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Author(s)	Miyoshi, Emako
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Emako MIYOSHI

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Emako MIYOSHI

1. Introduction

We have long history of eating gel-like foods in Japan and these food hydrocolloids are very important for a wide range of food application, because many food hydrocolloids have been long used as texture modifiers, emulsion stabilizers, water absorption agents, gelling and thickening agents, and many other desirable characteristics. Since health authorities in most industrialized countries recommend a reduction of total and saturated fat, there is much interest in the potential of these polysaccharides for the formulation of low-fat and low-calorie foods.

Recently, with increasing of the global environmental problems, greater efforts have been made to develop the effective usage of traditional polysaccharides, because these polysaccharides are environmentally degradable and bioabsorbable. The biocompatibility of hydrocolloids can be used not only in the drug delivery system but also to supply wound dressings and replacements for human tissue. Even better is a human material replacement, either in the form of human skin or a membrane, which surrounds the placenta (human chorion amnion). The field of "Tissue Banking" has grown up rapidly to provide safe and sterile human tissue dressing, thus the medical applications have been rapidly advanced as a result of the basic research.

Theoretically, many scientists have made great effort to classify ‘gel' systems based on easily recognizable physical and rheological properties (te Nijenhuis, 1996). However, different types of gels have different structures and are studied by scientists with different backgrounds, i.e. physicists, chemists, chemical engineers, biologists, rheologists, etc., so that it might be difficult to describe a simple definition of a gel. Indeed, as D. Jordan-Lloyd stated in the introduction of ‘The problem of gel structure' in 1926, “the colloidal condition, the gel, is one which is easier to recognize than to define, and even recognition is confused by the fact that the limits between gel and sol, on the one hand, and gel and what may be termed curd, on the other, are not precise, but consist of a gradual change." Since this statement was made, scientific understanding has made significant advances and today there are many reviews, including in particular Hermans (1946), Flory (1974), Graessley (1974), Sherman (1969), Ferry (1980), E.R.Morris (1983), Clark and Ross-Murphy (1987), Morris and Ross-Murphy (1981), te Nijenhuis (1996).

Flory (1974) has proposed a classification of gels divided into four types: (1) well-ordered lamellar structures, including mesophases; (2) covalent polymer networks, completely disordered; (3) networks formed through physical aggregation, predominantly disordered, but with regions of local order; (4) particulate, disordered structures. According to this definition, undiluted cross-linked rubbers, which consist of one component, are also treated as gels. Almdal et al. (1993) have suggested that the term ‘gel' is used so indiscriminately that it has become ambiguous, and have proposed some phenomenological definition by focusing on the specific phenomenological characteristics; a gel is a soft, solid or solid-like material of two or more components, one of which is a liquid, present in substantial quantity. Hence, they stated that xylogels and undiluted systems should not be admitted as gels.

We regard a hydrocolloid gel as a material capable of supporting its own weight against gravity (i.e. maintaining its shape) over a practical timescale of days or weeks (Morris, 1983). Most hydrocolloid gels consist of molecular networks maintained by physical junction zones which can be disrupted by changes in temperature, pH, cation species, or consist of the temporary cross-linking which was formed simply by local chain entanglements resulting from topological constraints (Morris, 1982; Clark & Ross-Murphy, 1987; Clark, 1992; Rosss-Murphy, 1994). These gels belong to the third type of gels in Flory's classification (Flory, 1974) mentioned above. There are some physical gels, which contain some junction zones formed by covalent cross-linking, however, few polysaccharide gels include junction zones formed by covalent bonds.

The theoretical study of synthetic polymer by “tube” or reptation models (Doi and Edwards, 1986) has described successfully the difference between the viscoelastic behavior of covalently cross-linked gels and the entanglement systems.

Marvin and Oser (1962), Chompff and Prins (1968) and Graessley (1974) have proposed theoretical treatments to explain the dip of G" in the frequency spectrum. Bell et al. (1984) suggested that an appreciable reduction in G" corresponds to a slow dissipative process occurring on a time scale of at least several minutes, and reflects the ability of gels to flow and spread, given sufficient time for network rearrangement. However, both weak and strong gels give essentially the same mechanical spectrum, with $G' > G''$, and with both moduli largely independent of frequency, and η^* for both gels decreasing markedly with increasing frequency. Clark and Ross-Murphy (1987) have suggested that it is easy to define the difference between the polysaccharide strong and weak gels by the strain dependence.

As for the strain dependence of shear modulus (in terms of the reduced modulus G/G_0) of entanglement system, it is clear that a weak gel is much more strain dependent than the strong gel or the entanglement network. It has been reported (Ross-Murphy, 1984) that the strain dependence of G' was very similar for entanglement systems and strong gels, with the linear viscoelastic strain extending to approximately 25%. For weak gels, the linear viscoelastic strain is usually ＜5%. Therefore, it is possible to distinguish between strong gels and weak gels, because they should give rather similar mechanical spectra, but have quite different strain dependence. Moreover, Ross-Murphy and Shatwell (1993) have suggested that the differences between strong gels and weak gels are exhibited by large deformation measurement; at large deformation, strong gels rupture and fail and never recover without melting, and in contrast, weak gels recover and can flow without fracture.

There are number of other methods for determining the gel point, based on determining by the storage modulus G' at a certain frequency as a function of time or temperature. One method is to determine the instant or temperature at which G' becomes to be detected. Another method is to determine the cross-over point of G' and G" as a function of time or temperature. However, Ross-Murphy (1994) has investigated the gel point of gelatin aqueous solutions by both methods, and concluded that both were rather imprecise. Winter and Chambon (1986) have found experimentally that the mechanical behavior of crosslinking polymers could be described at the gel point by a power law relaxation shear modulus.

Moreover, it is important to perform large deformation measurements as well as dynamic viscoelastic measurements in linear viscoelastic regime, in order to clarify the structural changes of aqueous environment surrounding polysaccharides. Therefore, in this study, the rheological properties of water soluble or insoluble polysaccharides were investigated by the steady-shear viscosity measurement.

Cellulose consists of sufficient chain length to be insoluble in water or dilute acids and alkalis at ordinary temperatures, so that it isn’t easy to use itself in the food industry. However, the physical modification of the cellulose (microcrystalline cellulose) offers several properties and provides effective stabilization in variety of food product systems. The colloidal microcrystalline can easily disperse in water and form a unique gel network which gives the functional properties necessary of effectively suspend solid in food systems. Moreover, the colloidal microcrystalline cellulose dispersed in water has been used to simulated fat in various food applications such as ice cream, salad dressing, sauces and gravies.

Gellan gum, is one of widely used fermentation materials, may offer a solution to many of problems encountered in the current gelling agents (Phillips & Williams, 2000), because it can form a transparent gel in the presence of multivalent cations, which is resistant to heat and acid. Since gellan gum can provide a wide-range of gel textures by careful control of added salts, these gels can give the same texture as other polysaccharide gels or create new textures. It has been reported that the brittle gels such as gellan gum gels give better flavor release than more elastic materials.

The aim of this paper is to present our findings on the non-Newtonian flow behavior of water-soluble polysaccharide (gellan gum aqueous solutions) (Miyoshi et al., 1997a; Miyoshi & Nishinari, 1999, 2000; Miyoshi, 2003 2006, 2008a) or water-insoluble polysaccharides (micro-particulated cellulose suspensions) (Miyoshi et al., 1997b; Miyoshi, 2005, 2008a; Nishinari et al., 1998) comparing with some advanced references, and to show some useful results for various applications. Especially, our results investigating the rheological and thermal properties of these polysaccharides were obtained using steady-shear viscosity measurement, involving some theoretical approach.

2. Materials and Methods

2.1. Material

Cream-like suspensions consisted of micro-particulated cellulose with various sizes (1.1, 1.8, 3.2, 6.5 μm) (10wt%) were kindly supplied by Asahi Chemical Industries.

Dispersions of micro-particulated cellulose were prepared at different concentrations by adding the required distilled water to the required amount of cream-like suspensions of micro-particulated cellulose (10wt%), and by stirring at 25℃ overnight. The concentration of suspensions including micro-particulated cellulose were changed from 1~10wt%.

Purified sodium form gellan gum sample kindly supplied by San-Ei Gen F.F.I. Inc., Osaka, Japan was used in the present work. The contents of the inorganic ions Na^+, K^+, Ca^{2+} and Mg^{2+} were determined as Na 2.59%, K 0.009%, Ca 0.02% and Mg 0.001%, respectively.

The gellan gum solutions were prepared in the same way as described previously (Miyoshi et al., 1994; Miyoshi, 1996).

2.2. Experimental

Mechanical spectra and thermal scanning rheological measurements were performed within a linear viscoelastic regime with a Dynamic Stress Rheometer DSR from Rheometrics Co.Ltd., NJ, USA, using a parallel plate geometry of 50mm diameter with radial grooves to avoid gel slippage (Miyoshi et al., 1994; Miyoshi, 1996).

The steady-shear viscosity was measured at various temperatures under conditions of steady shear on a RFSI fluids spectrometer from Rheometrics Co., N.J. USA, using a cone and plate geometry of 25mm diameter, over a steady-rate range from 0.01 to $100s^{-1}$ over 10 min. The shear rate was changed stepwise from 0.01 to $100s^{-1}$ over 10 min.

The details of rheological measurements have been described previously (Miyoshi et al., 1994; Miyoshi, 1996).

3. Rheological Properties of Micro-Particulated Cellulose Suspensions

3.1 Steady-Shear Viscosity

Figure 1 shows the shear rate dependence of viscosity or shear stress for micro-particulated cellulose suspensions (6.5 μ m) of various concentrations at 25℃, respectively. Water showed a Newtonian flow behavior (Graessly, 1974), and had a viscosity of about 10mPas, irrespective of shear rate. The shear stress for water increased linearly with increasing shear rate. However, water containing only 1% micro-particulated cellulose drastically changed to a pseudoplastic behavior (Graessly, 1974); this suspension showed the Newtonian behavior only at very low shear rated and the steady-shear viscosity decreased with increasing shear rate. For a 1% micro-particulated cellulose suspension, a yield stress to disrupt an ordered structure before flowing freely. Moreover, for micro-particulated cellulose suspensions (＞2%), the viscosity drastically decreased with increasing shear rate, and the Newtonian plateau at low shear rate could not be accessed experimentally. With increasing concentration of micro-particulated cellulose, the yield stress became larger and the stress for these suspensions showed little shear rate dependence. The similar behavior has been shown in a xanthan gum solution (Morris et al., 1990). Therefore, with increasing concentration of micro-particulated cellulose, structures of suspensions may become more rigid.

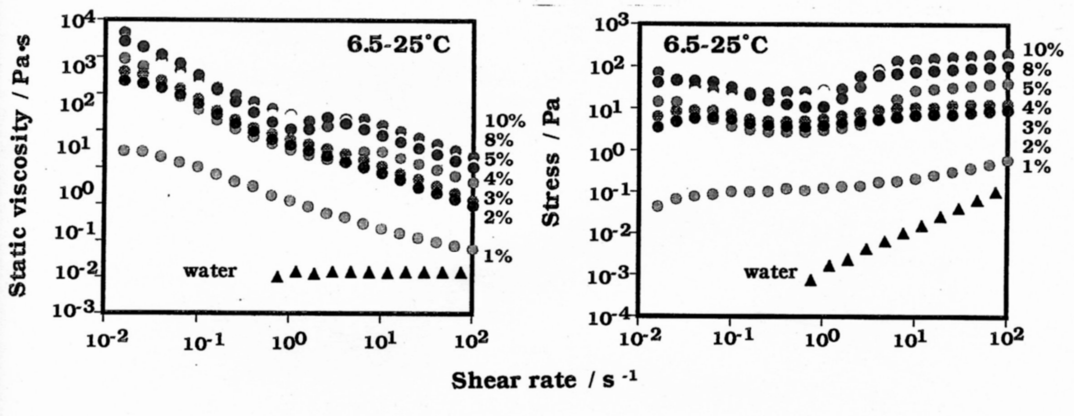

Figure 1

Shear rate dependence of viscosity or shear stress for micro-particulated cellulose suspensions (6.5μm) of various concentrations at 25℃.

Figure 2 shows the flow curve behavior for 10% micro-particulated cellulose suspensions (3.2 μ m) at 5, 25 or 60℃. This figure shows the effects of experimental temperatures on the flow curve of micro-particulated cellulose suspension during increasing and decreasing shear rate between 0 and 100s^{-1}.

At 5℃ and 25℃, similar flow curves were observed; these systems required a yield stress and the shear stress monotonically increased with increasing shear rate, and the flow curve during the decreasing process of shear stress was almost similar to that during increasing, although the final stress (observed at 50s^{-1}) at 25℃ was slightly larger than that at 5℃.

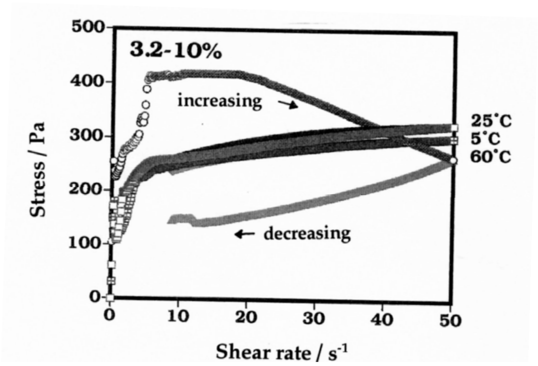

Figure 2

Flow curve behavior for 10% micro-particulated cellulose suspensions (3.2μm) at 5, 25 or 60℃.

Therefore, at 25℃ or 5℃, the orientation of micro-particulated cellulose could form a more ordered structure with increasing shear rate. However, when at both temperatures, the shear rate was applied to a 10% micro-particulated cellulose suspension up to 100s^{-1}, the shear stress showed a maximum at a certain shear rate slightly became smaller than that during the increasing process, which indicated the thixotropy. Therefore, with increasing shear rate, the suspensions conformationally became more immobile, so that the ordered structure may be easily broken by the fairly high shear rate. Micro-particulated cellulose suspensions at lower concentration that 10% showed a slight rheopecticity even by the applied shear rate up to 100s^{-1} (data not shown). Therefore, at a constant condition of applied shear rate, the flow properties depended on the concentration of micro-particulated cellulose.

The flow curve at 60℃ was remarkably different from that at 25℃ or 5℃, because it showed a significant thxotropic behavior. At 60℃, over the yield stress, the shear stress drastically increased up to a certain shear rate, and the maximum stress at 60℃was significantly larger that that at 25℃ or 5℃. However, over the maximum stress, the shear stress gradually decreased, so that the final stress (observed at 50s-1) at 60℃ significantly became smaller than that at 25℃ or 5℃. Moreover, the flow curve during the decreasing process of shear rate became markedly smaller than that during increasing process. In the dynamic visicoelastic measurement (data not shown), both moduli gradually increased with increasing temperature; therefore, the micro-particulated cellulose suspensions could form a more solid-like structure with increasing temperature. However, as illustrated in Figure 2, the ordered structures that formed at higher temperatures became much brittle, so that this structure may be easily broken by the large deformations.

Figure 3 shows the flow curve behavior for 10% micro-particulated cellulose suspensions with various particle size from 1.1 to 6.5 μ m at 5, 25 or 60℃. This figure shows the effects of particle sizes of micro-particulated cellulose on the flow curve during increasing and decreasing shear rate between 0 and 100s^{-1}.

At 5 ℃, micro-particulated cellulose suspensions with any particle size showed similar to that during decreasing shear rate, and the effects of particle size were vary small. Therefore, micro-particulated cellulose suspensions at 5℃ seemed to retain stable, structurally. At 25℃, any suspension showed a thixotropy, however, the flow curve changed depending on the particle size of micro-particulated cellulose. With increasing particle size, the yield stress became smaller and the dependence of stress on the shear rate became less conspicuous. For micro-particulated suspensions with particle size of 6.5 μ m, the maximum of stress was the smallest, and the shear rate at maximum was observed at the lowest shear rate. At 60℃, any suspension showed a marked thixotropic behavior, and the differences depending on the particle sizes was smaller than those at 25℃, although both yield stress and maximum of stress were the highest for suspension with particle size of 1.1 μ m.

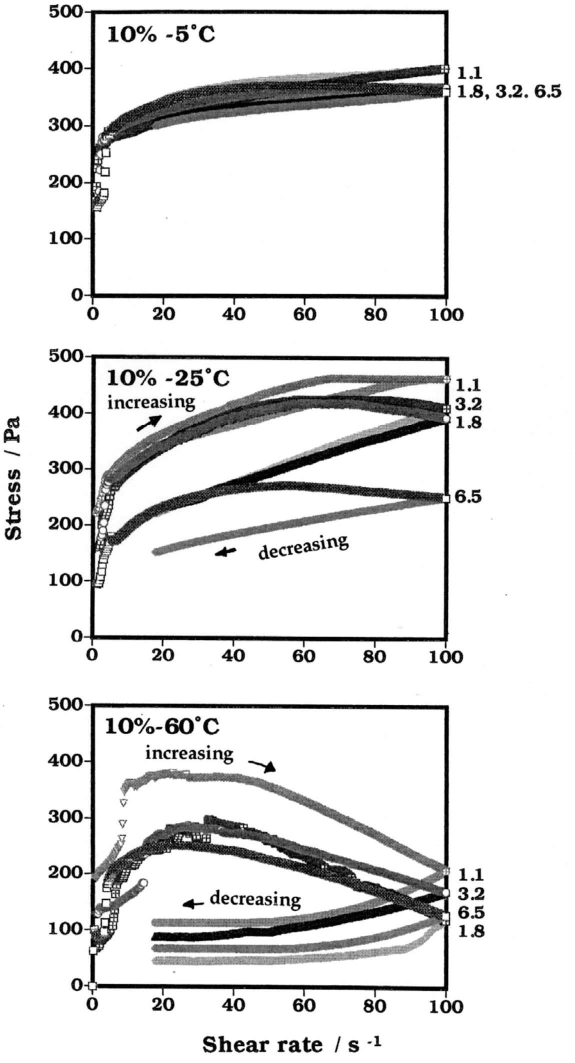

Figure 3

Flow curve behavior for 10% micro-particulated cellulose suspensions with various particle sizes (1.1, 1.8, 3.2, 6.5μm) at 5, 25 or 60℃.

3.2. Separating of Entropic and Energetic Terms of Storage Modulus G’

For the more detailed examination of these thermo-elastic phenomena of micro-particulated cellulose suspensions, it is necessary to investigate the thermo-dynamic quantities involving internal energy and entropy. Nishinari et al. (1984) have tried to separate the entropic and energetic terms from elastic modulus of agarose gels. This treatment does not assume any molecular model such as a reel-chain model (Nishinari et al., 1985) or a zipper model (Nishinari et al., 1990), however, the internal energy and entropy contributions to the elasticity are directly obtainable from the experimental storage modulus-temperature plot. Therefore, it was tried to discuss in terms of an entropic and energetic contribution. However, as shown in Figure 2, in the case of relatively higher scanning rate (1.0℃/min), the large thermal hysteresis was observed. With decreasing scanning rate, these thermal hysteresis became smaller, therefore, for this analysis, we have chosen the thermal scanning rheological results obtained at 0.2℃/min.

Figure 4 shows the storage modulus G’ for micro-particulated cellulose suspensions (6.5 μm) of various concentrations as a function of temperature, and the separation into entropic G_s and energetic G_u contributions. Taking into account the possible errors, the experimental values G’ was approximated by parabolic functions having coefficients determined by the least squares method. Elastic modulus can be separated to entropic contribution and energetic contribution as has been done for agarose gels (Nishinari et al., 1984).

$$G \equiv G_t = G_s + G_u$$

$$G_s = -(T/\gamma)(\partial \Delta S_v / \partial \gamma)_T = T(\partial G/\partial T)_\gamma$$

$$G_u = (1/\gamma)(\partial \Delta U_v / \partial \gamma)_T = -T^2(\partial/\partial T)(G/T)_\gamma$$

where G and γ are the shear modulus and the shear strain, respectively. The quantities ΔS_v and ΔU_v represent the change in entropy density and internal energy density for the deformation at a constant volume.

The entropic contribution G_s and energetic contribution G_u for micro-particulated cellulose suspensions are shown by a broken curve and a dot-line curve together with observed (total) storage modulus G ($\equiv G_t$) (thick solid curve) in Figure 4 respectively. As described previously (Nishinari et al., 1984), the meaning of $G_s > 0$ is that if the entropy decreases by deformation, there will appear resistance against it; whereas the meaning of $G_s < 0$ is such, if the entropy increases by the deformation, the deformation will be promoted by itself.

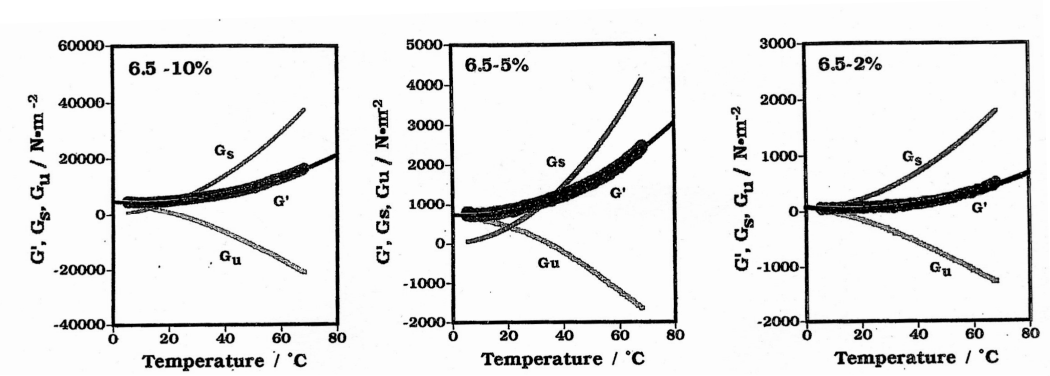

Figure 4

Storage modulus G’ for micro-particulated cellulose suspensions (6.5μm) of various concentrations as a function of temperature, and the separation into entropic G_s and energetic G_u contributions. Cooling and heating rate, 0.2°C/min; Freq. ω=1.0rad/s.

As illustrated in this figure, at any suspension, G_u was predominant over G_s at lower temperatures, however, G_s monotonically increased while G_u gradually decreased with increasing temperature, although the change of both G_s and G_u with increasing temperature became significant larger with increasing concentration of micro-particulated cellulose. This tendency was remarkably different from that of water-soluble hydrocolloids such as agarose, because for agarose gels, the entropic part decreased while the energetic part increased with increasing temperature (Nishinari et al. 1984). The increase of G’ with increasing temperature could be explained by the reduction of energetic nature or increase of entropic nature in micro-particulated cellulose suspensions. This may be attributed to the water-insoluble networks that are provided not by covalent bonds but rather than by secondary bonds between aggregates of particles. Since these bonds increased with increasing temperature, the entropic elasticity of micro-particulated cellulose may be supported by the secondary bonds such as hydrophobic bonds. However, with increasing temperature, Brownian motion, which is responsible for the entropic term, became more active, so that at higher temperatures, micro-particulated cellulose suspensions showing a larger elasticity became weaker by the large deformation (Figure 2 and Figure 3). The similar tendency of this figure was observed in suspensions with other micro-particle sizes (1.1 1.8 3.2 μ m), and the cross-over temperature of G_s and G_u didn’t depend so much upon the concentration or particle size of micro-particulated cellulose (data not shown).

It has been reported that the suspension of polystyrene latex showed a hexagonal or cubic arrangement by metallurgical microscope (Kose et al., 1973). If these micro-particulated cellulose suspensions are such a colloidal crystal, the entropy should increase by deformation. Thus, judging from the experimental finding and a thermo-dynamical analysis that G_s is always positive, the micro-particulated cellulose suspension isn’t a colloid crystal. It has been suggested that the structure tends to a more disordered state with increasing temperature, and that the elasticity originates from thermal motion of micro-particles. These micro-particles can't form a strong network by covalent bonds or by hydrogen bonds as in rubber-like materials or in true gels, but form a tenuous network structure by hydrophobic interaction. Since cellulose and its derivatives are known to be semi-flexible chains; the persistence length lie between 3 and 25nm and are larger than that of typical vinyltype polymer (~1nm), but markedly smaller than that of a typical stiff chain such as DNA (~50nm) (Kamide and Saito, 1987), the entanglement of molecular chains may not be so important as in solution of flexible polymers.

Consequently, these results suggested that micro-particulated cellulose suspensions showed an entropic elasticity and became a more elastic structure with increasing temperatures, however, this structural change accompanied with temperature was thermo-reversible. Moreover, the water-insoluble networks formed at higher temperatures were easily broken by the large deformation.

4. Non-Newtonian Flow Behavior of Gellan Gum Aqueous Solutions

4.1. Steady-shear viscosity of gellan gum

Figures 5 (a)~(d) show the shear rate dependence of steady-shear viscosity for 1%, 2%, 3%, 3.5% gellan gum solutions without salt at various temperatures. A 1% gellan gum solution showed a flow behavior close to the Newtonian flow at 40 or 30℃, and had a viscosity of about 10mPas (at 40℃) or about 100mPas (30℃), nearly irrespective of shear rate (Figure 5(a)). However, a 1% gellan gum solution changed to a shear thinning behavior at 20, 10 or 5℃. The range of Newtonian plateau at low shear rate gradually became narrower, and the viscosity became more shear-rate-dependent with decreasing temperature. Intermolecular entanglements disrupted by the imposed deformation could make new interactions at low shear rates, so that there is no overall change in the extent of entanglement, which corresponds to the Newtonian region in flow curves (Morris & Ross-Murphy, 1981). When the rate of disruption becomes greater than the rate of formation of new entanglements, the onset of shear thinning may occur. The extent of re-entanglement decreases with increasing shear rate, so that the viscosity for the solution may gradually decrease (Morris & Ross-Murphy, 1981). A behavior close to the Newtonian flow was observed at 40℃ for a 2% gellan gum solution (Figure 5(b)).

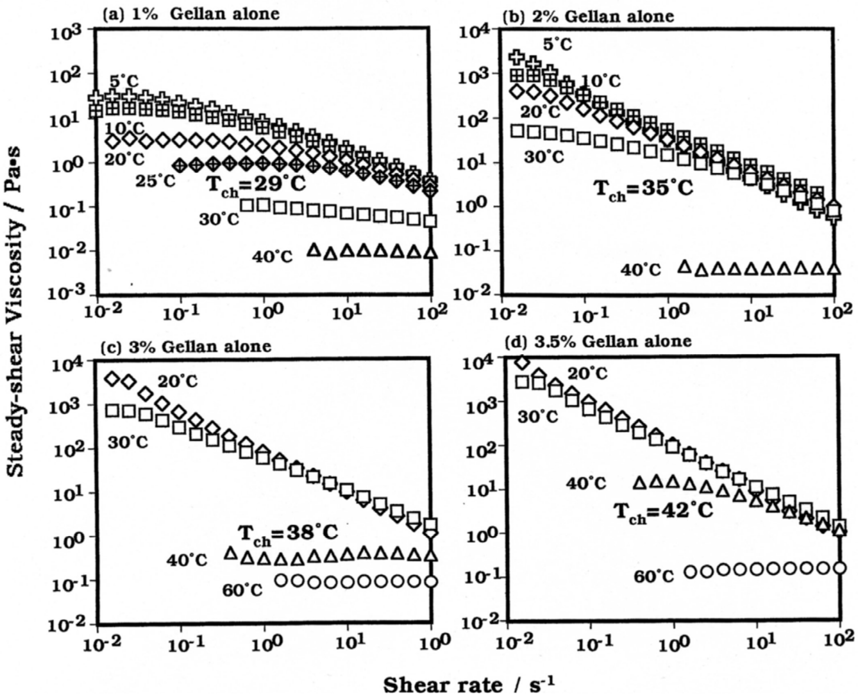

Figure 5

Shear rate dependence of viscosity for 1%, 2%, 3% and 3.5% gellan gum solutions without salt at various temperatures.

Steady-shear viscosity measurement indicated that gellan gum solutions tend to show more shear thinning behavior with the conformational change from coil to helix because the helix may be more easily orientated along the shear flow than coil. The range of Newtonian plateau at low shear rate gradually becomes narrower with development of an ordered structure of gellan gum solution.

For a 3% or 3.5% gellan gum solution (Figure 5(c), (d)) as well as a 1% or 2% solution (Figure 5(a), (b)), the flow curve showed a behavior close to the Newtonian flow at$>T_{ch}$ (38℃ for a 3% solution or 42℃ for a 3.5% solution, respectively) while it changed to the shear thinning behavior at$<T_{ch}$. However, at lower temperatures where gellan gum formed an elastic gel, the steady-shear viscosity measurement could not be performed.

Figures 6 (a)~(d) show the stress as a function of shear rate for 1%, 2%, 3%, 3.5% gellan gum solutions without salt at various temperatures. Open symbols represent flow curves for these solutions with increasing shear rate from 0.01s^{-1} to 100s^{-1}, and closed symbols represent those with decreasing shear rate from 100s^{-1} to 0.01s^{-1} after the increasing process of shear rate. For any solution, the stress increased linearly with increasing shear rate at higher temperatures than T_{ch}, and the yield stress seems to be very small. The slope of double logarithmic plots of stress against shear rate at higher temperatures (1% at 40 and 30℃, 2% at 40℃, 3% at 60 and 40℃, and 3.5% at 60℃) was approximately 1, as in the Newtonian flow. However, the yield stress was obtained by fitting the extrapolation to zero shear rate in the linear scale plot at relatively lower temperature (＜T_{ch}) (2% at 5℃, 3% at 20℃, and 3.5% at 30 and 20℃) (data not shown) and the stress did not show no remarkable increase with increasing shear rate, i.e. became markedly shear-thinning. For a 3.5% solution at 20℃, the parameter n in a Herschel and Bulkeley model $\tau - \tau_t = k\dot{\gamma}^n$ approached unlimitedly to 0, therefore this solution showed a marked shear-thinning behavior.

For 2%, 3% and 3.5% solutions at sufficient low temperatures (2% at 5℃, 3% at 20℃, and 3.5% at 30 and 20℃), the flow curves showed a maximum stress at a fairly low shear rate and then the steady-stress became little shear-rate dependent (open symbols). However, the flow curves for these solutions during the decreasing process of shear rate (closed symbols) showed no maximum stress, moreover the difference between flow curves during the increasing and decreasing processes became larger with decreasing shear rate.

For 2%, 3%, 3.5% solutions at relatively higher temperatures and 1% solutions at any temperature, the differences between flow curves during the increasing and decreasing processes were negligibly small, compared to those for 2%, 3% and 3.5% solutions at sufficiently low temperatures. This reason would be explained as follows. As illustrated in the previous study (Miyoshi, 2008b), at any temperature from 30℃ to 0℃, the mechanical spectra for a 1% gellan gum solution showed a typical behavior of a dilute polymer solution with $G' < G''$ throughout the accessible frequency range, and both moduli were strongly frequency dependent. Frequency dependence of moduli tended to $G' \sim \omega^2$, $G'' \sim \omega$ at 30～15℃, which is a characteristic feature of dilute polymer solutions (Doi & Edward, 1986). However, both moduli of this solution slightly deviated from this behavior at 0℃. Therefore, the individual helices of gellan gum molecules were formed at a certain temperature (T_{ch}) during cooling, and then these helices gradually aggregated with decreasing temperature. This ordered structure, however, does not lead to gel formation because the number of helical aggregates is not sufficient to develop a continuous network throughout the whole space. On the other hand, for the concentrated gellan gum solutions (＞2%), where the number of aggregated helices exceeds a critical value on cooling, the cross-over temperature of G' and G" appeared at temperatures lower than T_{ch} in the thermal scanning rheology, as described previously (Miyoshi, 1996). This transition corresponded to the sol-gel transition, because these solutions changed to a weak gel at temperatures lower than the crossover temperature (T_{sg}), as described previously (Miyoshi, 1996). Therefore, a 2% solution at 5℃, 3% solution at 20℃, and 3.5% solution at 30 or 20℃ behaved as a weak gel, and the flow curves for these stiff structures showed a distinct maximum stress at a fairly low shear rate.

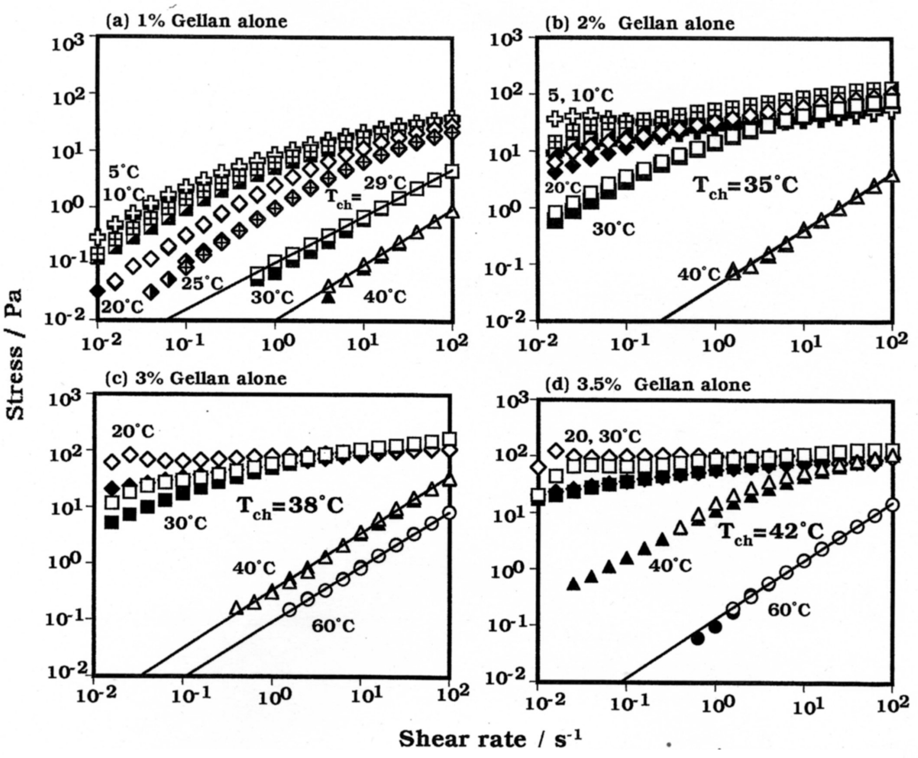

Figure 6

Stress as a function of shear rate for for 1%, 2%, 3% and 3.5% gellan gum solutions without salt at various temperatures.

It is difficult to understand that the stress slightly decreased with increasing shear rate. This might be attributed to one of or both the following factors; 1) These stiff structures (weak gels) might be ruptured at a certain shear rate which the stress showed a maximum; 2) Water exuded out from the solution forms a thin layer between cone (and/or plate) and the solution, and causes the slippage. After showing the slight decrease of stress, these solutions flowed and became strongly shear thinning fluids whose stress was much less dependent on shear rate. After increasing process of shear rate, weak gels would require enough time to recover their original properties when shearing is stopped, so that the shear stress in the flow curves for these systems during the decreasing process of shear rate became smaller than that during the increasing process of shear rate, especially at lower shear rate range. These systems could not flow by the shear stress lower than yield stress in the increasing process, however in the decreasing process, these structures have already been broken down by large deformation and flowed freely, so that the maximum, observed in these systems at low shear rate in increasing process could not appear. The distinction between weak gels and entanglement systems seems to be demonstrated using the Cox-Merz rule (Morris, 1982), as will be described in the next section.

4.2. Applicability of the Cox-Merz rule

It has been suggested that for solutions of entanglement systems such as xanthan gum (Ross-Murphy et al., 1983; Richardson & Ross-Murphy, 1983; Rochefort & Middleman, 1987; Ross-Murphy, 1994), galactomannan (Richardson & Ross-Murphy, 1987), gellan gum (Robinson et al., 1991; Cesaro et al., 1992), the steady-shear viscosity (η) and the magnitude of complex viscosity ［$\eta^* = (G'^2+G''^2)^{1/2}/\omega$］ superimpose closely at equivalent values of shear rate ($\dot{\gamma}$ /s^{-1}) and frequency (ω/rad･s^{-1}), i.e. these solutions obey the Cox-Merz rule. If the mechanical spectra for the solutions show a weak-gel behavior, η^* is significantly larger than η indicating that the weak gel networks can survive by small oscillatory deformation but may be ruptured by large deformation, so that these solutions tend to depart from the Cox-Merz superposition (Ross-Murphy, 1994; Morris, 1983).

Figures 7 (a)~ (c) show the shear rate dependence of steady-shear viscosity η and frequency dependence of the absolute value of complex viscosity η^* for 1%, 2%, 3% gellan gum solutions without salt at various temperatures. As shown in the previous study (Miyoshi, 2008b), a 1% solution behaved as a dilute polymer solution (with $G' < G''$ throughout the accessible frequency range, and both moduli were strongly frequency dependent) even if gellan gum molecules took a helix conformation. The shear rate dependence of η (closed symbols) , was in good agreement with the frequency dependence of η^* (open symbols) at any temperature from 30℃ to 5℃, which showed that the Cox-Merz superposition was well satisfied (Figure 7(a)).

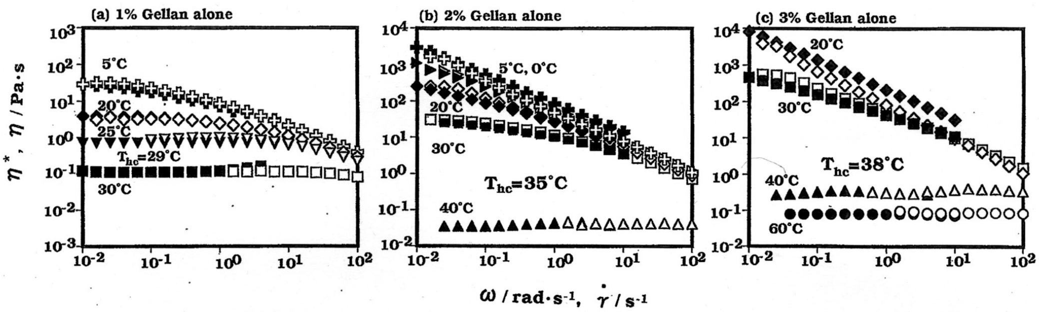

Figure 7

Shear rate dependence of the steady shear viscosity η and frequency dependence of the abusolute value of complex viscosity $|\eta^*|$ for 1%, 2%, 3% gellan gum solutions without salt at various temperatures ((a)~(c)).

The viscoelastic behavior for a 2% gellan gum solution was that of a dilute polymer solution at 40℃ and a concentrated polymer solution at 30 or 20℃ (which showed a cross-over of G' and G" at a certain frequency) (Miyoshi, 2008b), and this solution at these temperatures obeyed the Cox-Merz rule (Figure 7(b)). However, at 5 or 0℃, a 2% gellan gum solution changed to a weak gel behavior (Miyoshi, 2008b), so that η* (open symbols) was slightly larger than η, especially at high shear rate (frequency), indicating the departure from the Cox-Merz superposition (Figure 7(b)). For a 3% solution (Figure 7(c)), the Cox-Merz superposition was satisfied when this solution behaved as a dilute polymer solution (at 60 or 40℃) or a concentrated polymer solution (30℃) (Miyoshi, 2008b), while there was no evidence of the Cox-Merz superposition when this solution showed a weak gel behavior(at 20℃) (Miyoshi, 2008b).

These tendencies were similar to those of xanthan gum solutions, however, the departures from the Cox-Merz superposition seem to be more pronounced for xanthan gum (Ross-Murphy et al., 1983; Richardson et al., 1987; Rochefort & Middleman, 1987; Ross-Murphy, 1994) than for gellan gum in the present study. Xanthan gum shows the disorder-order transition on cooling or on addition of salt (Cesaro et al., 1992), which is analogous to that of gellan gum, however this transition temperature was significantly higher than that of gellan gum. Since for a polysaccharide such as xanthan gum, most of reports investigating the validity of Cox-Merz superposition have used the results obtained at room temperature (around 25℃), it has been reported that the mechanical spectra of xanthan solution around 25℃ did not change to the behavior of dilute polymer solution except at quite a low concentration of polymers (Ross-Murphy, 1994).

As is well known for biopolymers such as gellan or xanthan, even a subtle difference in molecular structure and molecular weight can lead to a significant difference in their rheological properties. Therefore, the reason why the difference between η* and η of gellan gum showing a weak gel behavior was markedly smaller than that of xanthan gum showing also a weak gel behavior seems to be related with the difference in molecular conformation and molecular weight.

For the present sample, the number average molecular weight M_n for soluble tetramethylammonium-type gellan determined by osmotic pressure measurement was shown as 5.0×10^4 at 40℃ and 9.5×10^4 at 28℃ (Ogawa, 1999). Therefore, M_n at 28℃ was twice as large as that at 40℃, which suggested an association of two molecules at 28℃ (Ogawa, 1999). In the ordered state for the present sample (where gellan gum molecules took a double helical conformation) the weight average molecular weight M_w for soluble tetramethylammonium-type gellan determined by light scattering measurement was shown as 2.38×10^5 at 27℃ (Akutu & Kubota, 1999). By comparison of M_w with M_n which obtained in the ordered (helical) form, the present gellan has a polydispersity index of approximately M_w/M_n=2.5, which substantially corresponded to that calculated for typical of polydispersion (M_w/M_n=2). The molecular weight of xanthan gum has been reported (Ross-Murphy et al., 1983; Richardson et al., 1987; Rochefort & Middleman, 1987; Ross-Murphy, 1994; Cesaro et al., 1992) to be approximately $1\sim7\times10^6$, which has been much larger than that of gellan gum.

It has been reported (Dentini et al., 1988) that both gellan gum and xanthan gum had significant larger values of Kuhn segment length than DNA (ca.120nm), and that all the microbial polysaccharides shown in the reference (Dentini et al., 1988) have approximately the same Kuhn segment lengths, although the statistical variation of Kuhn segment length for gellan gum was slightly larger than that for xanthan gum. From the chain stiffness drawn from static light scattering data (Dentini et al., 1988), it has been suggested that the Kuhn segments in xanthan gum behaved like truly rigid rods while those in gellan gum might have some flexibility. This fact might influence the differences of rheological behavior between xanthan gum and gellan gum mentioned above.

Graessley and Segal (1969) have suggested that as the molecular weight of polystyrene became larger, the shear-thinning behavior of polystyren solutions became more conspicuous. Therefore, the ordered structure of xanthan gum may be more easily broken down along the shear flow, compared to that of gellan gum, because the molecular weight of xanthan gum was much larger than that of gellan gum as described above. It has been reported that xanthan gum could form a weak gel at room temperature even at a low concentration (Ross-Murphy, 1994). However, the helices of gellan gum molecules can not form a weak gel if the concentration is not high enough (> 2.0%) and the temperature is not low (<7℃ for a 2.0% solution) (Miyoshi, 2008).

It has been reported (Robinson et al., 1987; Cesaro et al, 1992) that at higher temperatures, gellan gum solutions with a random coil conformation obey the Cox-Merz rule, while at temperatures below the transition, they tend to depart from this rule, as in the case of xanthan gum. Since the gellan gum solution (<2%) in the present work behaved as a dilute polymer solution even at temperatures much lower than the coil-helix transition (T_{ch}), the Cox-Merz rule was obeyed. However, the concentrated gellan gum solutions (≧2%) could behave as a weak gel since the sufficient aggregates of helices were formed at temperatures below the sol-gel transition temperature T_{sg}, so that the Cox-Merz superposition was satisfied at temperatures higher than T_{sg} but failed at temperatures lower than T_{sg}. The cr a function of concentration for gellan gum solutions itical-shear-rate value ($\dot{\gamma}_c$) of the onset of shear-thinning behavior as without salt at 30℃ is shown in Figure 8. At this temperature, the $\dot{\gamma}_c$ value decreased with increasing concentration of gellan gum; the concentration dependence of the critical shear rate was $\dot{\gamma}_c \sim c^{-3}$, which was in good agreement with experimental results obtained by Fouissac et al.(1993) and Mo et al. (1999). It has been suggested that in the semi-dilute regime for hyaluronate solutions with NaCl, the dependence of $\dot{\gamma}_c$ on M_w and c is given by $M_w^{-4.8}$ (Fouissac, 1993). We should investigate the flow behavior of gellan gum having different molecular weights with narrow molecular weight distribution to achieve a better understanding of the gelation mechanism.

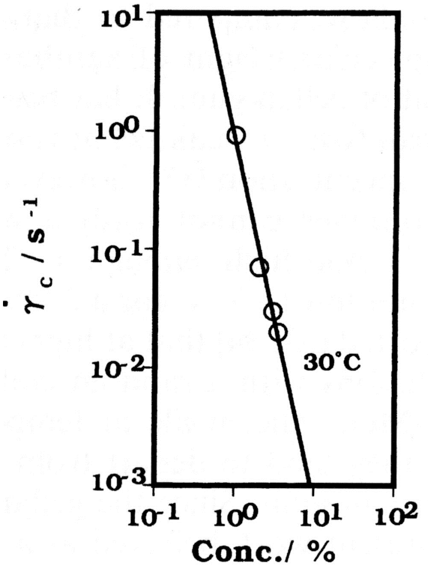

Figure 8

The critical-shear-rate value ($\dot{\gamma}_c$) of the onset of shear-thinning behavior as a function of concentration for gellan gum solutions without salt at 30℃.

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Structural Changes of Aqueous Environment Surrounding Water-Soluble or Water-Insoluble Polysaccharides

Emako MIYOSHI

Throughout the world there is a growing belief that natural foods are an integral part of a healthy life style. With an increased comsumption use of processed and simulated foods, health-conscious consumer needs reduced fat and enhanced fiber foods of all types, so that the food producers have sourced an increasing proportion the raw materials from nature itself. This objective can be achieved using natural type materials that have low calorific values, although foods containing such materials must match the quality of the original product and without adverse dietary effects.

Performing large deformation measurements as well as dynamic viscoelastic measurements in linear viscoelastic regime, is important to clarify the structural changes of aqueous environment surrounding polysaccharides. Therefore, in this study, it has been described our findings on the non-Newtonian flow behavior of water soluble polysaccharide (gellan gum aqueous solutions) or insoluble polysaccharides (micro-particulated cellulose suspensions) in comparison with some advanced references, and to show some useful results for various applications. Especially, our results investigating the rheological and thermal properties of these polysaccharides were obtained using steady-shear viscosity measurement, involving some theoretical approach.

Our results suggested that micro-particulated cellulose suspensions showed an entropic elasticity and became a more elastic structure with increasing temperatures, however, this structural change accompanied with temperature was thermo-reversible. Moreover, the water-insoluble networks formed at higher temperatures were easily broken by the large deformation.

Judging from our results, it was suggested that as gellan gum molecules took a coil conformation, gellan gum solution showed a behavior close to the Newtonian flow, while as gellan gum molecules took a helical conformation, gellan gum solution showed the shear thinning behavior. Furthermore, with increasing of ordered structure during cooling, the range of Newtonian plateau gradually became limited to very low shear rates.