

Gas-Filled Polymers. I. Void Morphology of Polyethylene

A. G. KOLBECK and D. R. UHLMANN, *Department of Metallurgy and Materials Science, Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*; and P. D. CALVERT, *School of Molecular Sciences, University of Sussex, Falmer, Brighton, England*

Synopsis

Morphologic studies of gas-filled polyethylene show a characteristic void structure, with an interior region containing distinct gas bubbles surrounded by a surface layer of void-free polymer. The voids in the bubbled region frequently show an elongated shape with the long dimension oriented parallel to the surface of the specimens. The gas-polymer interface within individual voids is composed of fibrils of the polymer extending into the interior of the void. Studies of the annealing temperatures required to obtain gas bubbles in the material and of the melting range of the ungasified polymer indicate that melting of the crystalline component of polyethylene is required for void formation.

INTRODUCTION

Plastic foam technology comprises an important branch of the commercial polymer industry. While an extensive literature exists dealing with the properties and morphology of foams having overall densities less than about 0.5 g/cm^3 ,¹⁻⁴ no work appears to have been reported that focuses primarily on higher-density gas-polymer systems. The present study was undertaken to investigate the high-density end of such systems, and in particular to clarify the transition from behavior typical of bulk polymers to that typical of foamed polymers. The present paper will consider the morphology of the voids produced in high-density and low-density polyethylene by heat treatment in the presence of inert gases. In companion papers, we shall describe the effects of various gasification treatments on the mechanical properties of both polyethylenes⁵ as well as polycarbonate and poly(vinyl chloride).⁶

EXPERIMENTAL METHODS

The semicrystalline polymers studied were commercial high-density and low-density polyethylene. Both materials were obtained in rolled sheet 0.25 cm thick. The density of the as-received HDPE was 0.953 g/cm^3 , while that of the LDPE was 0.922 g/cm^3 .

Heat treatment was carried out in an Inconel pressure cylinder, 45 cm long and 5 cm in diameter. The cylinder was wound externally with high-resistance nichrome wire capable of heating the interior to 600°C. Gas pressure was obtained from pressurized tanks of the desired gas (nitrogen, argon, or helium) and was admitted to the cylinder by a valve and tubing system entering from the side. Also connected into this tubing system were a pressure gauge and a Conax high-pressure feed-through. Access to the sample region was obtained by an end cap which was bolted onto the cylinder during the high-pressure heat treatments and sealed with a neoprene O-ring. The apparatus was capable of withstanding 1900 psi internal pressure.

Samples were heat treated in the form of strips 15 cm long and 2.5 cm wide. The strips were clamped at each end with binder clips to an aluminum plate of the same shape to increase temperature uniformity along the length of the sample and to prevent warping of the sample during the heat treatment. The sample assembly was then placed in the central region of the pressure cylinder for the heat treatment. Temperature was monitored with either a Leeds and Northrup 8686 potentiometer or an L&N Azar recorder, with the thermocouple embedded in the aluminum sample holder or in the sample itself. It was possible with the Conax feed-through to utilize two thermocouples simultaneously; calibration runs gave a temperature difference of approximately 1°C between a thermocouple embedded in the holder and one embedded in the sample. A 1° temperature variation along the length of the sample was also found.

The thermocouple in the gasifying system was calibrated by comparing the melting temperature of two materials, phthalic anhydride (mp 130–132°C, according to the manufacturer) and lead-tin eutectic (mp 183–184°C), as measured by the thermocouple and as measured by an indium-calibrated Perkin-Elmer DSC-1B scanning calorimeter at a slow heating rate of 1.25°C/min. All temperatures to be reported subsequently are corrected to agree with the DSC thermocouple as a standard.

The typical heat treatment cycle involved (1) pressurizing the cylinder at room temperature, (2) heating the system to the desired peak temperature, (3) annealing at that temperature for the desired time, (4) cooling the cylinder by forced air to about 50°C, and (5) depressurizing. In some cases, the pressure was released at the annealing temperature prior to cooling. In these cases, an entirely different gas bubble structure was obtained, resembling more a low-density foam than the lightly bubbled polymer obtained by depressurizing after cooling. To distinguish the two heat treatment processes—cooling before depressurization and cooling after depressurization—samples given the first type of heat treatment will subsequently be termed “gasified,” while those given the second type will be labelled “foamed.” The gasification process using the above heat treatment cycle, resulted in the case of HDPE in a material of density about 0.88 g/cm³ or higher, depending on the details of the heat treatment. With the foaming process, a much lower density was obtained.

All temperatures to be reported subsequently for specific heat treatments of particular samples are the highest temperatures attained during those heat treatments. Likewise the annealing time is defined to be the time between the attainment of a temperature within one degree of the desired peak temperature and the initiation of the cooling process.

A Vickers polarizing light microscope was used to characterize optically the morphology of the gas bubbles formed by the gasifying heat treatment. The technique found most effective was to view a thin slice of the specimen by reflected white light incident at an angle of about 30 degrees from the horizontal. The small thickness of the slice allowed the bulk polyethylene, which in thick films is normally translucent white, to be essentially transparent to the incident light, while the gas gubbles, being composed of large amounts of free surface, scattered the light readily even in very thin specimens. Using this technique, the morphology of the gas bubbles was easily resolvable at magnifications as low as 15X.

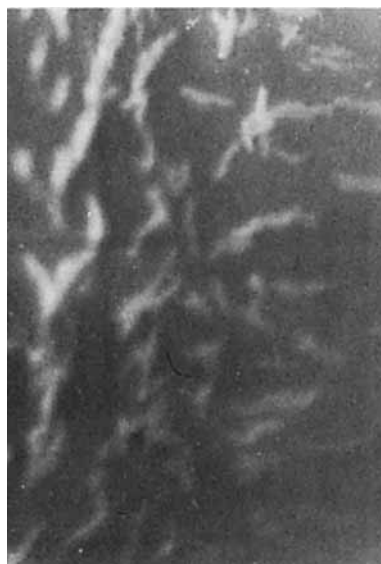
The scanning electron microscope (SEM) was also employed to study at high magnification the internal structure of the gas bubbles in high-density polyethylene. Successful high-magnification study was obtained by forming a fresh surface with a knife, shadowing the surface with gold, and viewing immediately in the SEM.

EXPERIMENTAL RESULTS

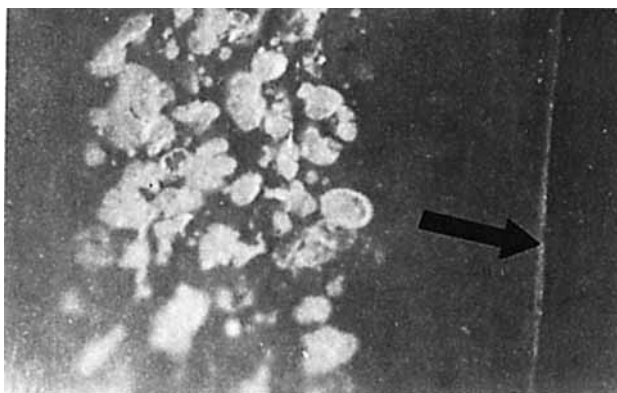
Gasification of High-Density Polyethylene, Optical Microscopy

Figure 1 shows two typical cross-sectional views, taken at low magnification under unpolarized, reflected light, of the void structure in N_2 -gasified HDPE. Similar micrographs of normal, ungasified HDPE are featureless, appearing the same as the surface regions of Figure 1b. In these and all subsequent micrographs, the surface of the sample, which is imaged as an edge in these cross-sectional views, will be marked by arrows.

Several points can be noted concerning this void structure. First, in all cases, including both HDPE and LDPE, a bubble-free surface layer is found. The thickness of the layer varies with the type of polymer investigated, the specific time and temperature conditions of the gasifying heat treatment, and the type of gas used as gasifying medium. For N_2 -gasified HDPE, the thickness of the surface layer is on the order of 0.05 cm. Second, the voids tend to show a specific orientation, particularly in the interior of the samples. It appears that the voids form more readily in platelet or rodlet shape parallel to the surface of the specimen. This observation was not completely general; at times an apparent orientation could be discerned in two directions—in one region of the specimen parallel to the surface, while in a neighboring region of the same specimen perpendicular to the surface. This effect is shown in Figure 1a. Other samples, as in Figure 1b, show no apparent orientation of the gas bubbles, but rather seem to be composed entirely of nearly spherical bubbles. The size of the voids in N_2 -gasified HDPE was about 0.03 cm for the diameter



(a)



(b)

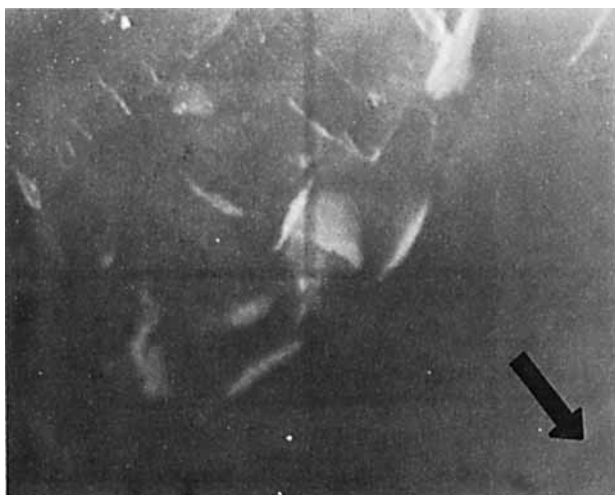
Fig. 1. Void morphology of N_2 -gasified HDPE. Heat treatment: (a) 152°C , 15 min, 1500 psi N_2 ; (b) 135°C , 30 min, 1500 psi N_2 . Magnification $40\times$. Arrow indicates surface of specimen.

of the spherical bubbles, while the dimensions of the oriented voids were about $0.03\text{ cm} \times 0.005\text{ cm}$.

Rotation of the specimen in the optical microscope had no effect upon the observed orientation of the voids; and the oriented structures seen in the SEM were similar to those noted in the optical microscope (compare Figs. 2a and 3). These observations indicate that the orientations were not artifacts of the illumination employed.



(a)



(b)

Fig. 2. Void morphology of Ar-gasified and He-gasified HDPE. Heat treatment: (a) 152°C, 15 min, 1500 psi Ar; (b) 152°C, 15 min, 1500 psi He. Magnification 40 \times . Arrows indicate surface of specimen.

It was not possible to focus on any sharp, distinct structure at magnifications greater than about 100 \times . This seems likely to be due to the structure of the phase boundary between the gas bubbles and the bulk polymer, as will be discussed below.

Figure 2 shows the void structure of argon- and helium-gasified high-density polyethylene. The Ar-gasified specimen is similar to the previously described N₂-gasified specimens, with similar surface layer thickness and void orientation. The bubbles themselves appear to be slightly larger,

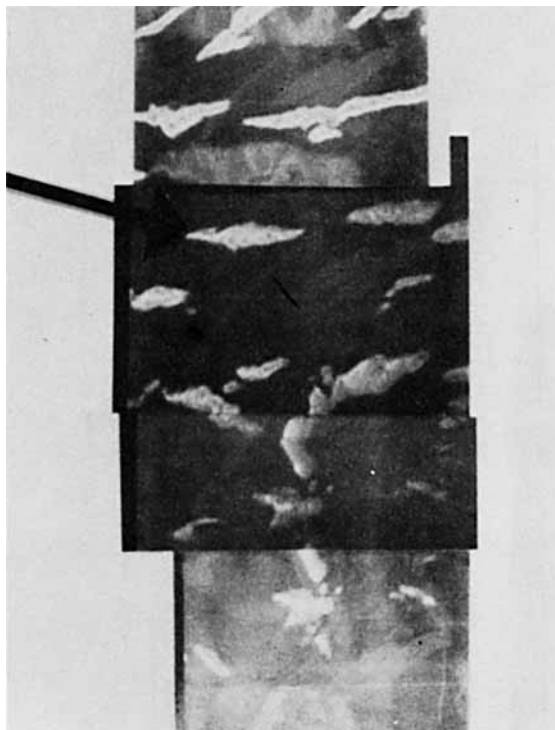


Fig. 3. SEM micrograph of void structure in Ar-gasified HDPE. Large arrow indicates void shown at higher magnification in Figure 4. Heat treatment: 152°C, 15 min, 1500 psi Ar. Magnification 45 \times .

about 0.10 cm \times 0.01 cm. The He-treated sample is quite different in appearance. The surface layers are 2-3 times as thick (approximately 0.12 cm) as those in the other two types of gasified material. In addition, the bubbles themselves are much fewer in number and more widely separated. Again the voids seem to show a preferred shape as either platelets or rods. The size of the voids in He-gasified HDPE is about 0.05 cm \times 0.005 cm.

The difficulty noted earlier of focusing at higher magnifications on the voids in N₂-gasified HDPE is more pronounced in He-gasified HDPE. Even at the low magnification of Figure 2b, the voids seem diffuse and ill defined; and this diffuseness proved to be general over several samples studied.

Scanning Electron Microscopy

Figure 3 shows a composite of a series of micrographs of Ar-gasified HDPE taken in the SEM at relatively low magnification. Comparing this micrograph with Figure 2a of Ar-gasified HDPE viewed in the optical

microscope, it seems reasonable to presume that the two techniques, optical microscopy and scanning electron microscopy, are consistent in representing the void structure. That is, no inconsistent artifacts are introduced between the two sample preparation techniques. The same characteristic void morphology is observed in the SEM, including the bubble-free surface layer and the tendency toward orientation of the bubbles parallel to the surface. Further, the size of the voids indicated by the SEM is approximately the same as found in the optical microscope.

Figure 4 shows the internal structure of the voids of Ar-gasified HDPE at higher magnification. The gas bubbles are clearly shown to be composed of many small fibrils extending outward from the walls of the voids. Very roughly, the fibrils in Ar-gasified HDPE are about 10^{-4} cm in diameter and 0.002–0.005 cm in length.

Similar SEM studies on N_2 -gasified HDPE showed a virtually identical internal void structure, with no noticeable differences between the fibrils in N_2 -gasified HDPE as compared to Ar-gasified HDPE.

The observation of a fibrillar structure as the boundary between gas and polymer provides an explanation for the observation noted earlier than in the optical microscope the boundary between gas and polymer appeared diffuse. At the relatively low magnifications of the optical microscope, where the individual fibrils could not be resolved, the existence of a boundary layer consisting of both gas and polymer would be expected to lend a diffuseness to the phase boundary.

Gasification of Low-Density Polyethylene

Figure 5 shows the two types of bubble morphology found in N_2 -gasified LDPE. The first structure (Fig. 5a) is similar to that found in gasified HDPE, with the characteristic bubble-free surface layer surrounding a region of oriented bubbles of size 0.04 cm \times 0.003 cm. The second structure (Fig. 5b), on the other hand, is very different from those seen in gasified HDPE. While the bubble-free surface layer is still present, its thickness is about one third that of the first structure (0.10 cm versus 0.03 cm). More important, the gas bubbles themselves are much smaller, on the order of 0.0025–0.0050 cm across, and more numerous than those in either N_2 -gasified HDPE or the first type of N_2 -gasified LDPE. The structure of Figure 5b may represent an interconnected bubble network. This is not certain, however, since the apparent interconnectivity may be due to the three-dimensionality of the specimen. (The image may be of several separate layers of the material, each with its own nonconnected set of gas bubbles being projected onto the plane of the photograph.)

The difference between the two types of N_2 -gasified LDPE is apparently due to a difference in gasification temperature, with the coarser, oriented morphology being observed for gasification at lower temperatures (below about 120°C), while the fine structure was found for gasification in the range of 130°C.



(a)



(b)

Fig. 4. Designated void from Figure 3. Magnification(a) 400 \times , (b) 1300 \times .

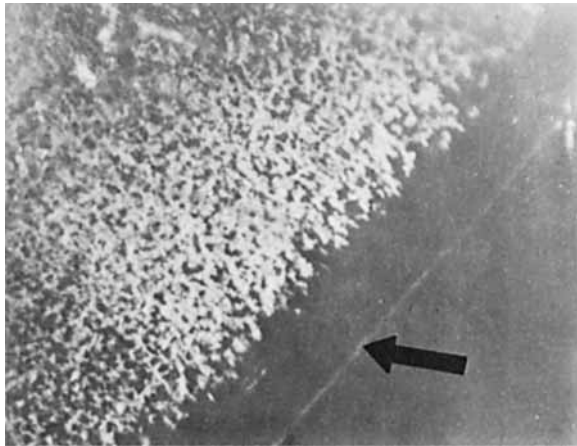
Experimental Requirements for Gasification

High-Density Polyethylene

To investigate the conditions in which gasification occurs (as indicated by the formation of gas bubbles in the interior of specimens), a series of HDPE samples were gasified under N_2 pressure at various temperatures for



(a)



(b)

Fig. 5. Void morphology of N_2 -gasified LDPE. Heat treatment: (1) 122°C , 30 min, 1500 psi N_2 ; (b) 133°C , 15 min, 1500 psi N_2 . Magnification (a) $40\times$, (b) $60\times$. Arrows indicate surface of specimen.

the same length of time. It was found for samples which were cooled before depressurization that, as the temperature of gasification was reduced in 1° increments from 136°C to 133°C, the number and size of the gas bubbles steadily decreased until at the lowest temperature no gas bubbles were observed. As the temperature was reduced, the void-free surface layer also increased in thickness.

To determine whether at temperatures of 133°C and below gas no longer entered the material during the annealing process, or whether gas was still entering the polymer but bubble growth was inhibited by insufficient supersaturation at the temperatures where appreciable diffusion was allowed, a series of samples were heat treated at various temperatures below 133°C for a constant length of time, then cooled rapidly (15–20°C/min) after depressurization of the apparatus. Presumably a lower ambient pressure would lead to greater effective saturation of the material. Results showed that gas bubbles formed to temperatures as low as 124°C, while for gasification at temperatures below this, no voids were found. That is, bubbles formed at temperatures 10° lower with the foaming process than with the gasifying process. Thus, bubble formation at higher temperatures, employing the gasifying rather than the foaming procedures, seems to be inhibited by insufficient supersaturation at the relatively high temperatures where transport should be most rapid, and inhibited by relatively slow diffusional transport at low temperatures (near room temperature) where the supersaturation after the release of pressure is relatively large.

An additional set of HDPE samples were treated at several pressures to determine the effect of gas pressure on the bubble morphology. Using 1000 psi of N₂ with the gasification, the void structure did not appear to vary significantly from that observed with gasification at 1500 psi, except that the critical temperature below which gas bubbles did not form was higher by 1°C (134°C). Gasification under a pressure of 500 psi N₂ is much reduced from that at higher pressures. Even at an annealing temperature of 150°C, well above the melting point of HDPE, only relatively few gas bubbles form, and these are individually much smaller than those formed at the higher pressures. At 137°C and 500 psi N₂, no gas bubbles were found while extensive void formation was noted at this temperature and higher pressures.

The result of a decrease in pressure is to raise the annealing temperature required for bubble formation. A gasification pressure of 500 psi is apparently near the critical pressure below which bubble growth is not found, since even with annealing at 150°C only very slight bubble formation is noted.

The observations presented above, that the temperatures required for gas bubble formation are in the range 120–135°C depending on the state of pressurization, suggest that melting of the crystalline structure in the material is important to the formation of gas bubbles (since the melting range of HDPE occurs in the same temperature interval). In an attempt to examine this relation more closely, the melting behavior of the as-received

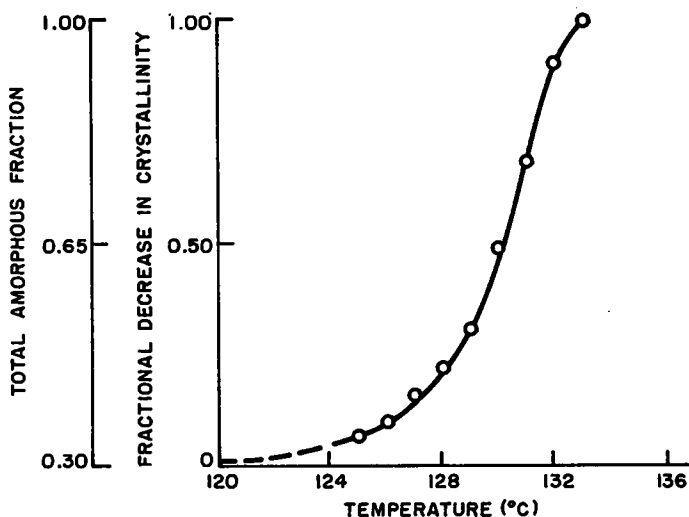


Fig. 6. Melting behavior of as-received HDPE.

HDPE was investigated in the Perkin-Elmer DSC-1B scanning calorimeter at a low heating rate of $1.25^{\circ}\text{C}/\text{min}$.

It should be noted, in comparing the DSC melting data taken at a pressure of 1 atm with the conditions required for gasification at approximately 100 atm, that the melting range of polyethylene increases as the material is pressurized.⁷ The magnitude of this increase is roughly 2° for a pressure of 1500 psi. Therefore, when considering the effect of melting on gasification, the critical temperatures (i.e., the temperatures below which no bubble formation is observed) must be lowered by 2°C to permit direct correlation with the DSC melting data.

Figure 6 is a plot of the fraction of the crystalline component melted as a function of temperature. The total crystallinity is estimated to be about 70%, using the value of 66 cal/g for the heat of fusion.⁸ The plot is therefore of the fraction of this 70% that is melted at any given temperature. It is evident from Figure 6 that the critical temperature below which bubble formation will not occur (133°C , adjusted to 131°C due to the effect of pressure on melting) in a gasification treatment at 1500 psi occurs in the same range as melting. Noting further that using the more favorable foaming process, the lowest temperature at which gas bubbles can be formed is $122\text{--}124^{\circ}\text{C}$, adjusted to $120\text{--}122^{\circ}\text{C}$, it appears that some degree of melting is indeed necessary to effect gasification, since from Figure 6 the $120\text{--}122^{\circ}\text{C}$ temperature interval is the same as that in which significant melting begins to occur.

Low-Density Polyethylene

Similar studies to those reported in the previous section were conducted on LDPE to determine the conditions at constant pressure and annealing time under which bubble formation occurs. With the gasification process

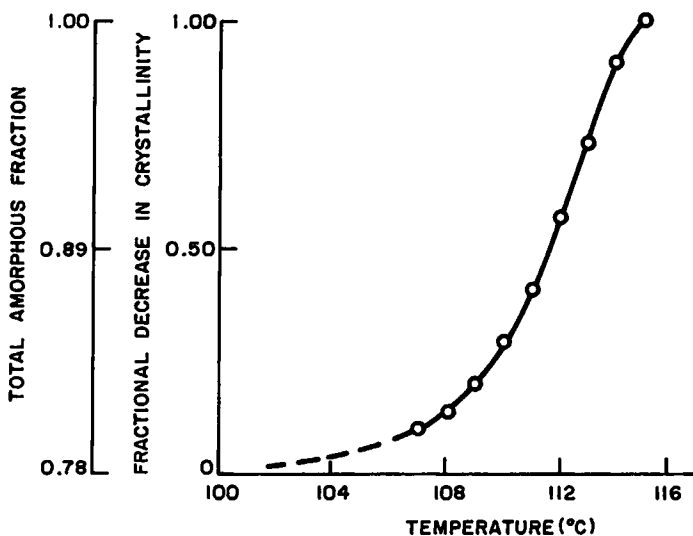


Fig. 7. Melting behavior of as-received LDPE.

at 1500 psi of N_2 , it was found that the temperature below which gas bubbles would not form was about $114^\circ C$ for LDPE. The degree of void formation in terms of size and number increased steadily above that temperature. With the foaming process bubbles were found to form at temperatures as low as $107^\circ C$, although at that temperature no bubbles were evident after the heat treatment until several days at room temperature.

The melting behavior of the LDPE was also studied. The fraction melted at a heating rate of $1.25^\circ C/min$ (of a total crystallinity of 22%) is indicated in Figure 7. After applying the $2^\circ C$ pressure correction to the critical gasification temperatures given above, it is apparent that the temperature region where some degree of bubble formation was observed with the foaming process is in the range where significant melting is beginning to occur. Again it appears that a relatively large degree of melting is necessary for the gasification process to lead to bubble formation, since with this process bubbles did not form below a pressure-corrected temperature of $112^\circ C$.

DISCUSSION

Experimental results for both HDPE and LDPE indicate that at least some degree of melting of the crystalline component is necessary for void formation. This can be related to two factors: (1) the melting process itself could be critical, with the diffusivity of gas in the molten polymer increasing to such an extent that appreciably more gas is dissolved in the amorphous phase; the supersaturation of the gas during the cooling process (which is the driving force for void formation) may then increase beyond

some critical amount required for bubble growth; or (2) the recrystallization of the polymer during the cooling process could be critical, with the growing spherulites rejecting dissolved gas during crystallization and creating locally large supersaturations which in turn cause void formation. It appears from the evidence found in the present study combined with that reported elsewhere on the sorption and diffusion of gases in polyethylene⁹ that a plausible argument can be made for a combination of the two factors.

Consider first the proposition that void formation occurs upon recrystallization of the polymer during the cooling process. The main source of evidence in support of this model is the work of Michaels and Bixler.⁹ These investigators have studied the solubility constant for a series of polyethylenes of various densities, ranging from 0.915 to 0.966 g/cm³. Their results showed that the solubility constant could be related in a linear manner to sample density, with samples of higher density and thus of higher crystallinity having a lower coefficient of solubility. Straight lines were obtained for solubility constant versus amorphous fraction for both nitrogen and oxygen. The extrapolation of this line from the highest density PE investigated 0.966 g/cm³, to the density of completely crystalline polyethylene, approximately 1.00 g/cm³, suggested that the solubility of both gases in polyethylene is zero for zero amorphous fraction. It was concluded that the crystalline phase of polyethylene has essentially zero solubility for these gases as compared to the solubility of the amorphous component.

In spite of the fact that these measurements were made at 1 atm pressure in the temperature range of 25–50°C, there is no reason to expect that their results should not apply at least qualitatively over the range of experimental conditions of the present investigation (110–150°C and 100 atm). Hence it is expected that the solubility of gas in the crystalline component of polyethylene is significantly less than in the amorphous material, most likely by an order of magnitude or more, and it can be readily understood why the bubbles form during the crystallization process. As the polymer melts, the solubility of gas in the initially crystalline regions increases by a large amount, and gas then diffuses into those regions. During the subsequent cooling process, gas should then be rejected at the crystal-liquid interface. This will lead to large supersaturations in small regions of the sample, which will in turn induce bubble formation.

Two observations must be accounted for by the model. The first has to do with the size of the spherulites as compared with the size of the voids formed during the gasification process. If bubble formation does occur during crystallization, one might at first expect the voids to be smaller than or comparable to the spherulites in size; yet it was found that the voids were at least a factor of 5 larger in their smallest dimension than the average diameter of the spherulites in HDPE. Rejection of gas during crystallization may, however, account for only the nucleation of the bubbles, with the subsequent growth and coalescence occurring by diffusion at the expense of gas in neighboring bubble nuclei and amorphous regions.

The second point to be clarified concerns the observation that only slight degrees of melting are required for gas bubbles to form. If bubble formation occurs by the rejection of gas during crystallization, it might be expected that significant melting would be required for void formation. It seems not unreasonable, however, that the solubility in crystalline PE is so low that during the recrystallization of even a few per cent of the crystalline component, the rejected gas causes supersaturation in local regions of the material sufficient to overcome the nucleation barrier to bubble formation. Growth of the voids to a size sufficient to allow their direct observation in the optical microscope then occurs by normal diffusion of gas to the bubble from the amorphous regions of the polymer.

The other important factor in the formation of gas bubbles following melting of PE involves primarily an increase in diffusivity of gas in polyethylene due to the melting of the crystalline component, and it acts in such a direction as to supplement the first proposed model based on bubble formation during recrystallization. It has previously been indicated⁹ that the diffusivity of gas in the amorphous component of semicrystalline polyethylene is smaller by a factor of about 10 than that in completely amorphous polyethylene (extrapolated from the melt). This was attributed to two effects: first, a tortuosity factor due to the fact that a given gas molecule must follow a very intricate path around the crystallites; and second, a chain-immobilization effect due to restrictions on chain movement in the amorphous phase caused by the presence of crystallites. While the tortuosity effect would not be expected to decrease significantly for annealing temperatures where the material is 5% melted, the chain-immobilization effect may well decrease significantly during the first stages of melting as crystalline features such as molecular links between lamellae and between spherulites are melted out. In this way, the diffusivity may increase significantly with increasing temperature in the interval over which melting begins to occur. This increase in diffusivity might then be sufficient to allow ready access of the gas to the interior of the sample, and thus to result in bubble formation during the time interval of the experiments.

The most reasonable model for the formation and growth of gas bubbles in polyethylene can then be summarized: nucleation of the bubbles occurs during crystallization of the material by rejection of gas from the crystallizing polymer. The melting process further aids bubble formation by reducing chain immobilization, which in turn causes an increase in diffusivity. The increase in diffusivity increases both the rate of absorption of the gas during annealing and the rate of growth and coalescence of the bubbles during cooling.

The growth and coalescence of the bubbles leads to a final morphology in the case of HDPE where the bubbles have a size at least five times larger than the size of the spherulites. Since the bubbles apparently form during crystallization, the attainment of their final size seems likely to involve a displacement of the spherulites themselves and a disruption of their internal structure. The bubbles would be expected to form initially in the

vicinity of the advancing crystal-liquid interfaces (either at the tips of the lamellae during primary crystallization or between the lamellae during secondary crystallization). Based on the observed behavior of other fluid particles at crystal-liquid interfaces,¹⁰ the bubbles should be rejected by the crystalline polymer-molten polymer interfaces and become concentrated in the interlamellar regions and the regions between the spherulites. Their growth from gas rejected during further crystallization and their subsequent coalescence could then result in the large bubbles which are finally observed. The most favored location for the interspherulitic gas bubbles would seem to be the nodal points where several spherulites come together; but this *a priori* preference may well be outweighed by details of the coalescence processes which take place in the interspherulitic and interlamellar regions. These coalescence processes can serve effectively to isolate the lamellae, either individually or in bundles as fibrils, and in this way a bubble-polymer boundary composed primarily of crystalline fibrils surrounded by the gas may reasonably be understood.

The observation of a void-free surface layer in all gasified specimens of both HDPE and LDPE is likely due to the diffusion of gas from the surfaces of the material as the specimens are cooled. The slow decrease in the solubility of the gases in polyethylene as the temperature is lowered¹¹ will give rise to a driving force for dissolution. The greatest contribution, however, will be associated with the large supersaturation which results from crystallization (due to the very low solubility of gas in the crystal phase). The gas phase above the surface of the specimen will act as a sink for the excess gas in the polymer, inhibiting the nucleation and coalescence of gas bubbles in a region near the sample surface. A rough estimate can be made of the depth of the affected zone using the well-known expression for the approximate size of a diffusion field: $x \approx (4Dt)^{1/2}$. Here, D is the diffusion coefficient, t is the time, and x is the scale of the diffusion field. Taking D to be on the order of 10^{-6} cm²/sec over the temperature range of interest¹¹ and t to be in the range of 15 min (between the occurrence of crystallization and the termination of the cooling process), a value is obtained for x of about 0.06 cm. Considering the level of the approximations, this estimate agrees well with the measured surface layer thicknesses which range between 0.03 and 0.12 cm.

The tendency of the voids in both HDPE and LDPE to form oriented parallel or perpendicular to the specimen surface is not understood in satisfactory detail. It seems likely to reflect some orientation in the specimen; but the relation of the usual descriptions of orientation to the complex growth and coalescence phenomena involved in forming the final bubble morphologies remains far from clear.

Financial support for the present work was provided by the Advanced Research Projects Agency, by the National Science Foundation, and by the International Business Machines Corporation who provided one of the authors (AGK) with the IBM Fellowship in Materials Science. This support is gratefully acknowledged.

This paper is based in part on a thesis submitted by A. G. Kolbeck in partial fulfillment of the requirements for the M.S. degree in Materials Science, M.I.T., 1972.

References

1. C. J. Benning, *Plastic Foams*, Interscience, New York, 1969.
2. R. E. Wright, *Resinography of Cellular Plastics*, ASTM STP 414, 1967.
3. J. D. Griffin and R. D. Skochdopole in *Engineering Design for Plastics*, E. Baer, Ed., Reinhold, New York, 1964.
4. R. E. Skochdopole and L. C. Rubens, *J. Cell. Plast.*, **1**, 95 (1965).
5. A. G. Kolbeck, D. R. Uhlmann, and P. D. Calvert, *J. Appl. Polym. Sci.*, **17**, 6395 (1973).
6. A. G. Kolbeck, H. Fujimoto, P.D. Calvert, and D. R. Uhlmann, *J. Appl. Polym. Sci.*, to be published.
7. E. Baer and J. L. Kardos, *J. Polym. Sci. A*, **3**, 2827 (1965).
8. P. H. Geil, *Polymer Single Crystals*, Interscience, New York, 1963.
9. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 393 (1961).
10. D. R. Uhlmann, B. Chalmers, and K. A. Jackson, *J. Appl. Phys.*, **35**, 2986 (1964).
11. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 413 (1961).

Received July 25, 1972

Revised September 1, 1972