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Review

Gelation and gel properties of polysaccharides gellan gum and tamarind xyloglucan

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Polysaccharide is used widely in food, cosmetic and pharmaceutical industries. The main use is to give appropriate texture to the products. Thus the polysaccharides used in such way are called texture modifier. Here two important texture modifiers, gellan and tamarind xyloglucan are introduced. The former one is a microbial polysaccharide with gelling ability. Gelling ability makes gellan valuable since only a few polysaccharides can form a gel. Most polysaccharides do not form a gel by themselves; however, some can form a gel under appropriate conditions. The latter one is a plant polysaccharide which forms a gel under appropriate conditions. Gelation and gel properties of gellan and tamarind xyloglucan are described.

Introduction

Some polysaccharides are used to enhance the quality of product by thickening and gelling, and by reducing the undesired defect of water release (syneresis) in some products, and by stabilizing emulsion and suspension [1]. The polysaccharides used in these ways are called texture modifier and creation of various kinds of texture modifier is required to make the products with desirable texture.

Gelling ability is an important property as a texture modifier and some polysaccharides can form a gel at low concentrations (~1%). There are only a few polysaccharides which have a gelling ability by themselves at low concentration whereas a lot of non-gelling polysaccharides are used as a thickener and stabilizer [2].

In the present article, recent insight about the gelation and gel properties of gellan gum and tamarind xyloglucan shall be

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Abbreviation: differential scanning calorimetry (DSC), epigallocatechin gallate (EGCG) described. Gellan gum is a polysaccharide which can form a gel at low concentrations. Gelation mechanism and gel properties of gellan have not been clarified well at the present stage. Tamarind xyloglucan, a polysaccharide obtained from tamarind seed, is a valuable thickener and stabilizer. We regarded tamarind xyloglucan as a representative of non-gelling polysaccharides. Understanding novel gelling conditions of tamarind xyloglucan would lead to create various kinds of texture modifier.

Gellan gum

Gellan gum is an extracellular polysaccharide produced by micro-organism *Sphingomonas elodea* (ATCC 31461) previously known as *Pseudomonas elodea*. Being a fermentation product, it can be produced on demand and with consistent quality. The primary structure of gellan gum is composed of a linear tetrasaccharide repeat unit: 1,3-β-D-glucose, 1,4-β-D-glucuronic acid, 1,4-β-D-glucose, and 1,4-α-L-rhamnose as reported by O'Neil et al. and Jannson et al. [3, 4].

Gellan gels in the presence of appropriate amount of cations are transparent, resistant to heat in the wide range of pH [5]. Brittle gellan gels have a good flavor release, suitable for gel products with new texture. For example, an assembly of brittle gel particle, called a microgel, has a specific texture like fluid gel which was produced from agarose gel [6].

Because of industrial importance of gellan gels, gelation and gel properties have been understood briefly. Some fundamental questions still remain to be answered. For example, what is the gelation mechanism like? In order to further understand gelation and gel properties of gellan gum, a collaborative research group was organized conjunction with the research group of polymer gels affiliated to the Society of Polymer Science, Japan, in 1989. The common gellan was

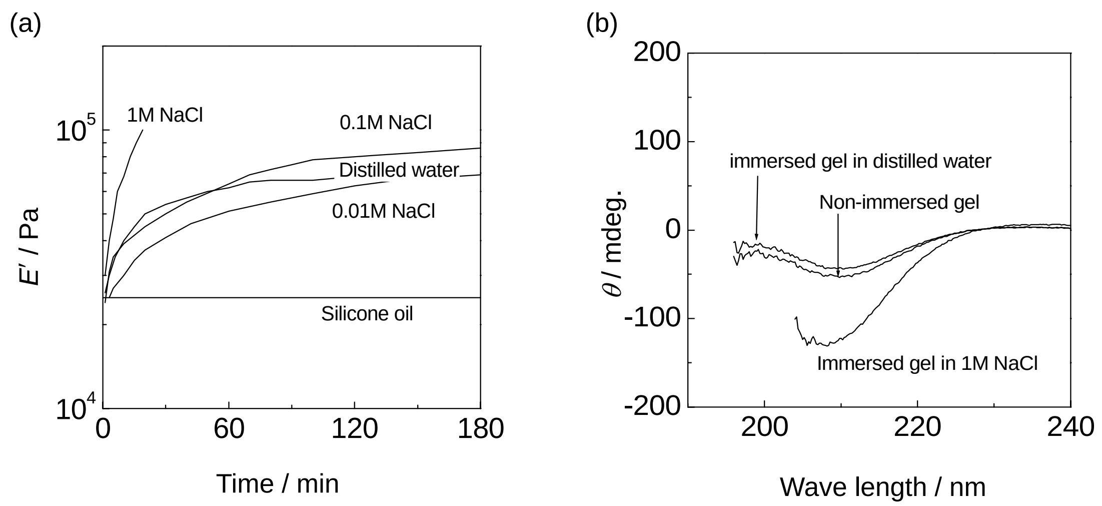

Fig. 1. (a) The storage Young's modulus and (b) the circular dichroism spectra of 1 wt % K-gellan gels affected by the immersion in NaCl solutions or distilled water.

used to study its properties with various techniques. The results of the collaborative studies were published in special issues of *Food Hydrocolloids* 7, 361-456 in 1993, *Carbohydrate Polymers* 20, 75-207 in 1996, and *Progress in Colloid and Polymer Science*, 114, 1-131 in 1999. Light scattering and osmotic pressure measurements showed that gellan changes from two single chains to one double helix on cooling and changes from one double helix to two single chains on heating [7, 8]. Rheological measurements showed that a gel formation occurs after the coil-to-helix transition on further cooling under appropriate conditions [9]. Proposed gelation mechanism is described in those special issues.

Gel properties also remain to be clarified. We found that rheological properties change dramatically under gel state at a certain temperature. At this characteristic temperature single peak appeared in differential scanning calorimetry (DSC) and spectra changed in circular dichroism. These thermally-induced physicochemical changes are believed to be due to a helix-coil transition of gellan; thus, we concluded that a helix-coil transition can occur even in gel state. Since gellan is a polyelectrolyte, gel properties are influenced by the salts. When the gellan gels were immersed in NaCl solutions, the elastic modulus of the gel increased and circular dichroism spectra changed as shown in Fig.1. This was also attributed to the helix-coil transition of gellan.

Tamarind xyloglucan

Xyloglucan is a major structural

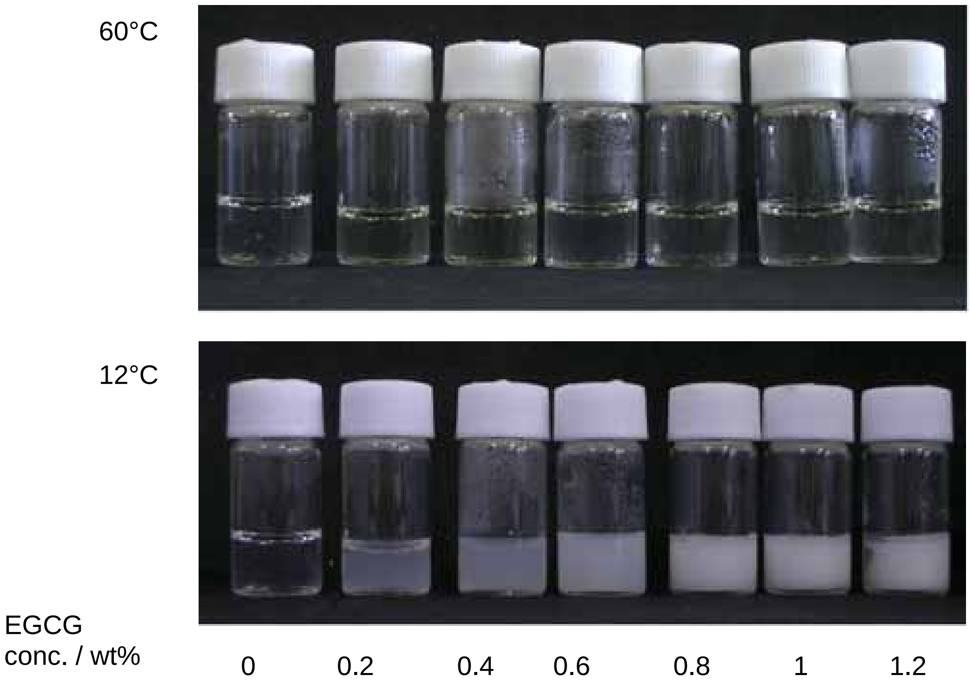

Fig. 2. The appearance of 1 wt % tamarind xyloglucan in the presence of epigallocatechin gallate (EGCG).

polysaccharide in the primary cell walls of higher plants. Tamarind xyloglucan is obtained from the endosperm of the seed of the tamarind tree, *Tamarindus indica*, a member of the evergreen family, that is one of the most important and common trees of Southeast Asia and widely indigenous to India, Bangladesh, Myanmar, Sri Lanka, and Malaysia [11]. Purified, refined tamarind xyloglucan is produced in Japan and is permitted as a thickening, stabilizing, and gelling agent.

Tamarind xyloglucan has a (1→4)-β-D-glucan backbone that is partially substituted at the O-6 position of its glucopyranosyl residues with α-D-xylopyranose [12]. Some of the xylose residues are β-D-galactosylated at O-2 [12].

Although tamarind xyloglucan itself does not form a gel, gel can be obtained under appropriate conditions, such as by adding some substances or removing substituents. Tamarind xyloglucan forms a gel in the presence of 40-65% sugar over a wide pH range [13]. It also forms a gel in the presence of alcohol [13] or by removing galactose residues from tamarind xyloglucan [14, 15]. In order to seek novel gelling condition of tamarind xyloglucan, we prepared a mixture of tamarind xyloglucan and epigallocatechin gellate (EGCG), a polyphenol abundant in tea leaves. The mixture formed a translucent or opaque gel (Fig.2) [16]. Rheological and DSC studies showed that the gelation occurred on cooling and gel melted on subsequent heating [16]. EGCG was most likely bound to tamarind xyloglucan chains for a gel network, which was detected as a DSC peak and two-dimensional nuclear Overhauser effect spectroscopy (2D NOESY) [16].

Since it has been reported that some mixtures of polysaccharides can form a gel by specific interaction, a mixture of tamarind xyloglucan and gellan was prepared in order to test whether or not the mixture shows a specific interaction leading to a synergistic gelation. From viscoelastic measurements we confirmed that the mixture formed a gel under the condition where individual polysaccharide does not form a gel at the experimental concentrations, indicating the synergistic gelation occurred [17]. In DSC measurements, the gelation was detected as a peak that appeared at higher temperatures than a peak arising from helix-coil transition of gellan alone [17]. It was also detected as a change in circular dichroism which was not observed in tamarind xyloglucan alone and gellan alone [17]. Judging from the results it was concluded that tamarind xyloglucan and gellan might associate to form a gel network.

Conclusion

Recent findings about gellan and tamarind xyloglucan are the helix-coil transition of gellan in gels, the gelation of tamarind xyloglucan by addition of epigallocatechin gallate, and the synergistic gelation of a mixture of tamarind xyloglucan and gellan. It should be noted that it is rare for the polysaccharide-polyphenol interaction leading to gel formation. It is also notable that only a few mixtures of polysaccharides show the synergistic gelation. These findings are expected to contribute to not only understand gelation mechanism of polysaccharides but also create new texture modifiers suitable for social requirement.

References

[1] Lapasin, R., and Pricl, S. (1995) Industrial applications of polysaccharides. In "*Rheology of Industrial Polysaccharides*". Chapman & Hall, New York, pp.134-161.

[2] Nitta, Y. (2005) Ph.D thesis, Osaka City University.

[3] Jansson, P. E., Lindberg, B., and Sandford, P. A. (1983) Structural studies of gellan gum, an extracellular polysaccharide elaborated by *Pseudomonas elodea*. *Carbohydr. Res*., **124**, 135-139.

[4] O'Neill, M. A., Selvendran, R. R., and Morris, V. J. (1983) Structure of the acidic extracellular gelling polysaccharide produced by *Pseudomonas elodea*. *Carbohydr. Res*., **124**, 123-133.

[5] Sworn, G. (2000) Gellan gum. In "*Handbook of hydrocolloids*", Edited by Phillips, G. O. and Williams, P. A., Woodhead publishing Ltd, Cambridge, pp. 117-135.

[6] Oomoto, T., Uno, Y., and Asai, I. (1999) The latest technologies for the application of gellan gum. *Prog. Colloid Polym. Sci*., **114**, 123-126.

[7] Takahashi, R., Akutu, M., Kuboka, K., and Nakamura, K. (1999) Characterization of gellan gum in aqueous NaCl solution. *Prog. Colloid Polym. Sci*., **114**, 1-7.

[8] Ogawa, E. (1999) Temperature dependence of the conformational properties of sodium-type gellan gum in aqueous solutions. *Prog. Colloid Polym. Sci*., **114**, 8-14.

[9] Miyoshi, E. and Nishinari, K. (1999) Rheological and thermal properties near the sol-gel transition of gellan gum aqueous solutions. *Progr. Colloid Polym. Sci*., **114**, 68-82.

[10] Nitta, Y., Ikeda, S., Takaya, T., and Nishinari, K. (2001) Helix-coil transition in gellan gum. *Trans. Mat. Res. Soc. J*., **26**, 621-624.

[11] Glicksman, M. (1986) Tamarind seed gum. In "*Food Hydrocolloids*, Vol. III", Edited by Glicksman M., CRC Press, Florida, pp.191-202.

[12] Gidley, M. J., Lillford, P. J., Rowlands, D. W., Lang, P., Dentini, M., Crescenzi, V., Edwards, M., Fanutti, C., and Reid, J. S. G. (1991) Structure and solution properties of tamarind-seed polysaccharide. *Carbohydr. Res*., **214**, 299-314.

[13] Nishinari, K., Yamatoya, K., and Shirakawa, M. (2000) Xyloglucan. In "*Handbook of Hydrocolloids*", Edited by Phillips, G. O., Williams, P. A., Woodhead Publishing, Cambridge, pp 247-267.

[14] Reid, J. S. G., Edwards, M. E., and Dea, I. C. M. (1988) Enzymatic modification of matural seed gum. In "*Gums and Stabilisers for the food Industry* 6", Edited by Phillips, G. O., Williams, P. A., and Wedlock, D. J., IRL Press, Oxford, pp.391-398.

[15] Shirakawa, M., Yamatoya, K., and

Nishinari, K. (1998) Tailoring of xyloglucan properties using an enzyme. *Food Hydrocoll*., **12**, 25-28.

[16] Nitta, Y., Fang, Y., Takemasa, M., and Nishinari, K. (2004) Gelation of xyloglucan by addition of epigallocatechin gallate as studied by rheology and differential scanning calorimetry. *Biomacromolecules*, **5**, 1206-1213.

[17] Nitta, Y., Kim, B. S., Nshinari, K., Shirakawa, M., Yamatoya, K., Oomoto, T., and Asai, I. (2003) Synergistic gel formation of xyloglucan/gellan mixture as studied by rheology, DSC and circular dichroism. *Biomacromolecules*, **4**, 1654-1660.

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