Texture of SS Cross-linked Gelatin Gels

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Received May 2, 1973

Relations among sensory properties, physical characteristics and the kinds of force supporting gel structure were studied by using thiolated gelatin.

Breaking stress of the gelatin gel was greatly influenced by contents of disulfide bonds in the gel. Young’s modulus of the gel was affected by its temperature. As to sensory properties of the gelatin gel, “hardness” highly correlated with Young’s modulus and “brittleness” correlated with breaking stress.

Therefore, it could be concluded that in the case of the gelatin gel, “hardness” was mainly attributed to hydrogen bonds and “brittleness” was to chemical bonds like disulfide linkages.

Since texture is well recognized as one of the important characteristics of foods, numerous reports are published as to sensory or physical measurements of food texture.1–3 Moreover, considerable attentions have been paid to the correlation between sensory evaluation and instrumental measurement to find out mechanical substitutes for sensory evaluations of food texture.4,5

In our preceding paper, we investigated the texture of soybean protein gels both objectively and subjectively.6 The gelation mechanism of the soybean protein is, however, too complicated to clarify how physical or chemical bonds affect the texture of gels. That is, disulfide bonds, hydrogen bonds, and hydrophobic bonds, all are reported to have important influence on the texture of soybean protein gels.7,8 However, comparatively little is known of the role of their bonds in gel texture.

Gelatin gel, a very popular food, is heat-reversible, and it has been reported that normal hydrogen bonding is a major mechanism responsible for gelation of the ordinary gelatin.9,10 If some sulfhydryl groups are artificially introduced into the ordinary gelatin, various gel samples different in ratio between disulfide bonds and hydrogen bonds can be prepared, which enables us to discuss the role of the bonding in gel texture in detail.

In the present study, gelatin gels different in contents of disulfide bonding were prepared and physical and sensory evaluation were carried out to discuss the effects of hydrogen and disulfide bonding on the texture of gelatin gel.

MATERIALS AND METHODS

Gelatin. Commercial products (Wako Chemical Co., Ltd.).

Thiolation of gelatin. Thiolated gelatin was prepared according to the method of Benesch et al.9 The contents of sulfhydryl groups introduced into gelatin were measured by amperometric titration with 0.1 N AgNO₃ in Tris-HNO₃ buffer (pH 7.6). Thiol contents of our thiolated gelatin were 66 moles per 10⁶ g protein.

Preparation of gels. The concentrations of gelatin in gel samples were 5%. To the gelatin, water was added and stirred with magnetic stirrer for 30 min at about 30°C. A slight excess of theoretical amounts of 30% H₂O₂ aqueous solution was added to the gelatin solution to oxidize sulfhydryl groups into disulfide bonds, and the solution was immediately poured into a glass tube (0.925 cm in diameter). Then, the samples were allowed to stand at 7, 15 and 20°C for 3 hr, followed by cutting into cylindrically shaped slices of 1 cm height. To prepare the gelatin gels varied in contents of disulfide bonds (10 and 33 moles of disul-
fide bonds per $10^6$ g protein, in this study), the sulphydryl groups of the thiolated gelatin were partly blocked with N-ethylmaleimide.

Young's modulus. Curd Meter Model 301 (Iio Electric Co.) and Travelling Microscope (Shimazu Seisakusho Co.) were used. A gel sample on a moving plate of Curd Meter was subjected to several given loads, and at each load the degree of deformation of the gel was measured with Travelling Microscope. Young's modulus of the gel was obtained as the tangent of stress-strain curve at the origin.

Breaking stress. Okada Gelometer (Chuo-Riken Co.) was used. Breaking stress was defined as the force to break the surface of gel.

Sensory measurements. A paired comparison method of incomplete design was used. Cylindrical gel samples were subjectively evaluated by five panel members by pressing and breaking the gel samples with spatula. The panel members rated comparatively each pair in three sensory attributes (hardness, brittleness and springiness) on a 11-point rating scale.

RESULTS

I. Physical characteristics of gels

Young's modulus. Relations among the contents of disulfide bonds, the temperature and Young's modulus of gelatin gels are shown in Fig. 1.

![Fig. 1. Correlation between Young's Modulus and SS Bonds in Gels at Various Temperature.](image)

Figure 1 shows that Young's modulus of gels decreases to one-fourth when gel temperature rises from 7 to 20°C, but Young's modulus only slightly increases with increasing contents of disulfide bonds at all temperature. Closer examination of this figure reveals that, to Young's modulus, the temperature of gels is more contributing factor than the content of disulfide bonds.

Breaking stress. Relations among the breaking stress, the content of disulfide bonds and the temperature of gels are shown in Fig. 2.

![Fig. 2. Correlation between Breaking Stress and Contents of SS Bonds.](image)

Figure 2 shows that the breaking stress is greatly affected by both the contents of disulfide bonds and the temperature of the gels.

II. Sensory characteristics of gels

Effects of the temperature or the content of disulfide bonds in gels on sensory attributes (hardness, springiness and brittleness) are shown in Fig. 3.

![Ordinate of Fig. 3 represents the score rated by panel members, after setting the score of an ordinary gelatin (not thiolated) as zero.](image)

Figure 3 reveals that all sensory attributes are affected more or less by both the temperature and the content of disulfide bonds. For example, on "hardness," the greatest effect of the temperature is exhibited of three sensory attributes, and the effect of temperature is greater than the content of disulfide bonds.
FIG. 3. Effects of Temperature and SS Bonds on Texture of Gels.

- gels with 33 SS bonds per 10^6 g gelatin; - gels with 10 SS bonds per 10^6 g gelatin;
- ordinary gelatin gels.

### TABLE I. CORRELATION COEFFICIENTS BETWEEN PHYSICAL MEASUREMENTS AND SENSORY RATINGS

<table>
<thead>
<tr>
<th>Sensory ratings</th>
<th>Physical measurements</th>
</tr>
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<tbody>
<tr>
<td>Springiness</td>
<td>Brittleness</td>
</tr>
<tr>
<td>Hardness</td>
<td>0.950&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Springiness</td>
<td>0.713</td>
</tr>
<tr>
<td>Brittleness</td>
<td>0.870&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>0.907&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Breaking stress</td>
<td>0.756</td>
</tr>
<tr>
<td>Brittleness</td>
<td>0.870&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>0.687</td>
</tr>
</tbody>
</table>

Significance of correlation is shown by a) for 1%.

On “brittleness,” however, the content of disulfide bonds have more significant effects than the temperature.

### III. Correlation between physical measurements and sensory evaluations

Correlation coefficients between sensory ratings and physical measurements are shown in Table I.

Table I shows that Young’s modulus highly correlates with “hardness,” and breaking stress correlates with both “springiness” and “brittleness.”

### DISCUSSION

In Figs. 1 and 2, the effects of both the contents of disulfide bonds and the temperature on Young’s modulus and breaking stress were shown. The results are summarized in Table II.

Table II clearly exhibits that Young’s modulus is considerably influenced by the temperature of gels, and to a lesser extent by the content of disulfide bonds. Breaking stress, however, is more affected by the content of disulfide bonds than the temperature.

Considering both the generally accepted theory that hydrogen bonding energy mainly depends on temperature and our observation that Young’s modulus of the gelatin gels receives a great effect of temperature, which is consistent with the results of Arakawa<sup>10</sup>, it can be concluded that Young’s modulus of the gel mainly depends on the hydrogen bonding. Breaking stress, however, is dependent on the content of disulfide bonds as shown in Table II.

In Table I, it was demonstrated that Young’s modulus highly correlated with sensory “hardness” and that breaking stress with sensory “brittleness.”

Now, all observations under the present condition of sensory test can be summarized...
TABLE II. EFFECTS OF SS BONDS AND TEMPERATURE ON PHYSICAL CHARACTERISTICS OF GELS

<table>
<thead>
<tr>
<th>Content of SS bonds (0→33 per 10^9 g protein)</th>
<th>Average change observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's modulus (dyne-cm^-2)</td>
<td>Breaking stress (g)</td>
</tr>
<tr>
<td>1.6</td>
<td>71</td>
</tr>
<tr>
<td>Temperature (20→7°C)</td>
<td>8</td>
</tr>
<tr>
<td>46</td>
<td></td>
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</tbody>
</table>

TABLE III. RELATION AMONG SENSORY EVALUATION, PHYSICAL CHARACTERISTICS AND BONDS

<table>
<thead>
<tr>
<th>Sensory evaluation</th>
<th>Physical characteristics</th>
<th>Type of bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>Young's modulus</td>
<td>Hydrogen bond</td>
</tr>
<tr>
<td>Brittleness</td>
<td>Breaking stress</td>
<td>SS bond</td>
</tr>
</tbody>
</table>

as Table III.

These results are of practical interest. For example, to modify “hardness” of protein gels, the introduction of chemical bonds like intermolecular disulfide bonds will be taken into consideration.

Acknowledgement. The authors are deeply indebted to Mr. Jun Toda for his valuable advices in the experiments and kind revision of this paper.

REFERENCES