$.

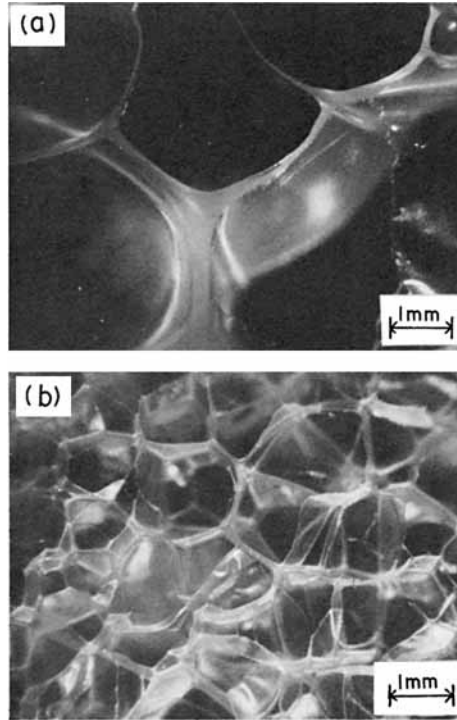


Fig. 7. Photomicrographs describing the effect of nucleating agent (talc) on cell size: (a) without talc; (b) with 0.25 wt % talc. The system is Rexene 143/FC-114 (15 wt %), and the extrusion conditions employed are: $T = 100^{\circ}\text{C}$, $\dot{\gamma}_{\text{app}} = 200 \text{ s}^{-1}$. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^{\circ}$.

blowing agent concentration, and nucleating agent concentration. With all the extrudates collected, we measured the extrudate diameter and foam density. With selected foam samples, we took photographs of the cell morphology (cell size and its distribution) in the extrudate cross section. Based on the ASTM D2856-70 standard test method, the open cell fraction of selected foam samples was measured by using an Air Pycnometer (Beckman Model 930).

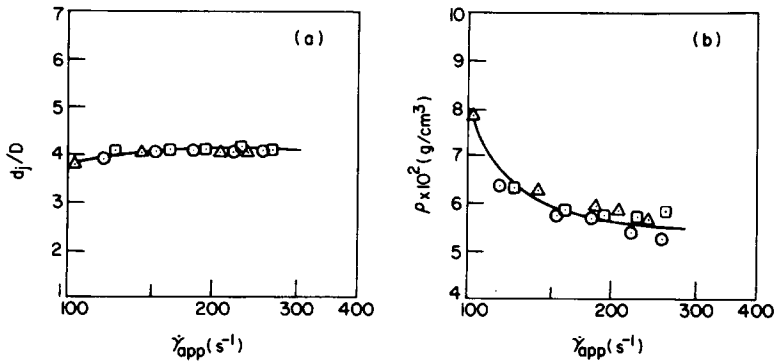


Fig. 8. Effect of die temperature on extrudate swell ratio and foam density. The system is Rexene 143/FC-114 (15 wt %)/talc (0.25 wt %). (○) $T = 100^{\circ}\text{C}$; (△) $T = 110^{\circ}\text{C}$; (□) $T = 120^{\circ}\text{C}$. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^{\circ}$.

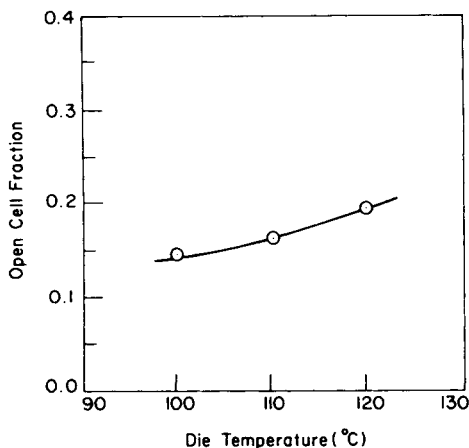


Fig. 9. Open cell fraction vs. die temperature for the system of Rexene 143/FC-114 (15 wt %)/talc (0.25 wt %), at $\dot{\gamma}_{app} = 190 \text{ s}^{-1}$. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^\circ$.

RESULTS

The Effect of Nucleating Agent on Foam Extrusion Characteristics

Plots of extrudate swell (d_j/D) ratio vs. apparent shear rate ($\dot{\gamma}_{app}$) are given in Figure 3, and plots of foam density (ρ) vs. apparent shear rate ($\dot{\gamma}_{app}$) in Figure 4, for the Rexene PE143/FC-114 system at two die temperatures, 110°C and 100°C, with various talc concentrations. Figure 5 shows the effect of talc concentration on open cell fraction. The following observations are worth noting in Figures 3–5: (1) The concentration of talc greatly influences the extrudate swell behavior and foam density, and a minimum foam density can be achieved

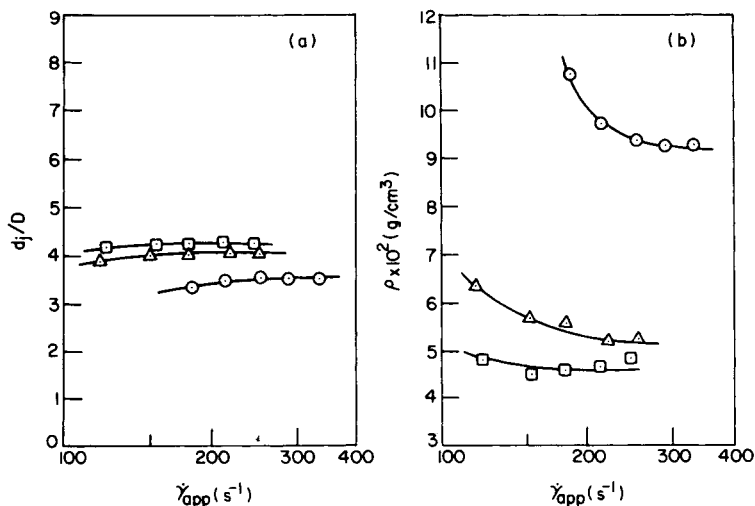


Fig. 10. Extrudate swell ratio and foam density vs. apparent shear rate for the Rexene 143/FC-114 system, with various FC concentrations: (\odot) 10 wt %; (Δ) 15 wt %; (\square) 20 wt %. The die temperature is 100°C and the talc concentration is 0.25 wt %. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^\circ$.

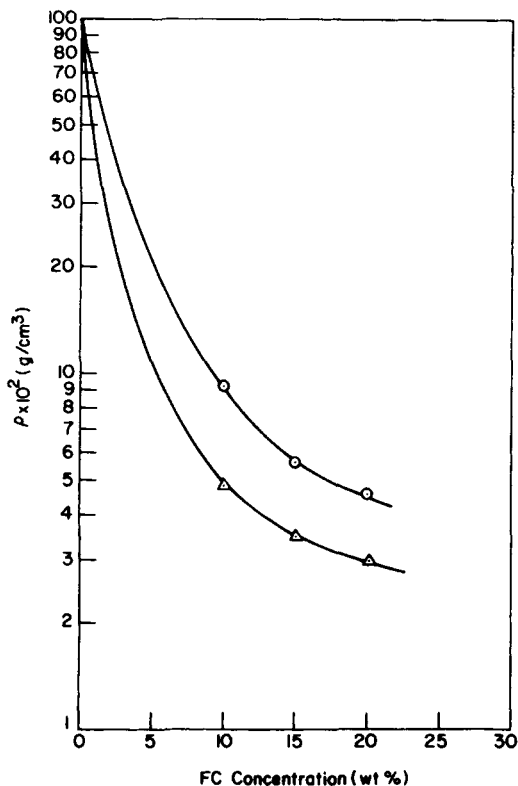


Fig. 11. Effect of FC blowing agent concentration on foam density in the extrusion of Rexene 143 containing 0.25 wt % talc: (○) FC-114; (△) FC-12. The die temperature is 100°C and the apparent shear rate is 200 s⁻¹. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^\circ$.

only over a certain range of talc concentration. (2) The die temperature, also, greatly influences both the d_j/D ratio and ρ . (3) At both the high talc concentration and high die temperature, the d_j/D ratio is decreased, and the ρ is increased as $\dot{\gamma}_{app}$ is increased. On the other hand, both the d_j/D ratio and ρ remain constant, although $\dot{\gamma}_{app}$ is increased, when optimum values of talc concentration and die temperature are chosen. (4) There appears to exist an inverse relationship between the d_j/D ratio and ρ . (5) The open cell fraction increases with talc concentration.

In reference to Figures 3 and 4, the rapidly *increasing* trend of ρ (and the rapidly *decreasing* trend of d_j/D) at high talc concentrations (0.75 and 1.0 wt. %) at 110°C, as $\dot{\gamma}_{app}$ is increased, may be attributable to the creation of local "hot spots,"⁵ which help gas bubbles collapse before the solidification of extrudate begins. The "hot spots" may also give rise to high open cell fraction at high talc concentrations (see Fig. 5). It should be pointed out that, during our foam extrusion experiments, the extrudates were cooled at ambient temperature (about 20°C), without using any special cooling device. At an optimum die temperature, as may be seen in Figure 6, the addition of talc decreases the foam density considerably, which is attributable to the presence of many small gas bubbles in the extrudate. Indeed Figure 7 gives photographs demonstrating the effect of talc, as nucleating agent, on foam morphology.

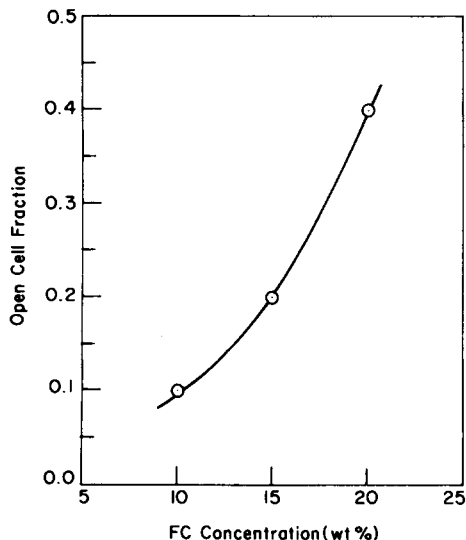


Fig. 12. Open cell fraction vs. FC concentration for the Rexene 143/FC-114/0.25 wt % talc system at 100°C and $\dot{\gamma}_{app} = 200 \text{ s}^{-1}$. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^\circ$.

The Effect of Die Temperature on Foam Extrusion Characteristics

Figure 8 gives plots of d_j/D ratio and ρ vs. $\dot{\gamma}_{app}$ for the Rexene PE143/FC-114 system with an optimum talc concentration (see Fig. 6), demonstrating that the die temperature between 100°C and 120°C has little influence on the foam density. It is also shown in Figure 9 that the open cell fraction changes little with the die temperatures investigated (100–120°C). However, it should be remembered (see Fig. 4) that the die temperature greatly influences the foam density when the talc concentration is not kept at an optimum value.

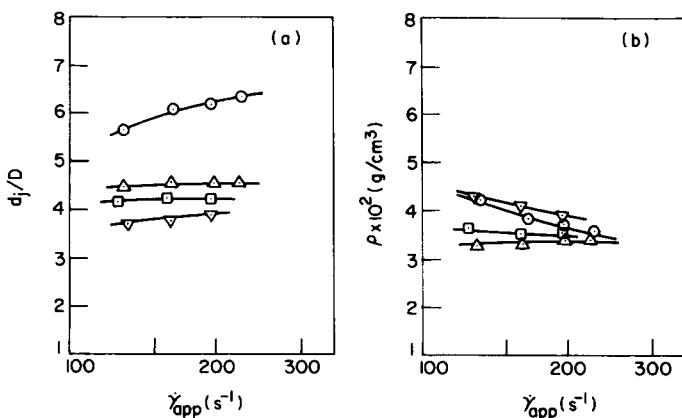


Fig. 13. Extrudate swell ratio and foam density vs. apparent shear rate for different values of capillary length-to-diameter (L/D) ratio: (\odot) 0; (Δ) 2; (\square) 4; (∇) 8. The die entrance angle (α) is 60° and D_R/D ratio is 8. The system is Rexene 143/FC-12 (15 wt %)/talc (0.25 wt %), and the die temperature is 100°C.

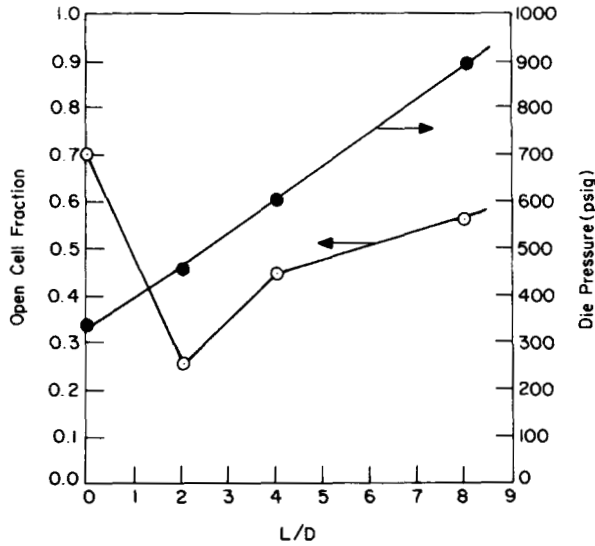


Fig. 14. Open cell fraction and die pressure vs. L/D ratio for the Rexene 143/FC-12 (15 wt %)/talc (0.25 wt %) system, at $T = 100^\circ\text{C}$, $\dot{\gamma}_{\text{app}} = 160 \text{ s}^{-1}$.

The Effect of Blowing Agent Concentration on Foam Extrusion Characteristics

Figure 10 gives plots of the d_j/D ratio and ρ vs. $\dot{\gamma}_{\text{app}}$ for the Rexene PE143/FC-114 system with an optimum talc concentration, at various concentrations of blowing agent. It is seen that, as the blowing agent concentration increases, d_j/D increases and ρ decreases. Figure 11 shows that FC-12 gives rise to lower foam density than does FC-114. Figure 12 shows that the open cell fraction increases with blowing agent concentration.

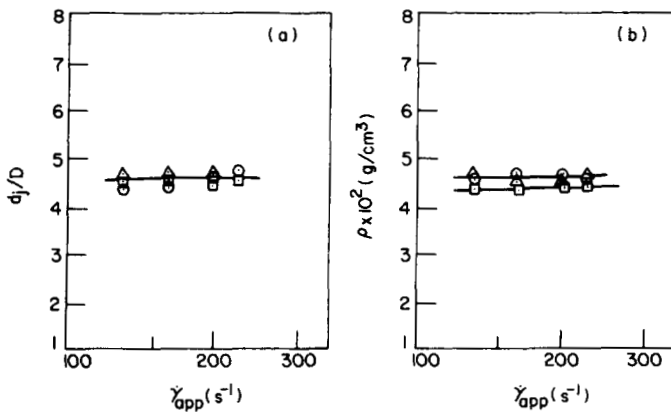


Fig. 15. Extrudate swell ratio and foam density vs. apparent shear rate for different values of die entrance angle (degrees): (○) 15; (△) 30; (□) 60. The L/D ratio employed is 2, and all other variables are the same as in Figure 13.

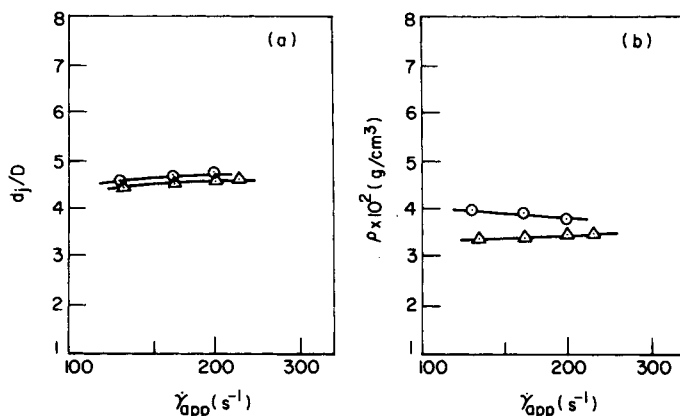


Fig. 16. Extrudate swell ratio and foam density vs. apparent shear rate for different values of D_R/D ratio: (○) 2; (△) 8. The L/D ratio employed is 2, and all other variables are the same as in Figure 13.

The Effect of Die Geometry on Foam Extrusion Characteristics

Figure 13 shows the effect of the capillary length-to-diameter (L/D) ratio on d_j/D and ρ for the Rexene PE143/FC-12 system, with talc as nucleating agent. It is seen that, as in the extrusion of virgin resins published in the literature,⁶ the d_j/D ratio increases as the L/D ratio decreases. Note that, except for an L/D ratio of 0 (i.e., a conical die), the d_j/D ratio increases very little with $\dot{\gamma}_{app}$. This observation is quite different from the situation where virgin resins are extruded. The effect of L/D ratio on ρ appears to be rather complex, as may be seen in Figure 13. The effect of L/D ratio on open cell fraction is also shown in Figure 14.

Figure 15 shows the effect of the die entrance angle on the d_j/D ratio and ρ , with other parameters kept constant. It is seen that little difference in the d_j/D ratio and ρ is observed with the three die entrance angles (15°, 30°, and 60°) employed.

Figure 16 shows the effect of the reservoir-to-capillary diameter (D_R/D) ratio on the d_j/D ratio and ρ , with other parameters kept constant. It is seen that the foam density is lower with a D_R/D ratio of 8 than with a D_R/D ratio of 2.

DISCUSSION

Extrudate Swell Behavior of Mixtures of Molten Polymer and Blowing Agent

It is a well-established fact today that the extrudate swell of molten polymer is associated with the elastic property of the melt and that the extent of extrudate swell depends, among many things, on shear rate, die geometry (i.e., L/D ratio, entrance angle, D_R/D ratio), and the extrusion melt temperature.⁶ There is, however, little information in the literature discussing the factors that influence the extrudate swell of mixtures of molten polymer and blowing agent.

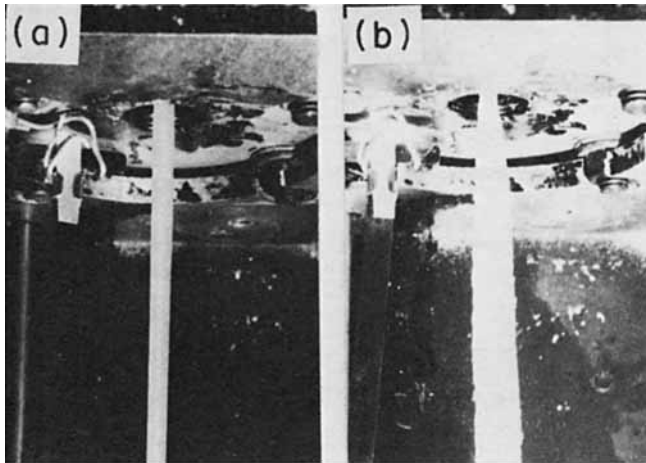


Fig. 17. Photographs describing the effect of FC blowing agent on extrudate swell behavior: (a) virgin Rexene 143 at $T = 160^{\circ}\text{C}$ and $\dot{\gamma}_{\text{app}} = 130 \text{ s}^{-1}$; (b) Rexene 143/10 wt % FC-114/0.25 wt % talc at $T = 100^{\circ}\text{C}$ and $\dot{\gamma}_{\text{app}} = 335 \text{ s}^{-1}$. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^{\circ}$.

The control of extrudate swell of such mixtures is of great importance in the control of the shape of extruded foam products. In foam extrusion, two factors contribute to extrudate swell: (1) the relaxation of stress (or the recovery of unconstrained elastic strains) of the polymer melt and (2) the expansion of blowing agent (i.e., gas bubbles) present in the polymer melt.

Figure 17 gives photographs demonstrating the differences in the extrudate swell behavior between a virgin resin (Rexene PE143) and a mixture of the same resin with a fluorocarbon blowing agent (FC-114). Note that the materials were extruded through a cylindrical die (D is 3.175 mm and the L/D ratio is 4). It is

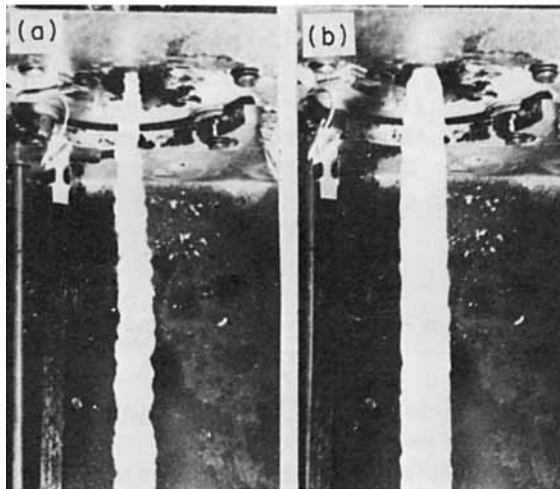


Fig. 18. Photographs describing the effect of nucleating agent on extrudate swell behavior: (a) Rexene 143/15 wt % FC-12 without talc, at $T = 100^{\circ}\text{C}$ and $\dot{\gamma}_{\text{app}} = 135 \text{ s}^{-1}$; (b) Rexene 143/15 wt % FC-12/0.25 wt % talc at $T = 100^{\circ}\text{C}$ and $\dot{\gamma}_{\text{app}} = 126 \text{ s}^{-1}$. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^{\circ}$.

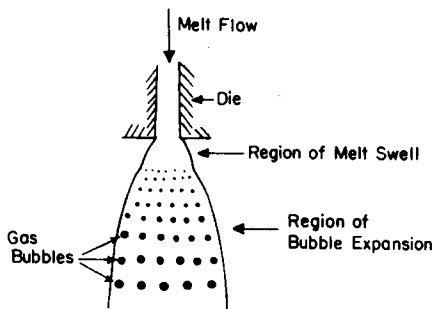


Fig. 19. Schematic depicting the mechanism of extrudate swell for a viscoelastic molten polymer containing a blowing agent.

seen in Figure 17 that the extrudate of the virgin resin swells quickly upon exiting from the die (although the die hole cannot be seen in the picture) and contracts slightly, due to the gravitational force, as it flows downward, whereas the extrudate of the mixture of Rexene PE143 and FC-114 swells initially due to the recovery of unconstrained elastic strains of the melt and then swells further due to the expansion of gas bubbles in the melt. It should be pointed out that the swelling behavior due to blowing agent in a mixture with molten polymer depends, among many other things, on: (1) the type and concentration of the blowing agent; (2) the extrusion rate or shear rate; (3) the type and concentration of nucleating agent; (4) the die geometry; (5) the cooling device. In the present study, the extrudates were cooled at ambient temperature, without using any special cooling device.

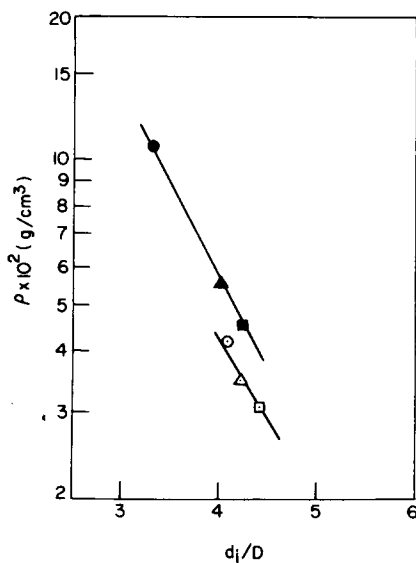


Fig. 20. Foam density vs. extrudate swell ratio for the Rexene 143/0.25 wt % talc system, at $T = 100^\circ\text{C}$ and $\dot{\gamma}_{\text{app}} = 185 \text{ s}^{-1}$. (a) FC-12 at various concentrations (wt %): (\odot) 10; (\triangle) 15; (\square) 20; (b) FC-114 at various concentrations (wt %): (\bullet) 10; (\blacktriangle) 15; (\blacksquare) 20. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^\circ$.

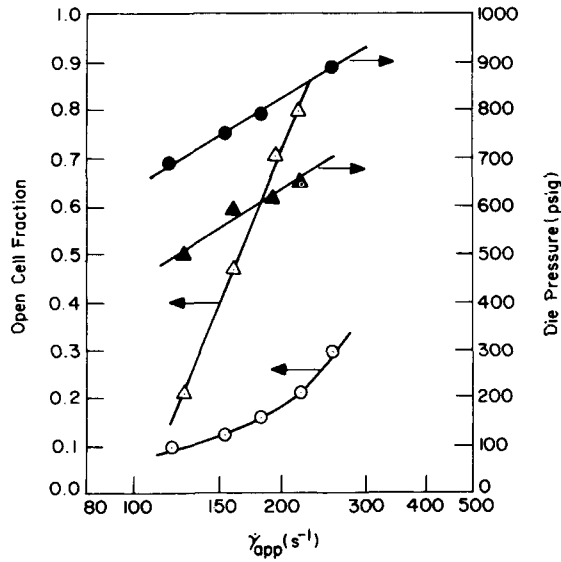


Fig. 21. Open cell fraction and die pressure vs. apparent shear rate: (○) open cell fraction for the Rexene 143/FC-114 (15 wt %)/talc (0.25 wt %) system; (△) open cell fraction for the Rexene 143/FC-12 (15 wt %)/talc (0.25 wt %) system; (●) die pressure for the Rexene 143/FC-114 (15 wt %)/talc (0.25 wt %) system; (▲) die pressure for the Rexene 143/FC-12 (15 wt %)/talc (0.25 wt %) system.

Figure 18 gives photographs demonstrating the effect of nucleating agent (talc in the present study) on the extrudate swell behavior of a mixture of Rexene PE143 and FC-12. It is seen that the presence of talc powders in the melt gives rise to a more uniform and larger extrudate diameter. The very irregular shape of the extrudate without nucleating agent [see Fig. 18(a)] is due to the rapid expansion of FC-12 gas bubbles in the melt upon exiting from the die.

With a proper choice of materials and processing conditions (e.g., a highly soluble blowing agent, a high extrusion rate, a very elastic polymer melt, a die having a small L/D ratio, a proper cooling device), one may observe extrudate swell behavior, as schematically shown in Figure 19. In other words, upon exiting the die, the initial swelling of extrudate is due strictly to the recovery of unconstrained elastic strains of the melt (i.e., the homogeneous mixture of polymer melt and blowing agent) and, then, the growth of nucleated gas bubbles takes over the swelling. Indeed such an observation is often made in commercial foam extrusion operations.

The Effect of the Type and Concentration of Blowing Agent on Foam Extrusion Characteristics

One should be reminded that, as shown in Figures 3, 4, 8, and 10, an inverse relationship appears to exist between the extrudate swell ratio and the foam density. In other words, the processing conditions that give rise to large extrudate swell produce low density foam. Figure 20 gives plots of foam density (ρ) vs. extrudate swell (d_j/D) ratio, at various blowing agent concentrations. It

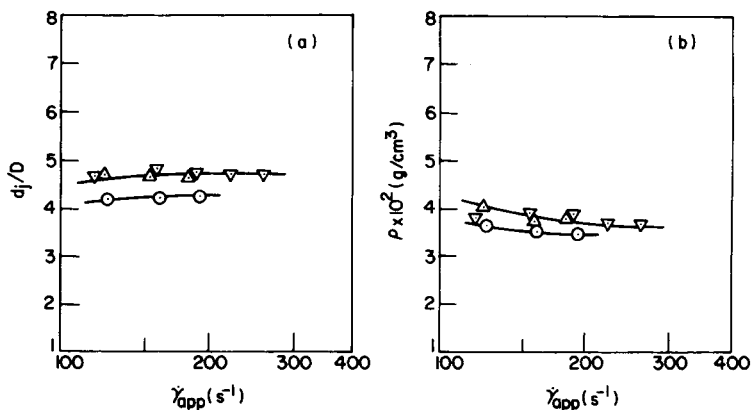


Fig. 22. Extrudate swell ratio and foam density vs. apparent shear rate for various grades of LDPE resin: (○) Rexene PE143; (△) Dow PE510; (▽) Norchem PE952. The blowing agent used is FC-12 (15 wt %), the talc concentration is 0.25 wt %, and the die temperature is 100°C. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^\circ$.

is seen that, for a given LDPE/FC blowing agent system, ρ decreases as d_j/D increases and that, for a fixed value of d_j/D , FC-12 gives rise to lower values of ρ than does FC-114.

However, as shown in Figure 21, over the range of shear rate investigated, FC-12 gives rise to greater open cell fraction than does FC-114. This is attributable to the fact that mixtures of FC-12 and LDPE are expected to have greater chance of premature foaming inside the die than mixtures of FC-114 and LDPE, because the viscosity of mixtures of FC-12 and LDPE is lower than that of mixtures of FC-114 and LDPE.³ Note in Figure 21 that the die pressure, measured during the foam extrusion experiment, for the FC-12/LDPE system is lower than that for the FC-114/LDPE system, supporting the independent viscosity measurements reported earlier.³ Note further that FC-12 has a much lower boiling point ($-29.9^\circ C$) and lower solubility in the polyethylene melt than FC-114 (its boiling point is $3.8^\circ C$). Thus, once foaming occurs inside the die the bubbles of FC-12 are expected to grow much faster than those of FC-114, which can then induce more bubble collapse during the expansion of extrudate and, consequently, may give rise to greater open cell fraction in the extrudate.

The Effect of Processing Variables on Foam Extrusion Characteristics

The extrusion rate (or shear rate), the melt temperature in the die, and the post-extrusion cooling temperature are the three most important processing variables influencing the foam extrusion characteristics. As shown in Figures 3, 4, 8, and 10, both the d_j/D ratio and ρ remain constant at and above a certain critical value of apparent shear rate ($\dot{\gamma}_{app}$). At a first glance this may seem somewhat peculiar, in view of the fact that the d_j/D ratio of homopolymer melts is known to increase with $\dot{\gamma}_{app}$.⁶ However, the experimental results given in Figures 3, 4, 8, and 10 may be explained by the following observations.

There is no doubt that, as the extrusion rate is increased, the extrudate swell of the *homogeneous* polymer melt will increase. On the other hand, the extent

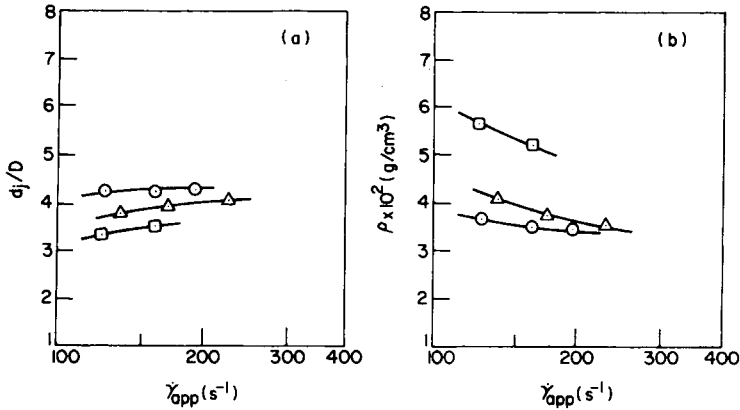


Fig. 23. Extrudate swell ratio and foam density vs. apparent shear rate for blends of Rexene 143 and Dowlex 2035: (○) pure Rexene 143; (△) Rexene 143/Dowlex 2035 = 90/10 (by wt); (□) Rexene 143/Dowlex 2035 = 70/30 (by wt). The blowing agent used is FC-12, the talc concentration is 0.25 wt %, and the die temperature is 100°C. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^\circ$.

of extrudate swell due to bubble growth is expected to decrease as the extrusion rate is increased, because the higher the extrusion rate, the less efficient the cooling of extrudate will be, which then brings about more cell collapse before the solidification of extrudate begins. Note in Figure 21 that the open cell fraction increases with shear rate, supporting the view presented above.

The choice of extrusion temperature is very important to the control of foam density. If the extrusion temperature is high, the blowing agent may come off from the polymer melt before the mixture of polymer melt and blowing agent reaches the die exit, giving rise to the coalescence of gas bubbles and, thus, the escape of the blowing agent from the extrudate. If this happens, the foam density will increase.

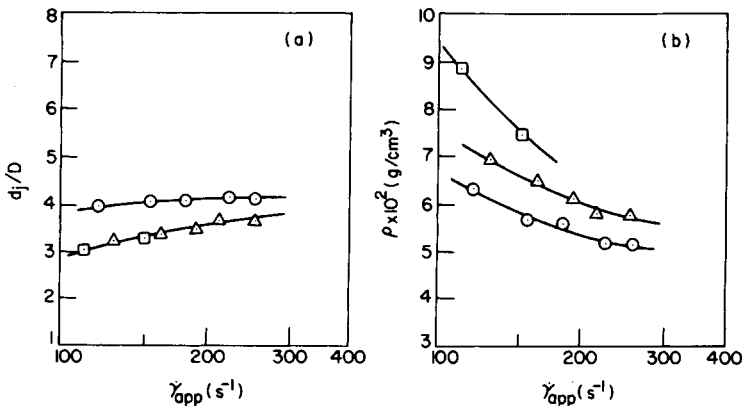


Fig. 24. Extrudate swell ratio and foam density vs. apparent shear rate for blends of Rexene 143 and Dowlex 2035. Symbols are the same as in Figure 23. The blowing agent used is FC-114, the talc concentration is 0.25 wt %, and the die temperature is 100°C. The die employed has: $L/D = 4$, $D_R/D = 8$, and $\alpha = 60^\circ$.

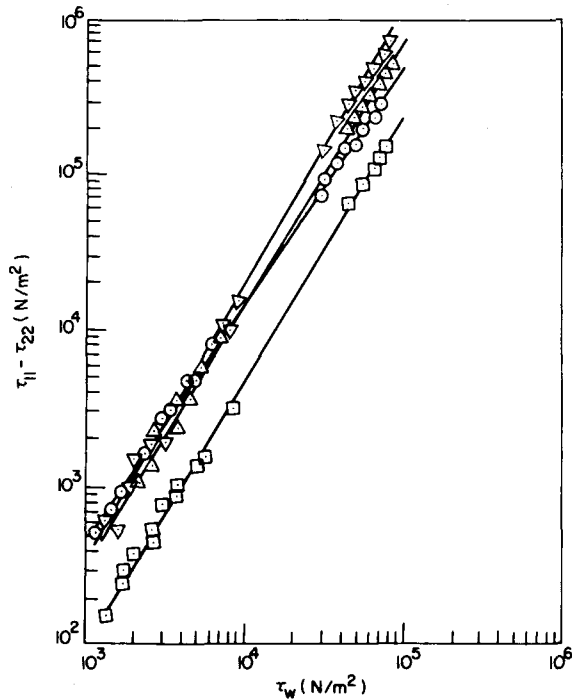


Fig. 25. First normal stress difference vs. shear stress: (○) Rexene PE143; (△) Dow PE 510; (▽) Norchem PE 952; (□) Dowlex PE 2035.

It should be noted that, in the extrusion of mixtures of low-density polyethylene and fluorocarbon blowing agent, the die temperature usually employed (say 100–110°C) is lower than the melting temperature of the resin itself (say, 115°C). This is due to the fact that the fluorocarbon blowing agent plasticizes the resin.

The Effect of the Rheological Properties of Resin on Foam Extrusion Characteristics

It is known today that the rheological properties of resin greatly affect its foaming characteristics. However, there is little information in the literature discussing the selection of resin for achieving good foaming characteristics. Figure 22 gives plots of the d_j/D ratio and ρ vs. $\dot{\gamma}_{app}$ for three different grades of low-density polyethylene, namely, Rexene PE143, Dow PE510, and Norchem PE952. It is seen that Rexene PE143 gives rise to a low d_j/D ratio compared to the other two resins. Although it shows that the foam density of Rexene PE143 is slightly lower than that of Dow PE510 and Norchem PE952, the difference between the two may be considered to be insignificant.

Figure 23 gives plots of the d_j/D ratio and ρ vs. $\dot{\gamma}_{app}$ for blends of Rexene PE143 and Dowlex 2035 containing FC-12 and talc, and Figure 24 gives similar plots for blends of the same resins containing FC-114 and talc. Note that Dowlex 2035 is a *low-pressure* low-density polyethylene, commonly referred to as *linear* low-density polyethylene. It is seen in Figures 23 and 24 that the blends give

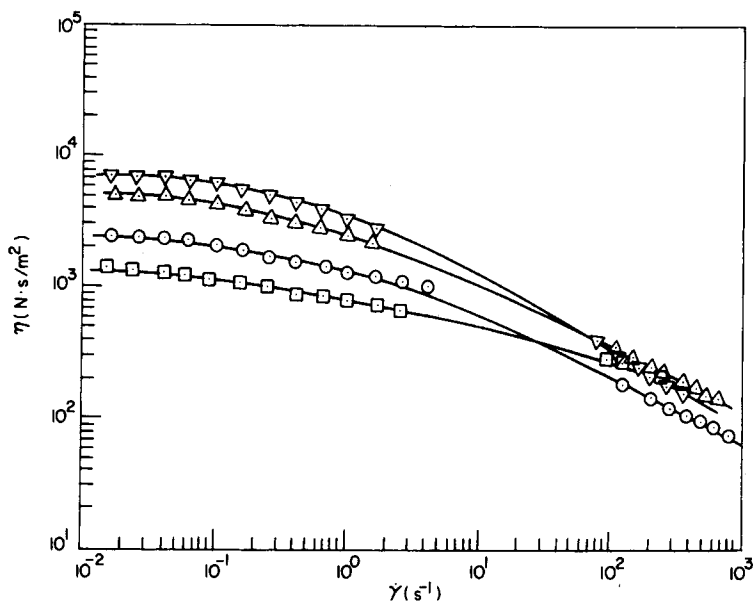


Fig. 26. Viscosity vs. shear rate at 220°C for the three high-pressure LDPEs and low-pressure LDPE employed. Symbols are the same as in Figure 25.

rise to lower d_j/D ratios and higher values of ρ than neat Rexene PE143 and that FC-12 gives rise to lower values of ρ than FC-114.

In order to explain the foam extrusion characteristics observed in Figures 22–24 from the standpoint of the rheological properties of the resins employed, let us look at the plots of first normal stress difference ($\tau_{11} - \tau_{22}$) vs. shear stress (τ_w) given in Figure 25, and the plots of viscosity (η) vs. shear rate ($\dot{\gamma}$) given in Figure 26, for the three *branched* LDPEs and one *linear* LDPE employed in extruding foams. It is seen in Figure 25 that, at high values of τ_w , Rexene PE143 is the *least* elastic of the three *branched* LDPEs, and that Dowlex 2035 is less elastic than any of the three *branched* LDPEs. Note that the foam extrusion experiment was conducted at τ_w values greater than 2×10^4 N/m² and $\dot{\gamma}$ values greater than 100 s⁻¹. It can now be concluded from Figures 25 and 26 that the d_j/D ratio of the extruded foam is controlled by the melt elasticity of the resin. Note in Figures 23 and 24 that an addition of the less elastic Dowlex 2035 to Rexene PE143 decreases the value of d_j/D ratio.

It should be pointed out, however, that the melt viscosity of a resin plays an important role in controlling the bubble growth *inside* the die. In order to demonstrate this, let us refer to Figure 27, which shows schematically the pressure profiles of two resins in a capillary (or slit) die. Note in Figure 27 that the greater the slope ($-\partial p/\partial z$) of the pressure profile, the larger the viscosity (η) of the resin,⁶ and therefore the viscosity of resin A is greater than that of resin B. One must be reminded that for a given combination of resin and blowing agent, there exists a critical pressure P_c at which bubbles nucleate and that, once bubbles nucleate inside the die, they will keep growing as the mixture of polymer melt and blowing agent approaches the die exit.¹ Therefore, in reference to Figure 27, with resin B, bubbles will start to grow much sooner than with resin A, and, thus, the ex-

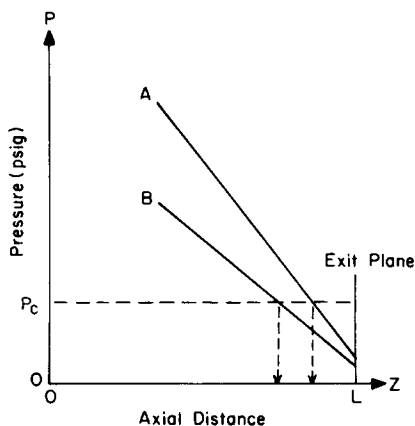


Fig. 27. Schematic describing the pressure profiles along the die axis, in which resin A is more viscous and, also, more elastic than resin B.

trudate of resin B will have larger bubbles than that of resin A. When bubbles are large in size, they tend to coalesce during flow, giving rise to foams of high density, i.e., the foam density increases due to the collapse of cells. On the other hand, high viscosity resins, while helping to suppress bubble growth inside the die, have other features that are *not* desirable from the standpoint of foam extrusion. High viscosity resins give rise to a shear heating problem at high extrusion rates, especially when the die temperature is very low, as in the foam extrusion process under discussion here, and thus limit the throughput.

One may now consider guidelines for selecting resins that would give good foam extrusion characteristics. In order to facilitate our discussion, let us look at the pressure profiles, shown schematically in Figure 28. It is seen that resin A, which is less viscous (i.e., having a pressure profile of smaller slope) than resin B, can completely suppress bubble growth inside the die if the pressure of the mixture of resin and blowing agent at the die exit plane can be kept greater than the critical pressure (P_c) for bubble nucleation. It has been amply discussed in the literature⁶ that viscoelastic polymer melts exhibit "residual stress" (i.e., nonzero gauge pressure) at the die exit plane and that the greater the "residual stress" of a resin, the larger the extrudate swell and, thus, the more elastic the resin is. Note in Figure 28 that resins A and B exhibit "residual stress." This is commonly referred to as "exit pressure," although it is a misnomer. It should be noted that the "exit pressure" of viscoelastic liquids increases with shear rate, whereas Newtonian liquids yield *zero* "exit pressure," regardless of how high the shear rate or the viscosity might be.⁶ Therefore, we suggest that the choice of resins for obtaining good foam extrusion characteristics be made on the basis of the measurements of pressure profiles in a capillary or slit die and that the processing conditions be chosen such that the "exit pressure" of the mixture of resin and blowing agent is greater than the critical pressure for bubble nucleation (P_c).

The Effect of Die Geometry on Foam Extrusion Characteristics

Figure 29 gives plots of ρ vs. d_j/D for the Rexene PE143/FC-12 system, for various values of L/D . It is seen that ρ decreases as the d_j/D ratio increases,

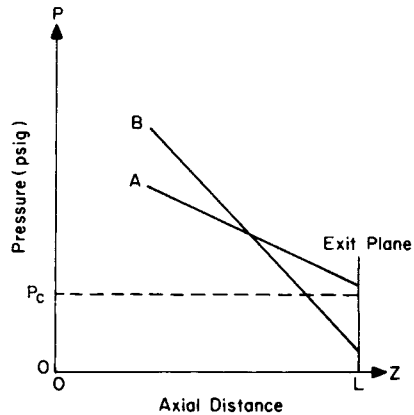


Fig. 28. Schematic describing the pressure profiles along the die axis, in which resin A is less viscous and yet more elastic than resin B.

regardless of the values of L/D and $\dot{\gamma}_{app}$ employed, and that a single correlation is obtained for L/D ratios of 2, 4, and 8. However, Figure 29 shows that the correlation between ρ and d_j/D obtained with an L/D ratio of 0 does *not* follow the trend observed with L/D ratios of 2, 4, and 8. Referring to Figure 13, one observes that the d_j/D ratio increases as L/D decreases, which is consistent with observations of homopolymer melts. However, the foam density obtained with an L/D ratio of 0 is greater than that obtained with L/D ratios of 2 and 4. Note that the die having an L/D ratio of 2 gives rise to the lowest foam density [see Fig. 13(b)] and, also, the least open cell fraction (see Fig. 14).

We will now attempt to explain the reason why the die having an L/D ratio of 0 gives rise to the foam density higher than the die having an L/D ratio of 2, while having a greater d_j/D ratio (see Fig. 13). An explanation for this seemingly anomalous observation may be given in terms of the die pressure, which was measured during the foam extrusion experiment. Referring to Figure 14, the die pressure, which was measured in the upstream end of the reservoir section, decreases as the L/D ratio decreases, which is expected intuitively. It appears that, under the particular extrusion conditions employed, the die pressure of 340 psi with the die having an L/D ratio of 0 (see Fig. 14) was not sufficiently high enough to prevent the occurrence of premature foaming inside the die, thus giving rise to high open cell fraction.

Note in Figure 14 that the open cell fraction for the dies with L/D ratios of 4 and 8 is greater than that for the die with an L/D ratio of 2, in spite of the fact that the die pressure increases with L/D ratio. This is attributable to the fact that, although there is less chance of premature foaming occurring in the *reservoir section* for the dies having L/D ratios of 4 and 8, premature foaming is expected to occur in the *capillary section* (i.e., die land) as the mixture of FC-12 and LDPE approaches the die exit. Therefore, the larger the L/D ratio of a die, the higher the open cell fraction will be. The observations made above suggest that an optimum die geometry is required for obtaining extruded foam products having low density.

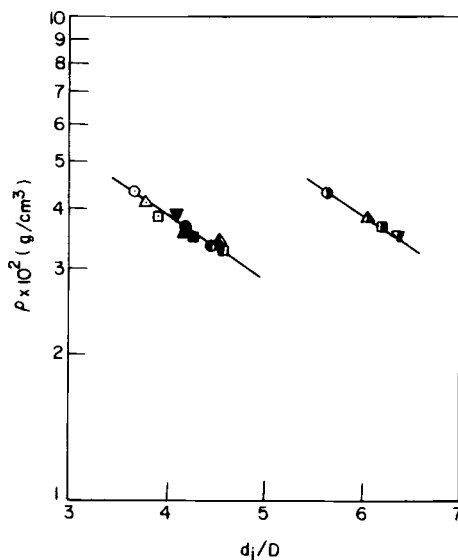


Fig. 29. Foam density vs. extrudate swell ratio for the Rexene 143/15 wt % FC-12/0.25 wt % talc system at 100°C. (a) $L/D = 0$ at various apparent shear rates (s^{-1}): (●) 130; (▲) 160; (■) 195; (▼) 225; (b) $L/D = 2$ at various apparent shear rates (s^{-1}): (●) 130; (▲) 160; (■) 195; (c) $L/D = 4$ at various apparent shear rates (s^{-1}): (●) 130; (▲) 160; (■) 195; (▼) 225; (d) $L/D = 8$ at various apparent shear rates (s^{-1}): (○) 130; (▲) 160; (□) 195.

CONCLUDING REMARKS

Many factors are involved in controlling the quality of foam produced by extruding mixtures of low-density polyethylene and fluorocarbon blowing agent. It appears that very intricate and complex relationships exist among the processing variables, the material variables, and the die design variables. In the present investigation, we have attempted to explain some of those complex relationships by conducting experiments in a systematic manner.

From the viewpoint of producing low density foams of low-density polyethylene by extrusion, the following observations are worth noting: (1) Too high a concentration of nucleating agent increases the foam density. (2) Too high a concentration of fluorocarbon blowing agent can give rise to cell collapse, yielding high density foams. (3) FC-12 gives rise to foam densities lower than does FC-114. (4) Linear (i.e., low-pressure) low-density polyethylene yields poor quality foams (i.e., high density foams and excessive cell collapses). This is attributable to the weak melt strength of the resin. (5) The three low-density polyethylene resins used, together with optimum values of blowing agent concentration (15–20 wt %) and talc concentration (0.25 wt %), and a die temperature of 100°C, have produced very good quality foams (i.e., uniform closed-cell foams with densities as low as 0.03 g/cm³). (6) Useful guidelines are suggested for selecting optimum die geometry that would produce good quality foams of low-density polyethylene. (7) A practical and efficient method is suggested for determining optimum extrusion conditions and selecting resins for foam extrusion operations.

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