

Study of Different Effect on Foaming Process of Biodegradable Bionolle in Supercritical Carbon Dioxide

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ABSTRACT: Microcellular foaming of biodegradable Bionolle in supercritical CO₂ has been produced. The effects of a series of variable factors, such as saturation temperature, saturation pressure, and depressurization time and step on the foam structures and density, were studied through measurement of density and SEM observation. The experimental results show that higher saturation temperatures lead to an increase in bulk densities; and different depressurization time and step result in different product

cell morphology. In addition, at some saturation temperature, the orientation of the cells can be found in the product morphology. XRD experimental results show that the foaming treatment with SC CO₂ increased the crystallinity of Bionolle. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2901–2906, 2006

Key words: supercritical CO₂; foaming; biodegradable; Bionolle

INTRODUCTION

Foaming of polymers using environmentally friendly physical blowing agents in their supercritical state has become of significant interest in the past decades. Supercritical fluids, especially CO₂, possess many advantageous properties including adjustable solvent strength, plasticization of glassy polymers, and enhanced diffusion rates. Moreover, CO₂ is a gas at ambient condition and this avoids creation of vapor-liquid coexistence upon release of pressure, and so damage to the cellular structure by capillary forces can be evaded. On the basis of the route to induce thermodynamic instability and initiate foaming process, application of SC CO₂ in producing polymeric foams can principally be classified as temperature-induced and pressure-induced phase separations. Compared with the former, the latter has its benefit in producing homogeneous and microcellular foam for the fast rate of phase change with little pressure gradient. In addition, it is the most potential and feasible alternative in

foam industries. Much work has been done using this method on foaming amorphous and semicrystalline glassy polymers such as PS, PMMA, PET, and PC^{1–4} with cell densities up to 10¹⁰/cm³ and average cell size varying from <10 to 50 μm depending on their specific condition.

It is well known that porous biodegradable polymers are required in biomedical applications such as tissue engineering and guided tissue regeneration. In the traditional techniques for generating porous biodegradable polymers, there exists a big drawback of utilizing organic solvents in the fabrication process and the residues of organic solvent may be harmful. Therefore, the pressure-induced technique using SC CO₂ to produce biocompatible polymer foams was employed. Most research has been focused on foaming of poly(lactic-co-glycolic) acid.^{5–7}

In this paper we use SC CO₂ in foaming Bionolle, one of the most important aliphatic polyesters. As biodegradable plastics have been receiving a great deal of attention from industrial and ecological view point, a number of plastics with biodegradability have been developed over the years. Biodegradable aliphatic polyesters of high molecular weight, consisting of dihydric alcohols and dicarboxylic acids (Bionolle), have been developed by Showa High Polymer Co. Because of their excellent biodegradability and superior mechanical properties, Bionolle is considered to be one of the most developed biodegradable synthetic polymers since the development of polycaprolactone. It is expected to become widely used as an alternative to ordinary plastics. In this work, we generated Bion-

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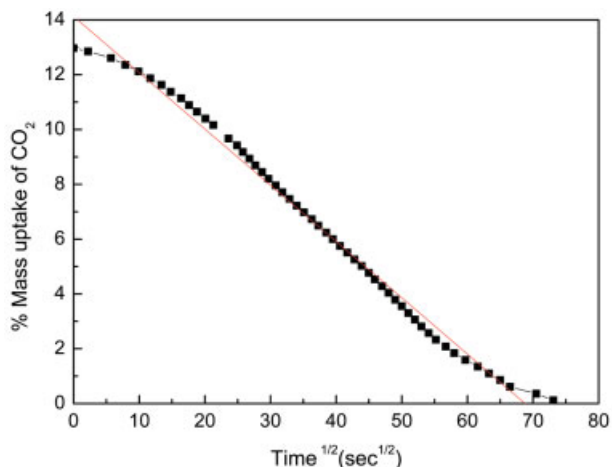


Figure 1 Mass uptake of CO₂ as a function of square root of desorption time after being saturated at 100°C and 16 MPa for 3 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

olle foams using SC CO₂. The effects of processing conditions on the cell morphology were studied.

EXPERIMENTAL

Materials

Bionolle (commercial grade) was supplied by CSIRO, CMIT of Australia in the form of white granules and was used as received ($T_m = 95.4^\circ\text{C}$). CO₂ (with the purity of 99.9%) is obtained from Zhengzhou Sanfa Gas Co.

Foam preparation

Reactions were run in a 50 mL high-pressure stainless steel reactor. A high-pressure syringe pump (Beijing Satellite Manufacturing Factory, DB-80) was used to charge CO₂ into the reaction vessel. A pressure gauge was connected to the reactor to observe the in situ pressure change of the system. In a typical experiment, the reactor was placed into a constant-temperature controller. Bionolle, in the form of granule (2 mm in diameter and 4 mm in length) or sheet, was weighed and placed into a glass tube (ϕ 20 mm \times 20 mm) in the steel vessel. Then the closed reactor was preheated in the temperature controller to a fixed temperature. Having been flushed for a few minutes with CO₂, the cell was filled up to the desired pressure. At this pressure the resin was exposed in SC CO₂ for a prescribed period of time. Finally, the valve of the reactor was opened and the pressure was quenched rapidly to that of the atmosphere. The time of depressurization was recorded to study its influence on the final product.

Foam characterization

The foams were characterized to determine their densities, cell sizes, and cell shapes. Density was measured using a gravity bottle with a capillary tube in its lid. The weight of bottle filled with distilled water was measured with an analysis balance at a presetting temperature. The sample was put into the bottle, and water of same volume as the sample overflowed along the capillary tube. The bottle containing both water and sample was weighed, thus the density was calculated using the following equation

$$\rho = w_1\rho_0/(w_1 + w_2 - w_3)$$

where ρ is the density of sample; ρ_0 is the density of water; w_1 is the weight of the sample; w_2 is the weight of bottle filled with water; w_3 is the weight of bottle containing both water and the sample.

The cell structures of foamed samples were studied using an AMRAY-1000B scanning electron microscope (SEM). The samples were prepared by freezing in liquid nitrogen, fracturing the surface, mounting the fracture on stubs with carbon paint, and sputter coating with gold forming a layer of approximately 100 Å in thickness. WAXD measurements were conducted to examine the crystallinity of the foamed materials. The apparatus was made up of an X-ray diffraction unit (D/MAX-3B, Rigaku Co., Japan) with a Ni-filtered Cu K α beam and a step length of 0.02°.

RESULTS AND DISCUSSION

Desorption kinetics

The desorption kinetics of CO₂ in foamed Bionolle was measured by a simple gravimetric method described

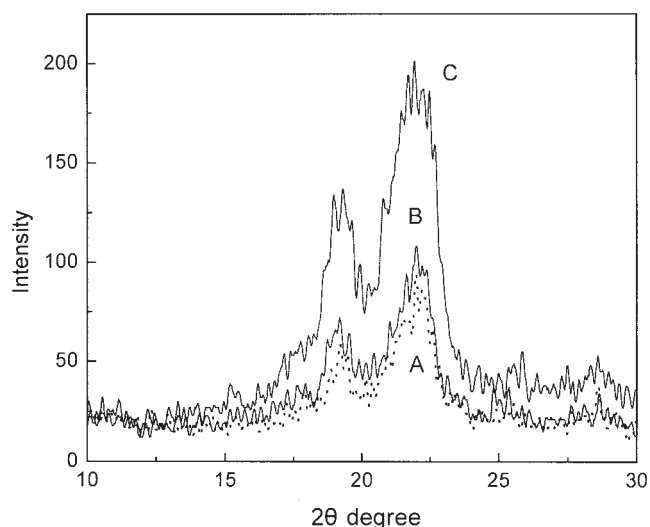


Figure 2 XRD diffraction curves of virgin Bionolle and foamed Bionolle saturated at (A) 80°C (B) 18 MPa, and (C) 20 MPa.

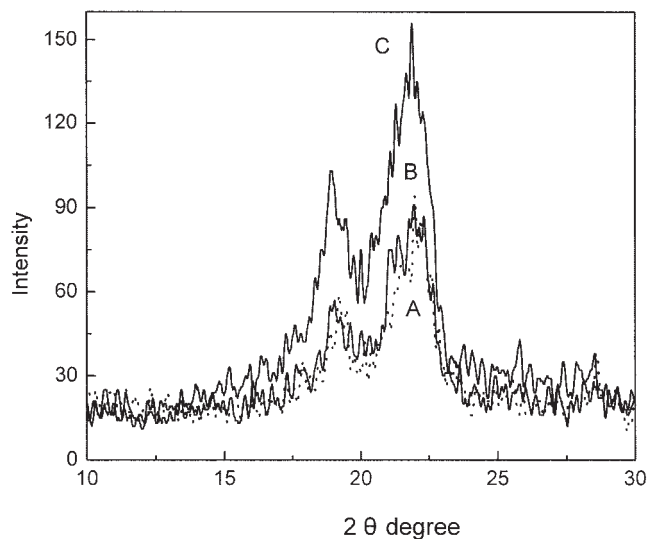


Figure 3 XRD diffraction curves of virgin Bionolle and foamed Bionolle saturated at (A) 16MPa (B) 75°C, and (C) 90°C.

by Berens.⁸ After CO₂ pressure was rapidly released to atmospheric, the weights of samples were recorded at intervals during the whole desorption process and the mass uptake were plotted versus the square root of desorption time (Fig. 1). It can be seen that in the part period of the desorption process, the plot appears linear in accordance with Fickian theory.

Crystallinity of the samples

It is well known that the absorption of CO₂ in polymer matrix can plasticize the material and in turn decrease

the glass transition temperature. Further, it can induce crystallization of the matrix and cause an increase in the melting temperature and melting enthalpy.⁹⁻¹² Here X-ray diffraction was performed to study the crystallinity of virgin and foamed Bionolle. The results are shown in Figures 2 and 3. After treated in SC CO₂, the degree of crystallinity was found to increase. At higher pressure under isotherm condition, the absorption of more CO₂ results in substantial swelling of the Bionolle and profound plasticization effect to the Bionolle, which favors polymer chains rearrange themselves into a lower free energy. Similarly, the higher temperature under isobaric conditions contributes to increasing mobility of polymer chain segments and a longer period for crystalline growth, so the crystallinity of Bionolle ascends markedly too (see Fig. 3).

Foam morphology

The polymer matrix firstly saturated with CO₂ at different conditions, then by the means of a rapid pressure drop. The solubility of CO₂ in the matrix decreased, thus the polymer became supersaturated and a large number of cells are nucleated.

Effect of the saturation temperature

Saturation temperature is an important parameter to control foam morphology. To study the influence of temperature, Bionolle samples were saturated at 16 MPa for 3 h, then rapidly depressurized for <3 s. A distinct change in morphology with different temperature is observed as presented in Figure 4. With the Increase in

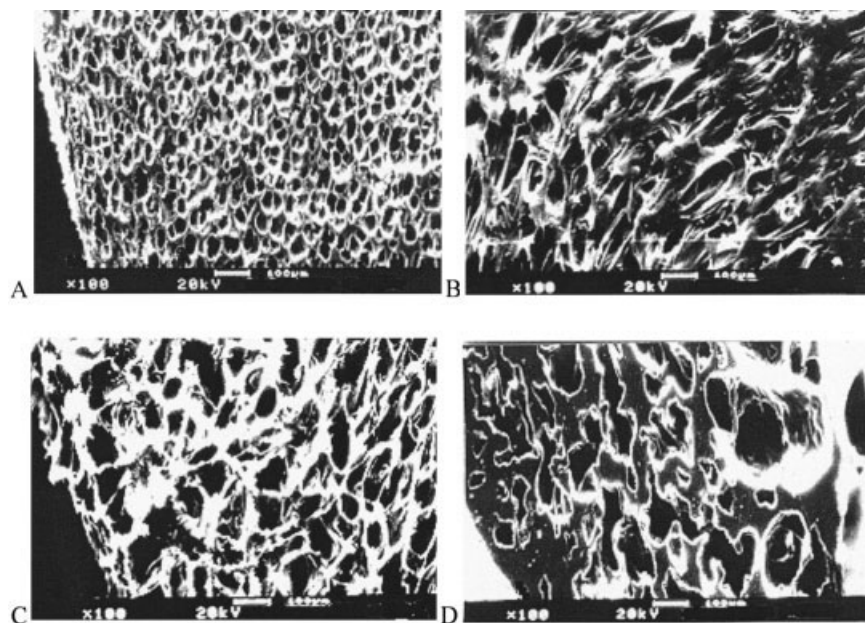


Figure 4 SEM micrographs of foamed Bionolle at 16MPa and at (A) 75°C, (B) 80°C, (C) 90°C, and (D) 100°C.

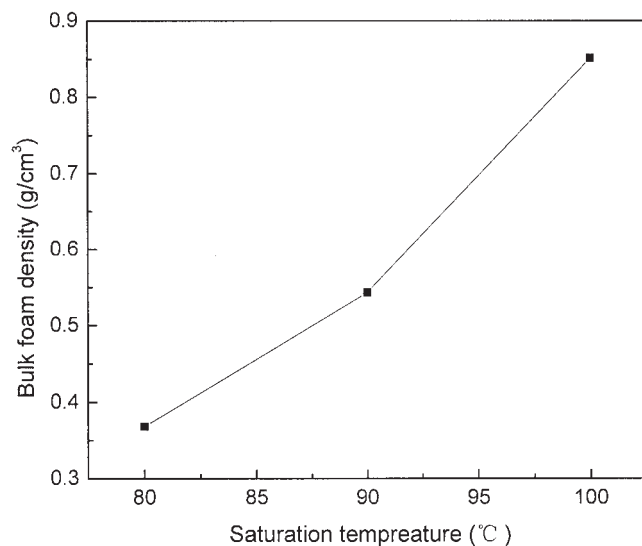


Figure 5 Influence of saturation temperature on the bulk density of foamed Bionolle saturated at 16 MPa.

temperature, the rate of nucleation decreases because of the increase of energy barrier,² while the polymer molecules is more mobile and the diffusion of CO₂ into the cell is more rapid. As a result, cell sizes increase and the shapes of cell turn interrupted, which is influenced by the coalescence and collapse of neighboring cells. At higher temperature (at 100°C, above the melting point of Bionolle), the pore sizes exhibit more asymmetry owing to much longer time for cells to grow and coalesce to much degree before they solidify.

The dependence of foam bulk densities on saturation temperature is shown in Figure 5. An increase in bulk density is observed with increase of temperature. The similar trend has been obtained with foaming of EVA-40 by Kemmere et al.¹³

Effect of the depressurization rate

The rate of pressure quench controls the time of nucleation and growth. The effect of depressurization rate on the foam structure was studied at 16 MPa and 90°C. Figure 6 shows that the cell sizes increase with the prolonging depressurization time. CO₂ gaseous nuclei formed after depressurization and when the depressurization time was longer, the gaseous nuclei would have more time to grow, and so larger cell were obtained. The bulk density increases with depressurization time as shown in Figure 7, since that at the fixed sites the cell had more time to contract and thus bulk volume decreased.¹⁴

The scale of depressurization time up to few minutes leads to a collapsed closed cell structure, as shown in Figure 6(C). When the saturation condition was fixed at a relatively higher pressure and lower temperature of 25 MPa and 80°C, different result was

obtained, seen in Figure 8. According to classical nucleation theory,² the energy barrier to nucleation decreases with increase in pressure, leading to a higher nucleation rate. Moreover, at lower temperature the viscosity of polymer matrix retards the cell growth. All these factors result in smaller pore size.

Effect of depressurization step

At the higher experimental pressure (25 MPa), the depressurization step on the product morphology was

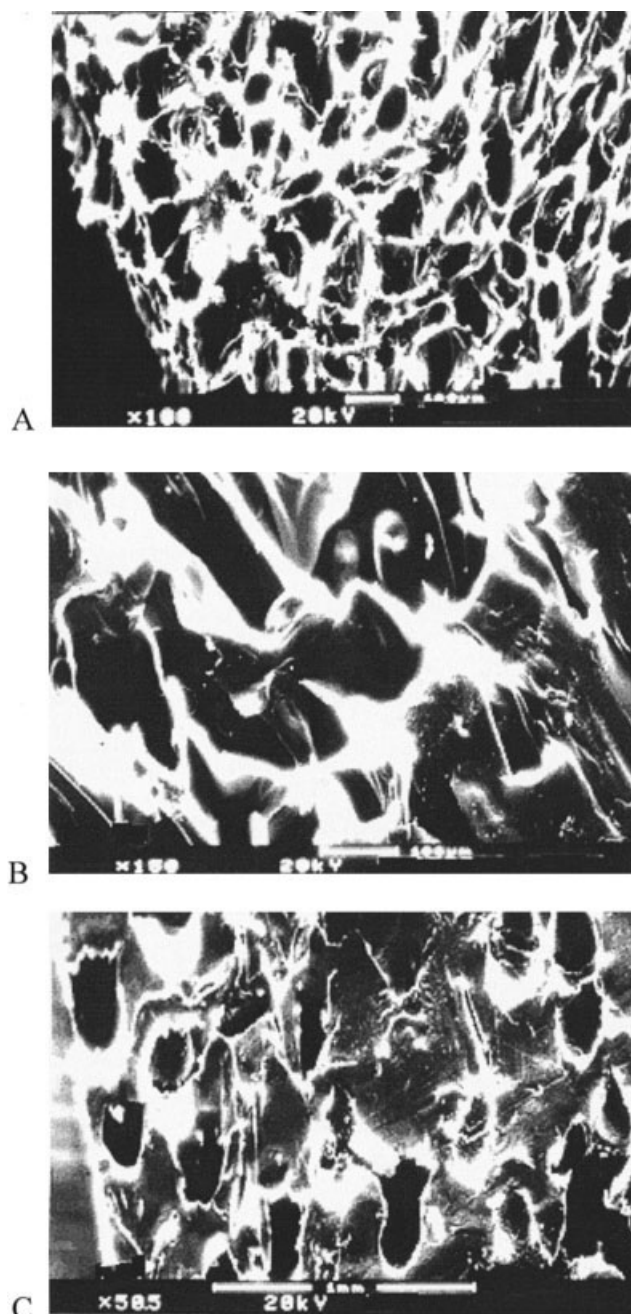


Figure 6 SEM micrographs of Bionolle foamed with CO₂ at various depressurization time: (A) 3 s, (B) 15 s, and (C) 200 s. Polymer saturated at 16 MPa and 90°C.

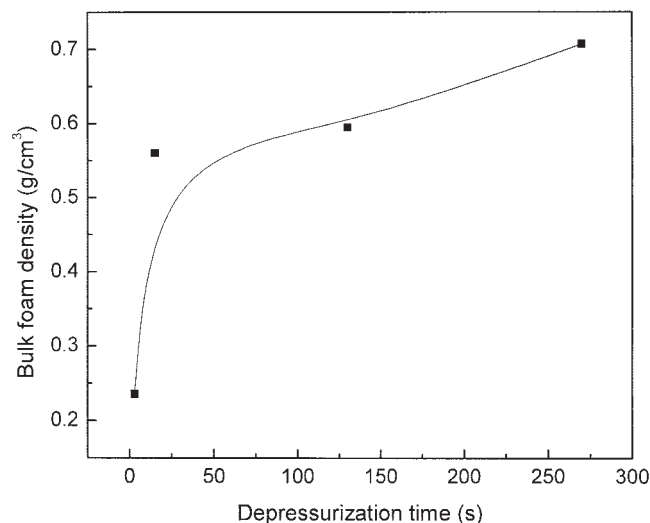


Figure 7 Influence of depressurization time on the bulk density of foamed Bionolle saturated at 16 MPa and 90°C.

studied. Instead of depressurizing directly to ambient pressure, the sample was first depressurized to 8 MPa, and then released to ambient pressure. With this two-step depressurization, foams exhibit spherical shape cells in the core region [Fig. 9(A)], while continuous and open cell structures similar to lacy morphology can be found in the edge region [Fig. 9(B)]. It is deduced that, in the core region, the cell growth encountered more resistance when compared with that in the edge region, and so the size of cell walls in the core region is thicker than that of edge region. With one-step depressurization at 25 MPa, the driving force coming from the pressure gradient drew the cell anisotropic enough expansion when compared with that with lower pressure, making the cell elongate into vegetable sponge structure [see Fig. 9(C)].

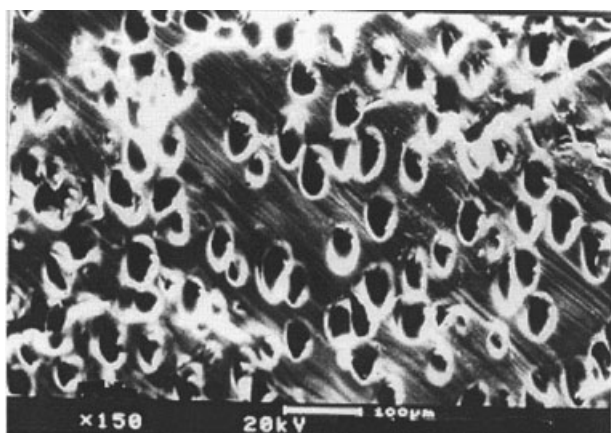


Figure 8 SEM micrographs of Bionolle foamed with CO₂ saturated at 25 MPa, 80°C, and depressurization lasting to 300 s.

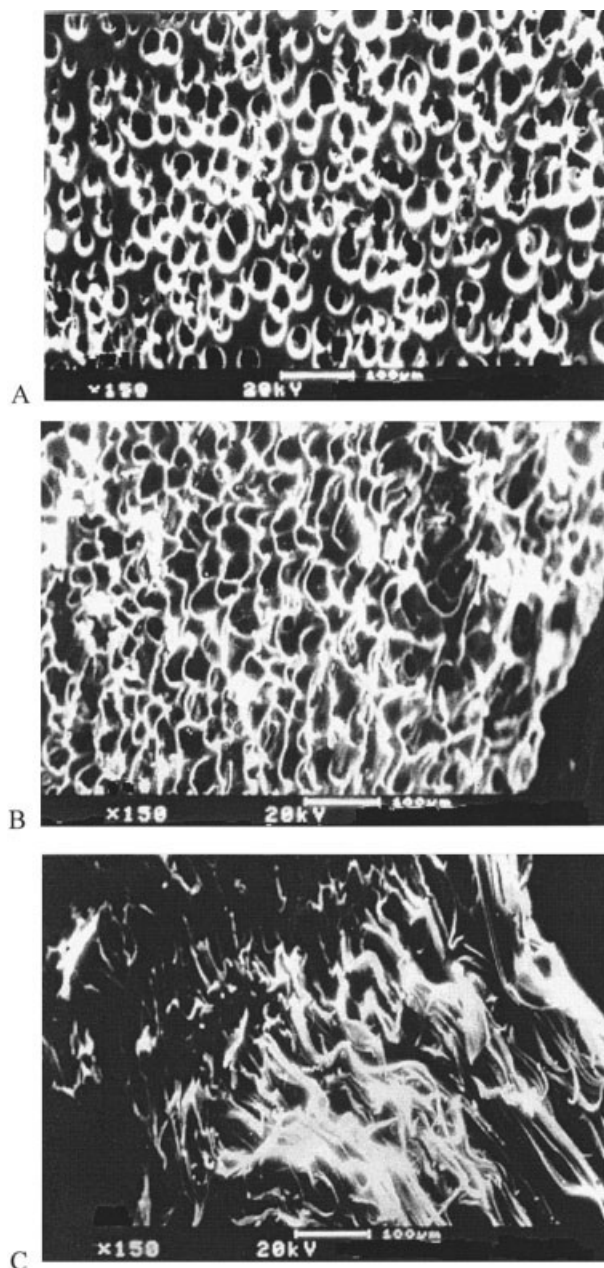


Figure 9 SEM micrographs of foamed Bionolle. (A) 25 MPa, 90°C, pressure was released to 8 MPa and then released to ambient pressure; (B) the edge region of sample A; (C) polymer saturated at 25 MPa, 90°C and rapidly depressurized to ambient pressure.

Oriented cell morphology

The SEM image displaced in Figure 10 illustrated that the orientation would occur in unconfined system. It can be attributed to that the cells grow along the direction in which the resisting force is low near the surface. The experimental temperature was 80°C and only at this temperature, the orientation can be found. It is deduced that temperature is a key factor for the orientation and it should be between the glass transition temperature and viscosity temperature. At this

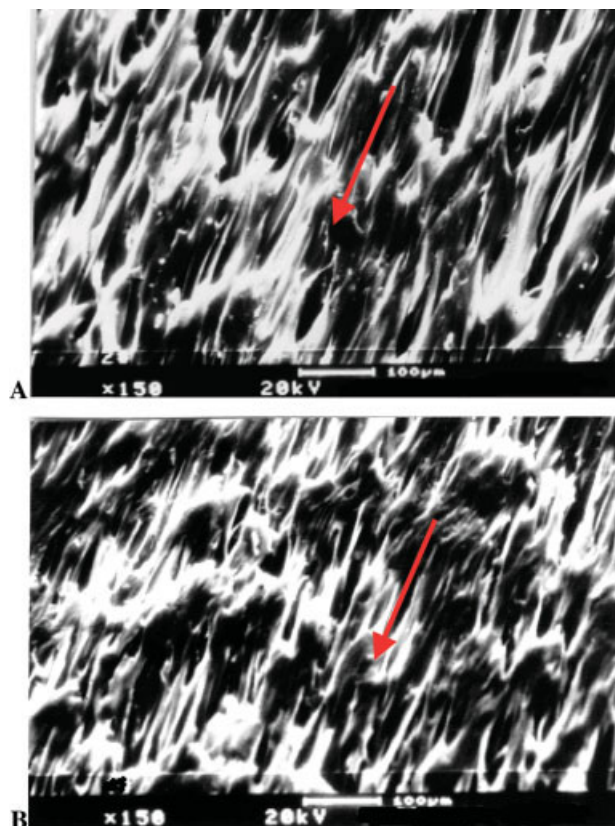


Figure 10 SEM micrographs of foamed Bionolle saturated at (A) 18 MPa and (B) 22 MPa, 80°C for 3 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

condition, the growth of cell was retarded by others and they were inclined to grow perpendicularly with the surface. The detailed mechanism need to be further studied.

CONCLUSIONS

The pressure-induced foaming technique using SC CO₂ allows the preparation of solvent-free foaming materials for medical and pharmaceutical application. Foaming of biodegradable Bionolle in SC CO₂ and the various factors affecting the microcellular structure have been studied in detail. The bulk density of the foam and the sizes of the cells increase with an increase in saturation temperature. Different depressurizing time and step have profound effect on the morphology of the product. The crystallinity of Bionolle is increased after foaming as shown by XRD. In addition, the orientation of the cells can be found in the product morphology at 80°C.

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