Mechanical properties of thin microcellular PET sheet

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Abstract: In this paper, the thin microcellular poly(ethylene terephthalate)(PET) sheets, having the controlled structures, were prepared by compression molding. The effects of the processing conditions on the microcellular PET tensile properties have been investigated. By comparing the importance of the individual processing parameters, the saturation time was the most important factor to determine tensile modulus, whereas the saturation time and the upper-plate temperature were the most important processing parameters that influence the tensile strength and specific tensile strength. The effects of the microstructure on the tensile properties of microcellular PET were also investigated systematically. The results indicated that the tensile modulus and strength increased with increasing foam density, but decreased slightly with increasing cell size. Following the experimental data, a new model was built to relate the tensile modulus and tensile strength with the foam density and the cell size.

Keywords: Microcellular; Foams; PET; Mechanical properties; Compression

Introduction

As a kind of novel materials, microcellular foam can be used in many applications, such as insulation, packaging, filters and so on [1-6]. However, these applications are closely related to their mechanical properties, and there are considerable literature dealing with the conventional foam mechanical property [7-10], but only a limited on the microcellular foams [11-15]. The mechanical properties of microcellular polymers are basically influenced by the properties of the original material (crystallinity, crosslinking, molecular orientation, etc.) and by microcellular structure and morphology. The relative density, cell size, cell density, and the degree of openness of the cells are the key structural parameters that control the properties. Mechanical properties are usually reported as a function of these structural parameters, or of processing parameters, such as saturation time, saturation pressure, foaming temperature and foaming time. In particular, since the foam density can be measured easily, it is very common to report and analyze the mechanical properties of microcellular foams as a function of the foam density. Several empirical and theoretical relationships between mechanical properties and foam density have been established. The advantage of this approach is that the foam density can be related to the cellular structure and geometry [16].

The earlier studies showed that the strength of microcellular polystyrene was lower than that of the unfoamed polymer, but its specific strength was higher [2]. Later, Waldman found a four fold increase in the fracture toughness in microcellular high-impact polystyrene in comparison to the unfoamed plastic [3]. A preliminary study of microcellular polyester composites was performed by Youn and Suh [17].
Then, Ozkul [11] carried out the work on the elastic and plastic mechanical responses of microcellular isotactic polystyrene, polyacrylonitrile, poly(4-methyl-1-pentene) and polyurethane. The Young’s modulus, the collapse stress, plastic deformations, time-dependent behavior and Poisson’s ratio were studied. Guriya studied the mechanical properties of microcellular ethylene-propylene-diene terpolymer rubber vulcanizates and ethylene-octene copolymer [18-19]. After that, the time dependent response, tensile toughness, impact behavior, compression behavior of microcellular polymers and their blends were studied as well [20-26].

Recently, Sun et al. studied the microcellular foaming and mechanical properties of polysulfones, polyethersulfone and polyphenylsulfone [27-28]. They found that the tensile strengths and moduli increased with increasing relative density, but they did not report the effect of cell size and cell density on the mechanical properties. Doroudiani et al. studied the impact and tensile properties of polystyrene foam [16, 29, 30]. Their results showed that foaming time was the most important factor to determine the impact strength, while foaming temperature was the most important factor to control the specific impact strength. Foaming time and foaming temperature were the most important processing parameters to influence the tensile modulus and strength. The tensile modulus and strength increased with increasing foam density, but they decreased slightly when the cell size increased. Kumar and Weller also examined the effect of the cell size on the tensile behavior of microcellular polycarbonate [14]. It was determined that the tensile behavior of microcellular polycarbonate was not affected by the average cell size, for the range of sizes studied. They found the bulk foam density as the only variable to determine the tensile strength. A number of other authors have tried to relate tensile properties of foams to the foam relative density and the properties of the microcellular foam matrix.

In our research, the thin microcellular PET sheet is prepared by compression molding invented by our research group [31-34]. In this paper, the effects of the processing parameters and microstructure on the mechanical properties were studied systematically. The objective of this work is to relate the tensile properties of thin microcellular PET sheets prepared by compression molding to the processing and microstructure parameters.

**Results and discussion**

*Preparation and mechanical properties of microcellular PET*

Microcellular PET can be successfully prepared by first preheating PET sheet with blowing agent matrix, next saturating PET sheet by blowing agent decomposition, and lastly making a pressure and temperature quench simultaneously [31]. Experimental results show that the processing parameters do affect the microcellular structures in microcellular foaming process by compression molding. The microcellular structure resulting from this type of foaming procedure can be readily controlled by manipulating preheat time, saturation time, saturation pressure, the upper-plate temperature, the lower-plate temperature, blowing agent content and the PET sheet thickness [31]. By controlling the processing conditions one can produce microcellular PET having the same density and different cell sizes and cell densities. For example, PET sheet saturated at 20 MPa, 187°C and 300 s and at 22 MPa, 187°C and 240 s exhibited the same foam relative densities of 0.638, but had average cell sizes of 47 and 35 μm, respectively. In order to conduct a systematic investigation of the effect of cell size and foam density on the properties of microcellular PET, it is very important...
to be able to produce microcellular PET specimens with controlled density and cell size in this way.

Fig. 1 shows the stress-strain curves of unfoamed PET and microcellular PET, saturated under a pressure of 20 MPa, at 187°C for 300 s, which produced foam with a relative density equal to 0.779. The stress-strain curves show an initial period of linearity followed by a change in slope.

Fig. 1. Tensile stress-strain curves for unfoamed PET and microcellular PET.

For unfoamed PET, this occurs at about 1.5% strain, while microcellular PET shows a change in slope at a strain of 2.5%. The linear slope determines the elastic modulus of the sample, so the elastic modulus of the microcellular PET is lower than unfoamed PET. The unfoamed PET has an obvious yield point, but the microcellular PET does not have an evident yield point. In the second region, the stress-strain relationship is nonlinear and all specimens fail by fast fracture. The ultimate strength and modulus of elasticity of all microcellular PET is less than those of unfoamed PET. However, the microcellular PET shows larger elongation at break. This is because the cell walls of the foam undergo both bending and axial deformations, which the slope of the stress-strain curve in the closed-cell microcellular foams is mainly determined by edge bending, face stretching, and pressure of the gas in the cells. Thus the tensile modulus, the maximum stress, and the breaking stress of microcellular PET are all lower than unfoamed PET, but the elongation at break of microcellular PET increases much under our experiment situation.

Effects of the processing parameters on the tensile properties

-Tensile modulus

Fig. 2 demonstrates how the tensile modulus varies with the main processing parameters. The tensile modulus decreases greatly (as low as one third that of the unfoamed PET) with the saturation time increasing. There is a decrease in the modulus with increasing saturation pressure, which corresponds to more expansion and a decrease in microcellular foam density. In this method, the upper-plate and lower-plates are set at different temperatures of the press differently to form a temperature gradient to control the blowing agent decomposition rate, a technique that we call nonisothermal foaming. In nonisothermal foaming, the lower-plate temperature is set at 197°C, and only the upper-plate temperature of the press is
altered. As the upper-plate temperature increases, the modulus shows a gentle decrease. This behavior can be attributed to a decrease in the microcellular foam density when the saturation temperature increased. Although the tensile modulus decreases with an increasing saturation pressure and the upper-plate temperature, the effects are much smaller than the saturation time. Analysis on the experiment data shows that saturation time is the most important parameter to control the tensile modulus, while saturation pressure and the upper-plate temperature are less important.

![Graphs showing the effects of processing parameters on the tensile modulus of microcellular PET.](a) (b) (c)

**Fig. 2.** The effects of processing parameters on the tensile modulus of microcellular PET. (a), (b) are saturated at 187 °C, (c) is saturated for 300s.

The tensile modulus is determined by the relative density, and the foam relative density decrease will lead to the tensile modulus decrease. This can explain why the microcellular PET reduces its modulus. In the foam literature, mechanical properties are often related to the relative density using a simple empirical equation: mechanical property $\propto A\rho^n$. The constant $A$ and the exponent $n$ are generally determined empirically. The coefficient $A$ is primarily related to the properties of the foam material, whereas $n$ depends on the deformation mode. The relationship between relative density and tensile modulus will be discussed later on.
- **Tensile strength**

From Fig. 3, we can see that the tensile strength of microcellular PET decreases significantly from 130MPa to 70 MPa as the saturation time increases from 180s to 600s or the upper plate temperature increases from 179 °C to 195 °C. Also, the tensile strength only decreases a little as the saturation pressure increases. This may result from two reasons: first, as the saturation pressure increases, the relative density decrease will reduce tensile strength; second, the tensile strength is normalized by mass increase for the smaller cell size and higher cell density generated at higher saturation pressures. An increase in the upper-plate temperature also generates more expansion, which cause a decrease in the tensile strengths of the microcellular PET. The tensile strength of PET reduces after microcellular processing. The reason for these results is that the relative density mainly affects the tensile strength, so the microcellular foam relative density decrease will lead to the tensile strength decrease.

![Fig. 3](image.png)

**Fig. 3.** The effects of processing parameters on the tensile strength of microcellular PET. (a), (b) are saturated at 187 °C, (c) is saturated for 300s.

- **Specific tensile strength**

In our experiment, the tensile strength is divided by the relative density of the microcellular PET to obtain the value, which is defined as specific tensile strength. From Fig. 4, we can see that the specific tensile strength with an increasing saturation...
time shows two different trends, one slightly increasing at shorter saturation times, another decreasing and level off at longer saturation times. The specific tensile strength did not significantly change as the tensile strength (see in Fig. 3) with the saturation time increasing. In other words, the decrease in the tensile strength as a result of foaming resulted entirely from a decrease in the foam relative density. The saturation pressure does not produce a consistent effect on the specific tensile strength. The specific tensile strength increases a little first, and then slightly decreases at elevated foaming temperatures.

![Graphs of specific tensile strength vs. saturation time and pressure](image)

**Fig. 4.** The effects of processing parameters on the specific tensile strength of microcellular PET. (a), (b) are saturated at 187 °C, (c) is saturated for 300s.

**-Elongation at break**

From Fig. 5, we can see that the elongation at break significantly decreases as the saturation time increases. This behavior can be attributed to a decrease in the microcellular foam density when the saturation time increased. The saturation pressure does not affect elongation at break obviously, and the elongation at break slightly decreases at elevated foaming temperatures.
Fig. 5. The effects of processing parameters on the elongation at break of microcellular PET. (a), (b) are saturated at 187 °C, (c) is saturated for 300s.

Effects of the microstructures on the tensile properties

Fig. 6. The effects of relative density on the relative tensile modulus and strength of microcellular PET.
The variation of the tensile properties of microcellular PET can be explained by considering the microcellular structure produced by microcellular foaming processing. The relative tensile modulus plotted in Fig. 6 increases with increasing relative density. The experimental data obtained from Fig. 6a were analyzed using Microsoft Excel computer software. A quadratic expression does not fit the data very well, as $R^2$ was equal to 0.7164. The trend of the variation of the tensile strength versus the relative density can be expressed by equation 1:

$$\sigma_r = 1.3057\rho_r - 0.2827$$  \hspace{1cm} (1)$$

where $\sigma_r$ is the relative tensile strength, $\rho_r$ is the relative density of microcellular PET. However, the linear expression does not fit the data well also, as $R^2$ was equal to 0.6498. The reason for these results is the effect of cell size. When the cell size increased, both the tensile strength and the specific tensile strength slightly decreased, and the value must be normalized by the mass decreased for the bigger cell size and lower cell density. This behavior can be attributed to the greater difficulty in bending the cell walls and struts within the unit cell in the foams with a smaller cell size. But when the cell size is small enough, the effect of cell size on the mechanical properties will decrease and be close to disappearing.

![Graph](image)

**Fig. 7.** The effects of relative density on the relative tensile modulus and strength of microcellular PET (samples with similar cell size).

To isolate the effects of cell size and foam density, two sets of results were extracted. In Fig. 7 (A), the relative tensile modulus of samples with similar cell sizes (40~44 $\mu$m) but different relative density are plotted. The data show a trend similar to that for the whole data set [Fig. 6a]. But the relative density and the relative tensile modulus fit equation 2 very well, and $R^2$ value for this curve fitting is 0.997.

$$E_r = 1.005\rho_r^2 - 0.009\rho_r + 0.0035$$  \hspace{1cm} (2)$$

where $E_r$ is the relative tensile modulus, $\rho_r$ is the relative density of microcellular PET. In Fig. 7b, the relative tensile strength for a series of samples with similar cell size (40~44 $\mu$m) but different relative density is also reported. The data indicate that, over this range of relative density, relative density affects the impact strength slightly. The relative densities and the relative tensile strength fit equation 3 very well, and $R^2$ value
is 0.925.

\( \sigma_r = 1.0036 \rho_r - 0.0021 \)  

(3)

The effect of cell size on the relative tensile modulus and the relative tensile strength is shown in Fig. 8. In our experiment, variations in saturation time, saturation pressure and the upper-plate temperature lead to variations in cell size. It appears that the tensile modulus [Fig. 8a] and the tensile strength [Fig. 8b] are depending on the cell size in a consistent way. They decrease slowly with the cell size increase; a quadratic expression fits the data very well.

The relative tensile modulus and strength can be expressed with equation 4(with R² equal to 0.9753) and equation 5(with R² equal to 0.9781):

\[
E_r = E_{r0} + 0.0002d^2 - 0.0207d + 1.2991 \quad R^2 = 0.9753
\]

(4)

\[
\sigma_r = \sigma_{r0} + 0.0001d^2 - 0.022d + 1.5197
\]

(5)

Where \( E_r \) is the relative tensile modulus, \( E_{r0} \) is the relative tensile modulus at the critical cell size \( C_0 \), \( \sigma_r \) is the relative tensile, \( \sigma_{r0} \) is the relative tensile strength at the critical cell size \( C_0 \), \( d \) is the cell size of microcellular foam. According to the initial aims of microcellular foam, the cell size in the microcellular foam is below the critical flaw size of the polymer materials; therefore, it will absorb the energy and increase the strength as additives (fillers) do when force is applied to microcellular foam [1-3]. That is to say when the cell sizes are smaller than the critical size, the tensile modulus and strength are only determined by the foam density, but when they are bigger than critical size, cell size will affect the mechanical property, thereby these relationships are not reasonable in these conditions. Thus, equation 4 and 5 only fit for \( d \geq C_0 \).

According to the results and discussion above, considering the effects of cell size on the mechanical properties, a new relationship about tensile modulus and tensile strength with the relative density and cell size are built as:

\[
E = E_0 \left( \frac{\rho}{\rho_0} \right)^n \left( \frac{C_0}{d} \right)^m \quad (d \geq C_0)
\]

(6)
\[ \sigma = \sigma_0 \cdot \left( \frac{\rho}{\rho_0} \right)^n \cdot \left( \frac{C_0}{d} \right)^m \quad (d \geq C_0) \]  

(7)

where \( E \) is the tensile modulus of microcellular foam; \( E_0 \) is the tensile modulus of unfoamed polymer; \( \sigma \) is the tensile strength of microcellular foam; \( \sigma_0 \) is the tensile strength of unfoamed polymer; \( \rho, \rho_0 \) are the mass densities of microcellular foam and unfoamed polymer; \( C_0 \) is the critical cell size of which the effect of cell size on the mechanical property can be neglected, it is below 29\( \mu \)m in microcellular PET prepared in our experiments. That is, in our experiment, the cell size will give some effect on the mechanical property, for the cell size is larger than the critical cell size as shown in Fig. 8. \( n \) and \( m \) are two coefficients determined by the properties of the material, according to the predictions of the current theory for conventional polymer foams and our experimental data, \( n \) is about 2 for the tensile modulus and 1 for the tensile strength respectively [7]; Then we can obtain the value of \( m \) according to our experimental data, which is about 0.4. So equation 10 and 11 fit for \( d \geq C_0 \), when \( d \leq C_0 \), \( m = 0 \).

**Conclusions**

The thin microcellular PET sheets were prepared with a wide range of controlled structures by compression molding, and the tensile property of the thin microcellular PET was studied. By controlling the processing conditions, we can control the microcellular PET structure. The processing-tensile property studies showed that the tensile modulus, tensile strength and elongation at break decrease with saturation time increasing, but the specific tensile strength increases first then decreases; the saturation pressure gives some effects on the tensile modulus and tensile strength, but have not much effects on the specific tensile strength and elongation at break; the tensile modulus, tensile strength, specific tensile strength and elongation at break are slightly influenced by the upper-plate temperature. From the research and statistical analysis of microstructure and tensile property, we can conclude that the tensile modulus and tensile strength of microcellular PET prepared under this condition mainly are determined by the relative density, but the microstructure have some effects as well. The effects of cell size and relative density are that the tensile modulus and strength increased with an increasing relative density, but they decrease slightly when the cell size increases. According to the results and analysis in our research, a new model which relates the tensile modulus and strength to the microcellular foam density and microstructure was built as:

\[ E = E_0 \cdot \left( \frac{\rho}{\rho_0} \right)^n \cdot \left( \frac{C_0}{d} \right)^m \]

\[ \sigma = \sigma_0 \cdot \left( \frac{\rho}{\rho_0} \right)^n \cdot \left( \frac{C_0}{d} \right)^m \]

which fits the cell sizes bigger than the critical cell size in our experiments.
Experimental part

Materials
The PET sheet (unfoamed PET) used in this work was a commercial-grade product with a thickness of 150 μm received from Oriental Insulation Materials Factory of China (Mianyang, China), it is semi-crystalline and biaxially oriented. Low density polyethylene (LDPE) pellet from Sinopec Beijing Yanshan Chemical Corporation Factory (Beijing, China), with a melt index 2 g/10min at 190 °C, was used as received. Azobisformamide (AC), commercial-grade product of Wuhan Honghua Chemical Reagent Corporation (Wuhan, China), was used as the blowing agent. The gas yield was about 200-220 ml/g and consists of nitrogen, carbon monoxide, carbon dioxide, and some ammonia. Dicumyl peroxide (DCP), Sinopharm Chemical Reagent Corporation, Ltd (Shanghai, China), was used without any further purification.

Foam preparation
The microcellular PET was prepared by mixing LDPE, AC, DCP in a two-roll mill, and then loading them with PET sheet in a hydraulic hot press under set experimental conditions [31]. Once the required foaming time and other conditions were reached, the pressure was released immediately and the mold was taken out of the hot press quickly. We then unloaded the mold, quenched it at room temperature within 30 s; and removed the microcellular PET sheet (microcellular PET) from the mold. Thus, the microcellular PET foam samples were ready for property characterization.

Foam characterization
The cell size of the foamed samples was calculated according to the images from OLYMPUS BX51 polarizing microscope (using a 100 x magnification camera lens). The cell structure parameters, such as the cell sizes and cell densities, were characterized by using the method suggested by Kumar et al. [35]. The cell size (D) was the average cell size measured from the photographs, usually more than 100 cells. The cell density (N_f), which is the number of cells per cubic centimeter of the foam, is calculated as:

\[ N_f = \left( \frac{nM^2}{A} \right)^{3/2} \]  

(8)

where \( n \) is the number of cells seen on the photographs, \( A \) is the area of the micrograph (cm²), and \( M \) is the magnification factor. In addition, the cell density (N_0) based on the pristine unfoamed sample is calculated as:

\[ V_f = \frac{\pi}{6} D^3 \times N_f \]  

(9)
where $V_f$ is the void fraction of the foamed material.

The relative density is determined according to ISO 1183-1987 because all microcells are closed as shown in Fig. 9. The mass of the sample in air and distilled water were measured with an analytical balance with an accuracy of 0.1 mg. The density of the sample ($d$) is calculated as:

$$
d = \frac{m_{\text{gas}}}{m_{\text{water}}} \times \rho_{\text{water}}
$$

where $\rho_{\text{water}}$ is the density of the distilled water at room temperature, and $m_{\text{gas}}$ and $m_{\text{water}}$ are the mass of the sample in atmosphere and in distilled water, respectively.

Then the density of the foamed sample is divided by the density of the unfoamed sample to obtain the relative density.

The microcellular PET were machined into dumbbell-shape specimens with a gage length of 80mm (ASTM D638 type II specimen). The specimen thickness varied with the foaming grade, and ranged from 150 $\mu$m to 500 $\mu$m. For each sample, at least five samples were tested and the average data is reported in this article. The tensile test was carried out at room temperature using a Shimadzu AG-A all-purpose testing machine (Japan) equipped with a 1000 lb load cell at a constant crosshead rate of 50 mm/min. The strain was calculated from the displacement of the crosshead, and the tensile modulus was determined by running a least-square fit through the initial linear portions of the stress-strain curves.

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