

Preparation and Characterization of Biodegradable Poly(butylene succinate)(PBS) Foams

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Abstract: In order to obtain crosslinked poly(butylene succinate) (PBS) foams with a closed-cell structure, a commercial-grade PBS was first modified in the melt using two different branching agents to increase the melt viscosity. The rheological properties of the branched and crosslinked PBS were examined by varying the amount of the branching agents. The complex viscosity of the crosslinked PBS increased with increasing amount of the branching agent. However, it decreased with increasing frequency. When 2 phr of the branching agent was added to PBS, the storage modulus (G') was higher than the loss modulus (G'') throughout the entire frequency range, showing that the addition of a branching agent increases the melt viscosity and elasticity of PBS effectively. Closed-cell PBS foams were prepared by mixing the chemical blowing agent with the crosslinked PBS. The effect of the foaming conditions such as temperature and time, and the amount of the crosslinking agent on the structure of the expanded PBS foams were also investigated.

Keywords: foam, poly(butylene succinate) (PBS), closed-cell, blowing ratio, chemical blowing agent, branching agent, rheological property.

Introduction

Foam materials have found many applications thanks to several attributes such as low density, high specific strength, poor heat conductivity and good sound insulation.¹ Typically, they are made of expanded polystyrene (PS), polyurethane (PU), poly(vinyl chloride) (PVC), etc.,² and they are especially important in packaging. However, wastes of these traditional foam products including polyolefins with closed-cell structure present some environmental problems. As biodegradable polymers were the focus of many studies in the last couple of decades, they acquired more attention due to their potential in the complex issue of plastic waste management.³

Aliphatic polyesters have become one of the important classes of biodegradable polymers.⁴ In recent years, a range of synthetic biodegradable resins based on synthetic aliphatic polyesters and their copolymers have been commercialized. Synthetic polyesters are generally produced by a polycondensation reaction of reactants that are obtained from the petrochemical feed stocks.⁵ Unlike other petrochemical-based resins that take centuries to degrade after disposal, these polymers break down relatively rapidly into carbon dioxide, water and humus under appropriate conditions when they are exposed to the combined attack of water

and microorganisms. Biodegradable aliphatic polyesters are known to meet advanced composting standards and usually break down in 12 weeks under aerobic conditions.⁶

One of the most promising synthetic aliphatic polyesters in this direction is poly(butylene succinate) (PBS), which is synthesized by the polycondensation of 1,4-butanediol with succinic acid. PBS has many interesting properties; biodegradability, melt processability, and thermal and chemical resistance. It has excellent processability, therefore, it can be processed into melt-blown textile fibers, multifilament, monofilament, flat, and split yarn, and also into injection-molded products, thereby making it versatile in many applications.⁷⁻¹¹

In general, foams can be produced by either chemical or physical methods, i.e., by using a chemical blowing agent (CBA) or a physical blowing agent (PBA). CBA is a chemical reagent or a compound that decomposes at elevated temperatures and normally produces a gaseous product under atmospheric pressure.¹² Most CBAs are solid particles, so they can be easily compounded with polymeric matrix followed by melt process using traditional equipments.¹³ Azodicarbonamide derivatives are widely used as chemical blowing agent.¹⁴ Among them, azodiformamide is the most popular one because of its high gas evolution volume, and good dispersibility. Also, it is relatively easy to form closed-cell structures by using azodiformamide.¹⁵ Moreover, the

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Food and Drug Administration (FDA) in the U.S. has recommended it for the manufacture of food contact articles. *N,N*-Dinitroso pentatetramine is another cheap and widely used blowing agent in the plastic industry.⁴ On the other hand, PBAs are usually volatile gases such as nitrogen, carbon dioxide and butane, and the blowing process requires special apparatus that has to be operated very carefully under strict conditions.

In the foaming process, the gaseous phase may be generated by the injection of a dissolved gas as in the case of foaming by a PBA or the release of a gas from a CBA. In processes where foam expansion is accompanied by heating, bubbles need to be stabilized by crosslinking the polymer. This is particularly true for a process employing a CBA that decomposes exothermically. Crosslinking stabilizes the expanding bubbles by sharply increasing the extensional viscosity of the polymer, thereby preventing the cell walls from draining. Crosslinking is also required for the process involving a PBA in which foam expansion is accomplished by decompression rather than by heating. Thus, to prepare low-density aliphatic polyester foam by using a decomposable CBA, it is necessary to crosslink the polymer. However, crosslinking generally is known to reduce the biodegradation rate. Jin and coworkers reported that the biodegradability of PBS that was crosslinked with benzoyl peroxide was remarkably decreased.¹⁶ Teramoto and coworkers found that the biodegradability of the crosslinked PBS copolymer was significantly suppressed not only by crosslinking but also by the crystallinity, even though crosslinking did not completely destroy biodegradability.¹⁷

In this work, we prepared crosslinked poly(butylene succinate) (PBS) foams with closed-cell structures using two types of branching agents. The effect of chemical blowing agents as cell nucleating agent and the rheological behavior of the crosslinked PBS were investigated. The density and morphology of the PBS foams were correlated with the blowing ratio and the cell structure. The effect of the foaming conditions such as temperature and time, and the amount of the crosslinking agent on the structure of the expanded PBS foams were also investigated.

Experimental

Materials. PBS used in this experiment was EnPol G-4560 (MI=1.5 g/10 min, T_m =115 °C), provided by IRE Chemicals Co., Korea. TPA[®] 100 and Desmodur[®] N3300, both aliphatic polyisocyanate from Bayer Chemical Co. (HDI trimer), were used as branching agent. ACP-4 (Kumyang Co.) was used as the CBA. Its main ingredients include azodicarbonamide, *N,N*-dinitroso pentatetramine, and urea activator. To minimize the moisture effect, all chemicals were dried in a vacuum oven at 30 °C for 24 h before use.

Preparation of PBS Foams. PBS pellets were fed into a torque rheometer (Haake Rheometer 90, Germany) and melted

at 120 °C for 5 min with a rotor speed of 60 rpm. Branching agent was then added to the melted PBS and compounded for 10 min at 120 °C to carry out crosslinking reaction. Then, ACP-4 was added and mixed for additional 10 min at 120 °C for complete melt mixing of the reagents. The final product was subsequently compression molded into bars (15 mm wide × 80 mm long × 5 mm thick) using a hydrodynamic press (130 °C, 5 min). The bars were then cut into specimens of 15 × 25 mm size and expanded in a forced convection oven at 150, 160 and 170 °C for 10, 20 and 30 min, respectively. PBS samples were coded in the following manner. When PBS was mixed with the branching agent, each sample was given two numbers separated by a hyphen. The first number is either 1 or 3, depending on the type of the branching agent. The second number means the amount of the branching agent in phr. For example, PBS 1-2 indicates a PBA/TPA[®] 100 mixture containing 2 phr of TPA[®] 100 as the branching agent. When the blowing agent was added to the mixture, each sample was given three numbers that were separated by hyphens. The third number means the amount of ACP-4 in phr. Thus, PBS 3-2-6 is the PBS foam containing 2 phr of Desmodur[®] N3300 and 6 phr of ACP-4.

Characterization of PBS Foams. The rheological properties of PBS, before and after crosslinking, were measured by a rotational rheometer (HCR 300, Physica, Germany) equipped with a parallel plate geometry (25 mm diameter) and the TEK 350 temperature controller. All samples were measured at the molten state at 170 °C with 1 mm gap distance. The foam density and the ratio of closed-cell and open-cell were measured by a gas pycnometer (Accupyc 1330, Micrometrics Co., USA). The blowing ratio was calculated using the following equation:

$$\text{Blowing ratio} = \frac{\text{the density of neat PBS (g/cm}^3\text{)}}{\text{the density of neat PBS foam (g/cm}^3\text{)}}$$

The cross-sectional morphology of the expanded PBS foam was observed with an optical microscope (i-Camscope, Somech, Korea).

Results and Discussion

In foaming operation, it is very important to have sufficient melt strength. The melt strength of a polymer generally depends on the viscosity, dynamic storage modulus and loss modulus. It is known that high molecular weight is required to impart high melt strength of a given polymer. However, it has been shown that it is inherently difficult to synthesize high molecular weight aliphatic polyesters through the polycondensation of diols and dicarboxylic acid.^{18,19} To overcome this limitation, the use of branching agents, as well as multifunctional alcohols and acids, was reported.¹⁹ In our study, it was necessary to increase the melt strength of PBS by crosslinking to achieve successful foaming. First of all, rheological measurements were made to evaluate the

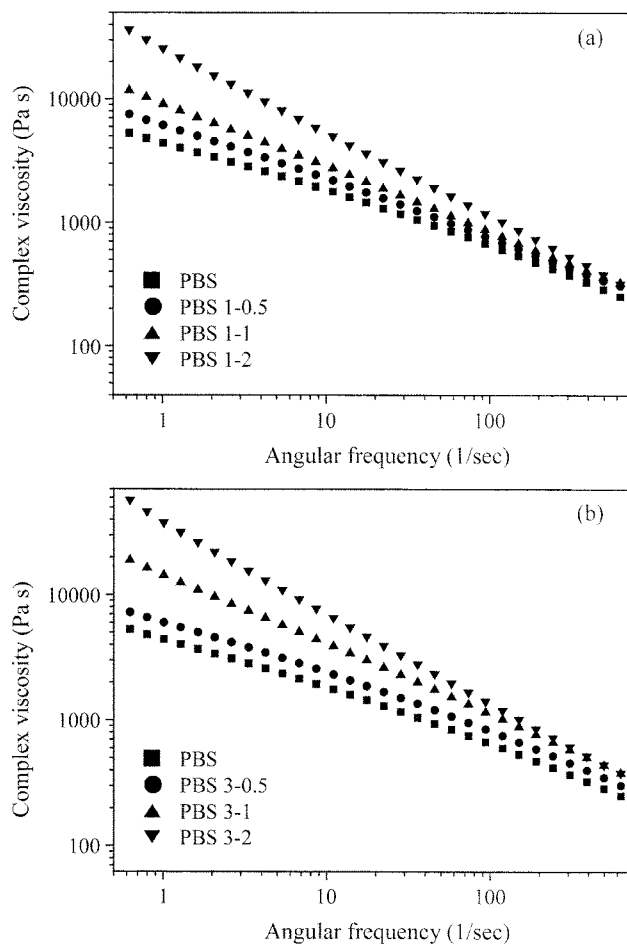


Figure 1. The complex viscosity of PBS reacted with different branching agents: (a) TPA[®] 100 and (b) Desmodur[®] N3300 (frequency=1 Hz, shear strain=0.5%).

viscoelastic properties of the polymer. Figure 1 shows the change in the complex viscosity of PBS at 170 °C as a function of the angular frequency. For all samples the complex viscosity decreased with an increasing frequency. The complex viscosity of the crosslinked PBS increased, as the amount of the branching agent was increased. The enhancement of the complex viscosity may result from the reduced polymer interchain slippage. Similar behavior was observed regardless of the type of the crosslinking agent. Figure 1 clearly indicates that PBS was effectively crosslinked by simple addition of the branching agents.

In Figure 2 changes in the storage modulus (G') and the loss modulus (G'') of PBS are shown with time. Both G' and G'' of neat PBS and branched PBS decreased with time, although the rate of the modulus change is different. It should be noted that PBS 1-2 (PBS reacted with 2 phr of TPA[®] 100 branching agent) was pre-loaded for 1 h at 170 °C, while the other samples were pre-loaded for 3 min at the same temperature. In fact, PBS 1-2 did not melt in 3 min at 170 °C so that the rheological measurement could not be

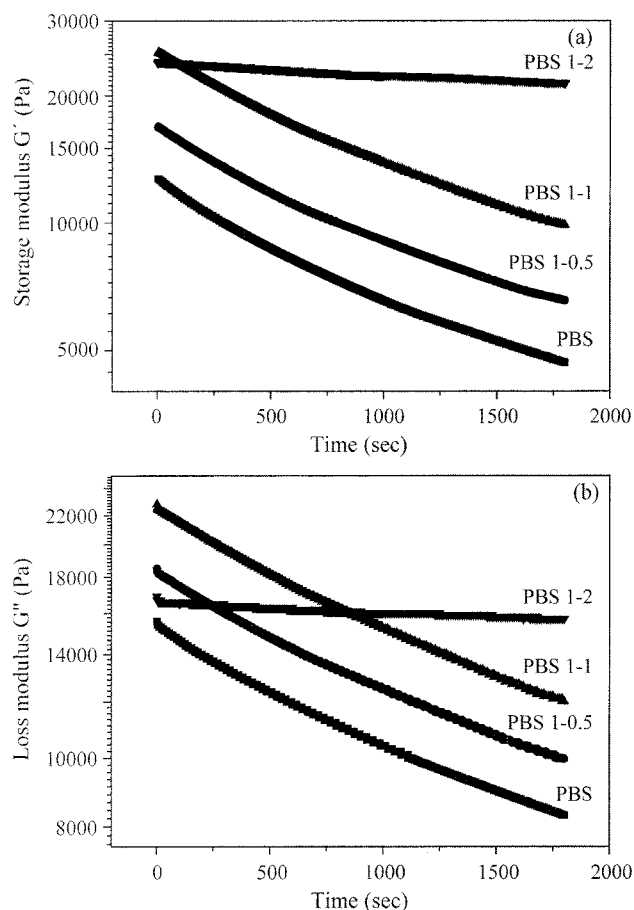


Figure 2. (a) Storage (G') and (b) loss (G'') modulus of the crosslinked PBS (frequency=1 Hz, shear strain=0.5%).

made. That is why the initial values of G' and G'' of PBS 1-2 are lower than those of PBS 1-1 in Figure 2(a) and (b). It can be deduced that the microstructure of PBS became fully crosslinked when 2 phr of TPA[®] 100 was added to PBS. PBS, that was reacted with less than 2 phr of TPA[®] 100, was only branched or partially crosslinked. Same results were obtained for the samples crosslinked with Desmodur[®] N3300.

Figure 3 shows the dynamic moduli (G' and G'') of the neat PBS and the crosslinked PBS as a function of the angular frequency. In Figure 3(a), (b) and (c), both G' and G'' increased with increasing frequency. At low frequencies G'' was higher than G' , and as the frequency increased, the gap between G' and G'' decreased and a crossover was observed so that G' became higher than G'' at high frequencies. It is a characteristic time-dependent viscoelastic feature of a thermoplastic polymer. However, as shown in Figure 3(d), when PBS was fully crosslinked with 2 phr of TPA[®] 100, G' was higher than G'' throughout the entire frequency range. Higher molecular weight and the enhanced entropy elasticity due to the crosslinking may have contributed to the high elasticity of the crosslinked PBS. This may be explained as follows: first of all, the higher the molecular weight of a polymer, the

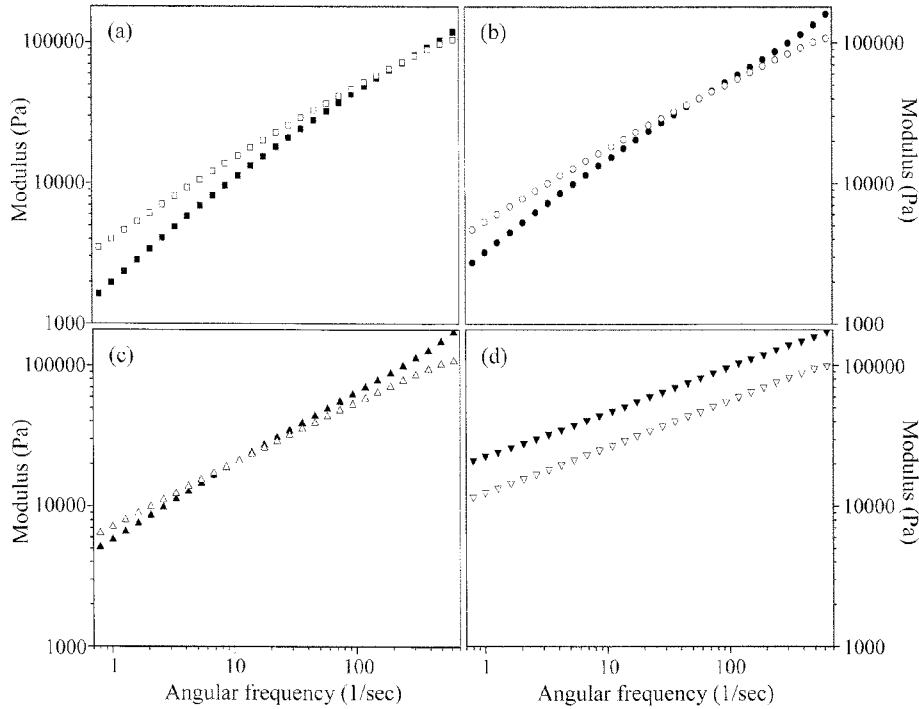


Figure 3. Dynamic modulus of PBS crosslinked by TPA[®] 100: (a) PBS, (b) PBS 1-0.5, (c) PBS 1-1, and (d) PBS 1-2 (filled symbol= G' , open symbol= G'').

higher the elasticity, because the higher degree of chain entanglement resulting from the high molecular weight restricts chain slippage, which is an irreversible deformation. Secondly, the entropy elasticity is expected to be enhanced by the higher extent of crosslinking. It can be concluded that the addition of the branching agent increased the melt viscosity and elasticity of PBS. And, the optimum branching agent content for PBS foam was determined to be 2 phr, based on the rheological data.

The foaming process usually includes cell nucleation, cell growth and cell stabilization.²⁰⁻²³ The nucleation starts to occur at initiation sites within the polymer melt that have supersaturated gases released from the blowing agent. Once the cell grows and reaches its critical size, the gas evolved as a result of the decomposition of the blowing agent propagates until it finally stabilizes (closed-cell) or ruptures (open cell).²⁴ Here all the discussions are based on an assumption that all the cells are closed ones. The gases released from the decomposition of the chemical blowing agent can hardly dissolve in the polymer matrix. Most of the available gases diffuse into the cells and increase the cell pressure. Since the pressure of the polymer matrix remains unchanged at the atmospheric level, a pressure difference is created between the inner cell and the environment. As a result, the expansion of the cell or the cell growth becomes dramatically accelerated. Cells may coalesce and coarsen as the side effects. Increasing the viscosity of the molten polymer can increase its melt strength and thereby reduce those negative side effects.

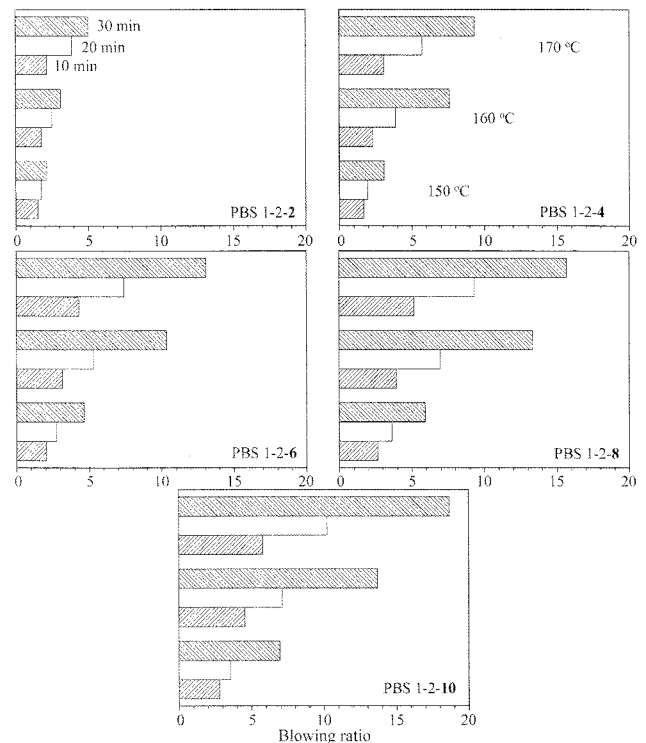


Figure 4. Blowing ratio of the PBS foam modified by TPA[®] 100 under various foaming conditions.

Figure 4 shows the blowing ratio of the PBS expanded by foaming at different temperature and time as well as by

varying the CBA content. When more blowing agent was added to the polymer melt, more gases were released to the system, and the growth rate was increased. As a result, a blowing ratio as high as 19 was obtained. Also, foaming temperature is a crucial factor in generating foams because the thermal decomposition behavior of the blowing agent is influenced greatly by heating. Thermal decomposition could be accelerated at higher temperature, resulting in a higher blowing ratio. In Figure 4, it is evident that the blowing ratio increased with the increase of temperature. The blowing ratio also increased with increasing the foaming duration up to 30 min. Same behavior was observed when PBS was foamed by Desmodur® N3300.

The structures of the cells of the crosslinked PBS foams were examined by optical microscope. Figure 5 shows the cells of PBS 1-2-6 produced at different foaming conditions. The CBA used in this work exothermically decomposed and caused yellowing. It can be seen that the cell size increased with increasing the foaming temperature and duration, but the cells became more and more irregular in shape. As the temperature increased, the melt viscosity decreased, which in turn made it easier for the cells to grow, resulting in larger cells. As can be seen from the micrographs, the majority of the cells were oval-shaped, and the cells were not ruptured, that is, closed-cells were formed. It means that the growing cells were effectively stabilized by

crosslinking, which stabilized the expanding cells by sharply increasing the extensional viscosity of the polymer, thereby preventing the cell walls from draining. When the ratio of the number of the closed cells to that of the open cells was determined, it was higher than 95% in all the PBS foams obtained in this study. It should be pointed out that the foams turned slightly yellow, because the blowing agents decomposed exothermically.

Conclusions

Biodegradable PBS was effectively crosslinked to yield closed-cell foams by controlling the amounts of the branching agent and the blowing agent. The crosslinked PBS showed much higher complex viscosity and the shear thinning behavior with a virtual absence of the Newtonian region in the viscosity versus angular frequency curve. Dynamic storage modulus of PBS reacted with 2 phr of the branching agent was higher than loss modulus in the entire frequency range, indicating that the PBS molecules were fully crosslinked. In the foaming process, higher blowing ratio was obtained when more blowing agent was added to the polymer melt. Also, the blowing ratio increased with the increase in the temperature and time. The blowing ratio as high as 19 was obtained. The majority of the cells were oval-shaped, and they were not ruptured, when examined

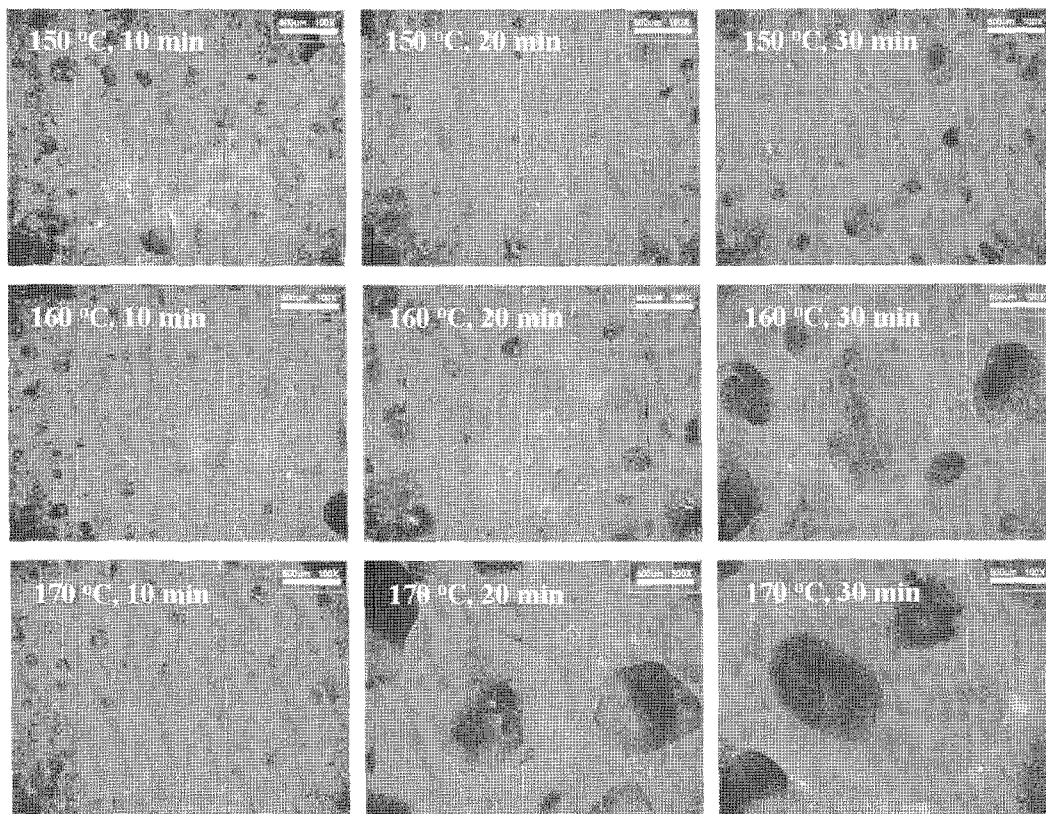


Figure 5. Cross-sectional microphotographs of the PBS (PBS 1-2-6) expanded under various conditions.

by optical microscope. The ratio of the number of the closed cells to that of the open cells was higher than 95% in all cases. The growing cells were effectively stabilized by crosslinking, which in turn sharply increased the viscosity of PBS.

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