Impact Strength of High Relative Density Solid State Carbon Dioxide Blown Crystallizable Poly(Ethylene Terephthalate) Microcellular Foams

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SUMMARY

In this paper, processing conditions for producing high relative density microcellular CPET foams using CO_2 as a blowing agent are described. Starting with solid CPET, foams with relative densities between 0.5 to 1.0 were produced. Results of instrumented impact tests conducted at various temperatures ranging from room temperature to -40°C are presented. The CPET foams exhibit excellent impact properties in the range of temperatures explored.

INTRODUCTION

The solid-state batch process has previously been applied to crystallized poly(ethylene terephthalate) CPET to produce a family of microcellular foams(1). An interesting phenomenon observed during the process characterization is the additional crystallization of CPET at room temperature in the presence of sufficiently high gas concentrations. This onset of crystallization during the gas uptake stage of the solid-state batch foaming process at sufficiently high CO_2 pressures has also been observed in poly(ethylene terephthalate) PET(1-5) but not in PETG(6). An immediate effect of the crystallization is an increased glass transition temperature (T_g), thus requiring higher foaming temperatures. Baldwin and Suh(1) observed that crystalline foams possessed smaller cell nucleation density compared to amorphous foams, accompanied by smaller cells. The mechanisms for these observations proposed by Baldwin and Suh(1), are: 1) the crystals act as heterogeneous cell nucleation sites, providing larger,

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stable nuclei and 2) the crystals act to stiffen the polymer matrix, thereby preventing the cells from growing large enough to coalesce. This crystallization is thus desirable for the microcellular process.

Figure 1 shows a schematic of the solid-state batch process in which the polymer is first saturated with a gas, and then heated to a temperature above the glass transition temperature of the polymer-gas system, which can be significantly below the T_g of the virgin polymer due to the plasticizing effect of the gas. This batch process has been converted to a semi-continuous process, shown schematically in Figure 2, that allows essentially continuous production of microcellular foam sheets(7,8). The words 'solid-state' underscore the fact that the polymer remains in the solid state during the entire process, which enhances the properties of the resulting foams.

This study undertakes to determine the impact behaviour of high relative density CPET foams. Both Gardner impact tests and instrumented impact tests were conducted. These impact tests were performed at varying temperatures between 22.2°C (72°F) and -40°C (-40°F).

Figure 1 Solid-state batch foaming process schematic

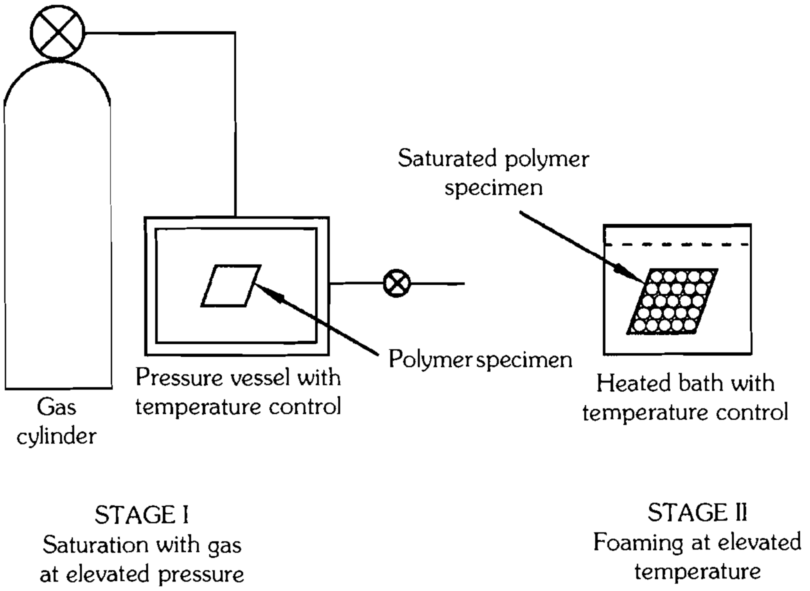
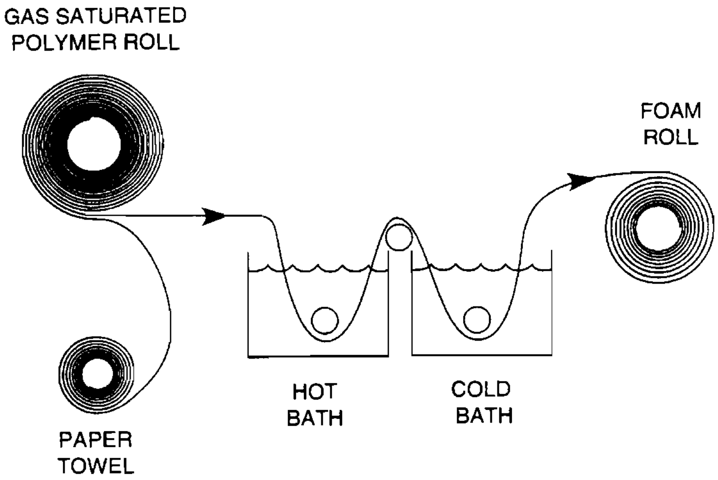


Figure 2 Semi-continuous foaming process schematic



EXPERIMENTAL

Material

Eastman Kodak's Eastapak™ CPET 12822 sheet 0.7 mm (0.028 in.) thick, with 8% impact modifier and 3% nucleating agent, was used in this study. The impact modifier is a cross-linked acrylic impact modifier (rubber) with a particle size less than 1 µm and the nucleating agent used is a LLDPE based nucleating agent containing some stabilizers. A small amount of inorganic nucleant is also added. The density of this composition was determined to be 1.30 g/cm^3 using ASTM D792-91 "Standard Test Methods for Density and Specific Gravity of Plastics by Displacement". The T_g and weight percent crystallinity (W_c) were determined to be 75°C and 10.4, respectively, using differential scanning calorimetry (DSC).

Solubility Measurements

Samples measuring approximately 25 mm x 25 mm were cut from the CPET sheet. Gas uptake curves were produced by taking the initial mass of the sample, and checking the gas uptake periodically by removing the sample from the pressure vessel and taking a mass measurement. Samples were measured on a Mettler AE 240 precision balance, with an accuracy of 10 µg. Three saturation pressures (3, 4 and 5 MPa) were chosen to monitor the CO_2 solubility and to demonstrate the crystallization of the CPET at increased saturation pressures. The CO_2 pressure or saturation pressure (P_{SAT}) and saturation temperature (T_{SAT}) were regulated to ±0.1 MPa and ±1°C respectively. The saturation temperature for all experiments was 25°C (77°F).

Specimen Saturation

Strips of material measuring approximately 5 m x 6.5 cm were cut from the CPET sheet. Seven strips were prepared to cover the testing conditions anticipated. These pieces of material were then paired with porous pieces of paper of the same size and wound into a roll. The rolls were then placed into a pressure vessel and pressurized with CO_2. The CO_2 pressure or saturation pressure (P_{SAT}) and saturation temperature (T_{SAT}) were regulated to ±0.1 MPa and ±1°C respectively. The vessels were then maintained at 5 MPa (725 psi) and 25°C (77°F). The results from the solubility measurements were used to determine the time needed to achieve maximum CO_2 concentration.

Specimen Foaming

After the samples were saturated, they were removed from the pressure vessel and processed using the semi-continuous process(7,8). To produce a sheet of foam, for example, a sheet of CPET was placed on a sheet of gas permeable material and the two layers of material were rolled to form a roll consisting of layers of polymer interweaved with gas permeable material. The roll was then passed through a hot bath and foamed at temperatures ranging from 50°C (122°F) to 90°C (194°F). All foaming was conducted at atmospheric pressure. It was found that a cold bath was not needed, as the foams cooled sufficiently quickly under ambient conditions.

Falling Weight Impact Tests (Gardner Impact)

Foams from the above foaming experiments were selected for impact testing based on their microstructure and feasibility in producing flat specimens. Twenty six specimens, measuring 50mm x 50mm were then cut from the corresponding processed sheet to assemble a sample set to be impact tested. The foams were then tested on a BYK Gardner Impact Tester with a falling weight capacity of 36.2 Joules (26.7 ft-lbs.). About 6 foamed specimens were needed to approximately determine the mean-failure height. Twenty additional samples were then tested to produce a statistically precise measurement of the impact strength. ASTM D5420-

93 "Standard Test Method for Impact Resistance of Flat, Rigid Plastic Specimen by Means of a Striker Impacted by a Falling Weight (Gardner Impact)" was followed, employing tup geometry GE (striker diameter: 12.70 ± 0.10 mm, support plate inside diameter: 16.26 ± 0.025 mm). Immediately before impact testing, 10 samples from each sample set were measured for thickness, weighed for concentration of gas still in the matrix, and their densities were calculated using ASTM D792-91. From these measurements an average thickness, average gas concentration, and average density for each sample set was determined. A relative density for each sample set was then calculated from the foam average density and the density of the parent material. All impact tests were conducted at room temperature and atmospheric pressure.

Instrumented Impact Tests

Circular samples 65 mm in diameter were cut from the sheets of foam produced using the semi-continuous process. Seven relative densities were tested at four different temperatures. Each temperature required 10 samples for testing to account for any variance. These foams were then tested on a Dynatup® Instrumented Impact tester and data was collected using data acquisition software on a PC following ASTM D3763-97a "Standard Test Method for High Speed Puncture Properties of Plastics Using Load and Displacement Sensors". These data points were analyzed and several points of interest were charted in data tables. A relative density for each sample set was then calculated from the foam average density and the density of the parent material. All impact tests were conducted at atmospheric pressure.

RESULTS AND DISCUSSION

Solubility Measurements

Figure 3 shows the CO_2 uptake for CPET at several saturation pressures, and the distinctive knee in the 5 MPa curve signifies crystallization as seen in previous studies(1-3). As the sorption curve passes through the knee (maximum), the polymer begins to reject the CO_2, indicative of crystallites forming, thus decreasing the solubility. Figure 4 shows data that has been corrected for the weight percent crystallinity of CPET after various equilibrium gas concentrations are achieved. This corrected gas concentration assumes that the crystallized polymer rejects the CO_2, and so these corrected values represent the CO_2 present in the amorphous

Figure 3 CO_2 uptake for CPET saturated at several saturation pressures at 25°C

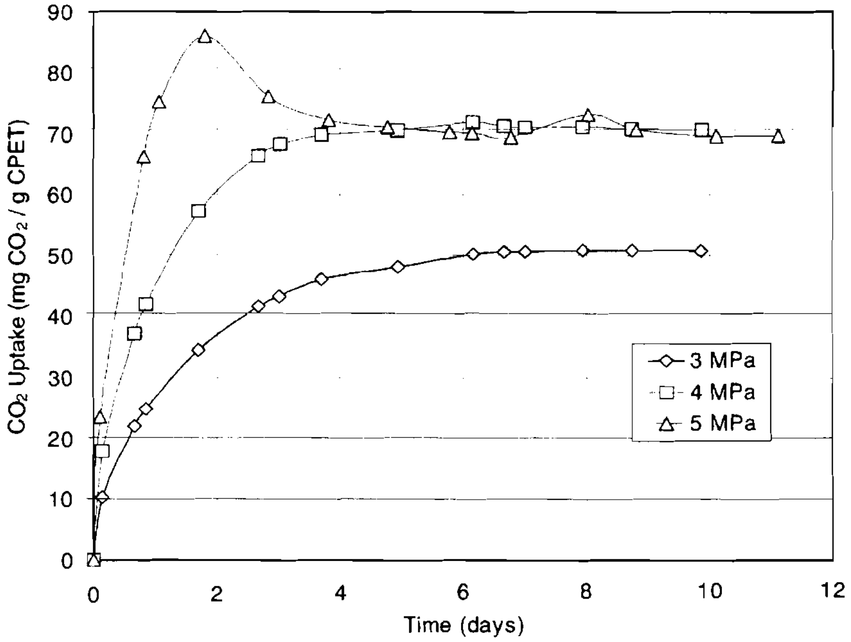
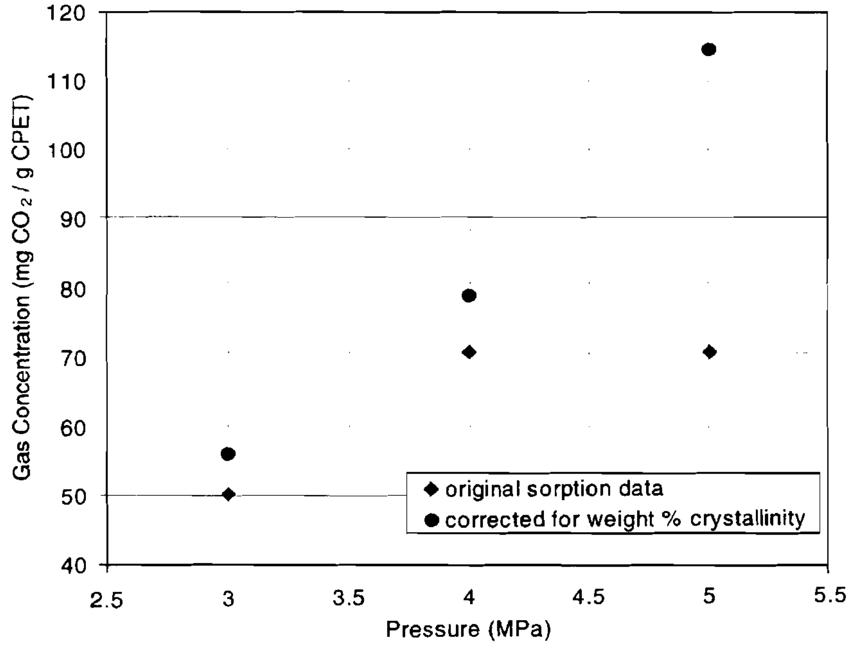


Figure 4 Equilibrium CO_2 gas concentrations corrected for weight percent crystallinity of CPET at 25°C



CPET. This corrected data fits the expected linear increase in equilibrium gas concentration that can be seen with increased saturation pressure seen in nearly all polymer/gas systems investigated thus far.

Foaming Experiments

The relative density, the density of the foam divided by the density of the virgin material, is plotted in Figure 5 as a function of foaming temperature for saturation pressures 3,4, and 5 MPa. Comparing data at 3 and 4 MPa, we see that with increasing saturation pressure a lower foaming temperature is needed to produce the same density foam. For the 5 MPa specimens, notice the dramatic increase in the foaming temperature needed to achieve an equal relative density compared to the 3 and 4 MPa samples. This is due to the increase in weight percent crystallinity as shown in Table 1. Table 2 gives the relative density and thickness achieved after foaming at particular conditions. Note that the saturation cycled (saturated but not foamed) specimens increased in thickness by nearly 5% over the virgin CPET.

Figure 5 Relative density versus foaming temperature for CPET saturated at several saturation pressures

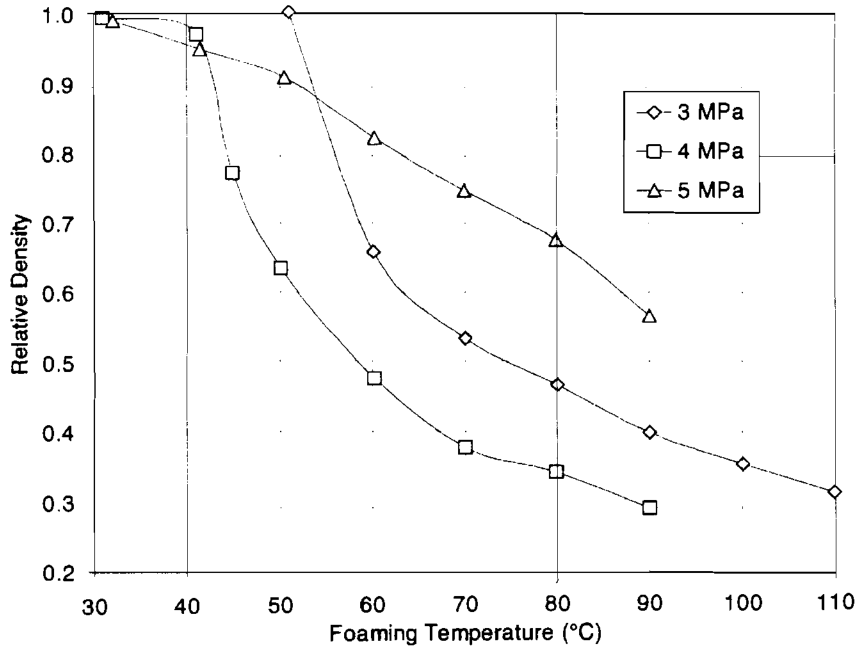


Table 1 Weight percent crystallinity for CPET saturated at various saturation pressures

Saturation pressure (MPa)	Weight % crystallinity
Virgin CPET	10.4
3	10.4
4	10.4
5	38.5

Table 2 Processing conditions and the resulting specimen density and thickness

Saturation pressure (MPa)	Foaming temperature (° C)	Relative density[1]	Specimen thickness (mm)
*	*	1.00	0.73
5	**	1.00	0.76
5	50	0.95	0.81
5	60	0.89	0.86
5	70	0.74	0.96
5	80	0.67	1.01
5	90	0.56	1.06

1. Normalized by CPET density of 1.3 g/cm^3
* Virgin CPET
** Saturation cycled CPET

Falling Weight Impact Tests (Gardner Impact)

Figure 6 shows the Gardner impact strength plotted as a function of relative density for CPET saturated at several pressures. The highest impact strength is seen in the virgin CPET at 14.1 J/mm. CPET that was saturated at 3 MPa (435 psi) and 4 MPa (580 psi) show an immediate loss of impact strength and remain fairly steady regardless of the foam relative density. CPET saturated at 5 MPa (725 psi) shows a very different behaviour, with only about a 10 percent loss in impact strength at a density reduction of nearly 40 percent. This remarkable behaviour was what lead to further investigation of impact properties using the instrumented impact equipment.

Instrumented Impact Tests

Each instrumented impact test produced a load versus time plot. The software on the Dynatup® impact tester automatically integrated the load versus deflection data, both of which vary with time during the dynamic test, to obtain energy to the point of maximum load, and the total energy to failure. The typical test lasted for approximately six milliseconds.

Figure 6 Gardner impact strength versus relative density for CPET saturated at several saturation pressures at 25°C. Twenty specimens were tested at each condition

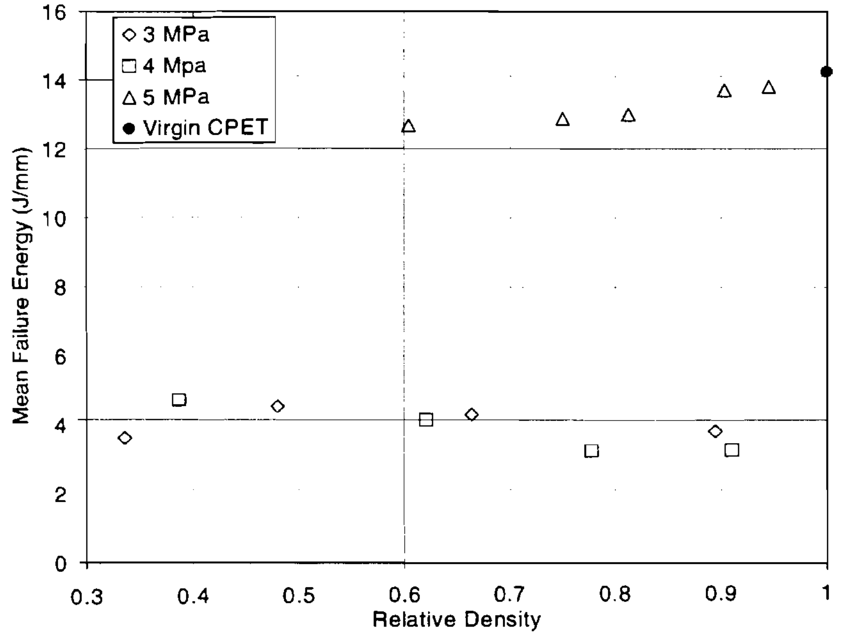


Table 3 shows the normalized failure energy data for different relative densities at different testing temperatures. The numbers for failure energy are average for ten tests. Note the first two rows show data at relative density of 1.0. The first row gives data for the as-received, unprocessed CPET specimens that we have designated as 'virgin' CPET in this paper. The second row gives impact data for 'saturation cycled' CPET specimens. These specimens were saturated with 5 MPa CO_2 and were left to desorb at room temperature for at least two months before testing. These saturation-cycled specimens provide a better approximation to the impact properties of the foam matrix material as compared to virgin CPET.

First, we note that as temperature drops, the normalized failure energy of virgin CPET drops from about 11.4 J/mm at room temperature to 5.4 J/mm at -28.9°C. Unfortunately data for virgin CPET at -40°C was not obtained, but we estimate it to be about 4 ± 1.5 J/mm for the purpose of making a general comparison. By contrast, we see that the saturation cycling clearly reduces the impact strength of CPET. This is likely due to the increase in crystallinity of the saturation cycled specimen to about 40 weight percent, compared to 10 weight percent for virgin CPET (See Table 1), rendering the saturation cycled specimens more brittle.

Table 3 Normalized failure energy in J/mm and standard deviation for instrumented impact testing of CPET at various temperatures. Ten specimens were tested at each condition

	22.2° C (72° F)		-17.8° C (0° F)		-28.9° C (-20° F)		-40.0° C (-40° F)	
Relative density	Failure energy (J.mm)	Std. Dev.	Failure energy (J/mm)	Std. Dev.	Failure energy (J/mm)	Std. Dev.	Failure energy (J/mm)	Std. Dev.
1.00*	11.37	0.15	8.12	0.60	5.40	2.13	—	—
1.00**	4.65	2.20	0.83	0.48	0.87	0.48	0.57	0.37
0.95	5.98	1.03	1.93	1.00	1.77	1.26	—	—
0.89	6.38	0.24	1.83	1.18	0.64	1.38	—	—
0.74	6.74	0.34	6.50	0.91	4.82	1.62	3.02	1.28
0.67	6.25	0.29	5.49	1.74	3.47	1.66	3.05	1.34
0.56	4.92	0.95	5.28	1.98	5.75	1.44	4.08	2.40

*Virgin CPET
**Saturation cycled CPET

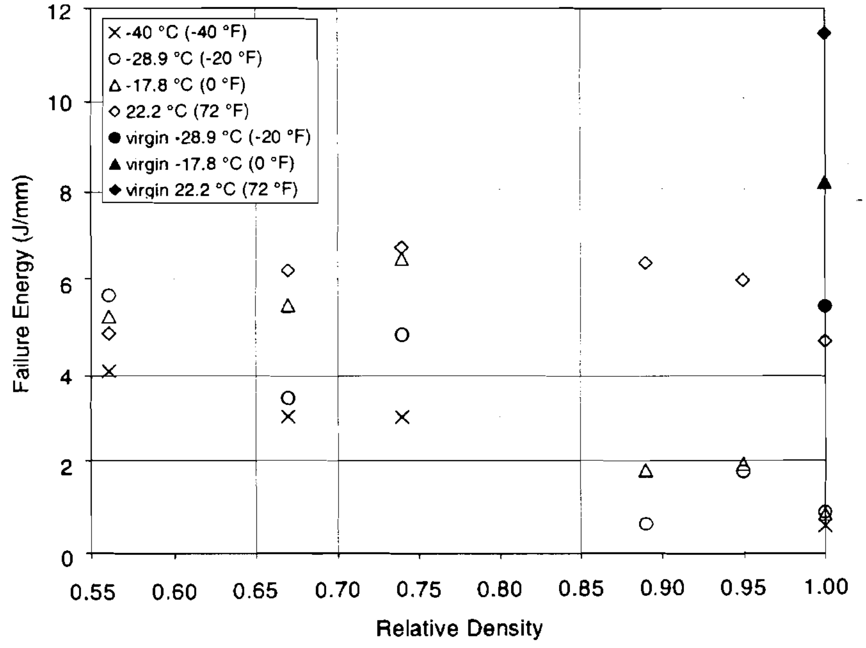
The failure energy data in Table 3 has been plotted in Figure 7 as a function of the foam relative density. The earlier observation from Figure 6, namely that the Gardner impact strength is maintained by microcellular CPET to nearly virgin CPET levels up to a reduction in density of 40%, is not repeated with the room temperature tests. However, this earlier observation seems to be collaborated with the lower temperature tests. For example, the data at -28.9˚C shows that failure energy initially decreases to approximately 1 J/mm for relative densities in the 0.9 to 0.95 range. However, for lower relative densities, the failure energy increases to about 5.5 J/mm, the same as for virgin CPET. This is an amazing result. To put it differently, microcellular CPET with a reduction in density of 25 to 50%, has an impact strength comparable to the virgin CPET at -28.9˚C.

The room temperature data for microcellular CPET is given in the second column in Table 3. We see that the normalized failure energy for all microcellular specimens tested lies in the 4.9 to 6.7 J/mm range. Thus it appears that in the 0.55 to 0.95 relative density range the impact strength is essentially constant at about 50% of the impact strength of the virgin CPET.

The data in Tables 2 and 3 can be used to estimate the impact strength of microcellular CPET foams. First the foam thickness is estimated, and then the impact strength can be determined. To illustrate this, consider an example of a target CPET specimen with a 30% reduction in density, and let us estimate the impact strength at room temperature. At a saturation pressure of 5 MPa (725 psi), it would take a foaming temperature of approximately 74°C (166°F) to achieve this density reduction. Interpolating the thickness data in Table 2, we estimate that this specimen would have a thickness of 0.98 mm. From Table 3, the normalized failure energy at room temperature is found to be 6.46 J/mm. After adjusting for thickness, the foam in our example will have a failure energy of 6.34 J.

Figure 8 plots normalized failure energy to maximum load as a function of the foam relative density. Data at various temperatures is included. The maximum load is simply the highest load recorded during the dynamic impact test. The trends discussed above with reference to Figure 7 can also be seen in Figure 8.

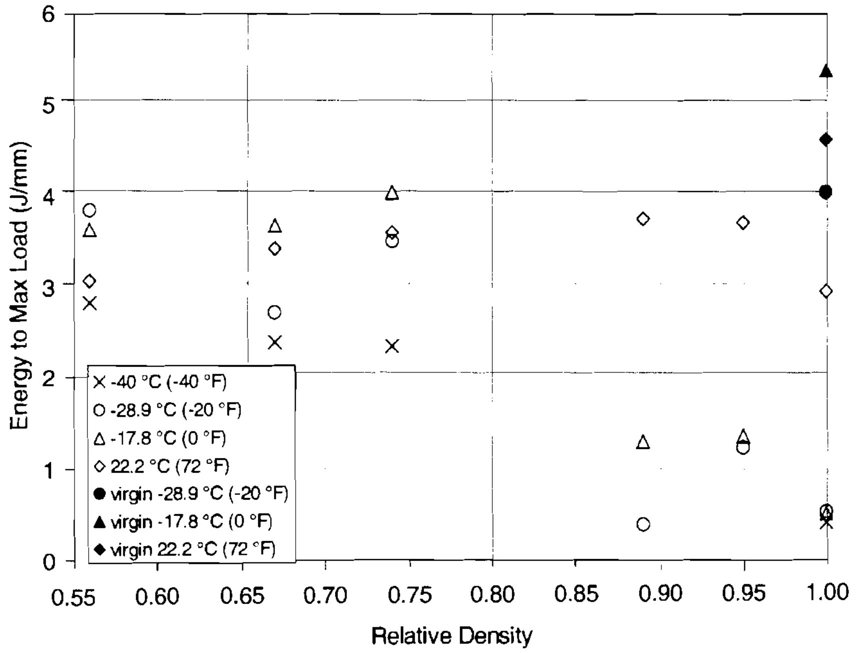
Figure 7 Failure energy for instrumented impact testing of CPET foams at various temperatures. The filled symbols give data for the unprocessed virgin CPET. The non-filled data at the relative density of 1.0 corresponds to saturation-cycled CPET



CONCLUSIONS

This study has brought out some unique properties of solid state microcellular CPET. In microcellular CPET foams obtained from fully crystallized specimens by saturating them with CO_2 at 5 MPa, it was found that up to 50% reduction in density is possible without a significant drop in impact strength. In fact, at lower temperatures, in the -17.8°C (0°F) to -40°C (-40°F) range, the impact strength of CPET foams appears to be comparable to that of the virgin polymer.

Figure 8 Energy to maximum load for instrumented impact testing of CPET at various temperatures



This result is very significant and has far reaching commercial implications, especially in applications where impact strength is important. Clearly, for such applications, substantial reductions in density and thus in material costs are possible without sacrificing the performance under impact loads.

ACKNOWLEDGMENTS

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