

Pullulan Foams Prepared Using Only Subcritical Water

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ABSTRACT:

A new foaming method applicable to polysaccharides has been established. Using this method, pullulan foams have been successfully obtained as molded products after a few minutes of heating under subcritical water conditions. Because the raw material is just a mixture of pullulan and water, nothing other than water vapor is emitted throughout the process. The transmission observation using X-ray CT has revealed that the pullulan foams have the so-called open cell structures. The cell diameter decreases with increasing the preparation temperature and with decreasing the water content of the mixture. The mechanical behavior of the pullulan foams against compression deformation can be explained in the framework of a simple model for elastic-plastic foams with open cell structures proposed by Gibson and Ashby. The rigid mechanical properties are maintained even at high temperatures, indicating the high heat resistance of the pullulan foams.

Keywords

polysaccharide, foaming, pullulan, subcritical water, plastic molding

1. Introduction

Currently plastics of synthetic polymers are causing a lot of environmental problems such as marine pollution and depletion of petroleum resources. Since polysaccharides are obtained from natural resources other than petroleum and intrinsically have biodegradability as well as biocompatibility, extensive replacement of plastics of synthetic polymers with those of polysaccharides would truly make a contribution to the decarbonation and to the so-called green transformation. Although polysaccharides have promising nature in this respect as raw materials of plastics, there is an inevitable disadvantage regarding the processability. That is, the usual procedures of polymer processing, where source polymers heated to be melts are injected into molds and then solid plastics are formed inside the molds on cooling, are not applicable to polysaccharides, because most polysaccharides do not become melts by heating and occur thermal decomposition instead. Until now, to overcome this difficulty in processing polysaccharides, derivatives of polysaccharides have been used as raw materials for molding, because several partially modified polysaccharides become molten state at high temperatures [1, 2]. As another approach, solutions of polysaccharides have been prepared to form thin plastics like films and fibers by casting solutions into a mold and evaporating solvent [3, 4]. However, the procedures such as synthesizing derivatives and preparing solutions obviously require additional time and energy. Therefore, it is urgently necessary to establish direct and energy-saving methods for

processing natural polysaccharides into molded plastics.

Foaming of polymers has been established as one of the important ideas of creating polymer plastics [5–9]. Foamed plastics show unique properties such as light weight, impact absorption, and thermal insulation. Nowadays foamed plastics have become indispensable materials in our daily lives. Conventional foaming methods of polymers can be classified into two groups; namely, the physical and chemical methods. In the physical method, liquid with a low boiling point is dispersed in a polymer and is allowed to vaporize into bubbles by quick increase in temperature and/or by quick decrease in pressure. In the chemical method, bubbles are formed by gases produced by chemical reactions among reagents added in a polymer. As a result, the conventional methods emit gases that are potentially harmful to the environment like carbon dioxide during foaming. Regarding foaming of polysaccharides, physical foaming of cellulose acetate with acetone and ethanol has been reported in the early studies [5]. Cellulose acetate foams have served as core materials in aircraft, housing, fuel cell, and containers due to the excellent thermal resistance in addition to the general advantages of polymer foams mentioned above. Since then, it seems that physical foaming of cellulose has been carried out for mixtures with other synthetic polymers [10, 11] as well as for various cellulose derivatives [12, 13]. In this context, starch is another base polysaccharide that is widely used for composite foams with synthetic polymers and with natural fibers owing to the abundance and the low cost price. Currently there are several

methods for foaming starch such as extrusion, baking, freeze-drying, and solvent exchange, all of which have particular control parameters to suit various applications [14]. Since starch is a food-related polysaccharide, the ecological aspects of foaming methods have been also taken into consideration. For example, extrusion has been used to produce expanded snack foods; starch is kneaded with water as the physical blowing agent at above 100 °C under a high pressure and the mixture is extruded from a die, resulting in the formation of low-density cellular structure by the evaporation of water [14]. With respect to the processing of polysaccharides, baking, or compression, is far more suitable for applications that require finely molded shapes like containers, where the foams are formed from the mixture of starch and water by pressing under heating in a mold accompanying simultaneous water evaporation [15].

Pullulan is a linear polysaccharide produced by a filamentous fungus *Aureobasidium pullulans*. The repeating units of D-glucose are uniquely linked by a periodical sequence of α -1,6-, α -1,4-, and α -1,4-glycosidic bonds [16, 17]. Pullulan is produced from the fungus through an established industrial process so that the products have well-controlled molecular characteristics regarding the molecular structure, the molecular weight, and the purity [18]. This fact indicates that pullulan is one of the ideal raw materials for polysaccharide plastics for advanced applications such as regenerative medicine materials requiring biocompatibility. On the other hand, when starch is applied to such an advanced use, the aspect that starch is basically a

mixture of amylose and amylopectin with the proportion that is dependent on the origin would cause instability in the properties of the materials [19]. However, as far as we know, there are no reports about pullulan processed into molded plastics. Since pullulan does not become melt and easily dissolves in water without gelation, transparent films of pullulan have been prepared by casting the aqueous solutions [20–23]. Consequently, we have focused on finding a direct and energy-saving method for molding pullulan. Among the foaming methods for starch mentioned above, the baking method seems to be the most appropriate for producing molded pullulan plastics. However, the foaming process in the baking method is actually carried out for starch-based feedstock, or starch-based dough, which is prepared previously by stirring starch into plenty of hot water followed by chilling to allow gelation to occur [15, 19]. This means that the same procedure cannot be applied to aqueous systems of pullulan, which do not form gels.

Taking what described in the earlier paragraphs into consideration, we have considered that foaming pullulan is a promising strategy to solve the urgent problem of plastics. In this study, a new method to mold pullulan is introduced. In fact, foamed pullulan is successfully molded using only water without any previous processes for gelation nor for modifications. Pullulan just mixed with water can be directly molded into cylindrical cellular structures after a few minutes of heating under subcritical water conditions. Here, subcritical water condition refers to a high-temperature and high-pressure region existing below the critical temperature of water of 374 °C; water under

these conditions exists in the liquid state even above 100 °C. It is noted that the foaming process is basically similar to that of extrusion, where the water in the mixture changes from liquid to gas after the pressure is released [14]. Regarding the pullulan foams obtained at various conditions, the cellular structure has been firstly characterized in terms of the density together with the transmission observation using X-ray CT. Then, the mechanical behavior against compression deformations of the specimens has been examined. The internal buckling phenomena of pullulan foams by the compression has been also elucidated with the X-ray CT observation.

2. Experimental Section

2.1 Pullulan

Pullulan sample was kindly supplied by Nagase Viita, Japan. According to the manufacturer, the weight average molecular weight and the number average molecular weight for the pullulan were 3.84×10^5 and 9.84×10^4 respectively by the gel permeation chromatography. The pullulan sample was used without further purification.

2.2 Foaming Procedure

Pullulan was mixed with distilled water at the water content by weight (c_w) of 0.20 – 0.28 and was manually kneaded in a plastic bag until the mixture appeared seemingly homogeneous.

Then each mixture was put on the bottom of a brass mold having a cylindrical shape of the diameter of 5 mm and the height of 3 mm at 20 °C. The mold was covered with a brass plate and was heated up to a target temperature ranging 140 – 200 °C using a hydraulic hot press machine, during which the mold was kept hermetically sealed. After keeping the sealed mold at the target temperature for 2 min, the mixture was opened to atmospheric pressure by releasing the compression by the press machine. It was observed that pullulan foams were formed within a few seconds after the compression release. To ensure that no foaming occurs during the heating under compression, it was confirmed that the mixture stayed almost the same as the initial state when the mixture was cooled down to the room temperature without releasing the compression, except for unavoidable slight water evaporation inside the mold. The pressure varied from about 0.4 MPa at 140 °C to about 1.6 MPa at 200 °C depending on the target temperature, indicating that in any case pullulan coexisted with subcritical water inside the mold before the compression release. The amount of the mixture put in the mold was changed with the pullulan content so that the obtained foams completely filled the mold. Pullulan foams were dried under vacuum at 80 °C for 12 h just before use for the characterization processes. The weights of pullulan foams reduced slowly and slightly due to evaporation of water residue and attained constant values during the vacuum treatment.

2.3 X-Ray CT Observation

Cellular structures of pullulan foams were observed by an X-ray CT device FLEX-M345 (Beamsense, Japan). A series of CT projections was obtained every 0.25° with rotating the cylindrical specimens over 180° at 20°C . A three-dimensional image of the internal structure was acquired from the CT projections. The internal buckling phenomena of pullulan foams were observed using a custom-made sample holder equipped with a manual compression mechanism.

2.4 Mechanical Measurement

Compression deformation measurements were conducted with a universal testing instrument EZ-LX (Shimadzu, Japan). The cylindrical specimens with the initial height of 3 mm were compressed at a constant speed of 1 mm/min until the nominal strain (ε) of 0.5 at 20°C . The nominal tensile stress (σ) was estimated from the obtained force and the initial cross section of the specimens. To evaluate Poisson's ratio regarding the compression deformation, the side view of the specimen under the compression was monitored with a camera. Compression measurement at 100, 150, and 200°C in addition to at 20°C were performed with another universal testing instrument AGS-5kNX (Shimadzu, Japan) equipped with a constant-temperature chamber under the same conditions as mentioned above except the temperature. To secure the reproducibility, two successful results were at least collected for each condition.

3. Results and Discussion

3.1 Effect of Preparation Temperature

Figure 1 shows (a) a photo and (b) a 3D-image of a pullulan foam obtained from a mixture of $c_w = 0.20$ at 200 °C. It is clearly seen from the 3D-image that the pullulan foam has the so-called open cell structure, where a lot of spherical blank spaces surrounded by pullulan walls are partly connected to the neighbors. Since pullulan has no crystallinity, the cell walls are probably made of amorphous pullulan [21, 22], that is to say, pullulan plasticized with water under compression would be expanded by the vigorous evaporation of water at the compression release and the walls would be formed when pullulan becomes glassy by losing water. Similar open cell structures have been observed for pullulan foams prepared at 140 °C and 170 °C. The cell diameters for the pullulan foams prepared at 140, 170, and 200 °C from the same mixture of $c_w = 0.20$ are displayed as histograms in Figure 2 (a)–(c) respectively. The distribution of the diameters has been evaluated using ImageJ Fiji software for a certain cross section image along the center axis of each cylindrical foam constructed from the CT projections; in practice, the diameter corresponds to the major axis of a blank space approximately considered as a ellipsoid. It has been confirmed that more than 98% of cells are counted in these histograms ranging up to 500 μm . As expected from the histograms, the arithmetic mean of the cell diameter (d_m) decreases as

the preparation temperature increases, from 121 μm for 140 $^{\circ}\text{C}$ to 100 μm for 200 $^{\circ}\text{C}$. On the other hand, it has been found that values of the density (ρ) of these pullulan foams coincide with each other at $5.3 \times 10^2 \text{ kg m}^{-3}$ regardless of the preparation temperature. Figure 3 shows σ - ε relations during the compression deformation for the pullulan foams. Typical behavior of elastic-plastic foams can be observed for each curve; that is, σ initially increases owing to linear elasticity and turns to decrease by yielding, followed by a plateau due to plastic deformation. The second increase in σ observed in the terminal region about $\varepsilon > 0.4$ is considered as densification of the cell structure by large compression. Moreover, the three curves appear almost the same quantitatively with respect to the linear elasticity region, the yielding point, and the plastic deformation, except for the terminal region about $\varepsilon > 0.4$. Also, Poisson's ratio for the elastic deformation has been estimated around 0.1 being independent of the preparation temperature. These results suggest that the mechanical properties of the pullulan foams are primarily determined by the density rather than the distribution of the cell diameters reflecting the preparation temperature.



FIGURE 1 (a) Cylindrical pullulan foam obtained from a mixture of $c_w = 0.20$ at 200 °C and (b) 3D-image of its inner cellular structure.

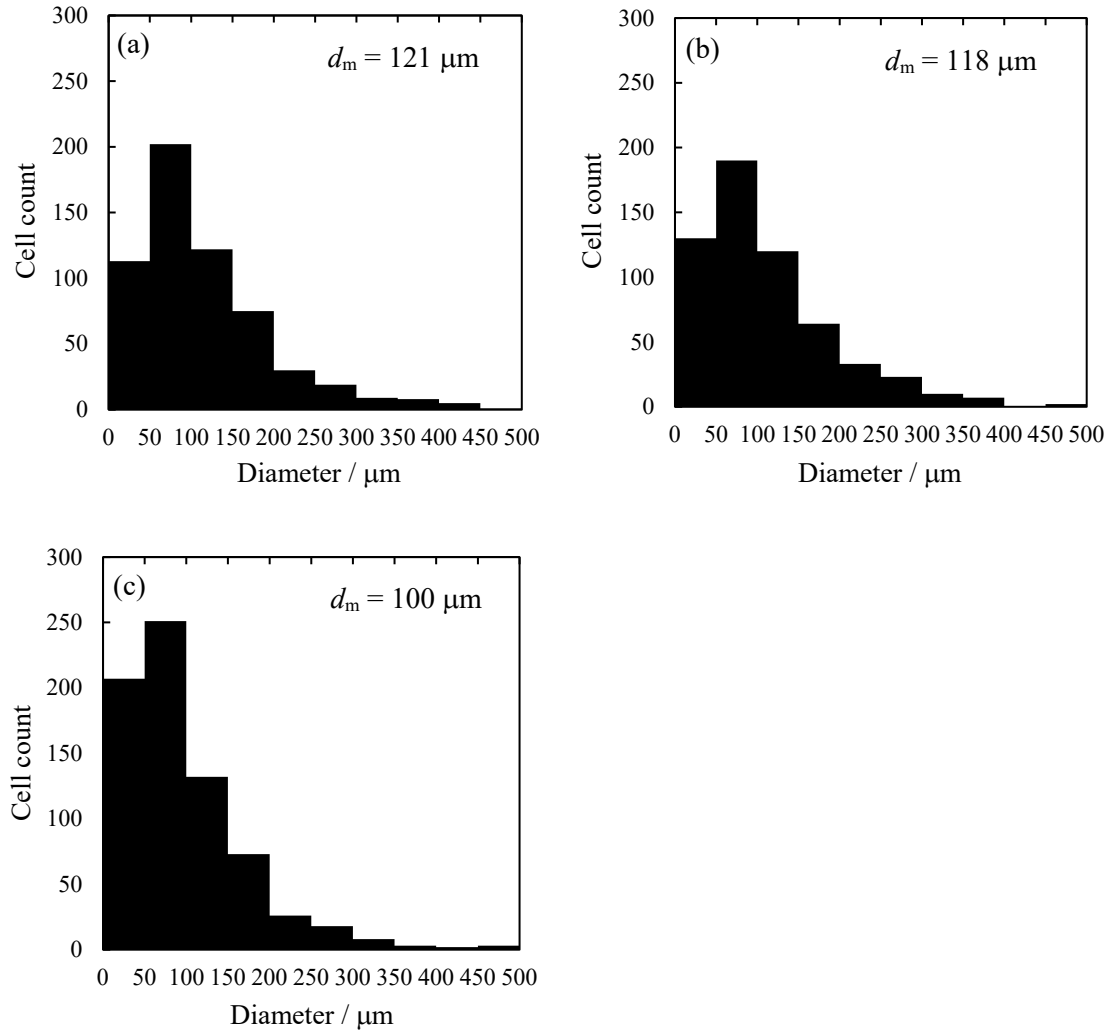


FIGURE 2 Histograms of cell diameters for pullulan foams obtained from a mixture of $c_w = 0.20$ at (a) 140 °C, (b) 170 °C, and (c) 200 °C. Arithmetic mean of the cell diameter (d_m) decreases as the preparation temperature increases.

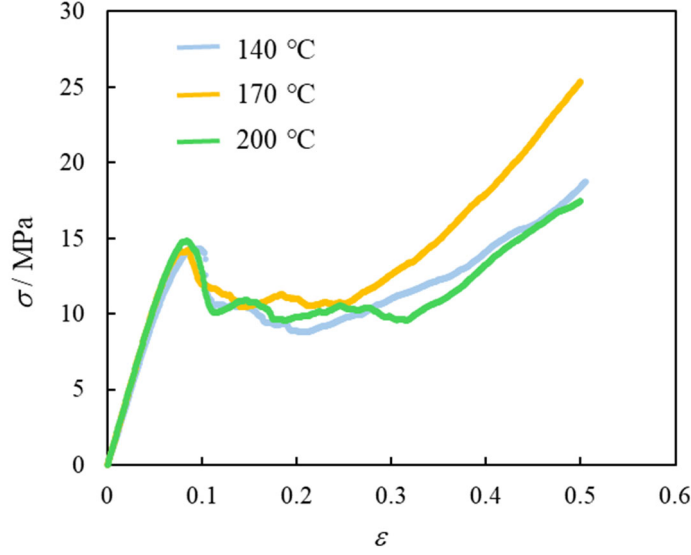


FIGURE 3 Stress-strain relations during compression deformation for pullulan foams obtained from a mixture of $c_w = 0.20$ at different temperatures.

3.2 Effect of Water Content

3D-images of pullulan foams obtained from mixtures of $c_w = 0.25$ and 0.28 at $200\text{ }^{\circ}\text{C}$ are shown in Figure 4. It has been confirmed that pullulan foams having similar open cell structures can be prepared only in a narrow range of c_w of 0.20 – 0.28 , as demonstrated in the figure. Since the cellular structure tends to be less homogeneous at higher c_w , the upper limit has been determined based on the histograms like Figure 2, where more than 98% of cells have the diameter less than $500\text{ }\mu\text{m}$. At c_w lower than 0.20 , it is practically difficult to prepare homogeneous mixture of pullulan and water. Table 1 shows ρ and d_m together with c_w for pullulan foams prepared at $200\text{ }^{\circ}\text{C}$. The value of ρ decreases with increasing c_w , while d_m exhibit opposite dependence on c_w .

Compression deformation curves for the pullulan foams differing in ρ are compared in Figure 5.

Although these curves commonly exhibit the deformation behavior of elastic-plastic foams, which is described above, there are quantitative differences throughout the process. Young's modulus (E_0) corresponding to the initial slope of the linear elasticity region increases with ρ . Furthermore, it is seen that yield stress (σ_y) as well as yield strain (ε_y) increases with ρ . The values regarding yielding estimated from the curves are also included in Table 1.

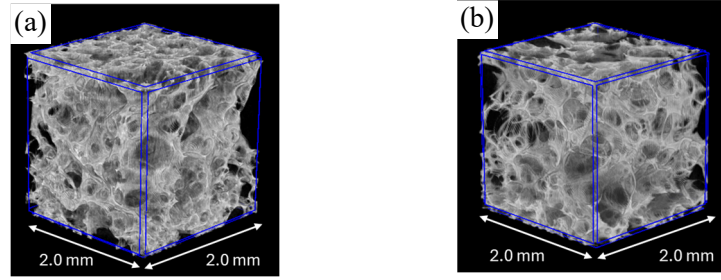


FIGURE 4 3D-images of inner cellular structures for pullulan foams prepared at 200 °C from mixtures of (a) $c_w = 0.25$ and (b) $c_w = 0.28$.

TABLE 1 Structural and mechanical characteristics for pullulan foams prepared from mixtures of different c_w .

c_w	$\rho / \text{kg m}^{-3}$	$d_m / \mu\text{m}$	E_0 / MPa	σ_y / MPa	ε_y
0.20	5.3×10^2	100	2.2×10^2	15	0.084
0.25	3.8×10^2	133	1.4×10^2	7.6	0.073
0.28	3.5×10^2	155	1.1×10^2	4.7	0.059

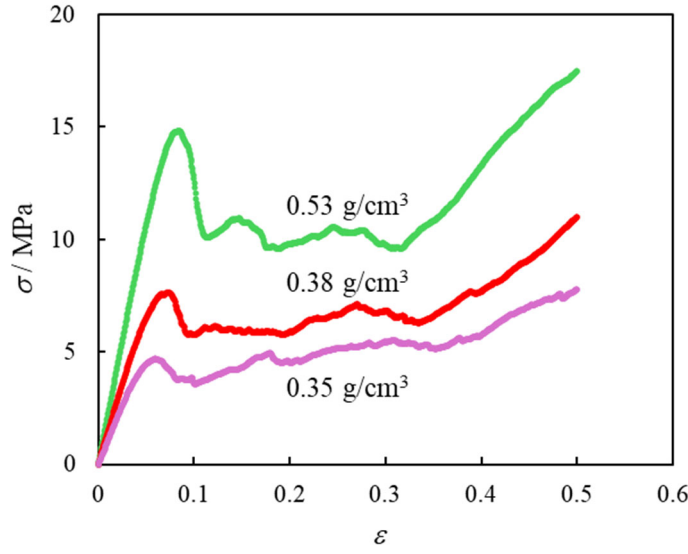


FIGURE 5 Stress-strain relations during compression deformation for pullulan foams having different densities. Although curves commonly exhibit deformation behavior of elastic-plastic foams, Young's modulus as well as yield stress increases with density.

In the simple model proposed by Gibson and Ashby, the open cell structure is represented by a cubic array framed with beams having a common length l and a square cross section where adjoining cells are staggered so that beams meet at the midpoints [6]. When the linear elasticity of the foam is interpreted as deflection of the beams by a load, E_0 is given by

$$E_0 = \frac{C_1 E_s I}{l^4} \quad (1)$$

where C_1 is a constant, E_s is Young's modulus of the solid material of the beam, and I is the second moment of area of the beam. Using dimensional arguments about the deformation process, the following equation is obtained from eq 1

$$\frac{E_0}{E_s} = C_1 \left(\frac{\rho}{\rho_s} \right)^2 \quad (2)$$

where ρ_s is the density of the solid material. Figure 6 shows the double-logarithmic plot of the relative modulus E_0/E_s against the relative density ρ/ρ_s . All values of E_0 obtained in this study in addition to those in Table 1 are plotted using $E_s = 3.5 \times 10^9$ Pa and $\rho_s = 1.48 \times 10^3$ kg m⁻³ according to our result about a pullulan film at 20 °C. It is seen that a straight line with a slope of 2 fits the data points well as drawn in the figure, where $C_1 = 0.51$ is employed as the parameter. This result indicates that the linear elasticity of the pullulan foams can be explained by the simple model based on a cubic array consisting of uniform beams. It should be noted that this model is consistent with the result obtained in the previous section that the density seems dominant in the mechanical properties of the pullulan foams. The value of C_1 lower than unity has been obtained for freeze-cast foams of bacterial cellulose and alginate. The lower mechanical properties have been explained by the imperfect foam structures that are slightly wavy and as a result misaligned with the loading direction in addition to variations in their local microstructure [24]. Concerning Gibson and Ashby model for extruded starchy foams, conflicting results have been reported about the degree of cell connectivity [25–29]. For closed cell structures, Gibson and Ashby predicts a power law-type relationship similar to eq 2, but with another power index of 3 [6]. The mechanical properties of extrusion-cooked maize foams have shown good agreement with the closed-cell model [25]. Wheat-based foams containing sucrose and sodium bicarbonate have also exhibit mechanical properties which are well fitted by the closed-cell model, regardless of the extrusion

conditions [26]. On the other hand, failure in fitting to the power laws has been reported for the mechanical properties of foams made of starch blends, where obtained values of the power index have been significantly smaller than that for the open cell structures [27]. Another research group have shown that the power index for starch foams depends on contained bran concentration; it becomes larger with the bran concentration from that for open cell structures to that for closed cell structures [28].

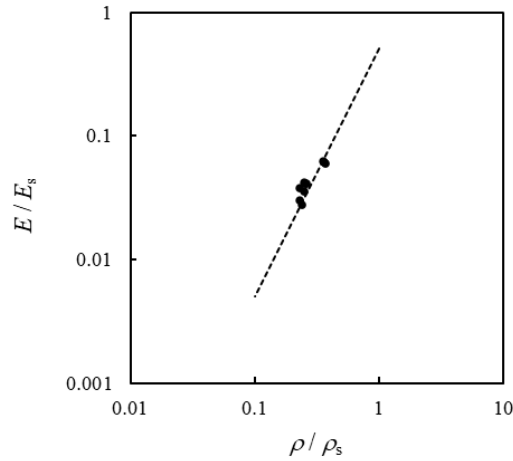


FIGURE 6 Double-logarithmic plot of E_0/E_s against ρ/ρ_s . All values of E_0 obtained in this study are plotted where the values of E_s and ρ_s are our result about a pullulan film. The dotted line in the figure has a slope of 2.

Next, the yielding properties of the pullulan foams are focused. Figure 7 displays CT-images of a single pullulan foam from mixtures of $c_w = 0.25$ during compression. It should be emphasized that these CT-images have been taken on the same section at different strains as indicated in the figure. Careful comparison of these images reveals the following facts. At $\varepsilon =$

0.027 that is before yielding (cf. Table 1), the cells appear almost the same as those at $\varepsilon = 0$ due to small strain within the linear elasticity. On the other hand, at $\varepsilon = 0.18$ that is after yielding, almost all the cells seem deformed along the direction of compression and the cell walls buckle under compression in places as indicated by red circles for examples. This result strengthens the explanation that the turning point from increase to decrease in the stress-strain curves is attributed to yielding, or plastic collapse, of the cell structure. In the framework of Gibson and Ashby, the yield stress of the open-cell foam is given by

$$\frac{\sigma_y}{\sigma_{ys}} = C_2 \left(\frac{\rho}{\rho_s} \right)^{3/2} \left[1 + \left(\frac{\rho}{\rho_s} \right)^{1/2} \right] \quad (3)$$

where C_2 is a constant and σ_{ys} is the yield stress of the solid material [6]. Here we have employed the equation including density correction for higher density foams. As shown in Figure 8, double-logarithmic plot of σ_y/σ_{ys} versus ρ/ρ_s can be represented by eq 3 well with $C_2 = 0.32$. Although σ_{ys} for pullulan is unknown as far as we know, $\sigma_{ys} = 1.2 \times 10^8$ Pa has been used assuming the reported relation $\sigma_{ys}/E_s \approx 1/30$ for rigid polymers holds for pullulan. An earlier study on composite solid foams mainly composed of starch and fibers has reported that fit of the yield stress to the Gibson-Ashby relationship can be improved when considering the walls of the solid

foam as composite materials.

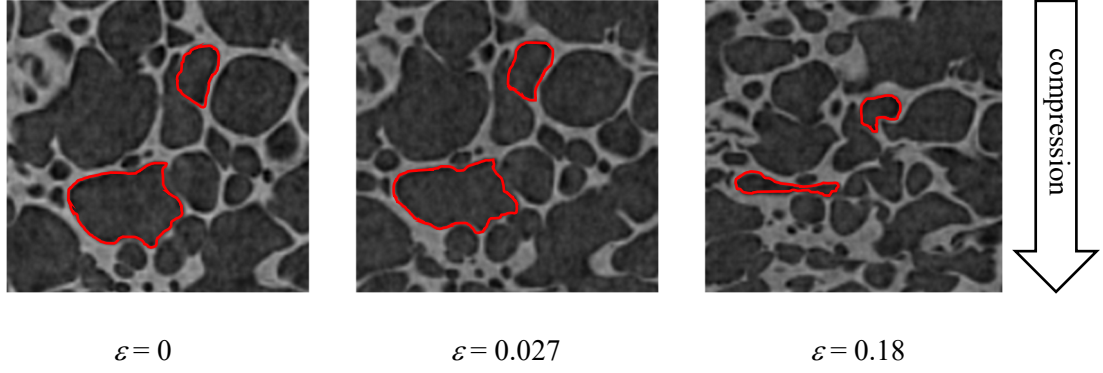


FIGURE 7 Yielding process of pullulan foam from mixtures of $c_w = 0.25$. CT-images of a single pullulan foam are taken on the same section at strains shown below each image. Cell walls buckle under compression in places by yielding, as indicated by red circles.

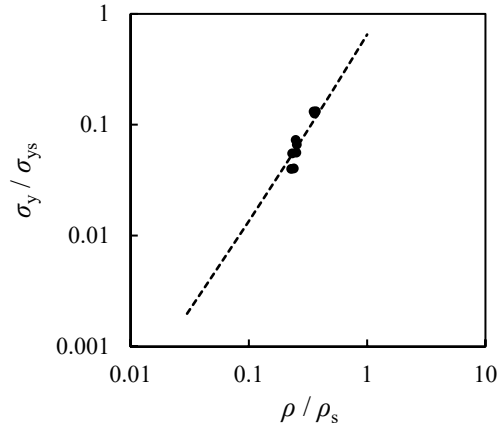


FIGURE 8 Double-logarithmic plot of σ_y / σ_{ys} against ρ / ρ_s . The value of σ_{ys} for pullulan has been estimated assuming the reported relation for rigid polymers, $\sigma_{ys} / E_s \approx 1/30$. The dotted line according to eq 3 fits the data points well with $C_2 = 0.32$.

3.3 Compression at High Temperatures

As described in the introduction, polysaccharides including pullulan do not become melts at high temperatures. This implies that foamed plastics made of pullulan are expected to exhibit high heat resistance compared to conventional plastics of synthetic polymers. In our preliminary dynamic tensile test with increasing temperature for a pullulan film, the glass transition temperature (T_g) for pullulan has been estimated to be 242 °C. Against this background, heat resistance of pullulan foams has been examined by compression deformation measurement at high temperatures. Figure 9 shows the stress-strain curves for the pullulan foams obtained from a mixture of $c_w = 0.25$ measured at 20, 100, 150 and 200 °C. It is seen that curves become smooth at high temperatures maintaining the whole compression behavior of elastic-plastic foams until 200 °C. It is also obvious that E_0 as well as σ_y decreases as temperature increases. Effects of increasing temperature in the range of below T_g on the mechanical properties of glassy polymer solids are explained by thermal expansion that lowers the van der Waals forces and by thermal acceleration of short chain movements in the solids. The dependence of E_s on absolute temperature (T) can be expressed as

$$E_s = E_s^0 \left(1 - \alpha_m \frac{T}{T_g} \right) \quad (4)$$

where E_s^0 is Young's modulus of the solid material at 0 K and α_m is a constant resulting from both thermal effects mentioned above [6]. Combining with eq 2, the temperature dependence of

E_0 for the open cell structures is given by the following equation:

$$E_0 = C_1 E_s^0 \left(1 - \alpha_m \frac{T}{T_g} \right) \left(\frac{\rho}{\rho_s} \right)^2 \quad (5)$$

Figure 10 shows the temperature dependence of E_0 for the pullulan foams. It is noted that all data points measured in this study in addition to those estimated from Figure 9 are collected in this figure. The data points can be well fitted by eq 5 with the parameter $\alpha_m = 0.67$ as indicated by the dotted line. In fact, E_s^0 has been estimated from E_s about pullulan films at 20 °C ($= 3.5 \times 10^9$ Pa) using eq 4. It has been demonstrated that although pullulan solid are softened to a small extent with increasing temperature, the pullulan foams as a whole remain rigid, exhibiting high heat resistance as cellular plastics. As for starch foams, it has been reported that the dynamic modulus drops near T_g of about 137 °C on heating; the reduction in the modulus appears more obviously as the amylose content decreases [29]. Since amylose is a crystalline polysaccharide, starch foams with low amylose content are considered to behave like pullulan foams regarding the temperature dependence of mechanical properties. Although it is impossible for us to conduct the tensile test above 200 °C at the present stage, it is anticipated that the pullulan foams maintain the rigidity up to slightly below T_g .

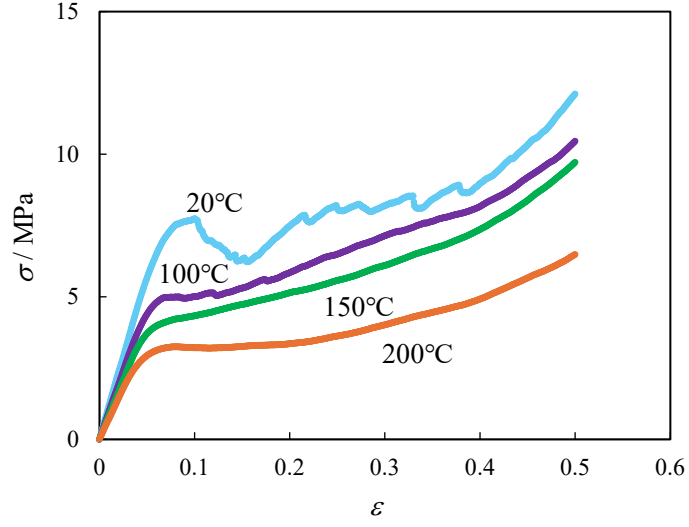


FIGURE 9 Stress-strain relations at different temperatures for pullulan foams from a mixture of $c_w = 0.25$. Curves maintain the whole compression behavior of elastic-plastic foams until 200 °C, while E_0 as well as σ_y decreases as temperature increases.

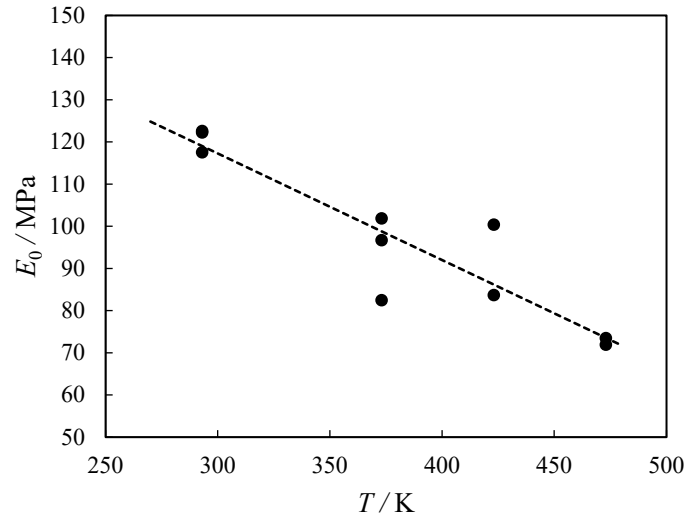


FIGURE 10 Temperature dependence of E_0 from 20 °C to 200 °C. Data points can be well fitted by eq 5 with $\alpha_m = 0.67$ as indicated by the dotted line, indicating that the pullulan foams are rigid cellular plastics with high heat resistance.

4. Conclusion

Cylindrical open cell foams have been prepared from pullulan by using only subcritical water. The molded products exhibit mechanical behavior of elastic-plastic foams against the compression deformation over a wide range of temperature from 20 °C to 200 °C. To our knowledge, this is the first report on a foaming process for water-soluble natural polysaccharides which do not form gels. Our continuous study shows that the same method can be possibly applied to other polysaccharides such as dextran and water-soluble cellulose derivative. We hope that modified approaches will be developed for various specific purposes based on ours, so that that this study will contribute to accelerate the green transformation worldwide. At the present stage, the pullulan foams can be considered useful in fields such as the environment, the medical care, the daily products, and the industrial manufacturing. Utilizing the eco- and bio-compatibilities, it is ideal for the pullulan foams to be applied to food, sanitary, and medical materials. Taking the rigidity and the heat resistance into account, the cellular plastics of pullulan are also attractive to materials for containers, structural core parts, and filters.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability

The data that support the findings of this study will be available on request.

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