

## Gas-Filled Polymers. II. Mechanical Behavior of Polyethylene

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### Synopsis

The mechanical properties of gas-filled polyethylene have been studied for material with density greater than about 0.85 g/cm<sup>3</sup>. The effect of gasification on the tensile properties of both high and low density polyethylene beyond a certain critical density reduction is to cause a general weakening of the material. The yield stress falls by about 25% over the range of density investigated, while the elongation to fracture decreases by an order of magnitude. A mechanism is proposed to this weakening and for the yielding and fracture phenomena observed for gasified polyethylene.

### INTRODUCTION

The morphologies of the voids observed in gasified polyethylene (PE) have been described previously.<sup>1</sup> The present paper will consider the tensile properties of this material and will attempt to relate the mechanical behavior to the void morphology of the gasified polymer.

The mechanical properties of gas-filled PE systems having overall densities less than about 0.5 g/cm<sup>3</sup>, approximately half that of the bulk polymer, have been investigated.<sup>2-5</sup> The values of the mechanical properties (modulus, yield stress, and elongation to fracture) in tension, compression, and flexure are invariably found to increase with increasing density of the material. As an example, the flexural modulus of foamed PE increases by an order of magnitude as the density changes from 0.05 g/cm<sup>3</sup> to 0.50 g/cm<sup>3</sup>, having a value of about 1000 psi at the 0.50 g/cm<sup>3</sup> end for a foam-formed from an LDPE resin and about 10,000 for one formed from an HDPE resin.<sup>2</sup> Likewise, typical values of the tensile strength for foamed PE are about 50 psi for a density of 0.02 g/cm<sup>3</sup> and 150-200 psi for a density of 0.1 g/cm<sup>3</sup>.<sup>2</sup> Ultimate elongation is found to be in the range of 100-200% over the same density range, increasing slightly with increasing density.

The present study is concerned with the mechanical properties of gas-filled polyethylene of relatively high density, above about 0.85 g/cm<sup>3</sup>, and with the transition in behavior between that expected for normal bulk polyethylene and that typical of foamed polyethylene. Little previous work appears to have been reported which considers such material. Ben-

ning<sup>3</sup> reports the tensile properties of a single specimen of foamed HDPE having a density of 0.89 g/cm<sup>3</sup>. He obtained a modulus of 129,000 psi, yield stress of 2000 psi, and elongation at fracture of 62%. No indication is given of the yielding and fracture phenomena associated with the tensile drawing of this specimen.

### EXPERIMENTAL METHODS

The materials used in the present investigation were the same as those studied previously,<sup>1</sup> viz., commercial high-density and low-density polyethylene obtained in rolled sheet 0.25 cm thick. The density of the as-received HDPE was 0.953 g/cm<sup>3</sup>, while that of the LDPE was 0.922 g/cm<sup>3</sup>.

The gasification procedure has been described previously.<sup>1</sup> Briefly, for samples intended for mechanical testing, the gasification treatment involved heating strips of the polymer under a pressure of 1500 psi of either nitrogen, argon, or helium to temperatures at or above the melting point of the particular polymer. After annealing at a specified temperature for the desired time, generally 16 to 60 min, the apparatus was cooled to room temperature prior to depressurization.

For LDPE the degree of gasification of the material after heat treatment could be readily determined by the change in opacity of the samples. That is, the opacity was found to increase significantly with the introduction of a relatively small number of gas bubbles. High-density polyethylene, on the other hand, showed an increase in opacity for large degrees of gasification (i.e., gasification at high temperature for long periods of time), but did not show a significant change in opacity for relatively small degrees of gasification. Hence, in order to obtain a quantitative measure of the degree of gasification of HDPE, density measurements were made using the gradient column technique described by Oster and Yamamoto<sup>6</sup> with toluene-monochlorobenzene or isopropanol-water as the gradient liquids. It was invariably found that, in cases where a visual distinction in degree of opacity could be determined, the more opaque sample showed a lower density.

Tensile tests were conducted on a table-model Instron machine at room temperature, with cross-head speeds of 0.2 in./min and in a few cases 0.02 and 2 in./min as well. Tensile samples were machined or stamped according to ASTM Standard D 638. For HDPE, two sets of dimensions were used. All samples had a nominal gauge width of 0.65 cm and a thickness of 0.25 cm, while the gauge length of the machined samples was 3.3 cm and that of the stamped samples was 5.1 cm. LDPE tensile specimens all had nominal dimensions 5.1, 0.65, and 0.25 cm for the gauge length, width, and thickness. Values of stress and strain were calculated from the force-elongation data on the basis of the initial cross section and the initial gauge length of the specimen. Exact dimensions of each sample were determined prior to tensile testing to take into account small variations, particularly of thickness, due to the heat treatment.

## RESULTS

## High-Density Polyethylene

Figure 1 shows a typical stress-strain curve found for ungasified HDPE. Prior to the tensile test, the sample had been annealed at atmospheric pressure in the temperature range at which the gasification heat treatments were conducted. Close agreement was obtained between the ultimate elongation (800–1000%) and yield stress (3500–4000 psi) found here for annealed HDPE and those reported elsewhere, for example, by Sandiford and Willbourn.<sup>7</sup> Figure 1 also shows the types of stress-strain curves found for specimens of gasified HDPE having density less than 0.953 g/cm<sup>3</sup>. The lower curve is typical of samples which showed a large density change upon gasification (to 0.92 g/cm<sup>3</sup> or less). Fracture occurred in the first portion (i.e., before yielding) of the “normal” stress-strain curve. The fracture process was abrupt and rapid, and generally occurred at relatively low stress levels.

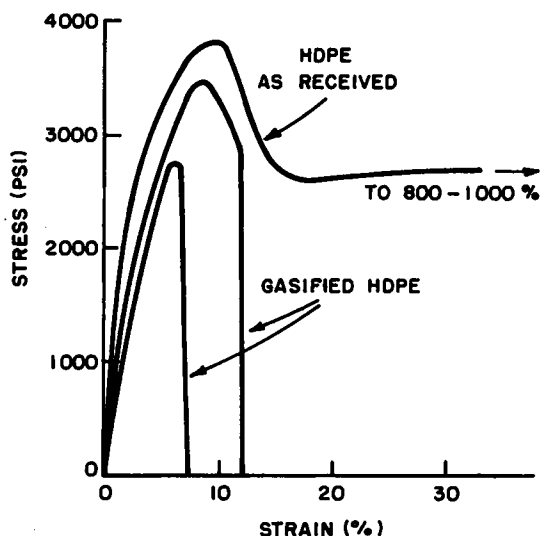


Fig. 1. Typical stress-strain behavior of HDPE.

A second type of stress-strain curve, shown as the intermediate curve in Figure 1, was found for more moderately gasified material (0.92–0.953 g/cm<sup>3</sup> in density). Here, the sample elongated beyond the yield point and was still capable of supporting a load, as indicated by the relatively low slope on the high-strain side of the yield maximum. After this yielding process, fracture occurred, as shown by the change in slope of the stress-strain curve. The maximum in the curve was accompanied on the sample by the formation of many whitened structures along the gauge length, most oriented roughly normal to the tensile axis of the sample. Some of these craze-like textures were, however, observed at angles as large as 45 degrees

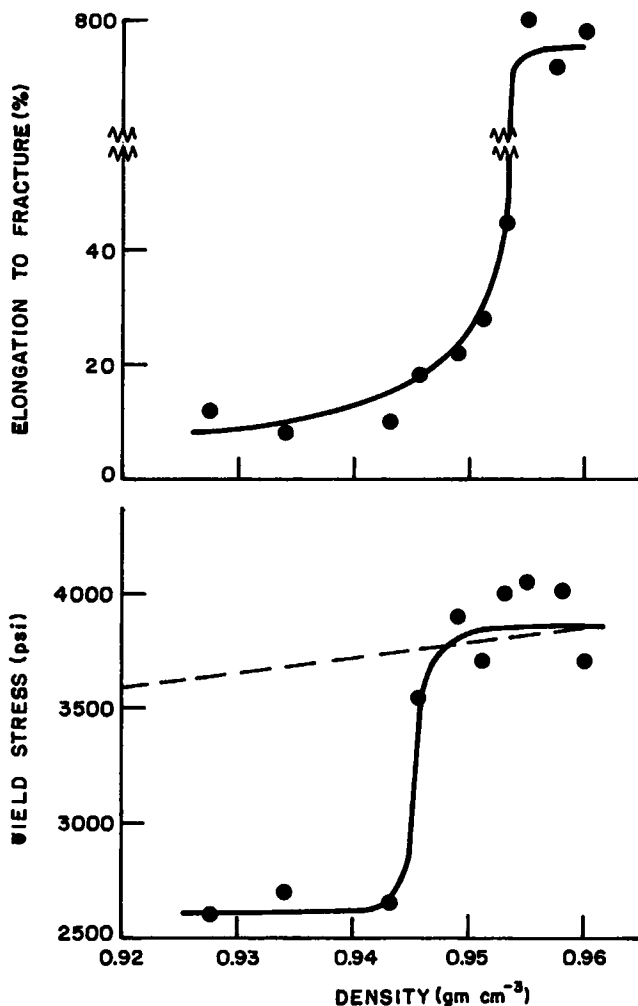


Fig. 2. Density dependence of yield stress and elongation to fracture for  $N_2$ -gasified HDPE. Heat treatment:  $134^\circ C$  and 1500 psi  $N_2$  for varying periods of time, ranging from 5 to 125 min. Solid curve, experimental data; dashed curve, law of mixtures.

to the direction of stress. During the yielding process following the yield point, these structures elongated until a crack initiated at one and propagated rapidly across the sample.

The stress-strain behavior as a function of density was determined for a series of HDPE specimens given gasifying heat treatments at the same temperature and pressure of nitrogen gas but for varying periods of time. Results are shown in Figure 2.

The most significant effect of the gasification was a large reduction in the elongation to fracture for even relatively lightly gasified samples. To appreciate this reduction, note that in Figure 2a all samples of density 0.954

or greater drew to 700% or more, while all samples with density less than 0.953 fractured at elongations of less than 60%, a reduction in elongation by more than a factor of 10. Further, the elongation-versus-density relation is monotonic, samples having lower density (and thus a higher degree of gasification) drew less than more mildly gasified specimens.

From the nature of the curve in Figure 2a, there are indications of a threshold in drawing behavior. For densities after the gasifying heat treatment of 0.954 or greater, the elongation to fracture was not appreciably affected; the samples still exhibited cold-drawing as would be expected of normal, gas-free polyethylene. As the density decreased to 0.953 or less, however, a sharp decrease in the ultimate elongation was observed.

The behavior of the yield stress as a function of density was similar to but less extreme than that of the elongation to fracture. At small density decreases, no appreciable decrease in the yield stress was noted. As the density of the specimens fell below 0.949, however, the yield stress dropped by about 30%. Again, a threshold reduction in density was required before the mechanical properties were affected, after which a significant decrease in magnitude was noted.

A simple law of mixtures analysis (sketched in Fig. 2b for a nominal control density of 0.96 g/cm<sup>3</sup>) predicts that the yield stress of the gasified samples will be reduced relative to the control samples by the ratio of the gasified density to the control density. It can be seen from Figure 2 that the observed reduction is substantially greater than this.

The forms of the curves obtained for both elongation to fracture and yield stress as a function of density are sigmoid-shaped. There is the suggestion of a plateau value for both parameters below a density of about 0.94 g/cm<sup>3</sup>.

The dependence of yield stress on strain rate is shown in Figure 3 both for ungasified control samples and for N<sub>2</sub>-gasified specimens having a density of 0.934 g/cm<sup>3</sup>. At all strain rates used, the yield stress of the gasified HDPE is significantly lower than that of ungasified material. Further, the elongation to fracture of these same gasified HDPE specimens was in all cases less than 20%, independent of the strain rate.

The results reported to this point on mechanical properties of gasified HDPE have been based on N<sub>2</sub>-gasified samples. Two other gases, helium and argon, were also used as the gasifying medium to determine the generality of the results found with N<sub>2</sub>-gasified HDPE. Results are listed in Table I. It can be seen that helium and argon are as effective as nitrogen in reducing the mechanical properties, particularly the ultimate elongation.

A series of N<sub>2</sub>-gasified HDPE samples were given secondary heat treatments at atmospheric pressure following the gasification heat treatment and tested in tension to determine whether the original mechanical properties could be recovered. These treatments involved remelting the specimens at atmospheric pressure and subsequently recrystallizing them. The resulting specimens exhibited a translucency and density similar to that of the original ungasified material. Their mechanical behavior is summarized

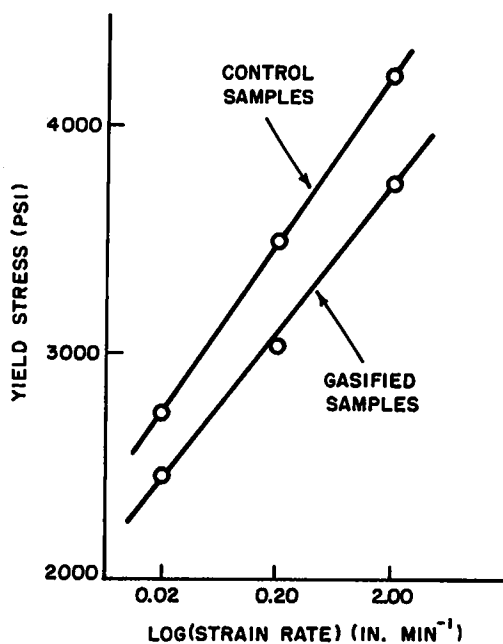


Fig. 3. Dependence of yield stress on strain rate for  $N_2$ -gasified HDPE. Heat treatment: control samples— $152^\circ C$ , 20 min, 1 atm; gasified samples— $152^\circ C$ , 20 min, 1500 psi  $N_2$ .

in Table II. It is seen that the elongation to fracture returned to values typical of normal, ungasified PE; but no such recovery was observed for the yield stress, which remained in the range of that for gasified PE. The form of the stress-strain curve for the recovered samples was the same as that of normal, ungasified HDPE (Fig. 1), and the yielding and neck formation processes appeared identical.

It is interesting that the ultimate elongation exhibited recovery after melting and recrystallization at atmospheric pressure, while the yield stress did not. (Recall the results shown in Fig. 2, where the elongation to failure appears to be more sensitive to the gasification process.) To deter-

TABLE I  
Effect of Helium and Argon Gas on HDPE<sup>a</sup>

Sample designation	Yield stress, psi	Ultimate Elongation, %
He 1	3410	14
He 2	3510	22
Ar 1	—	10
Ar 2	3400	12
Typical $N_2$	3500	20
Control (no gas)	3800	greater than 800

<sup>a</sup> Heat treatment:  $152^\circ C$ , 1500 psi He or Ar; strain rate: 0.2 in./min.

TABLE II  
Recovery of Mechanical Properties of HDPE<sup>a</sup>

Sample designation	Yield stress, psi	Ultimate elongation, %
Control	3700	greater than 1000
Gas 1	3030	9
Gas 2	3260	23
Recovery 1	3100	greater than 500
Recovery 2	3020	greater than 500

<sup>a</sup> Heat treatments: Control—152°C, 15 min, 1 atm, density 0.957 g/cm<sup>3</sup>. Gas 1 and Gas 2—152°C, 30 min, 1500 psi N<sub>2</sub>, density 0.93 g/cm<sup>3</sup>. Recovery 1 and 2—152°C, 30 min, 1500 psi N<sub>2</sub>, density 0.93 g/cm<sup>3</sup>; followed by 152°C, 15 min, 1 atm; recovered density 0.955 g/cm<sup>3</sup>. Strain rate: 0.2 in./min.

mine whether repeated heat treatments alone could cause a change in mechanical properties (the recovered samples had been melted and recrystallized twice prior to testing), identical tensile tests were conducted on twice-melted but ungasified specimens of HDPE. No significant variations were noted in the tensile properties of as-received, once-melted, and twice-melted HDPE. Thus, the 25% lower values of yield stress and initial modulus of the recovered HDPE samples must be associated with the gasification process, and the difference between the effects of recovery treatments on yield stress and ultimate elongation must be associated with differences between the processes involved in yielding and fracture.

All results reported to this point on the stress-strain behavior of gasified HDPE have involved gasification at temperatures in the range of 134–152°C, where melting of the crystalline component of the material, if not complete as in the 152°C heat treatments, is certainly extensive. To determine if melting was required to affect the mechanical properties, a series of samples were gasified at lower temperatures. Table III gives the results found for the elongation to fracture.

The data show that these low-temperature heat treatments give rise to neither of the effects most characteristic of the gasification at higher temperatures—an appreciable decrease in density or a large reduction in elongation to fracture. It would therefore seem that a significant degree of melt-

TABLE III  
Low-Temperature Heat Treatments of HDPE<sup>a</sup>

Sample designation	Density (after heat treatment), g/cm <sup>3</sup>	Ultimate elongation, %
1	0.96	greater than 500
2	0.96	820
3	0.96	500
4	0.953	30

<sup>a</sup> Heat treatments: Sample 1—102°C, 45 min, 1500 psi N<sub>2</sub>. Sample 2—122°C, 45 min, 1500 psi N<sub>2</sub>. Sample 3—129°C, 45 min, 1500 psi N<sub>2</sub>. Sample 4—134°C, 15 min, 1500 psi N<sub>2</sub>. Strain rate: 0.2 in./min.

ing is required to induce an amount of gasification sufficient to affect the stress-strain behavior.

### Low-Density Polyethylene

The stress-strain behavior of once-melted low-density polyethylene observed here was similar to that observed previously,<sup>7,8</sup> viz., a yield stress in the range of 1500–1800 psi and an elongation to failure of 350–500%. Yielding was observed at about 10% strain with the occurrence of a definite maximum in the stress-strain curve, followed by drawing at a relatively constant stress level. After drawing to about 50–100% strain, however a second yield point was found where the stress level dropped a second time. Cold-drawing then occurred at the new stress until failure took place, generally at a strain of 350–500%. The first yield point was accompanied by no distinct change in the nature of the specimen itself; the sample appeared to draw uniformly along the entire gage length. Simultaneous with the second yield point on the stress-strain curve, however, a sharp neck was observed to form. Further drawing then occurred by propagation of the neck.

Table IV presents data on the stress-strain properties of N<sub>2</sub>-gasified LDPE. It is seen that LDPE behaves qualitatively the same as HDPE. Gasification greatly reduces the elongation to fracture and has a similar but less dramatic effect on the yield stress. The form of the stress-strain curve is also similar to gasified HDPE (recall Fig. 1). The most typical curve was similar to the intermediate case shown in Figure 1, exhibiting a definite yield point, but retaining the ability to support a load after yield, before the occurrence of fracture. The yield and fracture processes observed on the LDPE samples themselves appeared quite different, however, from those observed with gasified HDPE. The HDPE was found to yield by the formation of craze-like structures along the entire gage length, and to fracture without the formation of a distinct neck. Gasified LDPE, on the other hand, yielded in all cases with the formation of a definite, sharp neck. The fracture process then occurred within the necked region before significant propagation of the neck. It was noted that the fracture appeared to

TABLE IV  
Mechanical Properties of Gasified LDPE

Sample designation	Yield stress, psi	Ultimate elongation, %
Control 1	1520	475
Control 2	1680	350
Control 3	1670	485
Gas 1	1430	14
Gas 2	1560	77
Gas 3	1560	38

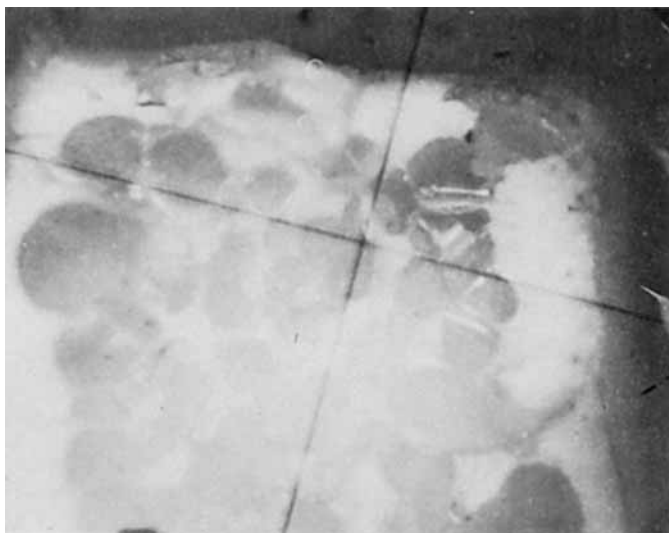
\* Heat treatments: Control 1—as cut from LDPE sheet. Control 2 and 3—133°C, 5 min, 1 atm. Gas 1—133°C, 15 min, 1500 psi N<sub>2</sub>. Gas 2 and 3—131°C, 5 min, 1400 psi N<sub>2</sub>. Strain rate: 0.2 in./min.



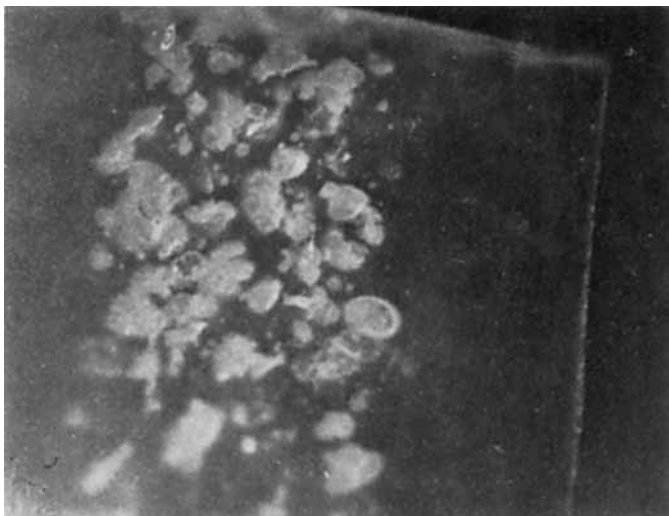
initiate in the interior of the specimen, with the edges being the last section of the sample to separate.

### Fracture Surface Morphology

Figures 4a and 5a are optical micrographs of the fracture surfaces of, respectively,  $N_2$ -gasified and He-gasified HDPE obtained at room tem-

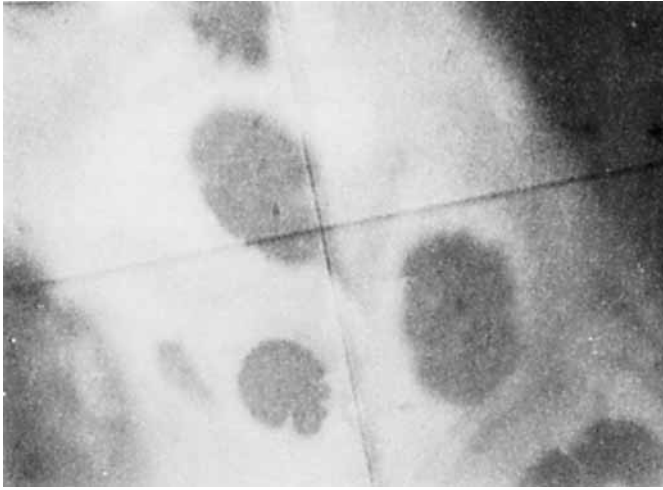


(a)



(b)

**Fig. 4.** Void morphology of  $N_2$ -gasified HDPE: (a) tensile fracture surface; (b) interior of unfractured material. Heat treatment:  $135^\circ\text{C}$ , 15 min, 1500 psi  $N_2$ . Magnification  $40\times$ .



(a)



(b)

**Fig. 5.** Void morphology of He-gasified HDPE: (a) tensile fracture surface (b) interior of unfractured material. Heat treatment: 152°C, 15 min, 1500 psi He. Magnification 40X.

perature by tension perpendicular to the surface shown. Fracture surfaces of Ar-gasified HDPE resembled closely those of N<sub>2</sub>-gasified HDPE. The most distinct feature of all these fracture surfaces is a void-filled central region surrounded by a whitened, void-free surface layer.

Figures 4b and 5b show the void structure of the same cross-sectional surface of unfractured N<sub>2</sub>-gasified and He-gasified HDPE. These micro-

graphs were obtained by viewing thin sections of the material with reflected light incident from 30 degrees to the plane of the specimen. In this arrangement, the bulk polymer appeared essentially transparent due to the small thickness of the specimen traversed, while the voids introduced by gasification process which are composed largely of free surface<sup>1</sup> scattered light extensively.

An obvious correlation is evident between the fractured and unfractured material: the surface voids on the fracture surface could readily be envisioned to have formed from the internal gas bubbles of the unfractured material. Considering the N<sub>2</sub>-gasified HDPE, the concentration of gas bubbles before fracture is about 1900–2200 cm<sup>-2</sup>, while the void density of the fracture surface is in the range 1700–2000 cm<sup>-2</sup>. Likewise, for He-gasified HDPE, the void densities of both fractured and unfractured material is about 250–350 cm<sup>-2</sup>.

Considering also the bubble-free surface layer, it can be seen that for both He-gasified HDPE and N<sub>2</sub>-gasified HDPE, the whitened surface layer of the fractured surface is approximately the same in thickness (0.06 cm for N<sub>2</sub>-gasified HDPE and 0.10 cm for He-gasified HDPE) as the bubble-free layer of the unfractured material. This provides further support for the relation between features seen on the fracture surface and those observed in the interior of the unfractured material.

## DISCUSSION

Simple two-phase mechanics, considering gasified polyethylene to be composed of a polymeric matrix and a system of discrete filler particles (the gas bubbles), cannot account for the mechanical behavior of the gasified material. Such models, based on the case of no adhesion between the matrix and filler particles (see, for example, Nielsen<sup>9</sup>) adequately predict the initial reduction of yield stress with void formation; they fail, however, to describe the plateau observed for the yield stress at relatively large density reductions (Fig. 2). Rather, the models predict a monotonic decrease in yield stress with increasing void content. The models also predict a gradual decrease in elongation to break with increasing volume fraction of voids, not at all in accord with the abrupt reduction by a factor of 30 or so observed for the elongation of gasified polyethylene.

Similar experiments performed on gas-filled glassy polymers<sup>11</sup> show even worse agreement with the simple theory. The mechanical properties of gasified polycarbonate and poly(vinyl chloride) appear to be nearly independent of void content, again at variance with the expectations of models based on simple two-phase mechanics. It seems clear, therefore, that an explanation for the mechanical behavior of gas-filled polymers must be based on the morphologies of the individual materials—not only because of the failure of gross mechanics to account satisfactorily for the phenomena but also because of the marked differences noted between semicrystalline PE and glassy polycarbonate and PVC.

Detailed consideration of the morphologies observed in fractured and unfractured specimens of gasified HDPE leads to clarification of the deformation processes of the material. Beginning with the surface layers, it can be seen that the opacity of the fractured and unfractured materials is quite different. The unfractured, gasified HDPE has a surface layer of the same degree of translucence as normal ungasified HDPE, while that of the fracture surface is opaque white, similar to that of the necked region of cold-drawn HDPE. Thus, as the gasified samples are pulled in tension, it is reasonable to deduce that the bubble-free surface layer cold-draws in a manner similar to normal HDPE and changes during the process from translucent to opaque white.

The bulk polymer between gas bubbles, which is translucent in the unfractured material, also changes to opaque white on the fracture surfaces. Again, this can be associated with localized cold-drawing of the material, aided in this case by some degree of stress concentration due to the presence of gas bubbles.

The void structures of the fractured and unfractured specimens are also related. The concentration of voids on the two surfaces has been shown to be nearly identical, with perhaps slightly fewer voids on the fracture surface than in the unfractured specimen. Comparison of Figures 4a and 4b of N<sub>2</sub>-gasified HDPE and Figures 5a and 5b of He-gasified HDPE indicates, however, that the average size of the individual voids on the fracture surfaces is somewhat larger than in the unfractured material. This increased size of the individual voids is particularly evident in the fracture surface of the He-gasified specimen and in those bubbles nearest the void-free surface layer of the N<sub>2</sub>-gasified HDPE.

Two phenomena can contribute to the enlargement of the gas bubbles. The first involves the internal structure of the gas bubbles themselves. Scanning electron microscopy<sup>1</sup> has shown that the boundary between gas and polymer at the bubble walls is diffuse and is composed of fibrils of the polymer extending into the bubbles. In many cases, these fibrils very likely bridge across the bubbles entirely. During the drawing process, the fibrils which are already extended across the bubble are forced to support a disproportionate fraction of the load, especially as compared to the material between the gas bubbles. This will lead to fracture of these bridging fibrils at relatively low overall stress levels. Such a process should lead to some degree of enlargement of the gas bubbles as the fibrils fracture.

The second and more important contribution to the increase in bubble size during deformation and fracture arises from the large structural rearrangements which take place in the regions between the bubbles. In these regions, cold-drawing is taking place; and the concomitant structural changes involving both the crystalline and amorphous components, together with local heating resulting from the deformation, should significantly increase the effective mobility of the gas molecules and facilitate the further growth and coalescence of the bubbles.

To summarize: at relatively low stress levels, the samples begin to fail by the expansion of the gas bubbles via further diffusion of gas to the bubbles and by physical enlargement at the diffuse bubble-polymer interface. As this occurs, increasing stress concentration on the remaining bulk polymer in the surface regions and between the bubbles leads to yielding and localized cold-drawing of this material. Overall fracture of the specimen then occurs when the internal void expansion has separated the sample to such an extent that the surface layer and interbubble regions, even in their strain-hardened cold-drawn condition, cannot support the applied load.

The rather sharp decrease in yield stress upon introduction of the first gas bubbles in the specimens very likely reflects the stress concentration associated with the bubbles. The decrease in yield stress is appreciably less than would be expected from a simple analysis of stress concentration due to holes in plates,<sup>10</sup> presumably because of the fibrils extending across the bubbles as well as orientation of the material adjacent to the bubbles. The apparent plateau in yield stress with increasing bubble content can be associated with the introduction of additional stress concentrators with relatively larger interbubble separations. With further increases in bubble concentration (decreases in density), a further decrease in the yield stress would be anticipated as the stress fields around the various bubbles overlap significantly. If the present investigation were extended to the range of lower densities, such a decrease in yield stress below the apparent plateau value should be observed. Previous data on PE foam structures (density  $<0.5 \text{ g/cm}^3$ ) indicate appreciably lower values for the yield stress (see discussion above).

The abrupt and substantial decrease in the ultimate elongation upon introduction of the bubbles (by a factor of about 30 in the case of HDPE and by a factor of about 15 for LDPE) reflects a failure in the process of stable neck formation. When either material contains bubbles, drawing is not observed. The physical basis of this change in behavior cannot be specified in detail at the present time, but seems to involve the microstructural changes which take place during crystallization in the presence of gas (with the glassy polymers, PVC, and polycarbonate, drawing continues to be observed with gasified specimens).

Gasified LDPE did not prove so amenable to investigation as gasified HDPE. The void structure of samples which were tested in tension occurred on too fine a scale to be readily studied in the optical microscope, even in the unfractured state. Further, normal ungasified LDPE shows no difference in opacity between drawn and undrawn material, eliminating the possibility of observing cold-drawing in the surface region. The observations of fracture surfaces of gasified LDPE are not, however, at variance with the fracture process indicated for HDPE. With a fine void structure found in the interior of the unfractured material, a relatively fine structure would be expected on the fracture surface. Likewise, the surface layer would be expected to cold-draw, which, in the case of LDPE, implies

that the layer would remain relatively transparent as compared to the great increase in opacity found upon cold-drawing HDPE. Such behavior was observed, with no appreciable differences being noticeable between the surface layers of fractured and unfractured material. The observed return of the elongation to failure to values typical of ungasified material upon remelting N<sub>2</sub>-gasified HDPE at atmospheric pressure may be anticipated from the absence of bubbles in the remelted specimens. The lack of recovery of the yield stress upon remelting seems to reflect "permanent" changes in the structure after the gas has been annealed out. This implies that although the bubbles close up, a weak zone, such as would result from fracture of some of the fibrils extending across the gas bubbles, remains in the material. The character of these structure changes remain, however, to be specified in satisfactory detail.

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