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Rheological properties and microstructures of Carbopol gel network system

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Abstract Carbopol gel systems have been studied using steady, oscillatory rheology, and cryoscanning electron microscopy (cryo-SEM) analysis in order to elucidate the nature of the different microstructures of the gel in relation to polymer concentration as well as triethanolamine (TEA) content. The effect of changing the concentration of Carbopol (0.1–4 wt%) for 0, 1, and 10 wt% TEA has been investigated. Cryo-SEM revealed that honeycomb structures were observed in the gel system depending on the amount of TEA and Carbopol while the irregular fibrous three dimensional gel network systems were seen at the lower level of polymer content even in the high concentration of TEA. In addition to that, as the amount of polymer was increased, strings of fibrous network became thicker and of honeycomb-like structure. Shape of storage modulus-shear stress curve in the dynamical

rheometric study was significantly changed as a result of variation in the microstructures while frequency sweep curve and yield values obtained from the model fitting in the steady rheological measurements couldn't reflect the structural difference of Carbopol gels. Two distinct relaxation phenomena were appeared with increase in polymer concentration as well as TEA concentration. Temperature dependence of the stress sweep experiment was measured and shown that the effect of temperature (1–80 °C) on the shape of the curve was the similar trend with that of TEA and polymer concentrations, although the temperature dependency on the increment was much weaker than TEA concentration.

Keywords Rheology · Carbopol · Cryoscanning electron microscopy · Temperature effect

Introduction

Poly(acrylic acid) polymers as an anionic hydrogel are widely used to improve the rheological properties of thickening systems. Those cover a wide range of applications from cosmetics to pharmaceutical uses for emulsification, stabilization and rheological control [1, 2, 3, 4, 5]. They are also used to control the release of medicaments from time-release tablets or from entrapped systems [6, 7, 8, 9] as well as known to be a highly efficient thickener by forming a networked

microgel structure in aqueous solutions [10]. Concept of microgel has been utilized in many hydrogel systems and applications as a vehicle for the drug and other active ingredient [11, 12, 13]. Microgel structure with interstitial spaces can help the suspended particles entrapped and stable for a sufficiently long time. There are various types of acrylic acid-based polymers commercialized [14]. In general, these polymers have poor ionic surfactant and electrolyte tolerance. Carbopol insensitive to electrolyte and ionic surfactant were therefore chosen in this study.

Rheological analysis of this hydrogel polymer is important, especially in the pharmaceutical applications, since its mucoadhesive performance is closely related to the rheological properties [15, 16, 17]. Rheological properties of Carbopol gels are extensively investigated and this polymer is known to form dispersion and show weakly viscoelastic properties, instead of dissolving in aqueous solution [18, 19, 20, 21, 22]. Early studies on Carbopol concluded that their unique rheological properties resulted from the interchain entanglements of the high molecular weight polyacrylate [23]. The Herschel-Bulkley model can be successfully applied to such a viscoplastic test media to analyze their rheological behavior [24]. High viscosity can only slow down the settling rate, and yield stress value is the predominant factor to provide a permanent suspension. The shear modulus (G°) represents interaction between swollen particles and should be proportional to the cross-link density [10]. Rheology of network dispersions was correlated to network structure and cross-link density determined from swelling ratio measurement of microgel networks [10]. More precise analysis of network gel structure, however, has not been fully understood. Carbopol 941, one of the most popular and commercially available poly(acrylic acid), was chosen as a thickener to study the rheological behavior in the presence of different amount of neutralizing agent, i.e. triethanolamine (TEA) [25].

The purpose of this study was to understand viscoelastic properties of Carbopol correlated to the direct analysis of microscopic network structure by cryo-SEM.

Experimental

Materials. Carbopol 941 was provided by BF Goodrich as a white powder form, which is synthetic, high molecular weight of $(21 \pm 3) \times 10^6$ [26], nonlinear polymers of acrylic acid cross-linked with a polyalkenyl polyether [27, 28] containing up to 20% soluble linear polyacrylate [20]. The cross-linking agents for all the Carbopol 900 series are allyl ethers of either sucrose or pentaerythritol [29], although the crosslinking agent used in Carbopol 941 is not known. All other reagents are of analytical grade. Chemical compositions of Carbopol used in this experiment are shown in Table 1. All polymer solutions were prepared using de-ionized water (Barnstead E-pure System, Barnstead/ThermoLyne Co., Dubuque, Iowa). The water had an electrical conductance of 18.2 M Ω cm.

Preparations of polymer gel. For the gel state suspensions, pre-mixed aqueous solution of 4 wt% of poly(acrylic acid) polymer was prepared with a four-blade marine impeller, as recommended by the manufacturer, at room temperature, 400 rpm (Heidolph RZR 2030, Germany) and diluted to the final concentrations. Neutralization of the poly(acrylic acid) polymer was accomplished with TEA. Gels produced at the final state have excellent clarity after being neutralized by TEA. Bubbles in a clear gel system must be controlled to satisfy marketing goals. The two major sources of bubbles are from mechanical entrapment and chemical generation. Mechanical bubble formation was minimized by careful dispersion of the polymer resins. In simple systems this can be handled by

Table 1 Chemical composition of Carbopol 941 in white powder form

Impurities	Typical values
Water	< 0.5%
Benzene	1800 ppm
Propionic acid	1200 ppm
Acetic acid	600 ppm
Acrylic acid	80 ppm
Heavy metals	10 ppm
Iron	1 ppm
Arsenic	< 1 ppm
Lead	< 0.3 ppm

allowing the dispersion to stand. In sophisticated systems vacuum de-aeration (or even vacuum mixing) readily eliminates bubbles. Another method to control bubble inclusion is to avoid disturbing the gel-air interface. A frequent cause of bubbles, especially myriads of tiny ones, is neutralizer that has become carbonated upon exposure to air. When added to the acidic acrylic acid resin dispersion, the CO₂ is liberated. To avoid this, store the neutralizing agents in closed containers. Here, simply, the centrifugation force was exerted to remove the entrapped gas bubbles.

Rheometric measurement. The rheology of aqueous polymer solutions was characterized using a Parr Physica UDS 200 mechanical rheometer (Stuttgart, Germany) at room temperature. Cone-and-plate geometry was used with a gap size of 0.05 mm, a radius of 50 mm, and an angle of 2° for steady state and frequency measurements. Another cone-and-plate geometry (0.05-mm gap size, 2°, 25-mm radius cone) was utilized to obtain dynamic storage (G') and loss (G'') moduli as a function of torque. In frequency sweep tests, G' and G'' were always determined in the regime of linear viscoelasticity where the material functions are only functions of the angular frequency. All measurements to study temperature effect were carried out fitted with a temperature control and a thermostated concentric-cylinder adaptor to avoid possible leakage of water by evaporation. Samples showing two relaxation behaviors in the stress sweep experiment were selected and heated from 25 to 80 °C while the samples with only one relaxation process were cooled down from 25 to 1 °C. The data reported here were reproducible within $\pm 15\%$. Before each dynamic experiment, a steady pre-shear was applied at a shear rate of 1 s^{-1} for 60 s, followed by a 120-s rest period. This procedure was necessary to erase any previous shear histories on the sample and to ensure that the sample establishes its equilibrium structure [30].

Cryogenic scanning electron microscopy (Cryo-SEM). Samples were mounted on a brass specimen holder and plunged into liquid nitrogen slush at -210°C . Rapid freezing supercools water and elevates its viscosity, thereby delays nucleation and the growth of ice crystals, and produces frozen samples with negligible freezing artifacts. The frozen specimen was fractured with a remotely controlled push rod in a Bio-Rad E7450 cryotransfer system (Bio-Rad, Hercules, CA) at -120°C under vacuum. Frozen Poly(acrylic acid) polymer/H₂O mixture in the specimen was partially sublimed away at -60°C and 2×10^{-9} bar for 10–90 min to expose the structure beneath the vitrified media. The mounted sample was transferred into a precooled Balzers MED 010 sputtering device (Balzers Union, Balzers, Liechtenstein) against a counter flow of dry nitrogen gas. Gold was sputtered on the specimen surface differentially at -180°C for 5 min. The specimen was then transferred to and examined by JEOL-JSM 840A (Japan Electron Optics Co., Japan) SEM with a modified oil-free evacuation system. All specimens were imaged under low acceleration voltage and low specimen current conditions, 5 keV, and 0.65×10^{-11} A, respectively, to reduce

the excessive charging and electron beam damaging to the specimens. The specimen temperature was kept lower than $-140\text{ }^{\circ}\text{C}$ during the entire imaging.

Results and discussion

Steady-state measurements of polymer gel

Typical shear stress-shear rate data for the aqueous poly(acrylic acid) polymer gels of different compositions are presented in Fig. 1 for shear rates ranging from 10^{-3} to 10^3 s^{-1} . As shown in Table 2, the data were analyzed by using conventional flow equations such as Bingham,

Casson, and Ostwald equations as well as the Herschel-Bulkley equation known as the model describing the flow behavior of the poly(acrylic acid) polymer very well. The yield stress value determination depends on the rheological method and model used [31]. Regression coefficients of each equations and parameters in Herschel-Bulkley model are shown in Tables 3, and 4, respectively. Ostwald and Herschel-Bulkley model were more satisfactory to describe the flow behavior while the Bingham and Casson model were digressed from the actual flow curves. Yield stress of poly(acrylic acid) polymers without TEA decreased with polymer concentrations. However, yield stress decreased with TEA content in the concentration ranges tested in this study. Yield stress values obtained from the equation were substantially low, compared with the literature reported previously [24, 32]. The difference comes from the fact that the extrapolation of the flow curves from $\dot{\gamma} \approx 0.1\text{ s}^{-1}$ to zero shear rate were done in the literature while entire shear rate ranges were fitted using models in this study to obtain the yield stress values. When the simple Bingham equation was applied over the entire shear rate ranges, yield stress values were well consistent with trends reported in the above literature (Table 4). In other words, the Bingham model was more suitable in terms of yield stress values in spite of the low regression coefficient values.

As shown in the flow curves re-plotting the viscosity as a function of the shear rate neutralizing agent, it was difficult to determine the zero-shear-rate viscosity since there was no clear Newtonian viscosity plateau region in the flow curves (Fig. 2). The power law can't generate the theoretical zero-shear-rate viscosity value (Table 2). The exponential form of flow model could determine the zero-shear-rate viscosity value at $\dot{\gamma} \rightarrow 0$, but the model was not reliable according to regression coefficients for all samples. The Cross model [33] in order to fit rheological behavior of Carbopol 941 (Table 5) should be modified in that the η_{∞} and p are assumed to be 0 and 1, respectively, in the following equation:

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{1 + (K\dot{\gamma})^p} \quad (1)$$

where η_0 is viscosity at $\dot{\gamma} \rightarrow 0$, η_{∞} is viscosity at $\dot{\gamma} \rightarrow \infty$, and p is the Cross exponent. η_0 of both samples with and without TEA increased clearly with polymer concentrations while it made only a slight difference with TEA concentration (Table 6, Fig. 3). Zero-shear-rate viscosity of all samples fell in the range of 10^3 due to the gel network. K values also showed the similar tendency. In this case, K value decreased dramatically with polymer concentrations when neutralizing agent doesn't exist in the solution. Steady-state measurements were not sufficient to analyze the overall rheological behavior of aqueous polymer gel system, considering a micro-structural point of view.

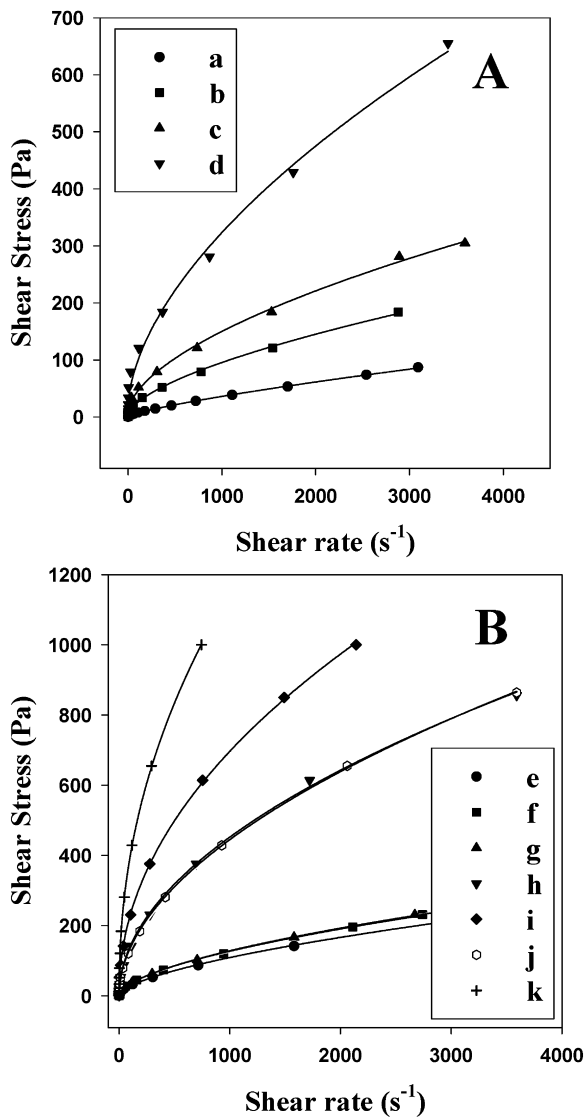


Fig. 1A,B Shear stress as a function of the shear rate for samples: A without TEA; B neutralized by TEA at $25\text{ }^{\circ}\text{C}$

Table 2 Flow models in shear rate-shear stress curve and shear rate-viscosity used in this study

Model	Model equation [$\tau = \tau(\dot{\gamma})$]	Parameters	
Bingham	$\tau = \tau_0 + \eta\dot{\gamma}$	τ_0	Bingham yield stress (Pa)
Casson	$\tau^{0.5} = \tau_0^{0.5} + \eta^{0.5}\dot{\gamma}^{0.5}$	η	Bingham viscosity (Pa·s)
		τ_0	Casson yield stress (Pa)
Ostwald	$\tau = K\dot{\gamma}^n$	η	Casson viscosity (Pa·s)
		K	Consistency (Pa·s ⁿ)
Herschel-Bulkley	$\tau = \tau_0 + K\dot{\gamma}^n$	n	Power law index
		τ_0	Herschel-Bulkley yield stress (Pa)
		K	Consistency (Pa·s ⁿ)
		n	Power law index
Model	Model equation [$\eta = \eta(\dot{\gamma})$]	Parameters	
Exponential Decay	$\eta = \eta_0 \cdot \exp(-K\dot{\gamma})$	η_0	Zero shear viscosity (Pa·s)
Ostwald	$\eta = K \cdot \dot{\gamma}^{n-1}$	K	Consistency (s)
		n	Consistency (Pa·s ¹⁻ⁿ)
Cross	$\eta = \frac{\eta_0}{1+K}$	n	Power law index
		η_0	Zero shear viscosity (Pa·s)
		K	Consistency (s)

Table 3 Regression coefficient (R^2) for various flow models in shear rate-shear stress curve

Concentration (wt%)			Bingham	Casson	Ostwald	Herschel-Bulkley
Class	Carbopol	TEA				
a	0.1	–	0.986	0.989	0.999	0.999
b	1.0	–	0.962	0.958	0.995	0.997
c	2.0	–	0.962	0.963	0.995	0.997
d	4.0	–	0.947	0.935	0.990	0.994
e	0.1	0.1	0.957	0.956	0.999	0.999
f	0.1	1.0	0.941	0.957	0.999	0.999
g	0.1	10.0	0.943	0.961	0.999	0.999
h	1.0	1.0	0.915	0.935	0.999	0.999
i	1.0	10.0	0.924	0.933	0.999	0.999
j	2.0	1.0	0.927	0.943	0.999	0.999
k	2.0	10.0	0.886	0.906	0.999	0.999

Table 4 Parameters of Herschel-Bulkley model in steady state experiments

Concentration (wt%)			τ_0 (Pa)	K (Pa·s ⁿ)	n
Class	Carbopol	TEA			
a	0.1	–	0.75 (2.47) ^a	0.16	0.78
b	1.0	–	3.67 (10.51)	1.23	0.62
c	2.0	–	7.72 (22.80)	2.53	0.58
d	4.0	–	16.07 (41.31)	5.66	0.58
e	0.1	0.1	1.94 (10.16)	1.50	0.62
f	0.1	1.0	2.23 (11.41)	2.12	0.59
g	0.1	10.0	2.08 (12.48)	2.07	0.59
h	1.0	1.0	2.58 (54.83)	13.28	0.51
i	1.0	10.0	1.59 (65.59)	24.60	0.48
j	2.0	1.0	6.00 (57.09)	11.51	0.53
k	2.0	10.0	2.65 (73.77)	47.25	0.46

^a() Bingham yield stress

Oscillatory rheological behavior

The dynamic rheology provides a more direct correlation with microstructure than steady rheology since the materials can be examined in their at-rest state without causing any disruption of their underlying structures

[33]. The viscoelastic behavior of the polymer solution is illustrated in Figs. 4 and 5 using frequency and stress sweep test at 25 °C.

The frequency spectrum for a given system offers a signature of the microstructure existing in the system [34]. The real images of microstructure were obtained by

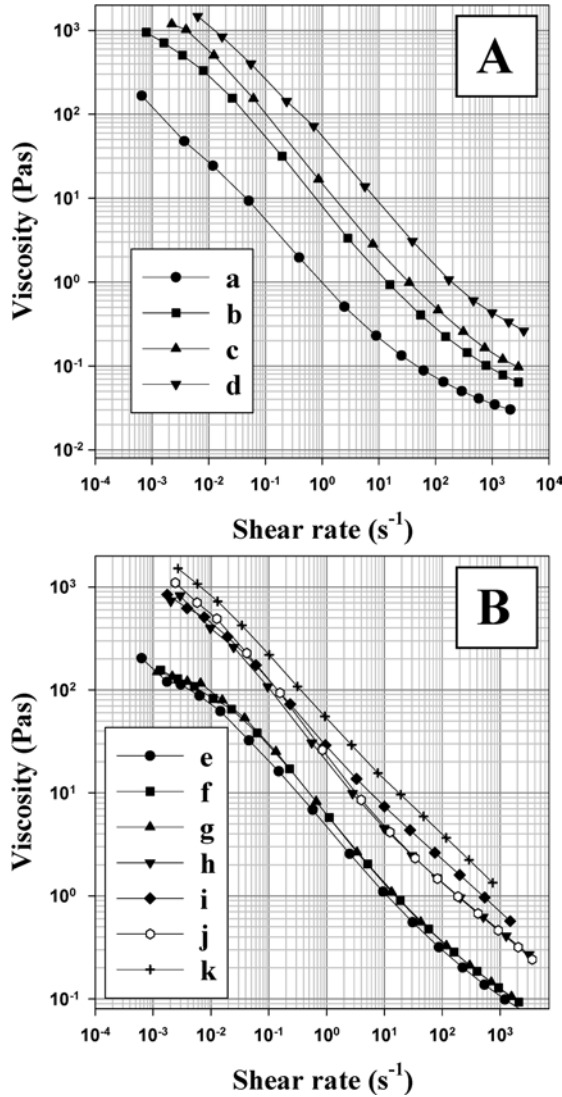


Fig. 2A,B Viscosity as a function of the shear rate for samples: A without TEA; B neutralized by TEA at 25 °C

Table 5 Regression coefficient (R^2) for three different flow models in shear rate-viscosity curve

Concentration (wt%)		Exponential decay (two parameter)	Ostwald	Cross	
Class	Carbopol TEA				
a	0.1	–	0.949	0.999	0.993
b	1.0	–	0.971	0.997	0.996
c	2.0	–	0.989	0.991	0.999
d	4.0	–	0.972	0.999	0.997
e	0.1	0.1	0.963	0.997	0.995
f	0.1	1.0	0.965	0.995	0.992
g	0.1	10.0	0.968	0.996	0.995
h	1.0	1.0	0.953	0.986	0.979
i	1.0	10.0	0.952	0.989	0.981
j	2.0	1.0	0.949	0.998	0.993
k	2.0	10.0	0.971	0.998	0.996

Table 6 Parameters of Cross model $[\eta = \eta_0 / (1 + K\dot{\gamma})]$ used to predict the rheological behavior in steady state experiments and shear modulus (G' at 1 Hz) from frequency sweep measurement data

Concentration (wt%)		η_0 (Pa · s × 10 ³)	K (s × 10 ²)	Go (Pa)	
Class	Carbopol TEA				
a	0.1	–	0.31	13.89	4.11
b	1.0	–	1.18	3.57	40.00
c	2.0	–	1.69	1.76	74.50
d	4.0	–	2.41	0.10	128.00
e	0.1	0.1	0.11	0.52	12.60
f	0.1	1.0	0.13	0.38	15.40
g	0.1	10.0	0.15	0.45	15.00
h	1.0	1.0	1.19	1.92	47.10
i	1.0	10.0	1.06	1.33	50.60
j	2.0	1.0	1.53	1.75	65.90
k	2.0	10.0	1.95	1.22	91.00

cryo-SEM and will be discussed in the following section. Storage modulus (G') and loss modulus (G'') are plotted in Fig. 4. G' was always larger than G'' , i.e., elastic component is dominant over viscous component. The Carbopol polymer gels without neutralization exhibited a frequency-independent elastic modulus G' that is about one order of magnitude higher than the G'' over the entire frequency range (Fig. 4A). The shear modulus was determined as the high-frequency limiting G' at the highest possible frequency to remove the inertia effects [35]. This type of dynamic response is a characteristic of gel-like materials [36] in good agreement with the previous results [10, 37]. The elastic modulus (G') of a gel system correlates with the rigidity (stiffness) of the network where G' is independent of the frequency. Thus, we expect that more rigid structures were formed with increasing polymer concentrations as shown in Table 6 and Figs 3 and 4A. However, when the Carbopol polymers were neutralized by TEA, both G' and G'' were no longer independent of the frequency showing polymer-like viscoelasticity (Fig. 4B). G' and G'' increased linearly with frequency from 10^{-2} to 10^{-1} Hz as shown in Fig. 4B. G' of unneutralized samples was lower than that of neutralized ones in low frequency ranges while higher in high frequency ranges as expected for samples containing the same amount of Carbopol [21]. It has also been suggested that a more rigid structure contributes to this behavior of unneutralized gel systems [21]. The constant G' at low frequencies means that it is sufficient to form the entanglement or cross-links at even low polymer concentration (0.1%) with or without TEA. Here an interesting feature could be seen at very low polymer concentrations of neutralized samples. G' of 0.1% Carbopol 941 neutralized by TEA showed almost constant values in low frequency ranges, and then increased with frequency while G' of the neutralized samples (1.0 and 2.0% Carbopol) monotonically increased. It is possible that monotonic increase in G' at

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