Coryneform Bacteria Strain C-8 の生成する粘質多糖と化工澱粉との協力効果(農芸化学科)

Synergistic Effect of Modified Starch on the Viscous Polysaccharide Produced by Coryneform Bacteria Strain C－8

Masakuni TAKO*, Sanehisa NAKAMURA* and Tomonori NAGAHAMA**

Summary

The synergistic effect of cationic starch and oxidized starch on the viscosity and dynamic viscoelasticity of Polysaccharide C－8 were investigated. The flow curves of a mixed solution of Polysaccharide C－8 and 0.5％ cationic starch showed a yield value and approximated to plastic flow behavior, but a mixed solution of Polysaccharide C－8 and 0.5％ oxidized starch approximated to pseudoplastic flow behavior at various concentrations. Dynamic modulus of the mixed solution of Polysaccharide C－8 and cationic starch increased remarkably at a concentration of 0.1％ Polysacharide C－8 in 0.5％ cationic starch and increased gradually after that, while dynamic viscosity increased in proportion to polysaccharide concentration. However, in the case of the latter it showed lower value than that of Polysaccharide C－8 itself. At pH 4.3, dynamic viscoelasticity of the mixed solution of the former showed the highest value than that of the other pH values.

Introduction

In order to apply the viscous Polysaccharide C－8[1] (D-mannose: D-galactose : D-glucose : D-glucuronic acid: pyruvic acid＝ 1 : 1 : 1 : 3 : 1) produced by coryneform bacteria strain C－8 for the food, we have previously investigated some rheological properties of it.[2～5] Polysaccharide C－8 showed comparable high viscosity to guar gum which was one of the highest viscous polysaccharides, and viscosity of it seemed to be scarcely changeable at pH 6～9 and also insensitive to heating for 30 minutes at 80℃. Polysaccharide C－8 was excellent in emulsion formation and film-forming properties,[2] also the behavior of non－Newtonian flow and dynamic viscoelasticity of it were consistent with that of guar gum[3].

* Department of Agricultural Chemistry, College of Agriculture, University of the Ryukyus

** Department of Agricultural Chemistry, Faculty of Agriculture, Kagoshima University

Sci. Bull. Coll. Agric. Univ. Ryukyus 30 : 247～254 (1983)

Viscosity and dynamic viscoelasticity of the mixed solution of Polysaccharide C-8 and gelatin were higher in those values than Polysaccharide C-8 itself.[4] This synergistic effect seemed to be due to the formation of ionic bonding between carboxyl groups of Polysaccharide C-8 and amino groups of gelatin. The physical properties of sweet bean jelly containing Polysaccharide C-8 were somewhat superior to that of guar gum.[5]

Accordingly, it is interested to investigate the synergistic effect of cationic starch and oxidized starch, which are used commonly to inner or surface coating or sizing in paper textile industries[6] as a fundamental polymer, on Polysaccharide C-8. Cationic starch has amino groups, so that much larger synergistic effect of it on Polysaccharide C-8 seemed to occure. In this paper, we describe the viscosity and dynamic viscoelasticity of a mixed solution of the Polysaccharide C-8 and modified starches.

Materials and methods

1. Preparation of Polvsaccharide C-8

Polysaccharide C-8 which was produced by culturing coryneform bacteria strain C-8 in a well-aerated medium containing soluble starch in a jarfermentor, was used[2] and purification of it was carried out by the same method as described in the previous paper. The molecular weight of it was calculated to be about 250,000 by viscometric method[2] and the viscosity of it was 400 cp at 0.5% concentration.

2. Preparation of mixed Solutions of Polysaccharide C-8 and modified starches

Commercial cationic starch and oxidized starch were supplied by Nippon Shokuhin Kagaku Kogyo Co., Ltd.; the former was prepared by reaction of potato starch with trimethylammonium chloride whose degree of substitution was about 0.2 per anhydrglucose unit and the latter by reaction of corn starch with hypochloric acid.

The modified starch was dissolved in hot water (85℃) to make 0.5% solution, and then Polysaccharide C-8, to be 0.1, 0.3 and 0.5% in concentration, was dissolved in addition.

3. Viscosity and dynamic viscoelasticity measurements

The mixed solutions were left to stand for 30 minutes, and then viscosity and dynamic viscoelasticity were measured. Viscosity and dynamic viscoelasticity measurement were carried out by use of rheogoniometer (Iwamoto Seisakusho Co., Ltd.) at 15 rpm (viscosity), 0.625 Hz (dynamic viscoelasticity) and 25℃ unless stated otherwise.

Shear rate, D, shear stress, S, and viscosity, η were calculated with equation of Margules[7). Dynamic viscoelasticity, η' and G', were calculated from Markovitzs equation[8).

Results

1. Flow curves

It was already reported that an aqueous solution of Polysaccharide C−8 showed pseudoplastic flow behavior[3). Fig. 1 shows flow curves of a solution of the Polysaccharide C−8 mixed with cationic starch, or with oxidized starch. In addition of cationic starch, the flow curve of 0.1% solution of Polysaccharide C−8 approximated to pseudoplastic flow behavior. However, 0.3 and 0.5% solutions showed plastic flow behavior, and the yield values of them were estimated to be 8 and 15 dyne/cm², respectively. From these results, it was assumed that intermolecular secondary bonding seemed to be formed between carboxyl groups of Polysaccharide C−8 and amino groups of cationic starch in higher concentration of the polysaccharide.

On the other hand, the solution of mixed with oxidized starch showed approximately pseudoplastic flow behavior in the concentrations tested, and the flow curves of 0.3 and 0.5% mixed solution shifted to the left over of Polysaccharide C−8 itself in the same concentrations. This results implied that molecular entanglement of Polysaccharide C−8 was inhibited by the existence of oxidized starch.

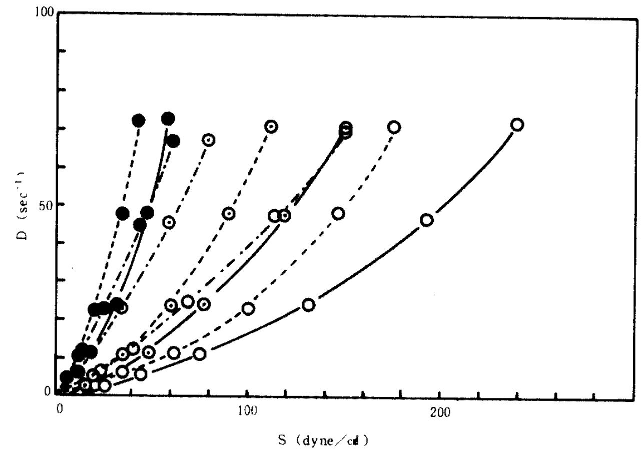

Fig. 1. Flow curves of Polysaccharide C−8 solution mixed with modified starches. Concentration of Polysaccharide C−8: ● 0.1% ◎ 0.3% ○ 0.5%
-·-·-· Polysaccharide C−8 only,
—— with 0.5% Cationic starch,
·········· with 0.5% Oxidized starch

2. Effect of polysaccharide concentration on dynamic viscoelasticity

The dynamic viscoelasticity-concentration relationship on Polysaccharide C−8 solution mixed with cationic starch or oxidized starch is shown in Fig. 2. Dynamic viscosity of the former mixture was higher but the latter was lower than that of the polysaccharide itself. On the other hand, dynamic modulus of the mixture with cationic starch increased remarkably at a concentration of 0.1% Polysaccharide C−8, and then increased gradually.

In the case of oxidized starch, dynamic viscoelasticity of the mixture showed lower valus than that of Polysaccharide C-8 itself.

3. Effect of pH

The viscosity of 0.5% Polysaccharide C-8 solution was essentially independent on pH 6～9 as described previously[2). The mixture with cationic starch, or oxidized starch were adjusted to pH values ranging from 3.0 to 11 with 0.1 N HCl or NaOH. Viscosity and dynamic viscoelasticity of them shown in Fig. 3 (A) and (B). The viscosity of the former mixture was relatively higher value showing about 6.6 and 5.3 poise at pH 4.3 to 8.2, while the latter mixture showed lower value than that of Polysaccharide C-8 itself in its viscosity.

Dynamic viscosity of the mixture with cationic starch was high value showing

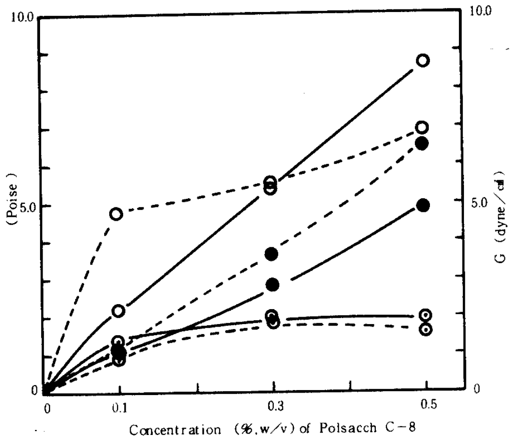

Fig. 2. Effect of polysaccharide concentration on the dynamic viscoelasticity of the solutions of Polysaccharide C-8 mixed with modified starches.
——— Dynamic viscosity, η'
--------- Dynamic modulus, G'
● Polysaccharide C-8 only
○ with 0.5% Cationic starch,
◎ with 0.5% Oxidized starch

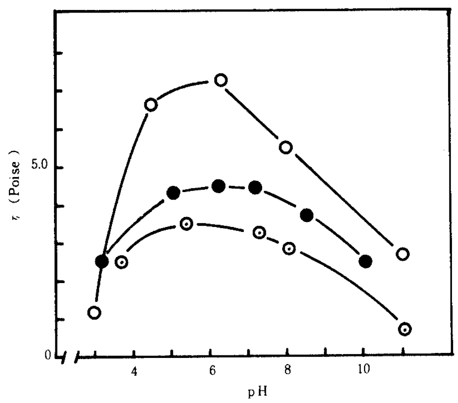

Fig. 3 (A). Effect of pH on the viscosity of Polysaccharide C-8 solution mixed with modified starches.
● Polysaccharide C-8 only, 0.5%
○ with 0.5% Cationic starch
◎ with 0.5% Oxidized starch
pH value of the solutions was adjusted with 0.1N HCl or NaOH.

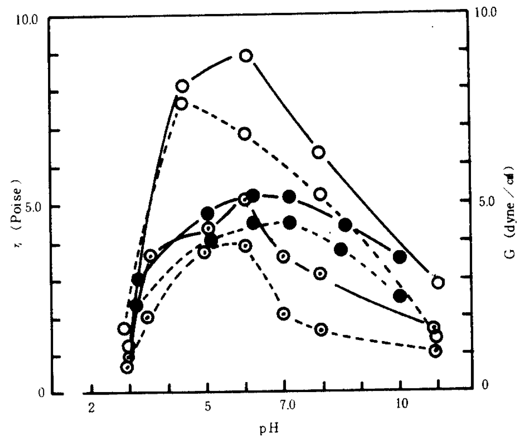

Fig. 3 (B). Effect of pH on the dynamic viscoelasticity of Polysaccharide C-8 solution mixed with modified starches.
● Polysaccharide C-8 only, 0.5%
○ with 0.5% Cationic starch
◎ with 0.5% Oxidized starch
——— Dynamic viscosity, η'
--------- Dynamic modulus, G'

about 8.2 and 8.8 poise at pH 4.3 and 6.4. However, a mixture with oxidized starch showed lower value than Polysaccharide C－8 itself. On the other hand, dynamic modulus of the former mixture was high value about 7.7 dyne/cm^2 at pH 4.3, and decreased gradually on the side of high pH value and also decreased rapidly on the side of low pH value. The latter mixture showed lower values than that of Polysaccharide C－8 itself.

4. Effect of temperature on dynamic viscoelasticity

The effect of temperature on dynamic viscoelasticity of the mixture with cationic strach were shown in Fig. 4. Dynamic viscosity of the mixture of 0.5 % Polysaccharide C－8 with cationic starch showed the highest value than that of 0.3 and 0.1 % Polysaccharide C－8. These solutions decreased in dynamic viscosity with increasing temperature. Dynamic modulus of the mixture of 0.1 % Polysaccharide C－8 showed a peak value between 0 and 10 ℃, and it decreased rapidly at the side of higher temperature.

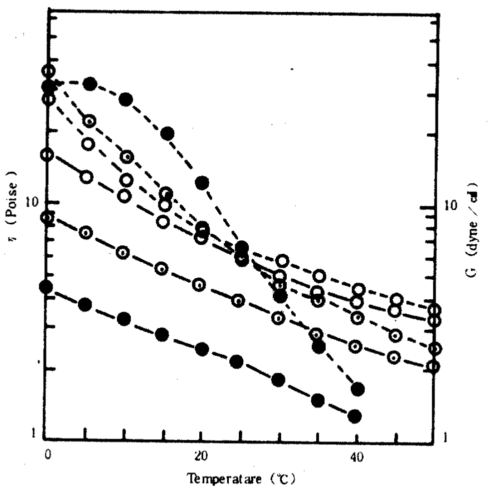

Fig. 4. Effect of temperature on the dynamic viscoelasticity of polysaccharide C－8 solution mixed with cationic starch at pH 4.0.
———— Dynamic viscosity,
.... Dynamic modulus
Concentration of polysaccharide C－8: ● 0.1 %, ◎ 0.3 %, ○ 0.5 %

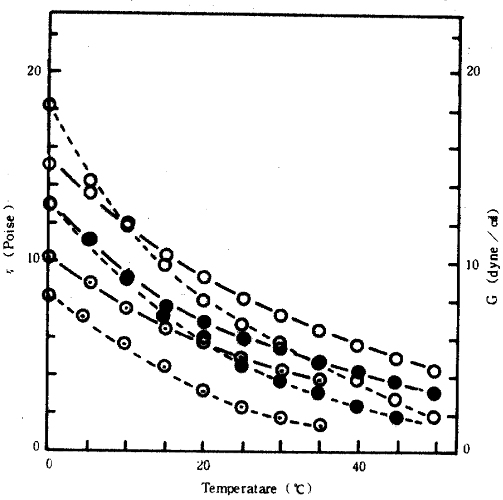

Fig. 5. Effect of temperature on the dynamic viscoelasticity of polysaccharide C－8 solution mixed with modified starches.
———— Dynamic viscosity,
.... Dynamic modulus
● Polysaccharide C－8 only, 0.5 %,
○ with 0.5 % Cationic starch
◎ with 0.5 % Oxidized starch

Fig. 5. showed the effect of temperature on dynamic viscoelasticity of the mixture with 0.5 % cationic starch, or oxidized starch in comparison with 0.5 % polysaccharide C－8 alone. Although the former mixture showed higher dynamic

viscoelasticity than that of the polysaccharide C−8 itself, the latter mixture showed lower value.

Discussion

The chemical structure of Polysaccharide C−8 has been proposed by Nagahama.[9] It mainly composes of β−1, 4 linked glycan (D−mannose, D−galactose, D−glucose, D−glucuronic acid) bearing single 1, 6 linked D−glucuronic acid residue as branches attached to D−galactose residue of the backbone. As it has acidic residues, glucuronic acid and pyruvic acid, dynamic viscoelasticity of a mixed solution of Polysaccharide C−8 and gelatin showed remarkable high values as described in the previous paper.[4] This synergistic effect seemed to be due to the formation of ionic bonding between carboxyl groups of the former and amino groups of the latter.

On the other hand, cationic starch is one of the modified starches having amino groups. It is used for inner or surface coating and sizing in paper and textile industries[6]. Considerable amounts of polysaccharide such as modified starches, guar gum, locust bean gum and sodium alginate[10] which have important functional effect on the sizing or coating, are used the manufacturing[11]. In this paper, dynamic viscoelasticity of the mixed solution of Polysaccharide C−8 and cationic starch or oxidized starch was examined by use of a rheogoniometer.

Flow curves of the solution of 0.3 and 0.5% Polysaccharide C−8 mixture with 0.5% cationic starch showed plastic flow behavior, since the yield values were estimated to 8 and 15 dyne/cm², respectively. This result indicates that the intermolecular secondary bonding is formed between the carboxyl of Polysaccharide C−8 and amino groups of cationic starch. It seemes to be a similar result to that from the mixed solution of Polysaccharide C−8 and gelatin[4].

The dynamic modulus of a mixed solution of Polysaccharide C−8 and cationic starch increased rapidly at the concentration of 0.1% of the former in 0.5% of the latter. This result indicates that the ionic bonding is formed remarkably at the above condition. The dynamic modulus of them showed also highest value at pH 4.3. These phenomenon have been also observed in a mixed solution of the Polysaccharide C−8 and gelatin . At the above condition, 0.1% Polysaccharide C−8 and 0.5% cationic starch, ionic bonding seemes to be formed strongly. At low temperature dynamic modulus of a mixed solution of them showed not so high value as that of a mixed solution of Polysaccharide C−8 and gelatin[4]. This result implies that intermolecular hydrogen and ionic bonding may not be formed as high as a mixed solution of Polysaccharide C−8 and gelatin.[4]

On the contrary, the negative synergistic effect on the dynamic viscoelasticity of a mixed solution of Polysaccharide C−8 and oxidized starch was observed at various polysaccharide concentrations. Decreasing a viscosity of them may be caused by contamination of hypochloric acid when oxidized starch was prepared.

The authors would like to express their deep thanks to Dr. Danji Nomura, professor of Kyushu Universtiy and Dr. Matsuo Kanie, emeritus professor of Kagoshoma University for their valuable advice.

The authors also thank Nippo Shokuhin Kagaku Kogyo Co., Ltd. for providing of the samples of cationic starch and oxidized starch.

References

1) Nagahama, T., Fujimoto, S. and Kanie, M. 1977 Isolation of the slime producing coryneform bacteria and their bacteriological characteristics, Agr. Biol. Chem., **41**: 9 ~ 16

2) Tako, M., Nagahama, T., and Nomura, D., 1977 Some rheological properties of the viscous polysaccharide produced by coryneform bacteria strain C − 8, J. Agric. chem. Soc. Japan, **51**: 389 ~ 395

3) ________ 1977 Flow properties of the viscous polysaccharide produced by coryneform bacteria strain C − 8, **51**: 397 ~ 403

4) ________ 1977 Synergistic effect of gelatin on the viscous polysaccharide produced by coryneform bacteria strain C − 8, J. Jpn. Soc. Food Sci. Tech. **24**: 565 ~ 569

5) Tako M., Nakamura, S. and Nagahama, T. 1982 Studies on the application of polysaccharide produced by coryneform bacteria strain C − 8, Sci, Bull. Agric. Univ. Ryukyus **29**: 79 ~ 85

6) Hjermstad, E. T. 1973 Industrial gums, Academic Press, p. 611

7) Harris, J., 1977 Rheology and non − Newtonian flow, Longman Inc., New York, p. 30

8) Markovitz, H., 1952 A property of bessel functions and its applications to the theory of two rheometers, J. Appl. Phys., **23**: 1070 ~ 1077

9) Nagahama, T. 1982 "Structure and charcteristics of the polysaccharide produced by coryneform bacteria strain C − 8," Symposium on structure and function of polysaccharides and glycoproteins (Annual meeting of the branch of west Japan, the Agricultural Chemical Society of Japan), October 16, 1982, Kagoshima p. 5

10) Whistler, R. L. 1973 Industrial gums, Academic Press, p. 62

11) Nakamura, K. water − soluble polymers, Kagaku Kogyo Sha, p. 174

琉球大学農学部学術報告　第30号（1983）

Coryneform Bacteria Strain C－8 の生成する粘質多糖と化工澱粉との協力効果

田幸正邦＊・仲村実久＊・永浜伴紀＊＊

要　約

Coryneform bacteria strain C－8 の生成する粘質多糖と陽性澱粉又は酸化澱粉との混合液の粘性および動的粘弾性を同軸二重円筒回転振動型のレオゴニオメーターを用いて測定し，以下の結果を得た。

C－8 多糖と陽性澱粉（0.5％）との混合液の流動曲線は前者の濃度 0.3 および 0.5％で降伏値を有し，塑性流動を示した。この結果，C－8多糖と陽性澱粉分子鎖間に二次結合が存在することが推察された。一方，C－8多糖と酸化澱粉との混合液は擬塑性流動性を示した。

C－8多糖と陽性澱粉との協力効果はpH 4.0～6.4で大きく，動的粘性は8.2～8.8 Poiseであった。C－8多糖と酸化澱粉との混合液の粘性はC－8多糖のみの溶液より低い粘性を示した。陽性澱粉 0.5％に対してC－8多糖 0.1％で動的弾性が著しく増大し，その後ゆるやかな増大が見られた。低温側では，C－8多糖と陽性澱粉との混合液の動的粘弾性は著しく増大した。

＊琉球大学農学部農芸化学科
＊＊鹿児島大学農学部農芸化学科