MICROCELLULAR FOAMING OF AMORPHOUS HIGH-T_g POLYMER USING CARBON DIOXIDE

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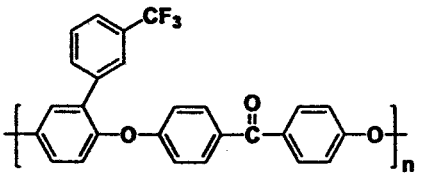
Introduction

Microcellular foaming of glassy polymers with carbon dioxide or nitrogen used as a physical blowing agent was first described by Martini and co-workers. [1] In general, microcellular foams are characterized by a cell size of around 10 μm and a cell density between 10^9 and 10^{15} cells/cm^3. Such foams have been successfully produced from polystyrene, polyester, polycarbonate, polypropylene, polyethylene terephthalate and polyvinyl chloride. In this work, we study the microcellular foaming process of amorphous high-T_g [2] fluorinated aromatic poly(ether ether ketone) themselves have low dielectric constants and high thermal stability. These closed-cell foams possess lower low dielectric constants and better thermal insulation properties than their matrix.

Experimental

Materials. FPEEK was synthesized by our lab. [3] The structure of FPEEK was shown in the **Scheme 1**. DMF was purchased from Tianjin Chemical Reagent Plant. Carbon dioxide having purity a larger than 99.9% was purchased.



Scheme 1. structure of the polymer FPEEK.

Film Preparation. Solutions of FPEEK were prepared by dissolving 20 wt % polymer in DMF. The solutions were cast onto glass plates which were then heated to evaporate the solvent at 100, 130, 160 and 210^{0}C for periods of 30min each. The transparent free standing films were stripped off the glass plate.

Microcellular Foam Formation. The fluorinated aromatic poly(ether ether ketone) sheet of approximately 0.1mm thickness was used in the experiments. The original, unsaturated material had a density of 1.32g/cm^3 and a glass transition temperature of 133^{0}C. Samples (approximately 40mm*10mm) were put into a carbon dioxide cylinder. The pressure within the vessel was regulated using a single stage regulator, and the gas sorption was carried out at 40^{0}C. The saturation time and pressure were 12h and 30Mpa, respectively. Then these samples were taken out of the chamber and dipped them for 5 seconds in a hot glycerol bath at 180^{0}C.

Instrumentation. The foamed polymer films were characterized to determine their mass densities, cell densities and cell size distributions. The microcellular morphologies of the foamed samples were investigated using a HITACHI X-650 scanning electron microsanalyze (SEM). The samples were freeze fractured in liquid nitrogen and sputter coated (Eik01 b.3 ion COATER) with gold at an argon pressure of 10^{-5} Torr for 4 min at a current of 10 mA. The cell densities were determined from SEM micrographs using a procedure described previously by Kumar et al. In this procedure, only the number of cells inside a window located in the center part of the foam was counted. The cell size was obtained by measuring the maximum diameter of each cell perpendicular to the skin. To determine the cell size distribution, the size of at least 150 cells in the core part of the cross section of the fractured foam sample was measured.

Results and Discussion

SEM micrograph for foamed FPEEK film is showed in **Figure 1.** It is clearedly visible that the foam. The microcellular foaming process using carbon dioxide as physical blowing was successfully applied to amorphous high-Tg poly (ether ether ketone).

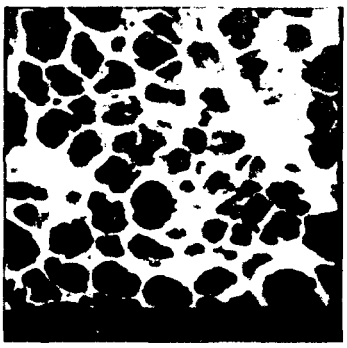


Figure 1. Micrograph of microcelluair polymer.

N_f V_f and N_0[4] are estimated from the scanning electron micrograph according to the following procedure. First a micrograph showing 100 to 200 bubbles is obtained, and the number of bubbles, n, in the micrograph is determined. If A is the area of the micrograph in cm^2 and M is the magnification factor, then ($n/A/M^2$) gives the area bubble density or the number of the bubbles per cm^2 of the foam. Assuming an isotropic bubble distribution, the square root of the area density gives a line-density or the number of bubbles per cm^2 of the foam. By cubing the line density, the number of bubbles per cm^3 of the foam, N_f can be estimated.

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

A second micrograph at a higher magnification is obtained at same location in the sample as the first micrograph, so that the average bubble diameter D would be determined. Because many bubble diameter measurements can be made on a single micrograph, the mean and standard deviation of the bubble diameter can be determined. In our experiments, the major and minor diameters of approximately 25 bubbles were measured in each of these micrographs. After determining the average bubble diameter, the volume occupied by the voids in one cm^3 of foam V_f can be estimated as

$$V_f = \left(\frac{\pi}{6}\right) D^3 N_f$$

and the volume occupied by the polymer in one cm^3 of foam is therefore approximated by $(1-V_f)$. Thus N_f bubbles in one cm^3 of the foam must have nucleated in $(1-V_f)$ cm^3 of the original polymer. Therefore, the number of bubbles nucleated per cm^3 of original unfoamed polymer N_0 can be estimated from

$$N_0 = \frac{N_f}{1 - V_f}$$

The results were showed in **table 1**.

Table 1. The results of the estimated values

N_f	V_f	N_0
$4.1*10^9$	0.72	$1.46*10^{10}$

Conclusions

Fluorinated aromatic poly(ether ether ketone) which has high T_g, can foam using supercritical technology. Microcellular foam structures were charactered by SEM. The mass, cell density, and cell size were estimated using some equations

References

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(4) Kumar, V. *J of Eng. For Ind.* **1994**, *116*, 413.