Effect of Adding Fructose on Uniaxial Tensile Behavior of Pullulan Films

by

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Plasticizing effect of fructose as an additive on the uniaxial tensile behavior of pullulan films was examined. At 100 °C, the tensile modulus determined from the stress-strain relation decreased as the fraction of fructose increased in a similar manner to glycerol, suggesting apparent plasticizing effect of this saccharide. Taking the melting point of fructose into consideration, this plasticizing effect was attributed to the “supercooled” liquid state of fructose in the pullulan films. At 29 °C, on the other hand, no plasticizing effect of fructose was observed even above the glass transition temperature. These trends were completely different from those obtained in earlier studies regarding κ-carrageenan and gellan films. The network structure of pullulan film having no crosslinks was considered responsible for the unique effect.

Key words:

Pullulan film, Fructose, Plasticization, Tensile modulus, Network structure

1 Introduction

Nowadays polysaccharides are recognized as versatile materials on the rise. Intrinsically, polysaccharides have the advantage of biocompatibility over conventional synthetic polymers, and can be plentifully obtained from natural resources such as land plants, seaweeds, crustaceans, and microorganisms. Although human beings have a long history of making good use of polysaccharides on the everyday basis, sound scientific knowledge of polysaccharides is still required in order to fully realize the potential of polysaccharide materials. Taking the biocompatibility of polysaccharides into account, making films with polysaccharides applicable for foods and medical items should be placed a high priority; accordingly, mechanical properties of polysaccharide films as well as the relevant factors have great importance. Among the additives, fructose in particular has exhibited interesting temperature dependence: At 100 °C, adding fructose softens both the κ-carrageenan and gellan films significantly, which can be attributed to the conventional plasticizing effect arising from a good solubility of fructose to the polysaccharide networks. On the other hand, at 29 °C (above \( T_g \) for fructose), \( E \) for each film with fructose is much larger than that at 100 °C, which is explained by the blending law for immiscible blends where fructose existing in the voids of the polysaccharide network is assumed to have a much lower modulus than the network. It has been concluded that the solubility of fructose to the network domains of κ-carrageenan and gellan drastically changes with temperature.

In the studies described above, κ-carrageenan and gellan films have been prepared from the aqueous solutions and therefore each system has reached the gelation point before forming a dry film; it is well known that aqueous systems of these polysaccharides become gels at respective certain concentrations. The resulting network structure would consist...
of crosslinks of aggregates of polysaccharide chains and continuous domain of polysaccharide between the crosslinks, as illustrated in Fig. 1(a); the latter would be the zone fructose dissolves into at the miscible conditions. There would be also voids without gellan in the film where fructose can exist even at the immiscible conditions. With respect to the network structure, pullulan films may have noticeable differences. Aqueous systems of pullulan can exist as solutions without gelation even at quite high concentrations in the process of film formation. In fact, the network structure of pullulan chains could be described by an amorphous state as drawn in Fig. 1(b), implying that the plasticizing effect of fructose might appear in a completely different way from the case of \( \kappa \)-carrageenan and gellan.

![Fig. 1 Schematic illustration of polysaccharide films; (a) film prepared via gelation, (b) film prepared without gelation. The crosslinks are represented by black circles on the polysaccharide chains drawn by solid curves in (a). Some voids existing in the film are indicated by dotted circles in (a).](image)

In this study, plasticizing effect of fructose on the uniaxial tensile behavior of pullulan films has been examined. The plasticizing effect in terms of \( E \) has been compared with that of another additive glycerol. It has been found that the effect of adding fructose reflects the difference in the network structure of the films, as expected.

### 2 Experimental

#### 2.1 Materials

The polysaccharide pullulan (Tokyo Chemical Industry Co., Ltd., Japan) was used without further purification. The additives fructose (Wako Pure Chemical Industries Ltd., Japan) and glycerol (Wako) were also used as received. The values of \( T_n \) and \( T_g \) of these additives quoted from literature are given in Table 1. The pullulan films were prepared in the following manner. Each additive was dissolved in water beforehand and the powdery pullulan was dissolved in the water with or without additive with stirring for 1 h at 50 °C. The concentration of additive was changed in the range of 0 – 18.8 g/L with the total concentration of solute fixed at 75 g/L, so that the weight fraction of pullulan (\( w \)) became 0.75, 0.80, 0.83 and 1. Then the solution was degassed under vacuum for 10 min prior to being spread on a glass plate; the glass plate was coated beforehand using a silane coupling agent (KBM-3063, Shin-Etsu Silicone, Japan). Then the solvent water was allowed to evaporate for 5 days until a transparent film with the thickness of ca. 0.15 mm formed on the glass plate. Preliminary tests demonstrated that transparent films were obtained at \( w < 0.75 \). The obtained film was cut into rectangular pieces of 10 mm × 30 mm. The cut films were dried further in a vacuum oven at 80 °C for 6 h until constant weights were reached. Each film to be tested was set with cramps in the heating box of the tensile apparatus and then served with a final drying process at 100 °C for 1 h just before measurement.

| Additive   | \( T_n \)/°C | \( T_g \)/°C |
|------------|---------------|---------------|
| Fructose   | 108           | 5             |
| Glycerol   | 18            | -100          |

#### 2.2 Measurement

Mechanical measurements were performed by using a tensile apparatus (TENSILO RTM-500, Orientec Corp., Japan) equipped with a heating box. Stress-strain relations were obtained for the pullulan films during the uniaxial deformation between the cramps at the speed of 1 mm/min.
until the nominal tensile strain ($\varepsilon$) reached 0.05 or until the film broke off. The measurement temperatures were 100 °C and 29 °C; the latter was chosen as the lowest temperature available in this study. The initial film length between the cramps was around 10 mm. The force measured with a load cell was converted to the nominal tensile stress ($\sigma$) using the cross section of the film before extension.

### 3 Results and discussion

Fig. 2 shows the stress-strain curves for the pullulan films with fructose (except $w = 1$) at 100 °C. The stress-strain relations are plotted until the end of deformation of $\varepsilon = 0.05$, except for $w = 0.75$. It is seen that $\sigma$ of each curve increases linearly with $\varepsilon$ in the low $\varepsilon$ region and the initial slope of the curve decreases as $w$ decreases, that is, as the content of fructose increases. Although the profiles of the curves in the larger $\varepsilon$ region are not very similar to each other, all the stress-strain curves in the figure seem to show the so-called brittle behavior. Similar effect of the additive on the stress-strain curve and its initial slope has been observed in our previous studies\(^3\), where the additives do not act as the conventional plasticizers and the decrease in the initial slope can be explained by the blending law at the immiscible conditions\(^6\).

![Fig. 2 Stress-strain curves for pullulan films with or without fructose at various $w$ at 100 °C.](image1)

Fig. 2  Stress-strain curves for pullulan films with or without fructose at various $w$ at 100 °C.

Fig. 3 shows the stress-strain curves for the pullulan films with fructose at 29 °C. Compared to Fig. 2, the profiles of the curves are close to that for the pullulan film without additive ($w = 1$) and the initial slopes of the curves are almost the same regardless of $w$. Apparently, the plasticizing effect of fructose on the tensile behavior of pullulan films disappears with decreasing temperature.

![Fig. 3 Stress-strain curves for pullulan films with or without fructose at various $w$ at 29 °C.](image2)

Fig. 3  Stress-strain curves for pullulan films with or without fructose at various $w$ at 29 °C.

The effect of adding glycerol, a common plasticizer for polysaccharide films\(^7\),\(^8\), on the tensile behavior at 100 °C is shown in Fig. 4. The curve of $w = 1$ is identical to that in Fig. 2. Each curve for the pullulan film with glycerol increases almost linearly with $\varepsilon$ and ends at $\varepsilon < 0.05$ due to the fracture of sample. The initial slope of the curve decreases as the content of glycerol increases, which is qualitatively similar to the case of fructose at the same temperature. The stress-strain curves for these pullulan films measured at 29 °C are given in Fig. 5. It is seen that the initial slope of the curve exhibiting a
linear relation between $\sigma$ and $\varepsilon$ decreases with $w$, although the effect of adding glycerol seems quite weak compared to that at 100 °C.

![Stress-strain curves for pullulan films with or without glycerol at various $w$ at 29 °C.](image)

Fig. 5 Stress-strain curves for pullulan films with or without glycerol at various $w$ at 29 °C.

![$w$-Dependence of $E$ for pullulan films with or without additive. $E(w)$ is normalized by $E$ at $w = 1$.](image)

Fig. 6 $w$-Dependence of $E$ for pullulan films with or without additive. $E(w)$ is normalized by $E$ at $w = 1$.

As shown in the figures, all the stress-strain curves obtained in this study have linear relation between $\sigma$ and $\varepsilon$ in the initial stage of deformation. Hence, the values of $E$ have been determined as the initial slopes of the stress-strain curves and are plotted in Fig. 6 against $w$. In the figure, $E(w)$ is normalized by $E$ at $w = 1$ ($E(1)$), where $E(1)$ at 100 °C and at 29 °C are $2.2 \times 10^7$ Pa and $2.5 \times 10^6$ Pa respectively, to show the effect of additives on $E$ more clearly. The data points for the pullulan film without additive at 100 °C and at 29 °C are inevitably overlapped. Here, it should be noted that good reproducibility of $E$ have been confirmed for all the systems examined with the maximum error of $3 \times 10^5$ Pa from the plotted values; this error would be small on the basis of the fact that $E \geq 10^7$ Pa. The small difference between the levels of broken lines might be attributable to hardening of the pullulan matrix. For the pullulan films with glycerol, the magnitudes of $E$ are significantly smaller compared to the broken lines and the plots of $E$ at 100 °C and 29 °C decrease with decreasing $w$ in a similar manner. This suggests that glycerol have some plasticizing effects on the mechanical behavior of the pullulan films. Since glycerol has $T_m$ of 18 °C, this additive is in the liquid state at all the conditions employed in this study. In our previous study\(^3\), it has been proposed that apparent plasticizing effect of glycerol on the polysaccharide films can be explained by the blending law for immiscible blends. It is assumed that the domain of glycerol in the liquid state existing in the voids (Fig. 1(a)) has a modulus being much lower than that of the matrix network of polysaccharide and therefore the overall modulus of the film decreases as the volume fraction of polysaccharide decreases. Getting back to the pullulan films, we consider that the immiscible-type of plasticizing effect of glycerol also holds true, even though miscibility between the matrix and the additive would have nothing to do with the plasticization due to the absence of pullulan domains (Fig. 1(b)). Moreover, $E$ at a given $w$ exhibits obvious temperature dependence; the larger $E$ at lower temperature could be explained by the increase in the volume fraction of pullulan in addition to the hardening of the pullulan matrix. Fig. 6 also shows that $E$ at 100 °C for both pullulan films are very close to each other at a given $w$. This indicates that fructose also exhibits the immiscible-type of plasticizing effect at this temperature. Although 100 °C is slightly lower than $T_m$ of fructose, as shown in Table 1, fructose still exists in the “supercooled” liquid state above $T_m$, as proposed in our previous studies\(^2\). It is reasonable that the magnitude of the immiscible-type plasticization is exclusively determined by the volume fraction of matrix, namely $w$. The pullulan films with fructose at 29 °C have almost the same $E$ being independent of $w$. It should be also emphasized that the level of $E$ is very
close to that for the pullulan film without additive, represented by the upper broken line, and significantly larger than that for the pullulan film with glycerol. The level of $E$ clearly indicates an absence of plasticizing effect of fructose for the pullulan film at this temperature. Our earlier results have demonstrated that $E$ for the $\kappa$-carrageenan and gellan films with fructose at 29 °C is almost the same with those with glycerol due to similar immiscible-type plasticization. Concerning pullulan films, there are no large voids in the polymer network, that is, no large domain of fructose, because of the homogeneous network structure of amorphous pullulan. This may accelerate the transformation of the “supercooled” liquid of fructose to the solid state. It is assumed that fructose in the solid state has a comparable modulus with the matrix network of pullulan in the glass state and gives complementary reinforcement to the film with changing $w$. It is interesting that the plasticizing effect of a saccharide additive in the solid state seems to appear in different manners depending on the network structure. For the $\kappa$-carrageenan and gellan films, $E$ at 29 °C are close to each other whether the additive is liquid or solid. This result has been interpreted that an additive in the solid state exists in the voids of the film as an assembly of micro-granules, so that the domain of the additives has a modulus being much lower than that of the polysaccharide. There are probably no such voids in the pullulan films.

4 Conclusions

Plasticizing effect of fructose as well as glycerol on the uniaxial tensile behavior of pullulan films has been examined. The plasticizing effect of liquid glycerol has been assigned to the immiscible-type one, as is the previous case of the $\kappa$-carrageenan and gellan films. On the other hand, the effect of adding fructose has appeared in completely different manners: At 100 °C, the immiscible-type plasticization has been recognized instead of the conventional plasticization observed for the $\kappa$-carrageenan and gellan films, which may reflect the amorphous state of the pullulan film. At 29 °C, the effect of adding fructose has disappeared apparently due to fructose in the solid state with comparable modulus with pullulan.

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