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CMC の非ニュートン流動と動的粘弾性(農芸化学科)

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Non-Newtonian Flow and Dynamic Viscoelasticity of Carboxymethylcellulose Solutions*

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Summary

Non-Newtonian flow behavior and dynamic viscoelasticity of carboxymethylcellulose (CMC) solutions were measured using a rheogoniometer and their rheological properties were analyzed. Aqueous solutions of CMC at concentrations of 0.5 and 1.0% showed pseudoplastic behavior and those of 1.5 and 2.0% showed plastic behavior. The flow indices of the former were 1.0 and the latter were 1.1 before refraction point and 1.6 after it. The situation of the refraction points for shear rate were consistent with that of xanthan gum at concentration of 1.5 and 2.0%. The activation energy of flow of 1.0% CMC solution was 4.58 Kcal/mole at a low temperature region and 5.95 Kcal/mole at a high temperature region. Dynamic viscoelasticity of CMC solutions was remarkably high at 2.0%, and loss tangent was evaluated to be 1.8. This result indicated that intermolecular secondary bonding was formed partially. Dynamic viscoelasticity of CMC solutions increased at low temperature but decreased with increasing temperature, while loss tangent also decreased from 1.8 to 1.2 with increasing temperature from zero to 65°C. Thus, intermolecular secondary bonds seemed to be attributed to intra- and intermolecular hydrogen bonding.

Introduction

In the previous paper,¹⁾ we reported the non-Newtonian behavior and dynamic viscoelasticity of the polysaccharide C-8 (D-mannose:D-galactose:D-glucose: D-glucuronic acid:pyruvic acid=1:1:1:3:1) which was produced by coryneform bacteria strain C-8, sodium alginate, locust bean gum and guar gum. Sodium alginate which consisted of β -1,4 linked D-mannuronic acid unit showed slight non-Newtonian (pseudoplastic) behavior, while locust bean gum which consisted

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of β -1, 4 linked D-mannose unit with a side branching unit of D-galactose on every fourth unit showed moderate non-Newtonian (pseudoplastic) behavior. Guar gum whose structure was the same as locust bean gum except the side chain attached on every other unit, furthermore, showed remarkable non-Newtonian (pseudoplastic) behavior as same as that of the polysaccharide C-8 and flow behavior indices, structural viscosity, activation energy of flow and frequency and temperature dependence on dynamic viscoelasticity of it were consistent with those of the latter. It was concluded that the mechanisms of non-Newtonian and dynamic viscoelasticity behavior of guar gum and the polysaccharide C-8 were agreed, and therefore mode of linkage of main chain and side one of the latter seemed to be similar to that of the former. It was also considered that the side chains of these polysaccharides, locust bean gum, guar gum and the polysaccharide C-8, remarkably participated in their non-Newtonian behavior. We also reported²⁾ on xanthan gum which consisted of β -1, 4 linked D-glucose unit with side branching of three sugar residues on every other unit.³⁾ It was concluded that the molecular chains of xanthan gum were associated in quaternary with hydrogen bonding, besides the side chains of it might participated in molecular aggregation.²⁾

Sodium carboxymethylcellulose (CMC) is a water-soluble cellulose derivative of the greatest commercial importance.⁴⁾ Although its non-Newtonian flow behavior and dynamic viscoelasticity have been reported by a number of workers,^{5)~11)} there has not been discussed on the correlation between its non-Newtonian behavior and molecular structure. As the structure of the backbone of CMC is similar to that of xanthan gum, we measured non-Newtonian behavior and dynamic viscoelasticity of CMC solutions and their rheological properties were analysed.

Materials and Methods

1. Preparation of CMC. Sodium carboxymethylcellulose was supplied from Taiyo Kagaku Co., Ltd. CMC was dissolved at 0.5% concentration in distilled water and filtered through Celite 545 layer, then in the presence of 1.0% NaCl, double volume of ethanol was added and polysaccharide was precipitated. After that, the polymer was dried in vacuum. The viscosity of 1.0% CMC aqueous solution was 250 cp at 15 rpm at 25°C.

Molecular weight of CMC was evaluated to be 120,000 by the viscometric method as previously described.¹²⁾

Average degree of substitution of carboxymethyl groups of CMC was calculated to be 0.8 per anhydroglucose unit.¹³⁾

2. Measurement of viscosity and dynamic viscoelasticity. Viscosity and dynamic viscoel-

asticity of the CMC solutions were measured with rheogoniometer (Iwamoto Serisakusho Co., Ltd.) at 15 rpm, 0.625 Hz and 25°C unless otherwise stated.

Shear rate, D , shear stress, S , and viscosity of CMC solutions were calculated with the equation of Margules.¹⁴⁾ On the other hand, dynamic viscosity, η' , and dynamic modulus, G' , of it were calculated with the modified equation of Markovitz¹⁵⁾ and loss tangent ($\tan \delta$) was calculated with the following equation

$$\tan \delta = \frac{G''}{G'}$$

$$G' : w\eta'$$

w : angular velocity.

Results

1. **Flow curve.** Flow curves of CMC aqueous solutions are shown in Fig. 1. The solutions containing 0.5 and 1.0% CMC displayed pseudoplastic behavior, while 1.5 and 2.0% solutions displayed plastic flow behavior, whose yield values were 6 and 10 dyne/cm², respectively. These yield values imply that intermolecular

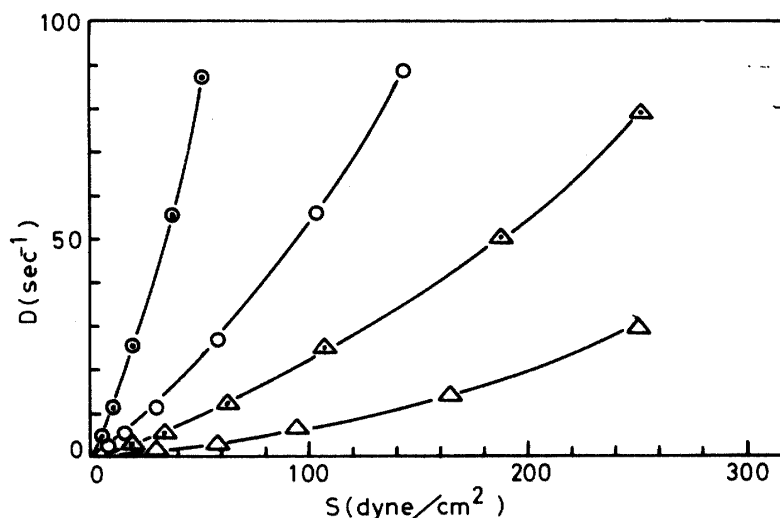


Fig. 1. Flow curves of sodium carboxymethylcellulose at various concentrations.

⊙ 0.5%, ○ 1.0%, △ 1.5%, △ 2.0%

secondary bonding is formed in the aqueous solutions at higher concentrations. Considering the above mentioned characteristic, the Herschel and Bulkley equation $D = K(S - S_y)^N$ is suitable for mathematical characterization of the flow of polymer. This equation has been used to describe the non-Newtonian flow of disperse systems, exhibiting a certain initial resistance to flow. Parameter K is the consistency index, N is the flow behavior index, S is the shear stress and S_y is the yield value. Parameter K and N have the same meaning as in the power law ($D = KS^N$). In order to evaluate its non-Newtonian flow behavior

quantitatively, log-log plots of the above results are shown in Fig. 2. The flow

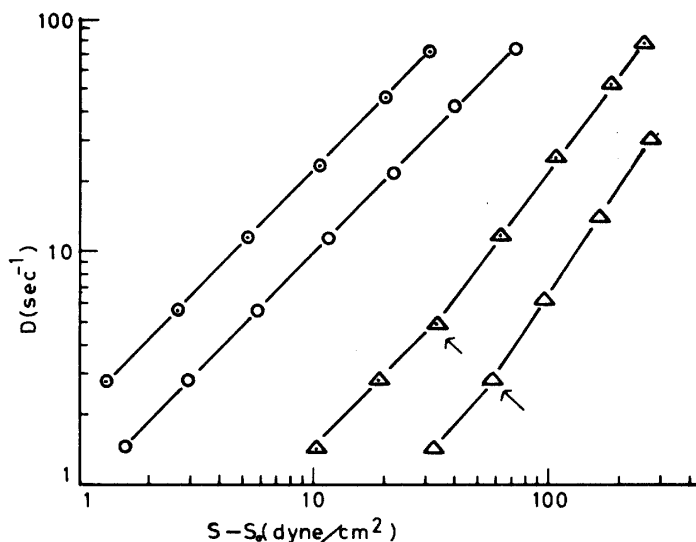


Fig. 2. Logarithmic plots of shear rate and shear stress for sodium carboxymethylcellulose at various concentrations.

⊙ 0.5%, ○ 1.0%, △ 1.5%, △ 2.0%.

← refraction point.

behavior indices, N , were evaluated to be 1.0 at 1.5 and 1.0% solutions, and 1.1 before the refraction point and 1.6 after the refraction point at 1.5 and 2.0% solutions, respectively. The refraction point of CMC seemed to be a breaking point of intermolecular secondary bonding and appeared at 2.8 and 5.9 sec^{-1} . In the case of xanthan gum, refraction points also appeared at 2.8 and 5.9 sec^{-1} as previously reported²⁾.

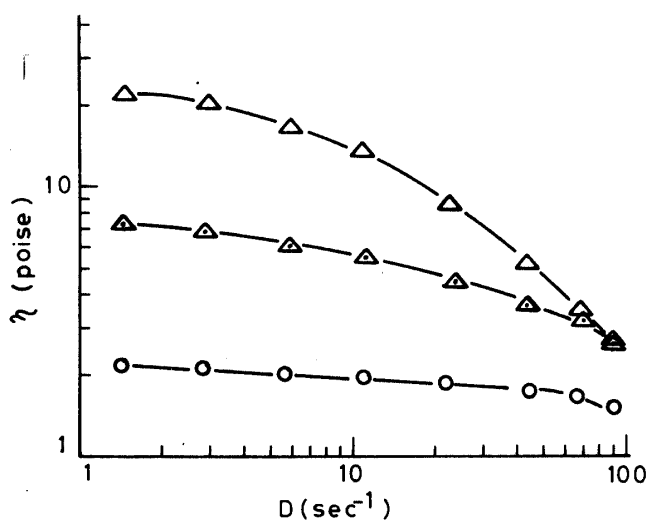


Fig. 3. Logarithmic plots of apparent viscosity and shear rate for sodium carboxymethylcellulose at various concentrations.

○ 1.0%, △ 1.5%, △ 2.0%.

2. Effect of shear rate on viscosity.

Fig. 3. shows the effect of shear rate on the viscosity of CMC at various concentrations. At 2.0%, viscosity decreased remarkably with increasing shear rate and its slope was evaluated to be 0.85 at high shear rate region. However, viscosity of 1.0 and 1.5% solutions slightly decreased for shear rate and their slopes were evaluated to be 0.2 and 0.4, respectively. Although the slope of 2.0% solution was larger than that of

xanthan gum²⁾ whose curves dropped linearly and its slopes were evaluated to be 0.8 at a wide range of the concentrations, CMC did not drop linearly. This result indicates that molecular chains of CMC are oriented remarkably for direction of shear rate at high shear rate region.

3. Activation energy of flow. The logarithms of the viscosity of 1.0% CMC solution are plotted against the reciprocals of the absolute temperature as shown in Fig. 4. Since the curve was divided into two straight segments, existence of two mechanisms of the viscous flow is indicated. The activation energy, E_v , in the equation of Andrade $\log \eta = \log A + E_v/RT$ was calculated to be 4.58 Kcal/mole at a temperature of 0~45°C and 5.95 Kcal/mole at a temperature of 45~70°C, respectively. This result was approximated to that of the CMC which had been reported by Nishida.⁷⁾

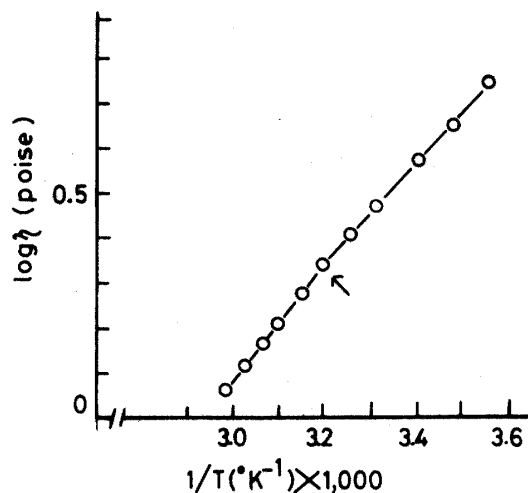


Fig. 4. Logarithm of apparent viscosity against reciprocal of absolute temperature for sodium carboxymethylcellulose at 1.0% concentration.

4. Effect of frequency on dynamic viscoelasticity. The effect of frequency on the dynamic viscoelasticity of CMC at various polymer concentrations are shown in Fig. 5(A). The dynamic viscosity of 1.0, 1.5 and 2.0% of CMC solution decreased with increasing frequency and their slopes were evaluated to be -0.2, -0.2 and -0.3, respectively, while the dynamic modulus of them increased with increasing frequency and their slopes were evaluated to be 1.2, 1.0 and 0.5, respectively. At 2.0% concentration, dynamic viscoelasticity modulus is about ten times higher than that of 1.5% solution. These results indicate that intermolecular secondary bonding is formed remarkably with increasing concentration. At 2.0% solution, dynamic

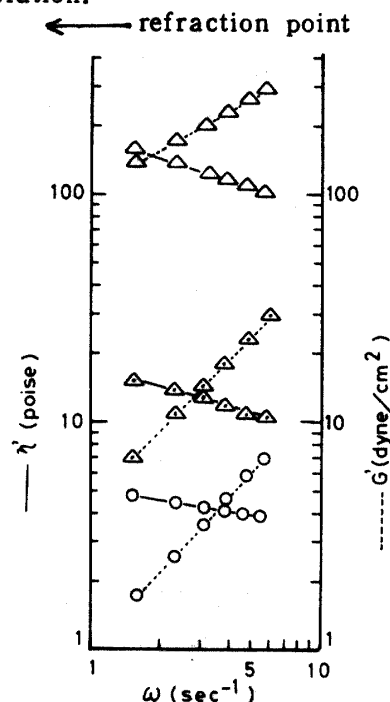


Fig. 5(A) Effect of frequency on dynamic viscoelasticity of sodium carboxymethylcellulose at various concentrations. ○ 1.0%, △ 1.5%, △ 2.0%.

viscoelasticity is about ten times higher than steady shear viscosity (Fig.3). These results indicate that intermolecular secondary bonding is stable for frequency.

The effect of frequency on loss tangent which calculated from the above results is shown in Fig.5(B). At concentration of 1.0% solution, it decreased from 14.5 to 3.5 with increasing frequency, while at 1.5% solution, it decreased from 3.2 to 2.4. The solution containing 2.0% of it kept a constant value of about 1.8 with increasing frequency. These results indicate that intermolecular secondary bonding of CMC is formed partially at this concentration.

5. Effect of temperature on dynamic viscoelasticity. The effect of temperature on dynamic

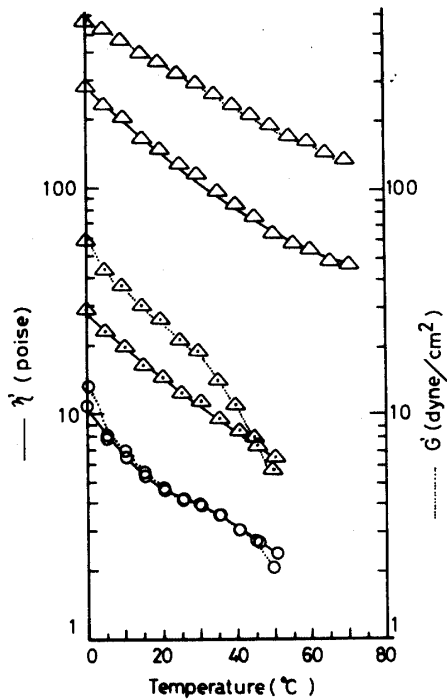


Fig.6(A). Effect of temperature on dynamic viscoelasticity of sodium carboxymethylcellulose at various concentrations and 0.625 Hz.

○ 1.0%, △ 1.5%, ▽ 2.0%.

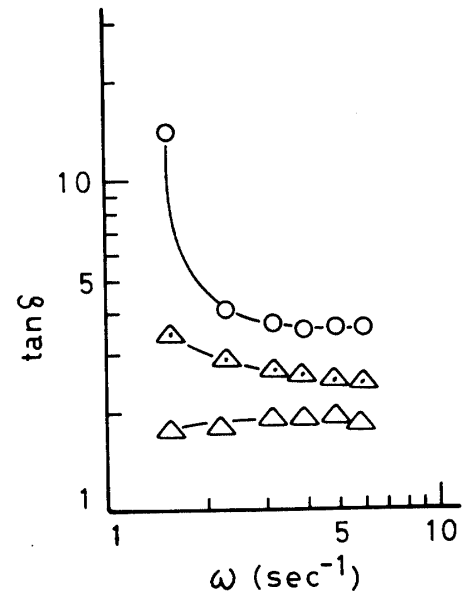


Fig.5(B) Effect of frequency on loss tangent of sodium carboxymethylcellulose at various concentrations.

○ 1.0%, △ 1.5%, ▽ 2.0%.

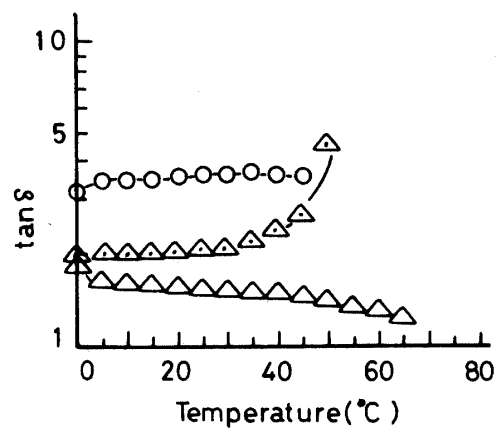


Fig.6(B). Effect of temperature on loss tangent of sodium carboxymethylcellulose at various concentrations.

○ 1.0%, △ 1.5%, ▽ 2.0%.

viscoelasticity of CMC at various concentrations is shown in Fig. 6(A). At 2.0% concentration, dynamic viscoelasticity showed remarkably high values about 280 poise and 570 dyne/cm² at 0°C and decreased with increasing temperature to 45 poise and 135 dyne/cm² at 70°C.

Loss tangent of 2.0% solution, as shown Fig. 6(B), showed 1.9 at 0°C, then decreased gradually and showed 1.2 at 70°C. These results indicate that intermolecular secondary bonding of it is stable for increasing temperature.

Discussion

It is well known that the aqueous solution of CMC shows a different degree of the degree of the substitution of carboxymethyl groups.⁵⁾ Namely, less uniformly substituted CMC contains more gel fragments than uniformly substituted one, the former shows a high degree of thixotropy⁶⁾. Consequently, it has a yield value. Such gel fragments of CMC originate from crystalline cellulose⁸⁾ which is mainly associated with intra- and intermolecular hydrogen bonds, indicating they may be associated with the bonds. On the other hand, much uniformly substituted CMC, whose degree of substitution is over 1.0, contains little gel fragment, therefore, and its non-Newtonian flow behavior approximates that of sodium alginate⁵⁾, exhibiting slight non-Newtonian flow behavior¹⁾. In such a high substituted CMC solution, having little gel fragment, the factor contributing to its non-Newtonian flow behavior is interpreted to represent interchain interaction, such as entanglements. In this experiments, we used a CMC, whose degree of substitution was evaluated to be 0.8.

Aqueous solution of CMC showed plastic flow behavior at high concentrations (1.5 and 2.0%). These results indicate that intermolecular secondary bonding is formed in aqueous solution. When the above results were adapted to the equation of Hershel and Bulkley, these curves were divided into two straight line at 2.8 and 5.9 sec⁻¹ of shear rates, respectively. These results were consistent with that of xanthan gum²⁾ which had such refraction points over the wide range of concentrations. Such situation of refraction points of CMC and xanthan gum for shear rates were different from that of locust bean gum, guar gum and the polysaccharide C-8, being situated at 10 and 20 sec⁻¹¹⁾. Furthermore, there was no refraction point in aqueous solutions of polysaccharide 271, which consisted mainly of α -1, 3 linked glycan¹⁶⁾. The compound seemed to exist in helical conformation, showing its flow curves of plastic behavior at high concentrations¹⁷⁾. The refraction point of CMC and xanthan gum²⁾ seemed to be a breaking point of molecular aggregation, while the refraction point of pseudoplastic fluids (locust bean gum, guar gum and the polysaccharide C-8) seemed to be a breaking point of the entanglements of molecular chains¹⁸⁾, which were participated main-

ly by the side chains of them¹⁾.

From the result of structural viscosity (Fig. 3), it was also evaluated that the molecular chains of CMC were oriented for shear direction at high shear rate region and 2.0% concentration. We have reported that xanthan gum is also a remarkably orienting polymer for direction²⁾. At 2.0% CMC solution, dynamic viscoelasticity as remarkably higher than that of 1.5% solution and kept high values during a variation in angular velocity, while loss tangent of it kept a moderate value about 1.8. This result indicates that intermolecular secondary bonding of CMC in aqueous solution is formed partially.

Nishida⁷⁾ reported that the dynamic viscoelasticity modulus of CMC solution decreased by an addition of urea. This result implies that its intermolecular secondary bonding is associated with hydrogen bonding.

Thus, the intermolecular secondary bonding of CMC in aqueous solution seemed to be associated with intra- and intermolecular hydrogen bonds at a high concentration partially.

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CMCの非ニュートン流動と動的粘弾性

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要 約

CMC, 分子量 120,000, 置換度 0.80, の水溶液は 1.5 および 2.0%濃度で塑性流動性を示し, それぞれの降伏値は 6 および 10 dyne/cm² であった。流動指数は 1.0%までは 1.0, 1.5 および 2.0%では屈折点前で 1.1, 後で 1.6 であった。ずり速度に対する屈折点の位置がキサントタンガムのそれらと一致した。動的粘弾性は 2.0%で急激な増大が見られ, $\tan \delta$ は周波数に関係なくほぼ一定 (1.8) であった。CMCのこのようなレオロジー特性は分子主鎖が部分的に会合していることによるものであることが認められた。

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