

THE BRITISH LIBRARY DOCUMENT SUPPLY CENTRE

Photocopy Declaration to be retained by the registered BLDSC Customer

To be completed by the Librarian of the user library when a declaration or similar undertaking has not otherwise been obtained

To the Librarian of the

Library

(Name of user library or library stamp)

1. I hereby request you to supply me with a copy of item specified on Request Number _____ which I require for the purpose of research or private study
2. I have not previously been supplied with a copy of this item by any Librarian
3. I undertake that if a copy is supplied to me in compliance with the request made above I will not use it except for the purpose of research or private study

Signature

Name

(BLOCK LETTERS)

Address

Date

N.B. the signature must be the personal signature of the person making the request

400028362

noplastics, and for poly-*cis*-isoprene indicates that the penetrant diffuses faster in the copolymer than in the glassy polymers but slower than in the rubber. The distinct difference in the time dependence of the birefringence and the force during adsorption certainly models the behavior of a glassy polymer.

Both models can be used to explain the stress and birefringence data because our observations represent an average of a sum of the events occurring at the macromolecular level. In view of this, we measured the wide- and small-angle x-ray scattering from dry and swollen stressed thermoplastics. No difference could be found for the two glassy thermoplastics. We believe that neutron scattering utilizing deuterated methanol would be much more sensitive than x-ray scattering and could provide a detailed picture of the morphological rearrangements which occur during swelling.

CONCLUSIONS

Swelling of stressed thermoplastics causes the stress and birefringence to decrease. It is found that the rate of the decay of the stress is faster than that of the birefringence, and both appear to be diffusion controlled. Two models are proposed to explain the data. Neutron scattering experiments are proposed.

The author wishes to acknowledge discussion with Drs. B. P. Hanlon, G. L. Gaines, Jr., and H. J. Frisch and the experimental assistance of J. Maglio.

References

1. J. F. Fetters and B. F. Kee, *J. Appl. Polym. Sci.*, **18**, 2355 (1974).
2. B. G. LeGrand, B. P. Hanlon, and W. R. Haef, *J. Polym. Sci. A2*, **15**, 65 (1972).
3. B. P. Hanlon and B. G. LeGrand, unpublished results.
4. B. H. Zimm and J. L. Lundberg, *J. Phys. Chem.*, **72**, 276 (1968).
5. J. L. Lundberg, *J. Macromol. Sci. Phys.*, **13**, 693 (1969).
6. C. E. Rogers, J. R. Semanick, and S. Kawai, in *Polymer Science and Technology*, Vol. 1, R. W. Lenz and H. S. Stein, Eds., Plenum, New York, 1975.
7. C. E. Rogers and J. Machin, *CHU (Can. Rev. Macromol. Sci.)*, **2**, 265 (1972).
8. B. G. LeGrand and G. L. Gaines, Jr., *J. Polym. Sci. C*, **34**, 45 (1971).
9. J. H. Gilks and E. A. DiMarzio, *J. Chem. Phys.*, **28**, 373 (1958).
10. R. E. Robertson, *J. Chem. Phys.*, **44**, 3950 (1966).
11. E. S. Stein and A. V. Tobolsky, *Text. Res. J.*, **18**, 302 (1948).
12. A. H. Gent and T. H. Kuhn, *J. Polym. Sci. A2*, **9**, 927 (1971), *Macromolecules*, **2**, 267 (1969).
13. B. G. LeGrand, in *Structure and Properties of Polymer Films*, R. W. Lenz and R. S. Stein, Eds., Plenum, New York, 1975.
14. L. R. G. Treloar, *The Physics of Rubber Elasticity*, 2nd ed., Clarendon Press, Oxford, 1958.
15. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.
16. D. W. McCall, *J. Polym. Sci.*, **26**, 151 (1957).
17. S. P. Chen, ACS, Los Angeles Meeting, *Polym. Prepr.*, **15**(1), 73 (1974).
18. C. Pao, M. Fukuda, C. Choi, and R. S. Stein, *J. Macromol. Sci. B*, **11**(1), 263 (1972).
19. J. S. Stein, *J. Macromol. Sci. B*, **11**(1), 243 (1972).

Received June 2, 1975

Revised August 14, 1975

A Study of Foam Extrusion Using a Chemical Blowing Agent

C. D. HAN, Y. W. KIM, and K. D. MALHOTRA, *Department of Chemical Engineering, Polytechnic Institute of New York, Brooklyn, N. Y. 11201*

Synopsis

An experimental study of foam extrusion was carried out to determine the effect of processing variables on the quality of the foam produced. For the study, the chemical blowing agent azodicarbonitrile was used together with an activator and a nucleating agent to produce thermoplastic foams of low-density polyethylenes. The quality of foam was determined from photomicrographs and the tensile properties of extrudate samples. It was found that the percent elongation correlates with the foam density and that the cell structure (cell size and its distribution) correlates with the ultimate tensile properties of the foam produced. Also, an experimental study was carried out to observe the growth of gas bubbles in the polymer melt containing a blowing agent (foam) through a rectangular channel constructed of quartz. This experiment helped us to interpret the curved measure profile of the polymer melt containing a blowing agent as the melt approaches the die exit, whereas the polymer without a blowing agent shows a linear pressure profile.

INTRODUCTION

In recent years, the polymer processing industry has become increasingly interested in the production of extruded foams^{1,2} and injection-molded structural foams.³⁻⁵ This is because, in many cases, lower density can be achieved, which makes the technique economically attractive. Also, the use of a blowing agent together with polymers can give rise to products (e.g., syntactic wood) which otherwise would be very difficult to obtain. For instance, the use of thermosetting acrylic monomers in plasticized PVC foams allows the compounder to produce foams having a wide spectrum of hardness and deformation resistance.

In producing plastic foams, two types of blowing agent are used, chemical and physical. Chemical blowing agents are commonly used to produce high-density foamed polyolefins. Among many such agents, azodicarbonitrile has widely been used successfully in foam extrusion. Their function by decomposing at and above a critical temperature and releasing a gas, for example, nitrogen, carbon monoxide, or carbon dioxide. The bubbles thus initiated may be dissolved into the hot melt under high pressure and will grow when the pressure is reduced as the molten polymer flows through an extrusion die.

Physical blowing agents are gases such as nitrogen, dichlorotetrafluoroethane, *n*-pentane, and others. They are introduced either as a component of

1583

© 1976 by John Wiley & Sons, Inc.

400028363

the polymer charge or under pressure into the molten polymer in the barrel of the extruder.

When many bubbles are initiated, their ultimate size will be small. If few bubbles are initiated, they will become quite large, which is generally not desirable. Therefore, in order to control the initial bubble size, nucleating agents (e.g., sodium bicarbonate) are often used. In addition, catalysts are also often used to promote the efficiency of the blowing agent.

In the foam process, using either chemical or physical blowing agents, one of the most important and yet difficult problems from the processing standpoint is to achieve intimate mixing of the blowing agent and nucleating agent in the polymer melt, and cooling the melt to the foaming temperature. There are a variety of practical techniques for achieving this, and they are the very carefully guarded secrets of the industries concerned. The monograph edited by Frisch and Saunders¹⁴ describes various foam processing techniques.

In foam extrusion, as in conventional extrusion operations, the measurement of the rheological properties of the polymer melt, in this case containing dissolved gas, is of fundamental importance to the design of the processing equipment (e.g., screw and die designs). As one may surmise, the flow properties of a polymeric material in foam extrusion varies with the type of foaming agent, the amount of foaming agent, and also with the type and amount of other additives (e.g., plasticizers, modifiers, nucleators, etc.). Also important in foam extrusion is a better understanding of the mechanism of foam formation. In particular, the control of the nucleation and growth of gas bubbles is vitally important to the success of the process.

In this paper, we shall present our recent study of foam extrusion, which was concerned with achieving a uniform cell distribution and the desired physical properties of the foam produced by varying the processing conditions (i.e., temperature and pressure) and the geometry of the extrusion dies.

EXPERIMENTAL

In the present study we carried out three different types of experiment. They were (1) wall normal stress measurement in a capillary die, (2) visual observation of the bubble growth phenomenon in a transparent test channel, (3) flat film extrusion of thermoplastics using a chemical blowing agent.

Wall-Normal Stress Measurement

The apparatus used in this experiment was essentially the same as described in earlier papers by Han,^{10,16} except that a Statix Mixer (Kenics Corp., Thermogenizer) was installed at the extruder outlet. The mixer was used in order to improve the dispersion of the blowing agent in the molten polymer. A schematic of the experimental apparatus is given in Figure 1a.

High-density polyethylene (Union Carbide, DMDJ 4306) was used as base polymer, and azodicarbonamide (National Polychemical, Kenmore 125) as blowing agent. The polymer was mixed with the blowing agent by tumbling for about 2 hr, and the mixture was then extruded through a 1 in

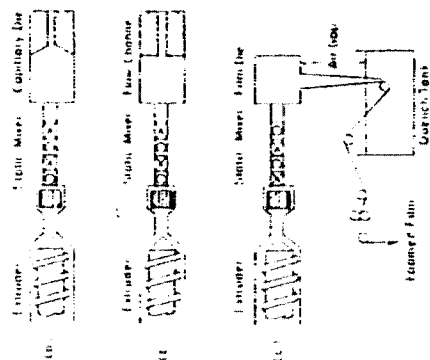


Fig. 1. Layout of experimental apparatus: (a) capillary extrusion apparatus, (b) flow visualization apparatus, (c) flat film extrusion apparatus.

diameter Killion extruder equipped with variable-speed drive and on-off temperature controllers.

In the measurement of wall-normal stresses in a capillary die ($L/D = 4$ and 20 , $D = 0.125$ in.), melt pressure transducers (Dynisco PT432) were used having a sensitivity of $\pm 1\%$ of the measured value. Details of the experimental procedures are described in earlier papers by Han.^{10,16}

Visual Observation of Bubble Growth in Extrusion

In this experiment, a rectangular flow channel constructed of quartz was used so that the growth of gas bubbles could be observed from the direction perpendicular to the direction of flow. The layout of the experimental setup is given in Figure 1b.

Motion pictures were taken of the bubbles flowing into and through the slit die section, using a special lens system to provide the proper magnification. The experiment was carried out under various extrusion conditions, i.e., for different values of temperature, flow rate, and die wall temperature.

Flat-Film Extrusion Experiment

The layout of the experimental apparatus is given in Figure 1c. In this experiment, a flat-film die was used. The die was designed in such a way that the die land length and entrance angle were independently adjustable, as schematically shown in Figure 2. In this experiment, as the extrudate emerges from the die, it is cooled by passing it through a water tank. The air gap is the distance between the die exit and the surface of the water.

Low-density polyethylene (Union Carbide, DYNJ 1) was used as base polymer, azodicarbonamide (National Polychemical, Kenmore 125) as blowing agent, solid Ba-Cd (Cincinnati Milatron, Advastab ABC 50) as activator,

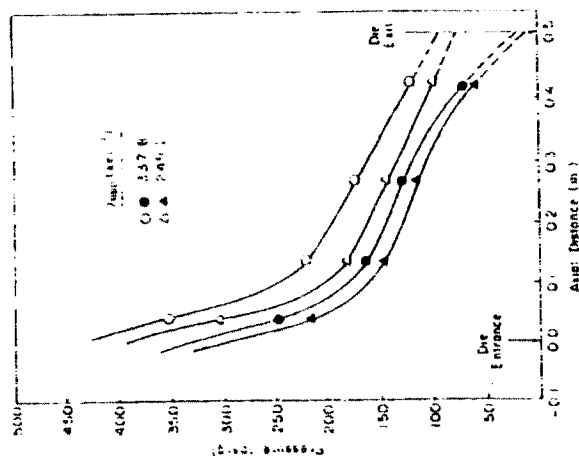


Fig. 4. Representative axial profiles for high-density polyethylene with and without blowing agent. Closed symbols are with blowing agent and open symbols without blowing agent.

one containing 0.3 wt-% of a blowing agent in a capillary having an L/D ratio of 4. It is seen that the pressure profile starts to deviate from a straight line somewhere in the capillary as the melt approaches the die exit and that the pressure drop at the die entrance is exceedingly large. Figure 4 shows axial profiles of wall normal stress of high-density polyethylene with and without a

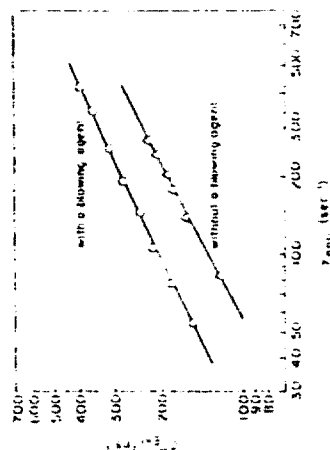


Fig. 5. Entrance pressure drop vs. apparent shear rate in the extrusion of high-density polyethylene with and without blowing agent ($T = 200^\circ\text{C}$).

blowing agent (azodicarbonamide) measured along a capillary with an L/D ratio of 4 ($D = 0.125$ in.). Two things can be seen in Figure 4. One is that, within the entire die length, the polymer with a blowing agent gives rise to lower wall-normal stresses than the polymer without a blowing agent. The other is that, after the melt passes the entrance region, the polymer with a blowing agent shows a curvature in its axial profile, whereas the polymer without a blowing agent shows a linear pressure profile.

That the pressure gradient is not constant in the capillary for the melt containing a blowing agent casts a doubt on the validity of determining the rheological properties from the wall normal stress measurements. In other words, the wall shear stress τ_w to be calculated from the expression

$$\tau_w = \left(-\frac{D}{4} \frac{dp}{dz} \right) \quad (1)$$

is not constant along the capillary for the melt containing blowing agent. In eq. (1), $(-dp/dz)$ is the pressure gradient at the position z , and D is the capillary diameter.

Another interesting observation that one can make in Figure 3 is the entrance pressure drop that occurs in the flow of polymer melt containing a blowing agent. Figure 5 shows plots of entrance pressure drop versus apparent shear rate for high-density polyethylene melts with and without a blowing agent. It is seen that the melt containing a blowing agent gives rise to much greater entrance pressure drops than the melt containing no blowing agent. The difference in the entrance pressure drop between the two curves in Figure 5 may be attributable to a possible evolution of the dissolved gas from the molten polymer in the form of small bubbles (i.e., as nuclei), as the melt passes through the die entrance.

Figure 6 gives pictures of the bubble growth phenomenon when a molten polyethylene containing a blowing agent is extruded through a transparent rectangular channel (see Fig. 1b) at different flow rates. It is seen that, (a) at low flow rates (see Fig. 6a) bubbles start to grow right after the die entrance, giving rise to a large number of big bubbles near the die exit; (b) at medium flow rates (see Fig. 6b), bubbles start to grow somewhere in the middle of the slit section; (c) at high flow rates (see Fig. 6c), the location where bubbles start to grow moves toward the die exit. In other words, as the flow rate is increased, the chances of bubble growth in the die become less. It should be pointed out that an increase in flow rate accompanies an increase in pressure.

From the experimental observations given in Figure 6, it may be concluded that the curved pressure profiles given in Figures 3 and 4 for the melt containing a blowing agent may be attributable to the rapid growth of bubbles as the melt approaches the die exit. In other words, there would be a critical value of pressure below which small bubbles start to grow. Of course, the critical pressure depends on the radius R of the initial bubble, interfacial tension σ , and the pressure difference Δp between the surrounding fluid (i.e., polymer melt in the present case) and inside the bubble. Thus, at equilibrium, the following force balance should hold¹⁸

$$\Delta p = \frac{2\sigma}{R} \quad (2)$$

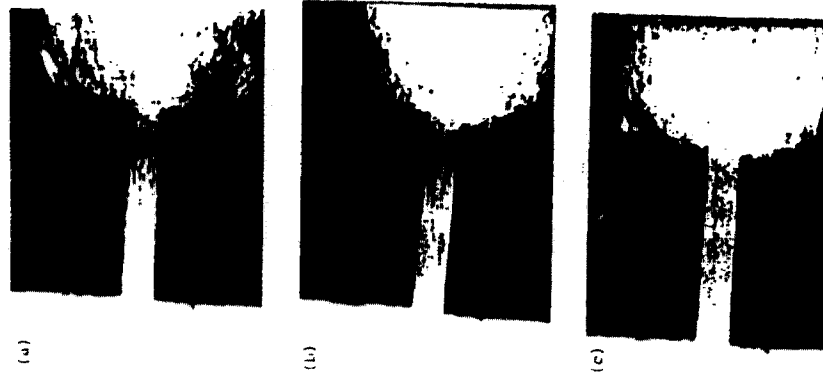


Fig. 6. Representative photographs showing bubble growth phenomena in the flow of a molten polyethylene containing blowing agent (acetic anhydride) through a rectangular channel at different flow rates: (a) $Q = 4.71$ cc/min; (b) $Q = 6.71$ cc/min; (c) $Q = 11.01$ cc/min.

Note that the interfacial tension σ may vary with the type of polymer used, and the radius R of the initial bubble depends on the type of blowing agent used as well as the additive (i.e., nucleating agent and activator).

To summarize, it has been shown above that the pressure profiles of a polymer melt containing a blowing agent in an extrusion die depend on the state of the bubbles dispersed in the melt. It should be mentioned that control of the bubble size and its distribution is vitally important to produce foams of uniform quality. During the extrusion operation, the size of the foam cell (i.e., bubble) changes with time because of diffusion of gas from the liquid phase into the cell and also, by possible coalescence of gas bubbles. Hence,

the stabilization of the foam cell is important. A better understanding of the mechanism of nucleation and growth of bubbles, and of the coalescence of bubbles, in a foaming process is very important to obtaining a product of desired quality.

Effect of Processing Variables on Foam Quality and Tensile Properties

Table II shows the effect of the die entry angle on foam quality. The thickness of the foam sheet produced is less for the smaller angle and the specific gravity is greater. Foam quality, as judged by appearance, is found to be better at the smaller angle. This may be due to the increased entrance pressure drops so obtained.

In order to determine whether the die land length would affect the foam quality, two extremes were used in our experiment. They were the die with zero land length, wherein the material exits immediately after the converging section, and the die fitted with a land length L of 0.4 in. Since the die opening h is 0.020 in., this would mean an L/h ratio of 20. Table III shows that the die length appears to have very little effect on the foam quality.

TABLE II
Variation of Foam Quality with Die Entry Angle

Die entry angle, degrees	Foam thickness, mils	Specific gravity	Tensile strength, psi	Percent elongation, %	Foam quality
90	15.8	0.536	760	185	fair, elongated bubbles present due to coalescence of bubbles and subsequent stretching
20	8.5	0.525	1040	240	better foam, fewer and smaller bubbles, more uniform appearance

* Operating conditions: screw temperature, 200°C; die temperature, 200°C; screw speed, 30 rpm; land length (L/h), 20; formula, 1; haul-off speed, 5.65 ft per min; air gap, 5 in.

TABLE III
Variation of Foam Quality with Die Land Length

Land length (L/h)	Foam thickness, mils	Specific gravity	Tensile strength, psi	Percent elongation, %	Foam quality
0	19.8	0.535	605	136	fair, nonuniform bubble size distribution, bubbles elongated due to stretching
20	23.5	0.540	545	144	same as above

* Operating conditions: screw temperature, 220°C; die temperature, 220°C; screw speed, 70 rpm; die entry angle, 20; formula, 1; haul-off speed, 5.65 ft per min; air gap, 5 in.

TABLE IV
Variation of Foam Quality with Screw Speed^a

Screw rpm	Die inlet pressure, psi	Foam thickness, mils	Specific gravity	Percent elongation, %	Tensile strength, psi	Foam quality
50	150	16.8	0.586	190	620	fair, some non-uniformity in bubble sizes, bubbles are elongated, overall thickness is uniform
70	220	21.2	0.580	120	600	rougher surface, non-uniformity in overall thickness due to surging at the extruder exit
95	270	28.0	0.570	135	600	same as above, but ripple marks caused by surging clearly visible

^a Operating conditions: screw temperature, 200°C; die temperature, 200°C; die entry angle, 20°; land length (L/h), 20; take-up speed, 5.65 ft per min; formula, $\frac{1}{2}$ air gap, 2 in.

Extruder screw speeds were increased from 50 rpm to 95 rpm, and Table IV shows how this affected the foam quality. From Table IV, one can see that the quality of foam deteriorates above 50 rpm screw speed. This implies that flow instabilities set in at higher shear rates. The die inlet pressure (i.e., the pressure in the reservoir) was measured by a pressure gauge located just after the adapter. As would be expected, the melt pressure increased with increasing screw speed. Based on this observation, it can be said that the effect of the land length on foam quality has not been fully established because the experiment was run under screw speed conditions (>50 rpm) which produces poor quality foam.

TABLE V
Variation of Foam Quality with Melt Temperature^a

Die temperature, °C	Die inlet pressure, psi	Foam thickness, mils	Specific gravity	Tensile strength, psi	Percent elongation, %	Foam quality
200	220	21.2	0.580	600	120	rough surface, non-uniformity in thickness due to surging at the extruder exit
160	325	23.0	0.615	800	150	surface still rough, but thickness is more uniform

^a Operating conditions: screw temperature, 200°C; die entry angle, 20°; land length (L/h), 20; screw speed, 70 rpm; take-up speed, 5.65 ft per min; formula, $\frac{1}{2}$ air gap, 2 in.

TABLE VI
Variation of Foam Quality with Air Gap Distance^a

Air gap, in.	Foam thickness, mils	Specific gravity	Tensile strength, psi	Percent elongation, %	Foam quality
7	22	0.530	745	125	fair, large elongated bubbles visible
6	33	0.545	820	175	good, bubble distribution is more uniform
8	42	0.555	820	180	same as above
16	56.8	0.530	735	205	same as above

^a Operating conditions: screw temperature, 180°C; die temperature, 180°C; die entry angle, 20°; die land (L/h), 20; screw speed, 70 rpm; take-up speed, 5.65 ft per min; formula, $\frac{1}{2}$.

Chemically blown foam is very sensitive to the temperature of the polymer melt. From Table IV, one sees that the surface of the foamed extrudate was rough. In order to obtain a smoother surface and more uniform foam, the temperature of the die was reduced from 200° to 160°C. The effect of this change is shown in Table V. Even though a smooth skin was not formed at the lower temperature, foam uniformity did improve. Since the die temperature was separately controlled, via a solid state thermostat control, it was quite easy to change it.

Figure 5 shows the relationship of ultimate tensile strength to specific gravity of the foam. Figure 8 is an attempt to show that the quality of foam, as judged by appearance, can be quantitatively determined by measuring percent elongation.

Interpreting the above, one can say that the tensile strength increases with specific gravity and is not much dependent on cell size or cell distribution whereas the percent elongation is strongly dependent on the foam quality.

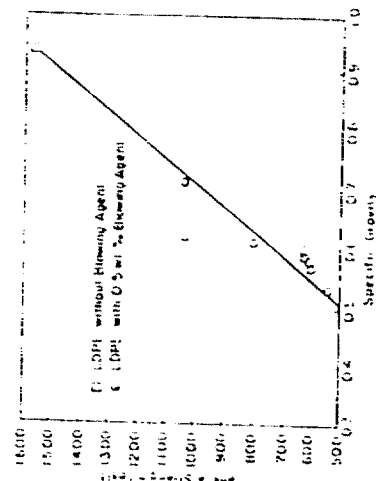


Fig. 5. Tensile strength vs. specific gravity for low density polyethylene foam with a blowing agent (azobiscarbonitrile).

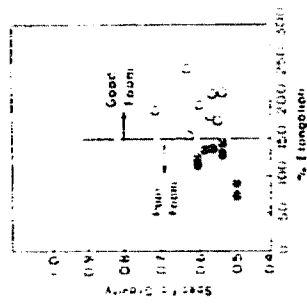


Fig. 8. Specific gravity vs. percent elongation for low density polyethylene foam.

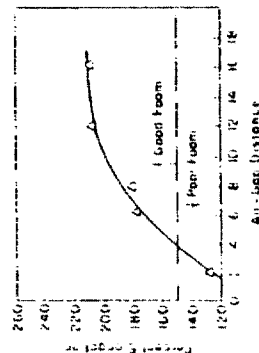


Fig. 9. Percent elongation vs. air gap distance for low density polyethylene foam.

Table VI shows how the foam quality generally improves as the air gap is increased in steps from 2 to 16 in. A further lowering of the water level resulted in inadequate cooling. It is further seen in Table VI that, as the air gap is increased, the following happens: (1) the thickness of the foam film increases but the width decreases; (2) the specific gravity remains unaffected; (3) the tensile strength remains fairly constant; (4) there is a dramatic increase in elongation with the increase in air gap from 2 to 6 in. On further increasing the air gap, the elongation increases slowly and then levels off. This is shown in Figure 9.

It has been shown in a previous study¹⁰ that the void morphology (hence, foam quality) is affected by the crystallinity of the polymer. It appears, then, that further research is needed to quantitatively relate the effect of the degree of the crystallinity of the polymer to foam quality and bubble distribution.

This work was supported in part by Kenics Corporation, for which the authors are very grateful.

References

1. W. T. Higgins, *Mod. Plast.*, 31(7), 99 (1954).
2. R. H. Hamann, *SPE J.*, 18, 77 (1952).
3. M. Nakamura, paper presented at the AICHE National Meeting, June 3-6, 1975, Detroit, Michigan.
4. A. C. Werner, paper presented at the AICHE National Meeting, June 3-6, 1975, Detroit, Michigan.
5. R. S. Hoon and H. K. Patel, paper presented at the 32nd ANTEC of the Society of Plastics Engineers, May 15-16, 1974, San Francisco, California.
6. R. S. Angel, *J. Cell Plast.*, 3(1), 490 (1967).
7. L. D. Cochran and C. W. Osborn, *SPE J.*, 25(9), 26 (1969).
8. A. C. Morris and J. Czerski, *Brit. Plast.*, 43(2), 56 (1970).
9. R. L. King and R. W. V. round, *Mod. Plast.*, 51(4), 70 (1974).
10. L. J. Schreiner, *Plast. Technol.*, 14(12), 35 (1968).
11. J. Donovan, *Brit. Plast.*, 43(2), 51 (1970).
12. J. F. Zappala, *J. Cell Plast.*, 7(1), 389 (1971).
13. R. E. Skochdopole and L. C. Kulkarni, *J. Cell Plast.*, 10(1), 91 (1965).
14. K. C. Frisch and J. H. Saunders, *Plastic Foams*, Parts 1 and 2, Marcel Dekker, New York, 1972.
15. C. D. Han and M. Charley, *Polym. Eng. Sci.*, 10, 148 (1970).
16. C. D. Han, *J. Appl. Polym. Sci.*, 15, 2867 (1971).
17. L. L. Byler and T. K. Kwei, *J. Polym. Sci. C*, 35, 165 (1971).
18. K. C. Frisch, *Plastic Foams*, Part 1, K. C. Frisch and J. H. Saunders, Eds., Marcel Dekker, New York, 1972.
19. A. G. Kolbeck, H. Fumoto, D. R. Uhlmann, and F. J. Calvert, *J. Appl. Polym. Sci.*, 17, 2895 (1973).

Received July 21, 1975

Revised August 14, 1975

AUTOMATED REQUEST TO The British Library DOCUMENT SUPPLY CENTRE

DY 77309

F

B COPY

03-Mar-89

01979

J. APPL. POLYMER SCI.

1976, VOLUME 20, PAGE(S) 1583-95

HAN, C.D.: ET AL

USER REF LUKE, J.A.

LIB

7
1
225

400028370