

Impact Strength of High Density Microcellular Poly(Vinyl Chloride) Foams

RICHARD P. JUNTUNEN, VIPIN KUMAR,* and JOHN E. WELLER

*Department of Mechanical Engineering
University of Washington
Box 352600
Seattle, WA 98195*

WILLIAM P. BEZUBIC

*Vinyl Building Products Group
CertainTeed Corporation
Jackson, MI 49203*

The impact strength of microcellular poly(vinyl chloride) (PVC) produced from an industrial formulation was investigated. The solid-state process with carbon dioxide as the blowing agent was used to prepare the specimens. Processing conditions were explored to produce microcellular PVC with a relative density of 0.6 and higher. These foams were impact tested by using a falling-weight impact tester. Impact strength of microcellular PVC was found to decrease linearly with relative density. The gas saturation pressure did not significantly affect the impact strength of microcellular PVC foams. Microcellular PVC foams with up to 40% reduction in density possessed a normalized mean failure energy of 3.8 J/mm (0.85 in.-lb/0.001 in.).

INTRODUCTION AND BACKGROUND

Interest in the microcellular plastics technology has grown steadily since the process was first discovered by Martini, Suh, and Waldman in 1982 (1, 2). The inventors hypothesized that if bubbles that were smaller than the critical flaw size in polymers could be introduced in large numbers, then the density of plastics could be reduced without sacrificing the mechanical properties. The motivation was to reduce the amount of polymer needed in many applications where the wall thickness is 1 mm or smaller. Since conventional foam processes typically produce cells larger than 0.25 mm, these processes were not suitable, owing to excessive loss of strength. The solid-state process was able to create cells in the 2–25 μm range and thus provided the potential to foam thin-walled parts. The two-stage batch solid-state process is shown schematically in Fig. 1.

In the first stage of the process, a polymer sample is placed in a pressure vessel, and high-pressure, nonreacting gas—typically, CO_2 or N_2 —is introduced. Over time, the polymer absorbs the gas and eventually becomes saturated. The length of time required to

saturate the polymer depends on temperature, polymer type, thickness, and often saturation pressure. After saturation, the polymer is removed from the pressure vessel and allowed to desorb some of the gas. The desorption step allows gas to escape from the surface layers, thus allowing formation of an integral skin during foaming (3). In the second stage of the process, the sample is placed in a heated bath which raises the temperature of the polymer to its foaming temperature, whereupon bubbles nucleate and grow. The foaming temperature is in the neighborhood of the T_g of the polymer, and the polymer remains in the solid state during the entire foaming process. Thus the phrase “solid-state foam” was coined in order to distinguish these foams from the conventional foams produced from polymer melt. Recently a semicontinuous process for production of foam sheets has been developed (4, 5) that makes industrial-scale production of these novel materials possible.

The bubble nucleation in this process results from the sudden reduction in the solubility of the gas as the gas-saturated specimen is heated to the foaming temperature. The plasticization of the polymer by the dissolved gas plays a key role in the cell growth process. Wonders and Paul (6) examined the plasticization behavior of CO_2 on several polymers and defined an

*Corresponding author. email address: vkumar@u.washington.edu

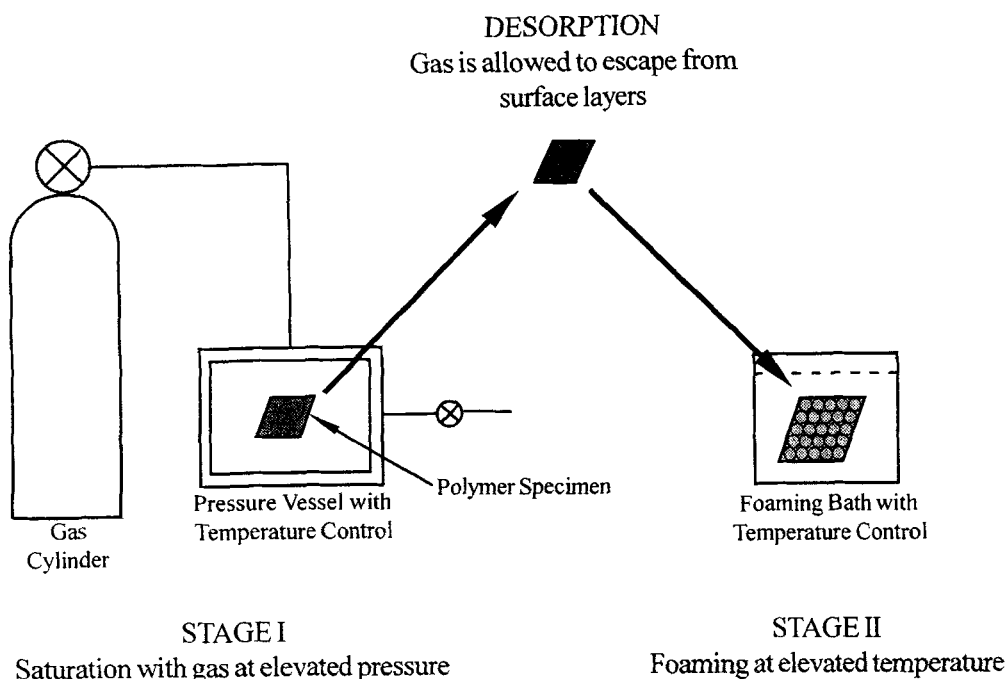


Fig. 1. Schematic of the solid state process.

effective glass transition temperature for the gas-polymer system. Chow (7) provided a theoretical model relating the glass transition temperature of a polymer to the temperature of the concentration of the dissolved gas. A model for cell growth in polymeric foams has been presented by Arefmanesh and Advani (8). This model was modified by Ramesh and Malwitz (9) to include the effects of gas concentration on diffusion, viscosity, and bubble growth.

Kumar and Weller (10) first produced microcellular PVC by using a relatively "neat" formulation and found that a wide range of densities could be produced. Several studies have followed which have explored the effects of additives on the microcellular microstructure (11), the effects of additives and foam density on the tensile properties (12), and the processing/mechanical behavior of PVC/(wood fiber) composites (13). To date, however, no data on impact properties of these materials have been reported. This study explores the relationship between impact strength and foam density for microcellular PVC foams by using a typical industrial PVC formulation containing additives such as calcium carbonate, paraffin wax, and calcium stearate.

EXPERIMENTAL

All experiments were performed on 1.07-mm thick PVC sheets provided by the Vinyl Building Products Group of CertainTeed Corporation. These sheets represented an industrial formulation and therefore contained a variety of additives. The density of the material used in this study was 1.43 g/cm³, and the glass transition temperature was between 80 and 90°C. Samples were cut into 10 cm × 10 cm squares and then

placed in a pressure vessel maintained at 40°C. Although it is common to saturate specimens at room temperature, an elevated temperature was used here to speed up the diffusion of gas in order to reduce the amount of time required to saturate the specimens. This temperature was chosen on the basis of previously published data (10, 11). All samples were saturated with CO₂ at pressures ranging from 2.76 MPa (400 psi) to 4.83 MPa (700 psi), which were controlled to ± 0.1 MPa (± 15 psi).

The time elapsed after a saturated specimen is removed from the pressure vessel up to the time of foaming is called the desorption time. Weller and Kumar (14) have shown that skin thickness is a function of both desorption time and foaming temperature. In this study desorption time was held constant at five minutes to ensure that a negligibly small skin thickness was produced.

After the desorption time had elapsed, the samples were foamed in a heated glycerine bath for five minutes in order to reach steady-state foam structure. The temperature of this bath was controlled to ± 1°C, and it will be referred to as the foaming temperature. After the foaming time had elapsed, all samples were quenched in room-temperature water, dried, and then left under atmospheric conditions for ten days prior to testing.

Sorption Experiments

Carbon dioxide uptake for the sorption experiments was measured by periodically removing samples from the pressure vessel and immediately weighing them on a Mettler AE240 precision balance with a resolution

of ± 10 micrograms. Sorption curves were measured for a temperature of 40°C and pressures between 2.76 and 4.83 MPa (400 and 700 psi). These experiments were performed to determine the length of time required to saturate the samples to equilibrium and to establish the solubility of CO₂ in our formulation at 40°C.

Process Space Experiments

Samples were saturated at four different pressures and were then foamed at various temperatures for five minutes in a glycerine bath. All samples were allowed to desorb gas for five minutes prior to foaming. By keeping the desorption time short, the skins formed were of negligible thicknesses. Specimens were foamed at temperatures in the 45 to 75°C range in 5°C increments. See Table 1 for the processing conditions used in this study.

Impact Tests

All samples were impact tested by using a Gardner impact tester according to ASTM D4226-98. In this

test method, a weight falls through a guide tube and impacts a striker resting on top of a supported specimen. The weight is dropped from various heights, rendering a procedure that determines the energy that will cause 50% of the specimens tested to fail. The technique used to determine mean failure energy is commonly called the Bruceton Staircase Method. Testing is concentrated near the mean, reducing the number of specimens required to obtain a reasonably precise estimate of the impact resistance. This test method permits the use of different striker diameters and specimen support plate geometries in order to obtain different modes of failure, permit easier sampling, or test limited amounts of material. There is no known means for correlating the results of tests made by different methods or procedures.

Prior to testing, all samples were conditioned at $20 \pm 3^\circ\text{C}$ and $50 \pm 10\%$ relative humidity for 10 days, when it was determined that approximately 20% of the carbon dioxide then was remaining in the sample. For each processing condition, a minimum of 20 independent drops was performed. Impact properties (mean failure energy) were calculated according to ASTM D4226-98.

Table 1. Processing Conditions, Density, and Thickness Measurements.

Experiment Number ¹	Saturation Pressure (MPa)	Foaming Temperature (°C)	Foam Density (g/cm ³)	Foam Relative Density ²	Foam Thickness (mm)
0	—	—	1.43	1.00	1.1
1	2.76	45	1.42	1.00	1.1
2	2.76	50	1.42	0.99	1.1
3	2.76	55	1.42	0.99	1.1
4	2.76	60	1.42	0.99	1.1
5	2.76	65	1.38	0.97	1.1
6	2.76	70	1.27	0.89	1.2
7	2.76	75	1.14	0.80	1.2
8	3.45	45	1.42	0.99	1.1
9	3.45	50	1.42	0.99	1.1
10	3.45	55	1.42	0.99	1.1
11	3.45	60	1.39	0.97	1.1
12	3.45	65	1.29	0.91	1.2
13	3.45	70	1.19	0.83	1.2
14	3.45	75	1.02	0.72	1.2
15	4.14	45	1.41	0.99	1.1
16	4.14	50	1.42	0.99	1.1
17	4.14	55	1.40	0.98	1.1
18	4.14	60	1.32	0.92	1.2
19	4.14	65	1.20	0.84	1.2
20	4.14	70	1.06	0.74	1.3
21	4.14	75	0.93	0.65	1.3
22	4.83	45	1.41	0.99	1.1
23	4.83	50	1.41	0.99	1.1
24	4.83	55	1.37	0.96	1.1
25	4.83	60	1.28	0.90	1.2
26	4.83	65	1.17	0.82	1.2
27	4.83	70	1.00	0.70	1.2
28	4.83	75	0.86	0.60	1.3

¹A total of 20 specimens was tested for each experiment.

²Normalized by PVC density of 1.43 g/cm³.

RESULTS AND DISCUSSION

Sorption of CO₂ in PVC

Figure 2 shows several sorption curves determined at 40°C for saturation pressures between 2.76 MPa (400 psi) and 4.83 MPa (700 psi). This Figure indicates that samples saturated at the higher pressures reach equilibrium in approximately 50 hours. Samples saturated at 2.76 MPa (400 psi) take about 100 hours to saturate, a result which indicates that the rate of gas diffusion in this system is concentration-dependent. Figure 3 relates the equilibrium CO₂ concentrations to saturation pressure. This Figure shows a linear increase in CO₂ concentration with saturation pressure as expected by Henry's Law. A datum from the work of Holl *et al.* (11) is shown to fit this trend also and is consistent with the solubility data from this study.

Microstructural Analysis

Figure 4 shows SEM micrographs of the PVC used in this study and a 0.78 relative-density foam. From a visual observation of the micrographs, it appears that the average cell size is smaller than 3 μm. Because the microstructure is irregular, precise image analysis of the average cell size and distribution could not be accomplished. All foam samples in this study showed similar microstructures. The solid additive particles of order 1-μm size can be clearly seen in the virgin PVC. The bubbles in the foam are nonhomogeneous as a result of additive particles providing nucleation sites that are not distributed uniformly. By contrast, PVC without additives shows a very homogeneous microstructure (10).

The PVC-CO₂ Process Space

A plot of relative density (density of the foam divided by the density of the unfoamed material) as a function

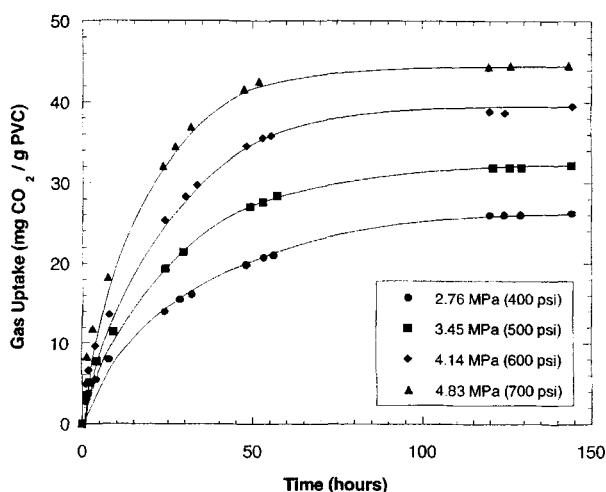


Fig. 2. Plot of CO₂ uptake in units of mg CO₂ per g of PVC, as a function of time. Specimens were 1.07 mm thick, and sorption temperature was 40°C.

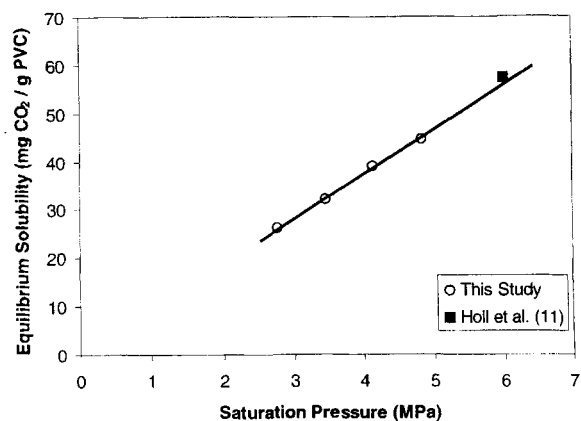


Fig. 3. Plot of CO₂ equilibrium gas concentrations for various saturation pressures, relating data from this study to work done by Holl *et al.* Sorption temperature was 40°C for both studies.

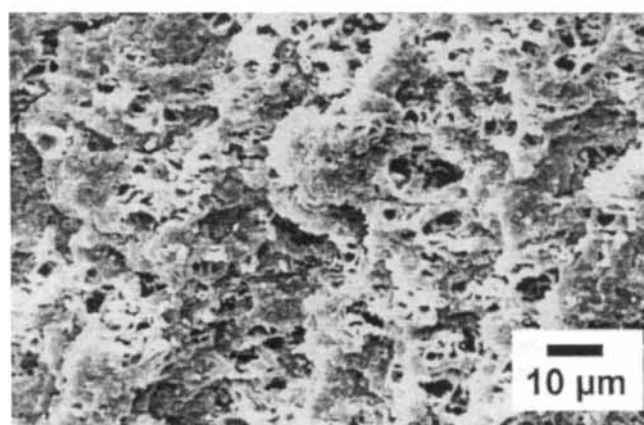
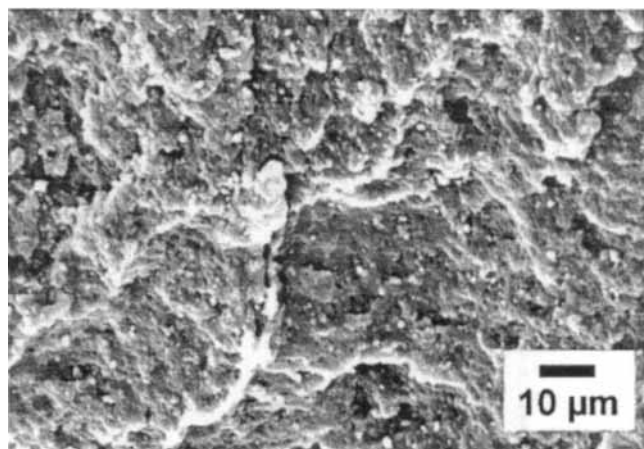


Fig. 4. Scanning electron micrograph of virgin PVC (top) and microcellular PVC (bottom); relative density = 0.78, saturation pressure = 500 psi, and foaming temperature = 70°C. Most bubbles lie in the range of 1 to 3 μm.

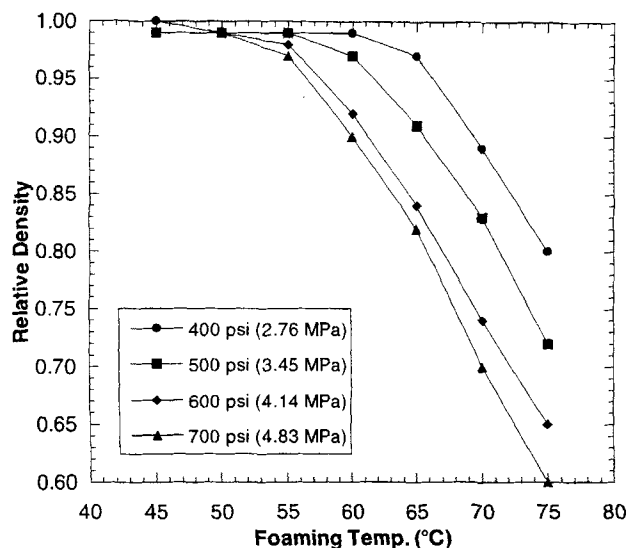


Fig. 5. Relative density of foams as a function of foaming temperature and saturation pressure. The process conditions span the useful range of produce PVC foams of 0.6 and higher relative density. Relative density is the foam density divided by the PVC density of 1.43 g/cm³.

of foaming temperature for various saturation pressures is shown in Fig. 5. This Figure shows that for each saturation pressure, there is a critical temperature below which foaming cannot occur. For example, at a saturation pressure of 4.83 MPa (700 psi), foaming will not occur below a foaming temperature of 50°C. This temperature is commonly referred to as the minimum foaming temperature and is always a function of saturation pressure (14). Figure 5 also shows that the minimum foaming temperature increases as saturation pressure or, equivalently, the equilibrium gas concentration goes down. Note that foaming can occur at temperatures significantly below the glass transition temperature of the original polymer, owing to plasticization by the absorbed gas. Although this behavior has been observed previously in the polycarbonate-CO₂ system (15), it also holds true in our system, which has a large number of insoluble additive particles. This result is significant because the minimum foaming temperature depends completely on the cell nucleation mechanism. Since material systems with large quantities of additives encourage nonhomogeneous nucleation (16), their cell nucleation can be very different from that in a polymer without additives.

Once the minimum foaming temperature has been reached, foam density decreases nearly linearly with increasing foaming temperature, a correlation that provides a simple means to control the density. At all saturation pressures, foams can be produced with relative densities between 1.0 (completely solid) and 0.65. It is also possible to produce two foams with the same relative density by employing different processing conditions, a result that opens the possibility for optimizing those conditions. Recall that higher saturation

pressures lead to lower saturation times, as shown in Fig. 2. Therefore, it may be advantageous to employ the largest possible saturation pressure in order to speed up processing.

Impact Behavior

Impact specimens were produced at the conditions shown in Fig. 5 (see also Table 1). They then were allowed to desorb any residual CO₂ for 10 days after foaming, thus allowing approximately 80 percent of the CO₂ to leave the samples prior to impact testing. All impact testing was performed according to ASTM D4226-98, with 26 test drops performed at each processing condition. The processing conditions and impact results are summarized in Tables 1 and 2. Figure 6 shows a plot of the normalized mean failure energy as a function of relative density. The mean failure energy for each processing condition was normalized by the average specimen thickness as per ASTM D4226-98. Impact resistance is observed to decrease linearly with relative density over the range of densities explored. Compared to the solid, unprocessed PVC normalized mean failure energy of 10.1 J/mm, a PVC foam with 25% reduction in density has an approximate normalized mean failure energy of 6.4 J/mm. We notice further that the data in Fig. 6 show no particular trend with respect to variations in gas saturation pressures. Thus, regardless of the processing conditions, two PVC foams with the same density can be expected to possess the same impact strength.

To use the data in Fig. 6 for design purposes, we first need to know the thickness of a foam specimen. For the specimens produced in this study, the foam thickness for different relative densities has been plotted in Fig. 7. Note that the relationship in Fig. 7 is for the processing conditions used in this study. Now consider, for example, a PVC foam with 25% reduction in density. Such a foam, with relative density of approximately 0.75, could be produced by saturating the PVC at 40°C and 4.14 MPa, then foaming at 70°C. This procedure would result in a specimen thickness of around 1.25 mm, and the resulting impact strength would be about 6 J/mm or 7.5 J for the foam in our example. This result compares to the 1.07-mm thick virgin PVC strength of 10.8 J. Thus a 25% reduction in density results in a 30% reduction in impact strength. As another example, consider an application where a minimum 60 in.-lb (6.78 J) impact strength is needed. What is the lowest density PVC foam that can be used? The reader can verify that PVC foam with a relative density of 0.7 has the required impact strength.

SUMMARY

In this study, we evaluated the impact strength of microcellular PVC foams of relative density 0.6 and higher. We found that the impact strength decreased linearly with density of the foam. At a relative density of 0.6, or 40% reduction from the PVC density, the

Table 2. Impact Resistance Data.

Experiment Number	Mean Failure Energy ¹ (J)	Standard Deviation (J)	Normalized Mean Failure Energy ² (J/mm)	Normalized Standard Deviation (J/mm)
0	10.8	1.4	10.1	1.4
1	10.7	1.5	10.0	1.4
2	11.4	0.6	10.6	0.5
3	11.7	1.5	10.7	1.4
4	10.8	0.4	9.9	0.4
5	10.7	3.1	9.4	2.7
6	9.6	1.9	8.2	1.6
7	8.4	1.2	7.2	1.0
8	10.6	1.0	10.0	1.0
9	10.9	0.6	10.3	0.6
10	10.8	1.3	10.3	1.2
11	11.2	1.7	10.3	1.6
12	10.6	1.2	8.9	1.0
13	9.2	1.6	7.9	1.4
14	6.8	2.1	5.4	1.7
15	11.5	2.5	10.6	2.3
16	11.6	1.8	10.6	1.7
17	10.7	1.3	9.8	1.2
18	10.3	0.9	8.8	0.8
19	9.7	1.4	7.8	1.1
20	9.0	1.5	7.1	1.2
21	5.2	0.9	4.0	0.7
22	10.8	1.3	10.1	1.2
23	11.8	1.0	10.9	0.9
24	10.7	0.7	9.8	0.6
25	11.2	1.3	9.6	1.1
26	7.5	1.3	6.2	1.1
27	7.7	1.9	6.2	1.5
28	5.3	1.3	4.1	1.0

¹A total of 20 specimens was tested at each condition.

²Mean failure energy divided by the foam thickness.

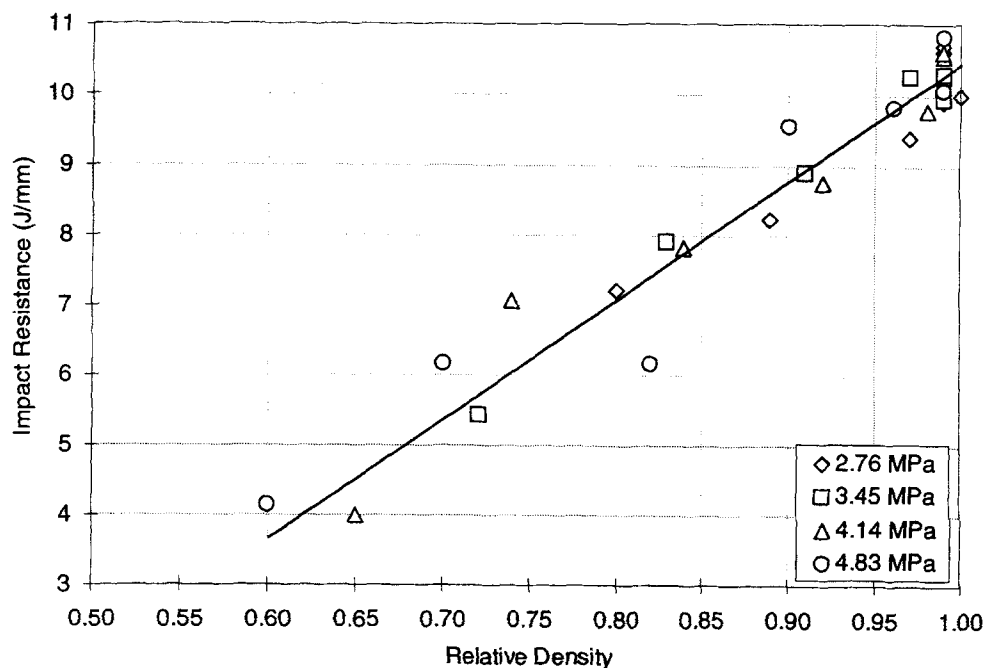


Fig. 6. Impact strength as a function of relative density for microcellular PVC foams. The solid line represents the best fit to the experimental data of Table 1. There is no significant effect of gas saturation pressure on the foam impact strength. The normalized mean failure energy and density for unprocessed PVC were 10.1 J/mm and 1.43 g/cm³, respectively.

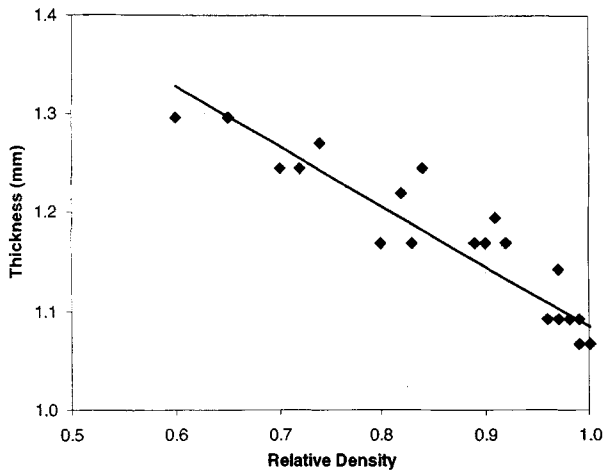


Fig. 7. Specimen thickness as a function of relative density. The unfoamed PVC thickness was 1.07 mm. For processing conditions, see Table 1.

foam impact strength was approximately 3.8 J/mm (0.85 in.-lb/0.001 in.). This value represents a loss of about 60% from the impact strength of virgin PVC of 10.1 J/mm (2.26 in.-lb/0.001 in.).

An important finding was that the carbon dioxide pressure had no significant influence on the impact strength at a given relative density. Therefore, the lowest possible CO₂ pressure can be employed in processing.

ACKNOWLEDGMENTS

Materials and financial support for this study were provided by CertainTeed Corporation, Vinyl Building Products Group, Jackson, MI. This support is gratefully acknowledged.

REFERENCES

1. J. Martini, F. A. Waldman, and N. P. Suh, *SPE ANTEC*, **28**, 674 (1982).
2. J. Martini, N. P. Suh, and F. A. Waldman, U.S. Patent 4,473,665 (1984).
3. V. Kumar and J. E. Weller, *Polym. Eng. Sci.*, **34**, 169 (1994).
4. V. Kumar and H. G. Schirmer, *SPE ANTEC*, **41**, 2189 (1995).
5. V. Kumar and H. G. Schirmer, U.S. Patent 5,684,055 (1997).
6. A. G. Wonders and D. R. Paul, *J. Membr. Sci.*, **5**, 63 (1979).
7. T. S. Chow, *Macromolecules*, **13**, 362 (1980).
8. A. Arefmanesh and S. G. Advani, *Rheol. Acta*, **30**, 274 (1991).
9. N. S. Ramesh and N. Malwitz, *ACS Symp. Ser.*, **669**, 206 (1997).
10. V. Kumar and J. E. Weller, *Int. Polym. Process.*, **8**, 73 (1993).
11. M. R. Holl, V. Kumar, M. Ma, and R. R. Kwapisz, *SPE ANTEC*, **42**, 1908 (1996).
12. V. Kumar, J. Weller, M. Ma, and R. Montecillo, *Cell. Polym.*, **17**, 350 (1998).
13. L. Matuana-Malanda, C. Park, and J. Balatincez, *Polym. Eng. Sci.*, **37**, 1137 (1997).
14. J. Weller and V. Kumar, *SPE ANTEC*, **43**, 2037 (1997).
15. V. Kumar and J. E. Weller, *J. Eng. Ind.*, **116**, 413 (1994).
16. J. Colton and N. P. Suh, *Polym. Eng. Sci.*, **27**, 493 (1987).