Preparation of microcellular composites with biomimetic structure via supercritical fluid technology

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Abstract **A new microcellular composite material with a biomimetic structure has been prepared via the supercritical fluid (SCF) technology. The resultant material has a clear biomimetic structure like bamboo and wood. The skin region is enriched with oriented high-strength thermotropic liquid crystal polymer fibrils, while the core region with polystyrene (PS) micro-cells. The diameter and density of micro-cells can be controlled by the processing parameters such as temperature and pressure. And the skin thickness can be controlled conveniently by varying the composition of polystyrene and liquid crystal polymer.**

Keywords: supercritical fluid, thermotropic liquid crystal polymer, polystyrene, biomimetic structure.

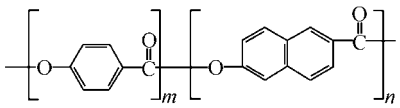
Microcellular polymer materials have extraordinary physical and mechanical properties, such as high anti-impact strength, high toughness, high strength/weight ratio, good thermal stability, long fatigue life, low dielectric constant, low heat conductivity, etc. They are applied extensively in food packaging, air plane and car components, sports equipment, fiber material, biomedical products, etc. Thus the microcellular materials are claimed as " novel materials for the 21st century"[1].

Supercritical fluids have not only densities like liquids and low viscosities and high coefficients of diffusion like gases, but also a controllable solvent property. They have been widely used in chromatograph and medicine industry[2], chemical synthesis[3], polymer synthesis and so on[4–6]. In recent years, the preparation of microcellular materials by using supercritical carbon dioxide (CO_2) has become a research topic for chemists. By using carbon dioxide having mild supercritical conditions (T_c =31.1℃, P_c=7.37 MPa), this technology is free of ozone-destroying chlorofluorocarbons (CFCs) and flammable hydrocarbons used in traditional foam plastics industry. So the preparation of microcellular materials by means of SCF carbon dioxide meets the demands of current green chemistry.

In the past decades, there has been much progress in producing and controlling microcellular plastics[7–10]. Microcellular structure can be obtained in amorphous polymers, semi-crystalline polymers and even the elastomers. In 1999, Beckmen et al. used one-step method to prepare microcellular fluorine materials[11]. However, little work has been done on the preparation of microcellular polymer composites[12]. This note reports a new kind of microcellular composites having a biomimetic structure via the SCF-CO_2 technology. The material has a biomimetic skin-core structure like bamboo and wood. The skin region is enriched with thermotropic liquid crystal polymer fibrils, while the core region with polystyrene (PS) micro-cells.

1 Experimental

(ⅰ) Sample properties. High-purity (99.9%) carbon dioxide (CO_2) was produced by the Beijing Analytic Gas Factory. Polystyrene (PS) with M_w of 243000 (the Yanshan Petrochemical Company in Beijing) was of PS666D brand. Thermotropic liquid crystal polymer (Product of the Hoeschst Celanese Company) was of Vectra A950 brand. Its chemical structure is as shown in scheme 1.



m/n = 73/27

Scheme 1

(ⅱ) Sample preparation. The sample was prepared in two steps. First, PS and Vectra A950 were blended and extruded. Then the extrudate was treated in SC-CO_2 for forming microcellular structure.

(1) All the PS and PS/Vectra A950 blends were prepared on the CS-194 Max Mixing Extruder and CS-183 Mini-Max Molder manufactured by the American Custom Scientific Instruments Company. The blending temperature was in the range of 275℃—290℃. Polymer blends have Vectra A950 in the weight range of 20%—60%. The resultant specimen was in the form of sheet, about 13.7 mm wide and 1.54 mm thick.

(2) All the sheets were put in a specially-made high-pressure chamber. First, it was flushed with a little CO_2 for 3—5 min to expel the air out. Then it was filled with CO_2 to the desired temperature and pressure. After being held at the pressure and temperature for some time till saturation was reached, the chamber was depressured quickly and held at the same temperature for half an hour to let cells grow. Finally, the sheets were cooled down and taken out for characterization.

(ⅲ) Sample characterization. Foamed samples were fractured in liquid nitrogen and characterized by a scanning electron microscope (SEM), Hitachi S-530. The cell density and cell diameter of the samples were measured from the SEM graphs.

2 Results and discussion

(ⅰ) Morphology of PS/Vectra A950 blends. Fig. 1 shows an SEM micrograph of fractured PS/Vectra A950 (60/40, by weight ratio) sheet in the melt flow direction. As liquid crystal polymers can be deformed easily into fibrils in the flow direction, this micrograph shows clearly a typical uneven skin-core structure. The closer to the core, the less the content and the degree of orientation of the liquid crystal polymer.

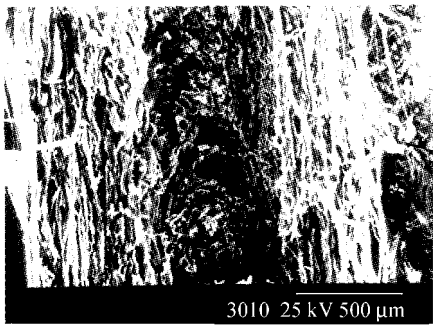


Fig. 1. SEM micrograph of PS/Vectra A950 (64/40) blend.

(ⅱ) Morphology of microcellular PS. As an amorphous polymer having a glass transition temperature at only 105℃, PS is easily made to have microcellular structure. At 60℃ and 15 MPa, microcellular PS was prepared in SC-CO_2 in one step. As shown in fig. 2, the distribution of micro-cells is very even, their diameters are in the range of 7—10 μm, and their distribution density is about 1.06×10^{10} m^{-2}.

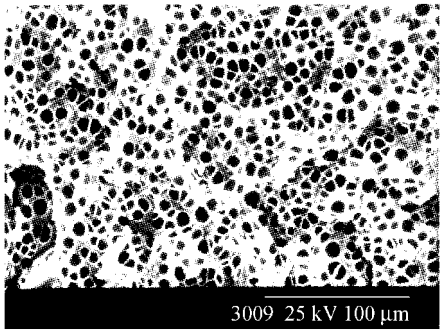


Fig. 2. SEM micragh of microcellular PS foamed at 60℃, 15 MPa for 6 h.

The most important controlling parameters in preparing microcellular PS are temperature and pressure in SC-CO_2. From a series of experiments, the dependence of cell diameter and cell density on the temperature and pressure is established in SC-CO_2. Plots in fig. 3(a), (b) show that low temperatures and high pressures favor the formation of smaller cell diameters and high cell densities in microcellular PS. With increasing SC-CO_2 pressure, the cell nucleus density increases, which leads to smaller cell diameters in the microcellular PS. Moreover, high pressures also have an effect of inhibiting the cell growth. Fig. 3(b) shows that the cell diameter increases and the cell density decreases with increasing temperature. The decrease of temperature mainly affects the micro-cells by changing the solubility coefficient, which leads to a smaller cell density. Higher temperature favors the cell growth, so the cell diameter increases as the temperature rises.

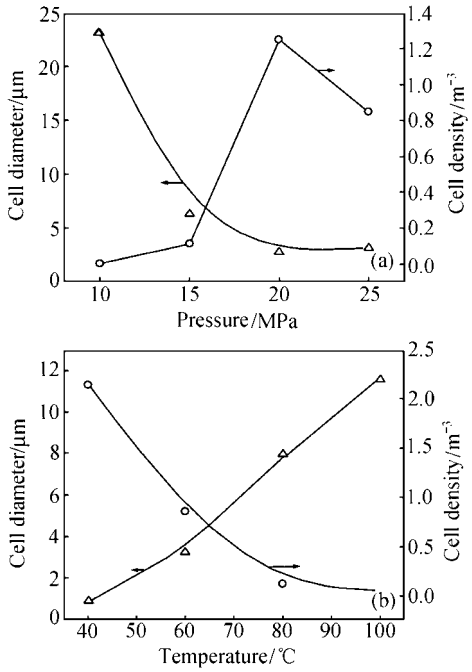


Fig. 3. (a) Dependence of cell diameter and cell density on pressure. (b) Dependence of cell diameter and cell density on temperature.

(ⅲ) Morphology of microcellular PS/Vectra A950 composites. Microcellular PS/Vectra A950 composites were prepared by the saturation in SC-CO_2 at 110℃ and 28 MPa with the same process as microcellular PS. Samples of two compositions of the PS/Vectra A950 composites, 70/30 and 40/60 (percent by weight), were studied. Fig. 4(a) is an SEM micrograph of PS/Vectra A950 (70/30, by weight ratio) in flow direction in the injection molding. The material has an interesting structure: Vectra A950 domains do not have any micro-cells, while PS has uniform micro-cells. Furthermore, the skin area (on the left) is enriched with oriented thermotropic liquid crystal fibrils, while the core area (on the right) with microcellular polystyrene (PS). Micro-cells in PS are uniform in their dimension with diameters of about 10 μm.

Fig. 4(b) shows an SEM micrograph of PS/Vercta A950 (40/60 percent by weight) composite in the flow direction of injection molding. It has a similar structure of PS/Vectra A950 (70/30 percent by weight) composite. However, due to a higher Vercta A950 content, the skin thickness is larger and the cell diameter of PS is smaller.

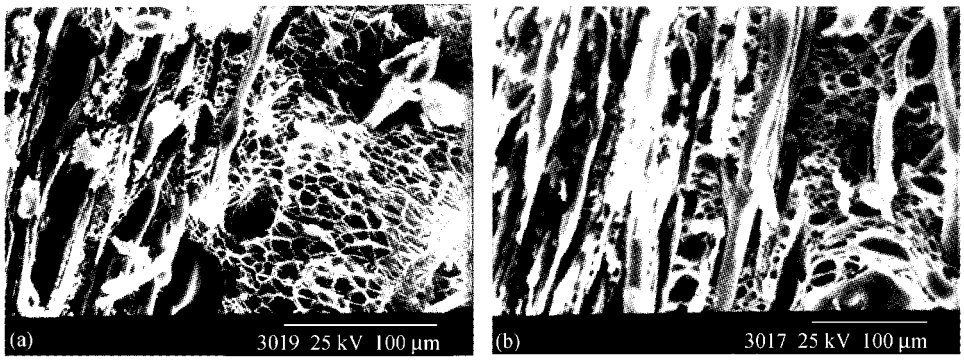


Fig. 4. SEM micrograph of the composites PS/VA 70/30 (percent by weight) (a) and PS/VA 40/60 (percent by weight) (b). The skin area is on the left and the core area on the right of the micrographs (a) and (b).

The structure shown in fig. 4(a), (b) is similar to that of some materials found in nature such as animal bones, bamboo and wood[14]. These natural materials have a compact and high-strength skin layer to support external loads, while their porous cores keep their toughness and decrease the whole weight. These two regions interact with each other to exhibit excellent performances of the resultant material. The PS/Vercta A950 composites in the present study have a biomimetic structure: in the outer skin area are highly oriented liquid crystal polymer fibrils, and in the core area is mainly the PS mcirocellular material. In this skin-core microcellular polymer composite, the liquid crystal polymer fibrils may give the material high strength and the microcellular PS in the core gives toughness and heat insulation. So these PS/Vectra A950 composites combine advantages of microcellular PS and Vectra A950 fibrils after being treated in SC-CO_2. Moreover, in this process we avoided the use of traditional blowing agent like ozone-destroying CFCs. So the research of this composite may enlarge the application of PS and liquid crystal polymers which may further develop into a new type of biomimetic material.

The relevant physical properties of the composites are being investigated. On the other hand, enhancing the interface adhesion between PS matrix and liquid crystal polymer phase and controlling the dimension and its distribution of the disperse phase are topics of further study.

3 Conclusions

A microcellular composite with a skin-core structure has been prepared via the supercritical fluid technology. The material has a biomimetic structure like bamboo and wood. The skin area is enriched with oriented high-strength thermotropic liquid crystal polymer fibrils, while the core area with polystyrene (PS) micro-cells.

The diameter and density of micro-cells can be controlled conveniently by temperature and pressure of SC-CO_2. The thickness of the skin can be controlled by varying the composition of PS and liquid crystal polymer.

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