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A feasible method to determine the critical DS for modified polysaccharide derivatives' gelation by gel point, t_g

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Abstract

The process of determining a critical DS to a polymer's gelation is a key link in identifying degradable polymers' cross-linking behaviors. A feasible method was developed from the rheological technique. In principle, it was a new application of gel point, t_g, in an overlapping field of polymers' modification and characterization, by which the gelling properties of carboxyl methylated guar gum (CMGG) and locust bean gum (CMLBG) were dynamically investigated by identifying their t_g. Differing from the routine research in rheology or synthesis chemistry, the present study focused on neither pure t_g nor pure DS but on their interrelation. The results demonstrated that CMGG/CMLBG's gel points could be observed only when their DS were 0.2. However, it was not guaranteed to yield the tested polymers' gel points unless the investigation was performed on a plateau region. Two preconditions, $\mathrm{DS} \leq 0.2$ and $\omega = 3-60\ \mathrm{rad\ s^{-1}}$, must be satisfied simultaneously besides γ of 0.5% was maintained in order to obtain the expected gel point. Since DS was regarded as a contradictory focus related to the polymers' hydrophilicity and cross-linking behavior, the value $\mathrm{DS} = 0.2$ was exactly the upper limit of CMGG/CMLBG's gelation. The significance of the present study rests not only in the first successful attempt in determining galactomannan-based derivatives' $\mathrm{DS}_{\mathrm{critical}}$ but also in its universal application for other polysaccharide-based derivatives because of a similarity in structure.

Keywords: Gel point; Degree of substitution; Gelation; Polysaccharide; Guar gum; Locust bean gum; Carboxyl methylation; Hydrogel; Super water absorber

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1. Introduction

Being a contradictory focus, DS is related not only to polysaccharide derivatives' properties in modification but also to their behaviors in cross-linking/gelling. On the one hand, DS should be as high as possible to reach the best improvement in hydrophilicity. On the other hand, it should be limited to the lowest level to ensure expected gelation results. From this aspect, a critical DS is a substitution level required for guar gum (GG)/locust bean gum (LBG)'s carboxyl methylation, and the upper limit permitted to CMGG/CMLBG's gelation as well. The process of determining the critical DS was therefore the key link in developing the degradable polysaccharides-based hydrogels or super water absorption polymers.

Using Lazik's work as reference (Lazik, 1998), a range of $0 < \mathrm{DS} < 1$ was deduced in our former study (Xing, 1999). This result was not applicable to the current research on CMGG/CMLBG's gelation behaviours, because it was too inaccurate to satisfy the quantitative requirement for $\mathrm{DS}_{\mathrm{critical}}$ determination. A superior method was subsequently developed to overcome the polyelectrolyte method's insufficiency. In principle, it was a new application derived from the gel point determination technique. What was concerned in our study was to combine an investigation of *degree of substitution*, DS, with an identification of *gel point*, t_g. The final goal was to determine $\mathrm{DS}_{\mathrm{critical}}$ by t_g. No similar information dealing with this topic has been reported yet so for.

The method we developed was performed using an automatic rheometer, by which the $\tan\delta(\omega, \mathrm{DS}) \sim t$ plots were dynamically demonstrated. The fact that a gel point, t_g, could be observed and determined only when $\mathrm{DS} \leq 0.2$ provided evidence: the value 0.2 was the expected critical DS that was crucial to CMGG/CMLBG's gelation. Based on this result, CMGG/CMLBG-based polymers were successfully gelled with the cross-linker, ethylene glycol diglycidyl

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ether (EGDE). The low cross-linked products showed a good absorption capacity in water, even in normal saline. They could be used as substitutes to the polyacrylamide/ polyacrylic acid-based produces (Brannon-Peppas & Harland, 1990; Buchholz, 1994; Xing, 1999). This paper focused only on an introduction to the innovation method. As for the study of synthesizing and characterizing CMGG/CMLBG, it will be discussed in a subsequent article in progress (Xing, 2004).

2. Materials and methods

2.1. Materials

Carboxyl methylated guar gum (CMGG) and locust bean gum (CMLBG) with DS = 0.2, 0.3, 0.5, 0.7 and 0.9, powder in light yellow color, $M_w = 220,000–330,000$ g/mol, prepared at Institute of Chemistry, University of Osnabrück (Jarowenko, 1990; Whislter, 1984; Xing, 1999); ethylene glycol diglycidyl ether (EGDE), colorless viscous-liquid, $M_w = 174.2$ g/mol, $\geq 50\%$, Polysciences, Inc.

2.2. Rheological principle and technique

The rheological study was dynamically performed by a CSL 100 model rheometer equipped with a set of stainless steel plate-and-plate oscillation response (see Fig. 1). A typical plot is shown in Fig. 2. According to the principle developed by Winter and Chambon, the complex modulus, G^*, was expressed as $G^*(\omega, t) = K/t^n$ (Chambon & Winter, 1985; Winter & Chambon, 1986). Here G^* was the shear module of the tested sample; ω, the angle frequency; K, the force of hydrogel; t, the gel time; and n, the characterizing exponent of a critical hydrogel. $G^*(\omega, t)$ was further divided into two components, storage modulus, G', and loss modulus, G''. Moreover, $G''/G' = \tan\delta = \tan(\pi n/2)$, where $\delta = 0°$ for pure elastic fluid, $\delta = 90°$ for pure viscous fluid, and $0° < \delta < 90°$ for viscoelastic fluid (Kulicke, 1986). An oscillation course related to gelling initiation time, gelling starting time and gelling balance time was automatically plotted demonstrating a continuous change in $G''(t)$ and $G'(t)$. The point at which $\tan\delta$ no longer depended on the angular frequency, ω, was exactly the gel point, t_g (Kjøniksen & Nyström, 1996; Nijenhuis & Winter, 1989).

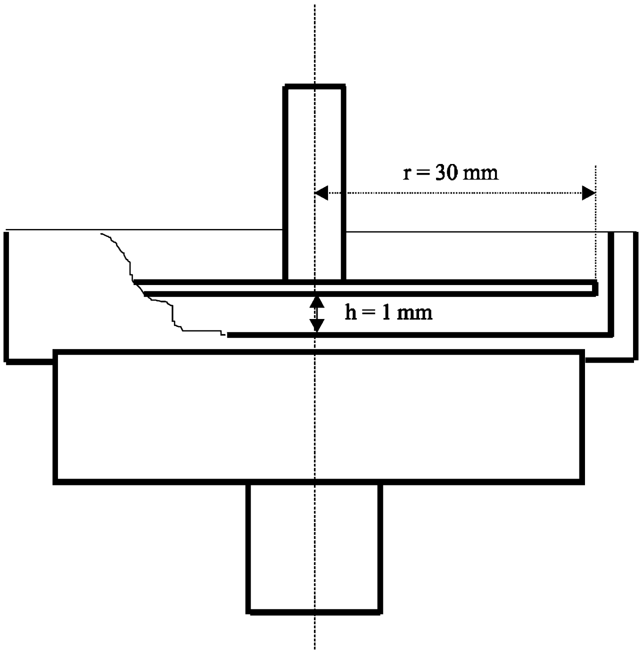

Fig. 1. A plate-and-plate oscillation response. $r = 45$ mm; $h = 1$ mm.

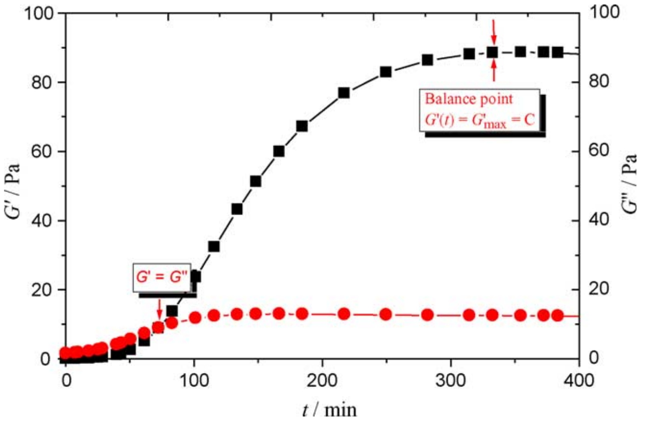

Fig. 2. Plots of $G' \sim t$ and $G'' \sim t$ for CMLBG. DS = 0.2; m(NaOH) = 0.9; $T = 50$ °C; $\gamma = 0.5\%$; $\omega = 6.28$ rad s^{-1}.

Drops of a 1–3% mixed viscous solution of CMGG/CMLBG sample and cross-linking reagent EGDE were placed on the surface of the concave stainless steel shallow pool (the down-plate) and allowed to spread. The rotating up-plate was positioned exactly on the surface of the viscous polymer solution. The whole oscillation response system was then sealed with liquid paraffin (flash point ≥ 200 °C) to reduce evaporation of the liquid while the gelation was dynamically determined. A skilled operation technique was specially required for the above preparation to avoid system analysis errors caused by manual operation such as interval time and non-homogeneity in liquid phase. Every operation, for example, must be finished in a limited time, and no air bubbles could be visible in the viscous polymer solution. In addition, all variables such as solution concentration, rheological parameters and even environment temperature should be kept to be the same to ensure experimental consistency and comparability.

3. Results and discussion

The present study consisted of two developing stages. The primary stage was involved mainly in investigating CMGG/CMLBG's gelling behavior through a function relation, like $G^* \sim t$. Here G^* was either the storage modulus, G', or the loss modulus, G''. Fig. 2 displays a typical signal–variable curve resulting from CMLBG's gelling with EGDE. Resembling the results from Chambon and Kjøniksen (Chambon & Winter, 1985; Winter & Chambon, 1986), the values of G'' were always larger than those of G' prior to reaching an intersecting point. Subsequently, G' greatly exceeded G''. A steep increment in G' appeared during a gelling period of $t = 100–250$ min. $\Delta G'$ decreased after the accelerating period, and finally reached a gelling balance, from which $\Delta G'$ dynamically maintained zero. Basically, the whole rheological process experienced two gelling regions and three states. The two gelling regions were divided by the intersecting point, from which the gelling behavior changed from a physical gelation to a chemical one. The physical gelation ($G' < G''$) was a dynamically reversible process, in which the formed bonds (hydrogen bonds) might be broken again by mechanical force such as vibration and temperature variation. The chemical gelling process ($G' > G''$) started to play a key role after the intersecting point. It was irreversible in gelling, because a three-dimensional structure was formed through covalent bonds. The point at which $G' = G''$ was regarded as the gel point, t_g. However, t_g obtained in this way was not a true gel point as that reported by Nijenhuis and Winter (1989). A change in t_g may occur due to a dependence existing between the angular frequency, ω, and the gel point, t_g. Despite this defect, the plot shown in Fig. 3 was still useful in demonstrating the gelling process for CMGG and CMLBG.

Additional oscillation behaviors were demonstrated in Fig. 3a and b. Differing from those shown in Figs. 2 and 3a, b, were the results from a double variable function $G'(\mathrm{DS}) \sim t$, in which an affect of DS on gelation was clearly demonstrated.

Surprisingly, no rheological change in gelling was observed at all in any case of $G'(\mathrm{DS} > 0.2) \sim t$. G' of CMLBG started to increase in $t =$ ca. 100 min. only when its DS descended to 0.2 (see Fig. 3a). The steep slope in $G' \sim t$ demonstrated that an accelerating gelation in CMLBG occurred in a period of $t = 100–350$ min, and then the gelation plateaued to a balance at $t = 500$ min, from which $\Delta G'(t)$ dynamically remained zero. CMGG-based samples yielded roughly similar results (see Fig. 3b). The gelation also took place only at DS = 0.2. What differed was that the gelling in CMGG increased slowly. A much longer time was needed to reach a dynamic gelling balance in comparison with that in CMLBG. Perhaps it resulted from GG's rigid structure (refer to subsequent structure figure and discussion). It should be noted that both Fig. 3a and b were the results from only a single angular frequency of $\omega = 6.28\ \mathrm{rad\ s^{-1}}$ for CMLBG and $4.71\ \mathrm{rad\ s^{-1}}$ for CMGG. The positions of the divided gelation regions and the three gelling states could be changed with ω due to a non-linear interrelation between $G'_i \sim \omega_i$ and $G''_i \sim \omega_i$, i.e. $G''(\omega_i)/G'(\omega_i) \neq G''(\omega_j)/G'(\omega_j)$. From this aspect, $G'(\mathrm{DS}) \sim t$ was, at best, a qualitative way to identify gelation process. To date, the study has not yielded expected results for determining a definite DS. A quantitative interrelation between $\mathrm{DS_{critical}}$ and t_g was expected to be found during the study.

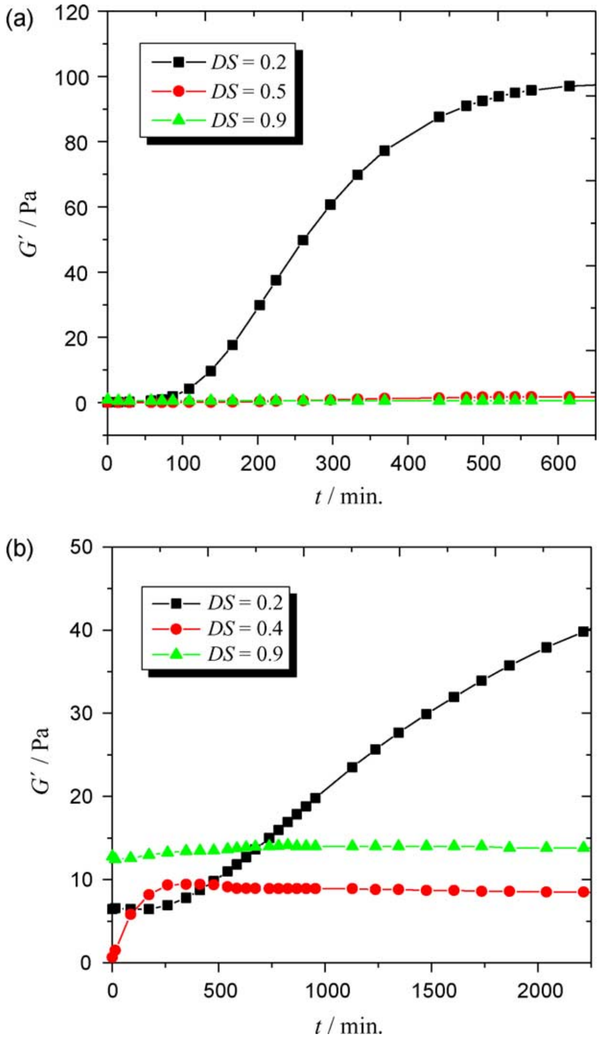

Fig. 3. (a) A gelation process of CMLBG where DS = 0.9, 0.5 and 0.2. $m(\mathrm{NaOH}) = 0.9$; $T = 50\ ^\circ\mathrm{C}$; $\gamma = 0.5$; $\omega = 6.28\ \mathrm{rad\ s^{-1}}$. (b) A gelation process of CMGG where DS = 0.9, 0.4 and 0.2. $m(\mathrm{NaOH}) = 0.9$; $T = 50\ ^\circ\mathrm{C}$; $\gamma = 0.5$; $\omega = 4.71\ \mathrm{rad\ s^{-1}}$.

The subsequent attempt was based on $G^*(\omega, \mathrm{DS}) \sim t$. Here, the dynamically oscillational modulus, G^*, was a function of a three-variable such as ω, DS and t. Meanwhile, G^* was substituted by a non-dimensional function, $G''/G' = \delta$, to eliminate affects of ω on t_g resulting from the non-linear relationship between $G(\omega_i, t)$ and $G''(\omega_i, t)$. The test was performed in a sequence of DS = 0.9, 0.7, 0.5, 0.3 and 0.2 in order to identify how DS was related to t_g on earth. The results showed that tan δ did not change with ω when the samples' DS were selected from 0.9 to 0.3. No t_g could be obtained at all no matter how ω varied because the curves obtained did not intersect each other. Even if some of them did, they were disorderly and unsystematic. This confirmed that gelation did not happen when $\mathrm{DS} \geq 0.3 \rightarrow$ not possible to get $t_g \rightarrow$ no interrelation existed between t_g and DS.

A group of alike geographic contour curves were finally observed when $\mathrm{DS} = 0.2$. The shapes of the curves greatly changed with varying ω. Most of $\tan\delta(\omega, \mathrm{DS} = 0.2) \sim t$ curves intersected with others, but the intersecting points were irregular at a wide ω range. A favorable turn occurred when the test angular frequency was limited within $100\ \mathrm{rad\ s^{-1}}$. The intersecting points obviously tended to draw closer when the ω range was further reduced to $3–60\ \mathrm{rad\ s^{-1}}$, even though some of them were still dispersed. It was easy to find an intersecting point for two arbitrary $\tan\delta(\omega) \sim t$ curves at this ω region. However, it was difficult to make three or more curves intersect at one point simultaneously because a selection of a ω value for the third curve did not accord with certain regularity. For example, it was not guaranteed that the third ω_3 would be found between ω_1 and ω_2, even though $\delta(\omega_1, \mathrm{DS} = 0.2) \sim t$ and $(\omega_2, \mathrm{DS} = 0.2) \sim t$ intersected at certain point where $t_1 = t_2$. Three $\delta(\omega) \sim t$ curves intersected exactly at the same point only when $\omega = 4.71$, 6.28 and $31.42\ \mathrm{rad\ s^{-1}}$ for CMGG and $\omega = 6.28$, 18.85 and $56.55\ \mathrm{rad\ s^{-1}}$ for CMLBG (see Fig. 4a and b).

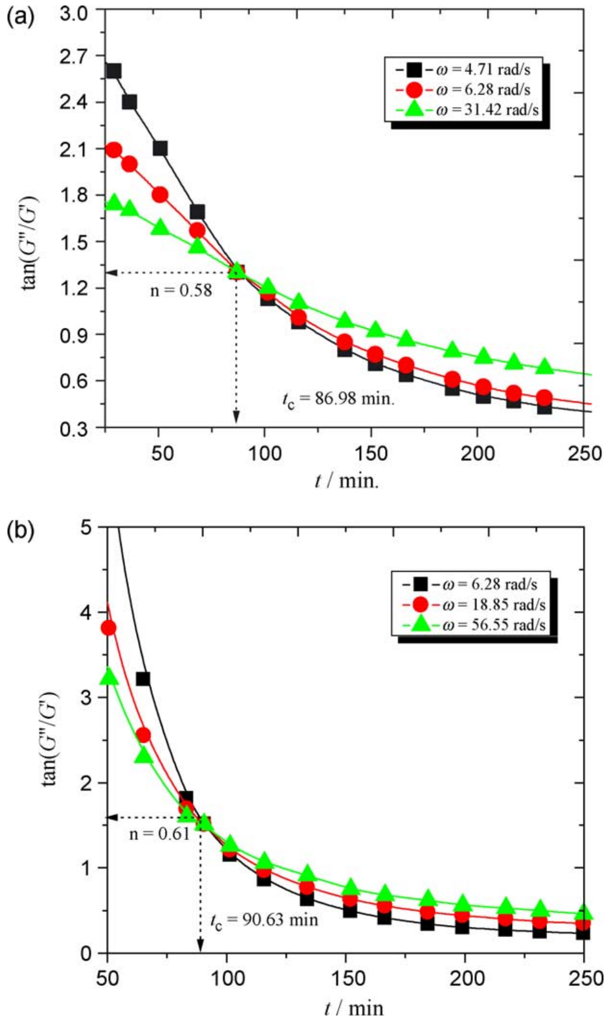

Fig. 4. (a) $\tan\delta$ as function of t and ω for CMGG. $\omega = 4.71$, 6.28 and $31.42\ \mathrm{rad\ s^{-1}}$; $\gamma = 0.5\%$; $\mathrm{DS} = 0.2$; $m(\mathrm{NaOH}) = 0.9$; $T = 25\ ^\circ\mathrm{C}$. (b) $\tan\delta$ as function of t and ω for CMLBG. $\omega = 6.28$, 18.85 and $56.55\ \mathrm{rad\ s^{-1}}$; $\gamma = 0.5\%$; $\mathrm{DS} = 0.2$; $m(\mathrm{NaOH}) = 0.9$; $T = 25\ ^\circ\mathrm{C}$.

The above results provided the first evidence that an interrelationship existed between t_g and DS. Both CMLBG's and CMGG's t_g were obtained when their $\mathrm{DS} = 0.2$. Since it was the highest DS at which t_g could be determined, $\mathrm{DS} = 0.2$ was the critical value permitted for CMGG/CMLBG to gel. However, it did not imply that t_g was definitely observed at $\mathrm{DS} = 0.2$. An important precondition to get t_g lay in performing the designed determination on a rheogical plateau region, on which the deformation, γ, and the angular frequency, ω, were limited to a specific range. The expected plateau region had to be determined prior to t_g test. Otherwise, the obtained results would have been disorganized. Fig. 4a and b further proved that the ω-range was $4–35\ \mathrm{rad\ s^{-1}}$ for CMGG and $6–60\ \mathrm{rad\ s^{-1}}$ for CMLBG. Those results basically accorded with the plateau region shown in Fig. 5, in which an upper line of $\gamma = 2\%$ and a range of $\omega = 15–50\ \mathrm{rad\ s^{-1}}$ were recommended. The true values were $\omega = 3–60\ \mathrm{rad\ s^{-1}}$ and $\omega = 0.5\%$. The reason for the difference in ω and γ might lie in a difference in test systems. To ensure a continuous and stable change in G' and G'', the low-density cross-linked samples were used for testing the plateau region. Dynamically, it was a 'frozen state', in which no phase change occurred during the whole oscillation process. The true testing system, however, was variable process in phase, in which the system varied from a liquid phase (physical gelation) to a solid one (chemical gelation). The response of a liquid state on ω might not be as sensitive as that of a solid on ω due to a difference in visco-elasticity.

Returning to Fig. 4a and b, the fact that the gel point could be dynamically determined by $\tan\delta_i(\omega_i, \mathrm{DS}) \sim t$ plot only when $\mathrm{DS} = 0.2$ suggests that when their DS is over this upper line, it is impossible to determine CMGG or CMLBG-based sample's gel point. As for any case where $\mathrm{DS} < 0.2$, gelling will certainly occur. However, due to

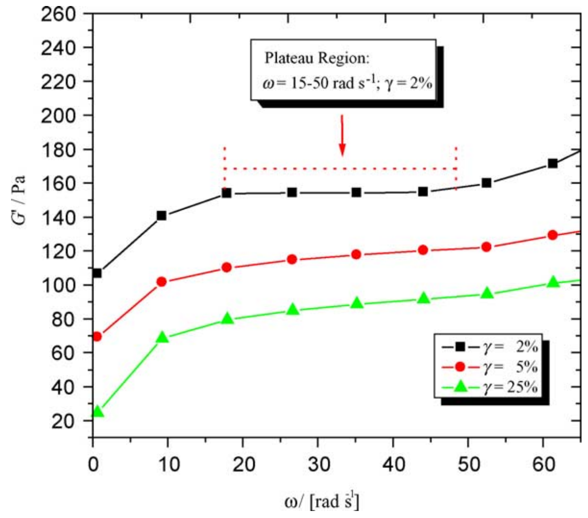

Fig. 5. A plateau region of low-density cross-linked CMLBG. $c = 3\%$; $\mathrm{DS} = 0.2$; $T = 25\ ^\circ\mathrm{C}$; $m(\mathrm{NaOH}) = 0.9$.

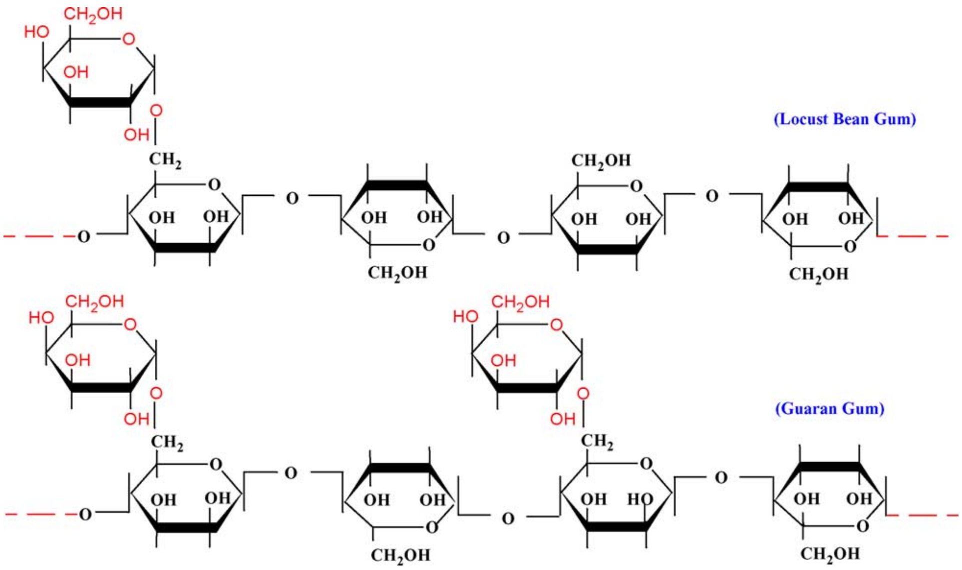

Fig. 6. The structures of guar gum (GG) and locust bean gum (LBG).

the lack of $-CH_2COO^-$ groups in any case of DS < 0.2, the system's hydrophilicity is too weak. Therefore, cases where DS < 0.2 should not be considered either.

The above study also provided some evidence for the gelling mechanism. The fact that the higher the test samples' DS, the weaker the gelation, demonstrates that the gelation of CMCC/CMLBG as a typical nucleophile addition did not occur between the carboxyl methylated groups ($-CH_2COO^-$) but rather between the original hydroxyl groups ($-OH$) with EGDE. Since the gelation strongly depended on CMGG/CMLBG' function level, a lower DS contributed more OH-groups to participating nucleophile addition. Additionally, the chemical activity of the alkalized mannopyranosyl/galactopyranosyl-based OH-groups also played a leading role in the overall gelling process.

Theoretically, a difference in gelation should be demonstrated between CMGG and CMLBG because of the difference in their chain structures. As shown in Fig. 6, the ratio of mannopyranosyl units:galactopyranosyl units is 4:1in LBG while it is 2:1 in GG (Daniel, Voragen, & Pilnik, 1994; Kudela, 1990; Maier, 1993; Seaman, 1989). Obviously, the molecular chains in CMLBG are more flexible than that in CMGG. A possible and reasonable result should be $t_{g(CMLBG)} < t_{g(CMGG)}$. The actual result, however, was $t_{g(CMLBG)}$ $(=90.6\text{ min})$ longer than $t_{g(CMGG)}$ $(=87.0\text{ min.})$. A further explanation is that C^1 and C^2-based OH-groups are arranged in *trans* in galactopyranosyl units (G) while they are in *cis* in mannopyranosyl units (M). OH-groups linked to G are more easily alkalized in comparison with those linked to M. The alkalized galactopyranosyl-based OH-groups tended to attack EGDE's epoxy cycles more because of their lower chemical potential and smaller space-resistance. The chemical activity of locust bean gum is lower than that of guar gum, because it has much less G units than guar gum does. As a result, that CMLBG's advantage in chain flexibility is offset by its disadvantage in active energy may be the main reason for $t_{g(CMLBG)} > t_{g(CMGG)}$. This conclusion, however, was contradictory to the results shown in Fig. 3a and b, in which CMLBG gelled faster than CMGG did. The true gelling process may be more complex, and requires further study.

4. Conclusions

Whether a gelation would take place, depended strongly on CMCC/CMLBG' DS. To figure out its leading role in gelling process, DS was introduced into the rheological function formula as the third variable. The new oscillation relation was expressed as $\delta(\omega, \mathrm{DS}) \sim t$, where $\delta = G''/G'$. Though being similar to an expression for gel point, t_g, the present study focused on neither pure t_g nor pure DS but on the interrelation between the two. The results proved that it is available to determine any CMGG/CMLBG's critical substitution by investigating the corresponding t_g.

A gelling behavior could be changed with ω, while the critical DS of CMGG/CMLBG was the only one for a defined polymer. The value at which the polymer's t_g occurred was exactly the critical DS. For CMGG and CMLBG, $\mathrm{DS}_{\mathrm{critical}}$ was 0.2, i.e. a gelling process could be observed and determined for CMGG/CMLBG only when DS was not greater than this limit. In accordance with DS's double meaning in relation to polymers' functioned level and gelling behavior, the value 0.2 was both the optimal DS required for improving GG and LBG's hydrophilicity and the upper limit for CMGG and CMLBG's gelation.

The dependence of $\mathrm{DS}_{\mathrm{critical}}$ on t_g could be demonstrated only when the gelling process was performed on the plateau region obtained prior to the test. It was not guaranteed, however, that an arbitrary $\tan \delta_i(\omega_i, \mathrm{DS}) \sim t$

curve could be made to intersect at the same point, even if the corresponding ω_i lay completely within the plateau region. The only way to ensure three or more curves would cross through a single intersecting point was to try randomly on the plateau region. The results proved that three curves of $\tan \delta_i(\omega_i, \mathrm{DS}) \sim t$ intersected perfectly at the gel point when $\omega = 4.71$, 6.28 and 31.42 rad s^{-1} for CMGG and 6.28, 18.85 and 56.55 rad s^{-1} for CMLBG, when the deformation, γ, was fixed at 0.5%.

The method developed and presented in the study is of universal application. It can be used in other modified polysaccharide derivatives such as carboxyl methylated starch (CMS) and cellulose (CMC) because their structures are similar to each other.

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References

Brannon-Peppas, L., & Harland, R. S. (1990). *Absorbent polymer technology*. Amsterdam: Elsevier.

Buchholz, F. L. (1994). Recent advances in super absorbent polyacrylates. *Trends in Polymer Science*, *2*(8), 277–281.

Chambon, F., & Winter, H. H. (1985). Stopping of cross-linking reaction in a PDMS polymer at the gel point. *Polymer Bulletin*, *13*, 499–503.

Daniel, J. R., Voragen, A. C. J., & Pilnik, W. (1994). *Starch and other polysaccharides* (*Vol. A25*). *Ullmann's encyclopedia of industrial chemistry*, VCH Verlagsgesellschaft mbH, pp. 1–21.

Jarowenko, W. (1990). *Encyclopaedia of polymer science and engineering* (2nd ed.). New York: Wiley.

Kjøniksen, A. L., & Nyström, B. (1996). Effects of polymer concentration and cross-linking density on rheology of chemically cross-linked poly(vinyl alcohol) near the gelation threshold. *Macromolecules*, *29*, 5215–5222.

Kudela, V. (1990). *Hydrogels* (2nd ed.) (*Vol. 7*). *Encyclopedia of polymer science and engineering*, New York: Wiley, pp. 783–807.

Kulicke, W.-M. (1986). *Fließverhalten von Stoffen und Stoffgemischen*. Basel: Hüthig & Wepf.

Lazik, W (1998). *Synthesis of cross-linked polysaccharides and their physicochemical properties in aqueous system*. Dissertation, University of Osnabrueck, Germany.

Maier, H. (1993). *Industrial gums* (3rd ed.). New York: Academic Press, pp. 181–226.

Nijenhuis, K. Te., & Winter, H. H. (1989). Mechanical properties at the gel point of a crystallizing poly(vinyl chloride) solution. *Macromolecules*, *22*, 411–414.

Seaman, J. K. (1989). *Handbook of water solution polymer and resins*. New York: McGraw-Hill.

Whislter, R. L. (1984). *Starch chemistry and technology* (2nd ed.). San Diego: Academic Press.

Winter, H. H., & Chambon, F. (1986). Analysis of linear viscoelasticity of a cross-linking polymer at the gel point. *Journal of Rheology*, *30*(2), 367–382.

Xing, H. (1999). *Comparative study of synthesis and characteristics on galactomannan-based super water absorbers*. Aachen: Shaker Press.

Xing, H (2004). *Synthesis and characterization of carboxyl methylated guar gum and locust bean gum*. Submitted for publication.