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Rheological investigation of specific interactions in Na Alginate and Na MMT suspension

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ABSTRACT

Here we report on a study of a rheological behavior of sodium alginate and montmorillonite suspension. We find that viscoelastic behavior of this suspension is dramatically affected with increasing volume fraction of montmorillonite platelets. Addition of montmorillonite generally leads to gel formation, which is attributed to interactions of montmorillonite and alginate via H-bonding and attraction between the positive edges of the platelets and the anionic backbone of the biopolymer. A critical concentration for the measured system was observed at 20 wt.% montmorillonite, where a crossover to a gel-like structure was detected. The observed gel has a rubber plateau, which develops further with higher montmorillonite concentration. In this physical gel the relaxation maximum was detected, which is associated with the breaking and reformation of the bonds between the platelets and the biopolymer. For this transient behavior, we find that a Maxwell type viscoelasticity quite well describes the relaxation time and the observed G' - G'' crossover. We believe that this gel-like behavior plays an important role in formation of highly ordered nanostructures that develop during the drying of these bio-nanocomposite suspensions.

KEYWORDS physical gel, rheology, alginate, montmorillonite, suspension

1 INTRODUCTION

The addition of clay platelets to polymers is a way to improve the properties of the unfilled material, lead to a significant increase in stiffness (Young's modulus), a decreased permeability and reduced flammability¹⁻⁴. The reason for such material property enhancement comes from the nature of the filler, i.e. its high aspect ratio, which imposes a tortuous path to the diffusing molecules and the good interaction between the filler and the polymer⁵. A variety of polymers have been used to produce such polymer clay nanocomposites (PCNs). In many systems the concentration of layered silicates rarely exceeds 5-10 wt.%, due to phase separation and loss of exfoliation. Recently, clay bio-nanocomposites have been made using biopolymers, such as chitosan, carboxymethyl cellulose, and xylogulcan. Using these biopolymers the concentration range of clay that can be successfully incorporated increases dramatically, with materials displaying unique properties, such as high level of alignment, and high volume fraction of the filler, which may result from favorable interaction between the biopolymer and the clay. All of the mentioned bio-nanocomposites have been produced via water casting of the biopolymer clay suspension^{6,7,8,9}. Due to the nanostructure and the high volume fraction of the clay, these materials display superior mechanical and transport properties, when compared to conventional PCNs.

The present work is motivated by a high order parameter achieved in Na Alginate/MMT bio-nanocomposite system. Investigating the rheological behavior of the initial suspensions of the biopolymers (anionic and cationic) and clay platelets may give some answers in understanding how these nanostructures are formed. The interaction between the clay platelets and positively charged polyelectrolyte, e.g. chitosan, is likely to occur due to the electrostatic interactions between $-\text{NH}_3^+$ groups and the negatively charged sites on the clay surface, leading to a dynamic

gel formation of the resulting suspension^{10,11}. Subsequently, alignment of the montmorillonite platelets results in a nacre-like, highly ordered, microstructure that is proposed to occur via water evaporation induced self-assembly⁶.

Miano et al. studied the influence of polyelectrolytes on the rheological behavior of montmorillonite suspension and found that face-edge interaction between montmorillonite platelets is inhibited by the presence of sodium polyacrylate, which is adsorbed on the edges of the clay particles¹². Jaber et al. measured the adsorption of negatively charged molecules on the montmorillonite platelets, where the interaction was hypothesized to occur on edges of the montmorillonite platelets via hydrogen bonding¹³.

Physical gelation occurs as a result of intermolecular association, leading to network formation. Unlike chemical bonding, where covalent attachments are typically permanent, these intermolecular associations are weak, reversible bonds or clusters produced by Van der Waals forces, electrostatic attractions, and/or hydrogen bonding¹⁴.

The present work is intended to study the effect of the addition of montmorillonite platelets on the structure and rheology of Na-alginate solutions. Na-alginate is a negatively charged polyelectrolyte copolymer composed from mannuronic (M) and guluronic (G) acid. The functional properties of alginate are related to the ratio of the copolymers (M/G) and the level of block formation. Alginate can be derived from brown algae, which is the main source for industrial use, and is also found in metabolic products of some bacteria, e.g. pseudomonas and azotobacter¹⁵⁻¹⁶. Commonly, alginates are used as food additives (E400-405), gelling agents, wound dressings, membranes for curing cement-based materials, and potentially for drug delivery^{17,18,19}.

Na-alginate suspensions with a wide range of montmorillonite concentrations were characterized, in which a critical concentration for a gel-like behavior was measured. The intermolecular associations are hypothesized to occur between the positively charged montmorillonite edges and the negatively charged alginate backbone and/or via H-bonding. The transient behavior of the obtained bio-nanocomposite suspensions is described well by the Maxwell type viscoelasticity. The results from this study suggest that the gel-like behavior of the suspensions causes a strain-induced orientation, during drying. This leads to a formation of a highly ordered structure.

2 MATERIALS AND METHODS

Na-alginate (Na-Alg) suspensions with various concentrations of Na-montmorillonite (Na-MMT) were prepared according to the following procedure. Commercially available MMT, the aspect ratio (width/thickness) of the Cloisite is roughly 250:1, (Cloisite Na⁺ (MMT), Southern Clay Products Inc., Rockwood) was dispersed in deionized water under vigorous stirring for 24 hours to achieve 3 wt.% exfoliated dispersion. During that time all of the Na-MMT got dispersed, without any remaining visual agglomerates. Na-Alg, (M/G=1.56, Mw=150 kg/mol) purchased from Sigma Aldrich was used as received. Na-Alg was dissolved using deionized water to form a 3 wt.% solution. The Na-MMT suspension was subsequently mixed with Na-Alg solution and was further mixed for 24 hours. The total solid content was kept at 3 wt.% but with different MMT concentrations, 0, 1, 5, 20, 40, 50, 60, 70, 75, 80, 90, 95, 98 and 99 wt.% with respect to Na-Alg + Na-MMT.

The Na-Alg MMT suspensions were examined by small amplitude oscillatory shear (SAOS) experiments on a TA Instruments AR-G2 Rheometer, using parallel plate geometry with

diameter of 40 mm. For each suspension, a strain sweep was performed, at the oscillatory frequency of 10 rad/s to determine the linear viscoelastic region. Frequency sweeps were performed in the linear viscoelastic region between 0.1 and 100 rad/s.

For time sweep experiment and for the dynamic oscillatory measurement at longer time scales (lower frequencies) we used a Couette geometry with stator radius 15.18 mm, rotor radius 14 mm and cylinder height 42.07 mm. The time sweep experiments were performed such that after sample loading, the samples underwent a pre-shear treatment at a shear rate of 100 s^{-1} for 120 s. All measurements were performed at 25 °C, using a solvent trap to avoid evaporation of water.

3 RESULTS AND DISCUSSION

For the Na-Alg solution and all the prepared suspensions, a strain sweep was performed at an oscillatory frequency of 10 rad/s to determine the linear viscoelastic region. The results are shown in figure 1, the dashed vertical lines indicate the strain used for the subsequent frequency sweeps. For Na-Alg suspension with Na-MMT concentrations higher than 40 wt.% we find that G' is higher than G'' , which is indicative of an elastic behavior rather than a viscous one, as is observed for the neat polymer solution and the pure Na-MMT suspension. A noticeable increase in G' is found upon the addition of Na-MMT platelets that at higher strains exhibits a sharp decrease, suggesting a critical strain for structure breakdown that imposes a limit of the linear regime²¹. For the Na-Alg with 99% wt.% Na-MMT we observe a similar behavior as is found for the pure Na-MMT suspension.

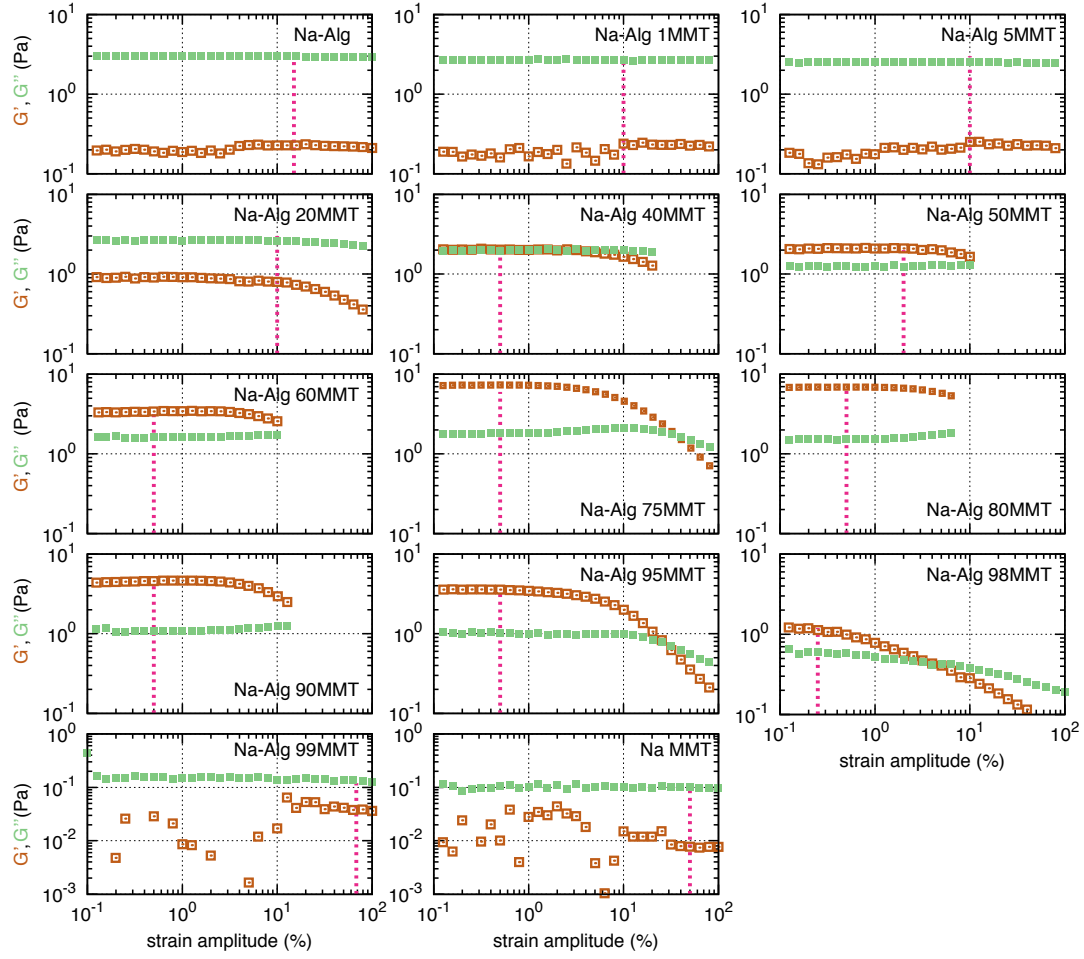


Figure 1 Storage (G') and loss (G'') moduli, as a function of applied strain amplitude for Na-Alg solution, Na-MMT and Na-Alg Na-MMT suspension at different clay concentrations to investigate the strain independence (linear viscoelastic regime). Total solid concentration of suspensions was fixed at 3 wt.%. The measurements were performed at a frequency of 10 rad/s. The vertical lines indicate the strain used for the frequency sweep measurement. Note the different scale-bars for G' and G'' in some of the figures.

Figure 2 shows the storage and loss modulus, G' and G'' , of a 3 wt.% Na MMT suspension (open circles) and a 3 wt.% Na-Alg (open squares) solution as a function of angular frequency measured by parallel plate geometry. The Na-Alg solution primarily liquid-like behavior, $G'' > G'$, showing scaling properties of approximately $G' \propto \omega^{1.5}$ and $G'' \propto \omega$. The deviation from the behavior of a fully relaxed homopolymer ($G' \propto \omega^2$ and $G'' \propto \omega$) might be attributed to polydispersity²². The aqueous dispersion of MMT exhibits a liquid-like behavior where the storage modulus scales with frequency as $G' \propto \omega^2$ and the loss modulus is linear in frequency $G'' \propto \omega$. The 3 wt.% MMT suspension behaves as a solid at very short time scale of 0.025 s (40 rad/s crossover). This can be attributed to face-edge interaction and a formation of a transient network. Abend and Lagaly reported similar behavior of Na-MMT in this concentration range²³.

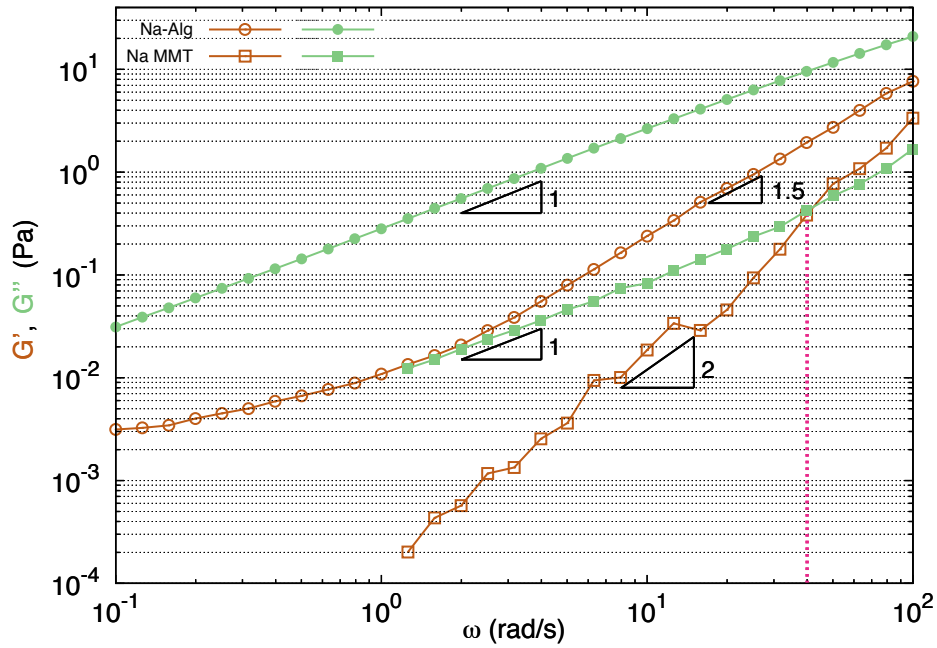


Figure 2 Storage (G') and loss (G'') moduli of Na-Alg solution and Na-MMT suspension as a function of angular frequency. Total solid concentration of both suspension and solutions is 3 wt.%. The vertical line at 40 rad/s indicates the $G'-G''$ crossover.

The storage and loss modulus for the systems with 1 and 5 wt.% Na-MMT platelets are shown as a function of angular frequency in Figure 3. The addition of Na-MMT platelets up to 5 wt.% has little influence on the storage moduli. We still observe a liquid-like behavior of the suspension with G'' values higher than the G' values at the studied frequency range. A decrease in the terminal slope was noticed for the 5 wt.% Na-MMT compared to 1 wt.% Na-MMT that could be a result of interaction between the Na-MMT and alginate that can cause reduced mobility. We also notice that the extrapolated high frequency crossover relaxation time remains unaffected (roughly at 300 rad/s) and the high frequency regimes overlap.

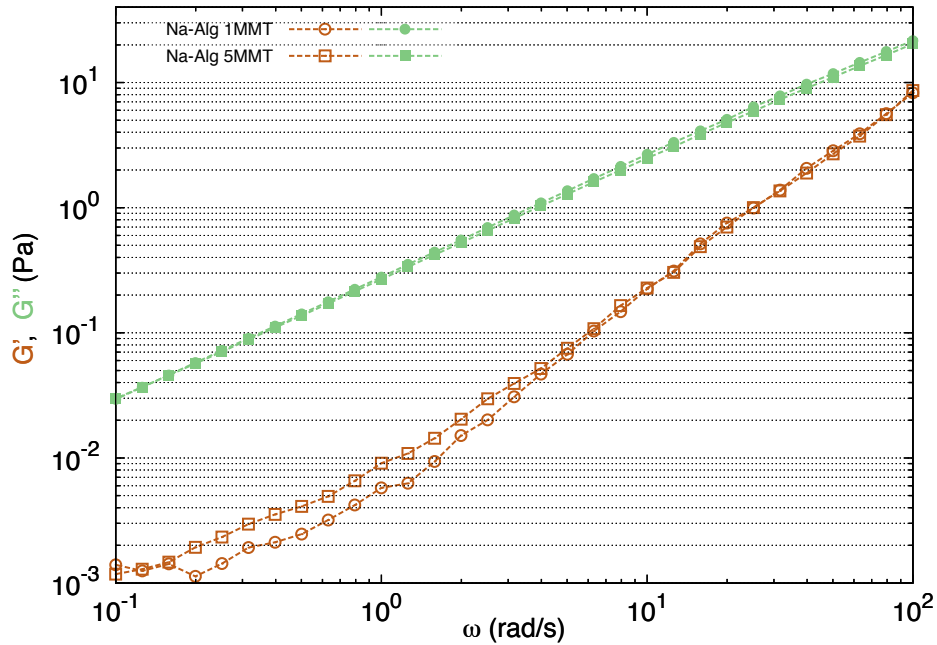


Figure 3 Storage (G') and loss (G'') moduli of Na-Alg suspension with 1 and 5 wt.% Na-MMT as a function of angular frequency. We observe a liquid-like behavior over the investigated timescales. Total solid content of the mixed suspension was 3 wt.%.

With further addition of Na-MMT, at 20 wt.%, a crossover appears and at lower frequencies with $G' > G''$ and frequency independence of G' , presented in Figure 4. The corresponding frequency of the cross-over is 0.1673 rad/s. G' dominance falls in the region at large time-scales, which suggests that over longer timescales the suspension behaves like a viscoelastic soft solid as the long-range rearrangements are very slow. Above the $G'-G''$ crossover point, we have a dominant viscous behavior, which implies that short-range rearrangements occur rapidly²⁴. The reason for the crossover could be a result of an interaction between the edges of the Na-MMT platelets, which can be positively charged, and the negatively charged alginate backbone²⁵. The Na-MMT platelets are linked to form a network structure, which can be disrupted by the flow. It is important to note that the formed cross-links appear to be transient that at rest allows the gel structure to rebuild to its initial structure. This is also characterized, as will be shown below, by a weak frequency dependence of the storage modulus and $G' > G''$ over the measured frequency range, indicating that the material behaves solid-like on the investigated time-scales. We also note that in broader terms the high frequency crossover seems to be independent of the MMT concentration up to 20 wt.%.

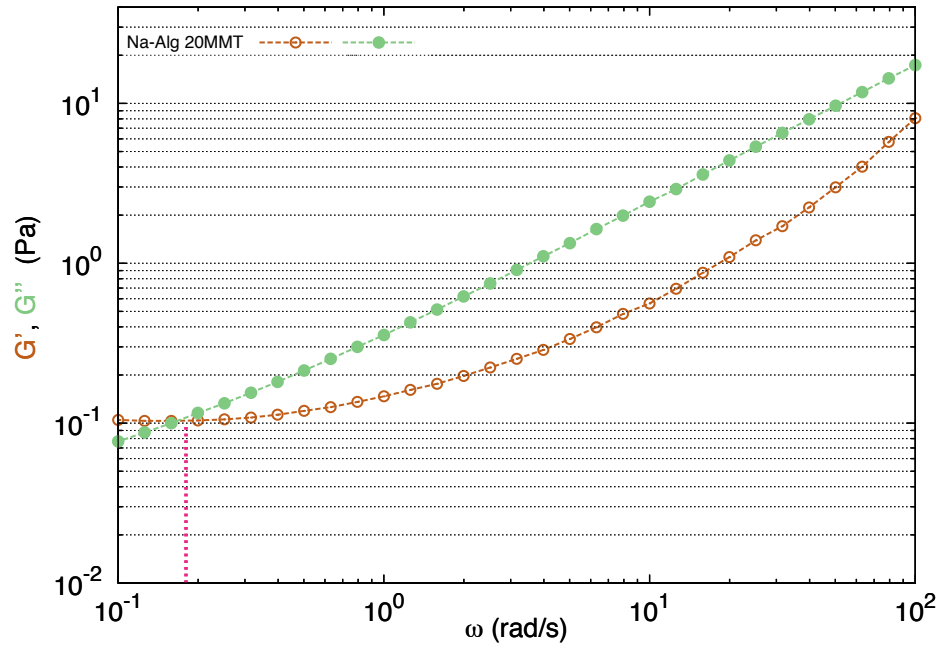


Figure 4 Storage (G') and loss (G'') moduli as a function of angular frequency for Na-Alg suspension with 20 wt.% Na-MMT. The measured G' - G'' crossover frequency is at 0.1673 rad/s.

The frequency dependence of the storage modulus for suspensions with Na-MMT concentration above 40 wt.% up to 98 wt.% can be seen in Figure 5. The storage modulus is greater than the loss modulus, compare figures 5 and 6, over the entire frequency range which corresponds to a solid-like behavior, and G' is nearly frequency independent, i.e. we detect a plateau modulus. This plateau implies that for these time scales the suspension behaves as an elastic body. Aforementioned suggests the formation of an associative network, which could be attributed to the large number of connections between the polymer and the Na-MMT platelets. With further addition of the Na-MMT platelets to the suspension a substantial increase in the plateau modulus is measured, suggesting that a strong reinforcement occurs in the system, in addition the plateau modulus is observed over a much larger frequency range. This plateau modulus is analogous to a classic rubber plateau.

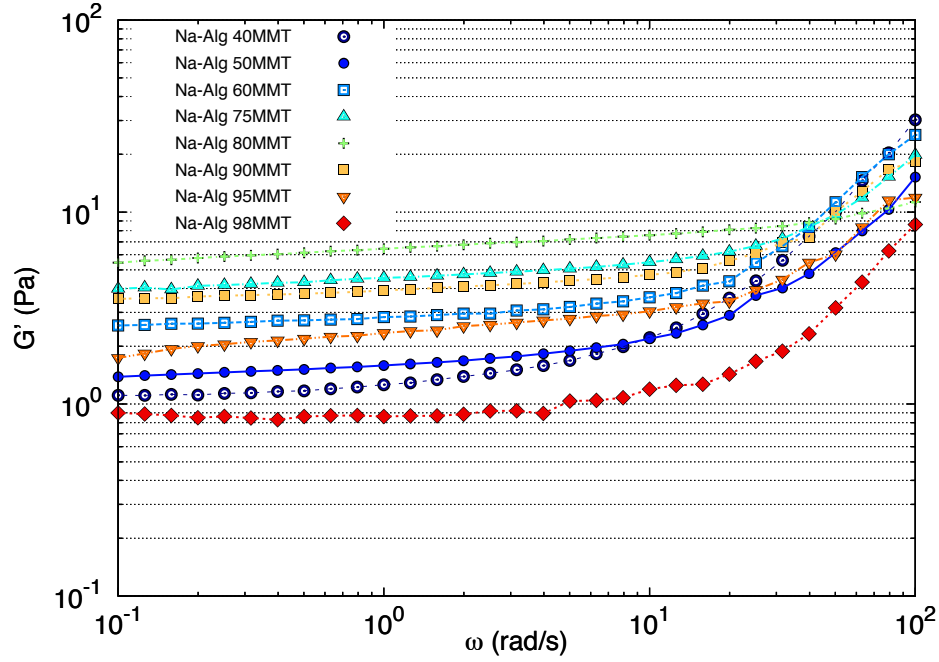


Figure 5. Storage moduli of Na-Alg with 40, 50, 60, 75, 80, 90, 95, and 98 wt.% Na-MMT as a function of angular frequency. The total solid concentration is 3 wt.%.

In Figure 6, we observe that, at lower frequencies, the Na-Alg/MMT bio-nanocomposite suspensions show a distinct minimum in the loss modulus. This minimum shifts to higher frequency values with increasing in Na-MMT concentration. Further we observe that the minimum becomes less shallow and wider at higher volume fractions of Na-MMT platelets. Because the interactions that form a continuous network are of a transient nature (physical cross-links), a structural relaxation that is characterized by a $G' - G''$ crossover and $G'' > G'$, is expected to occur at much longer timescales than measured here. This means that a maximum in viscous dissipation will be present at lower frequencies and will be followed by a decrease in the storage modulus, so that relaxation will take place and the suspension will start to flow²⁶. The relaxation can be attributed to the breaking and reforming of the transient MMT-alginate bonding. Such

behavior is, as mentioned, characteristic for physical gels where the continuous network is portrayed by reversible links formed from temporary associations between the chains.

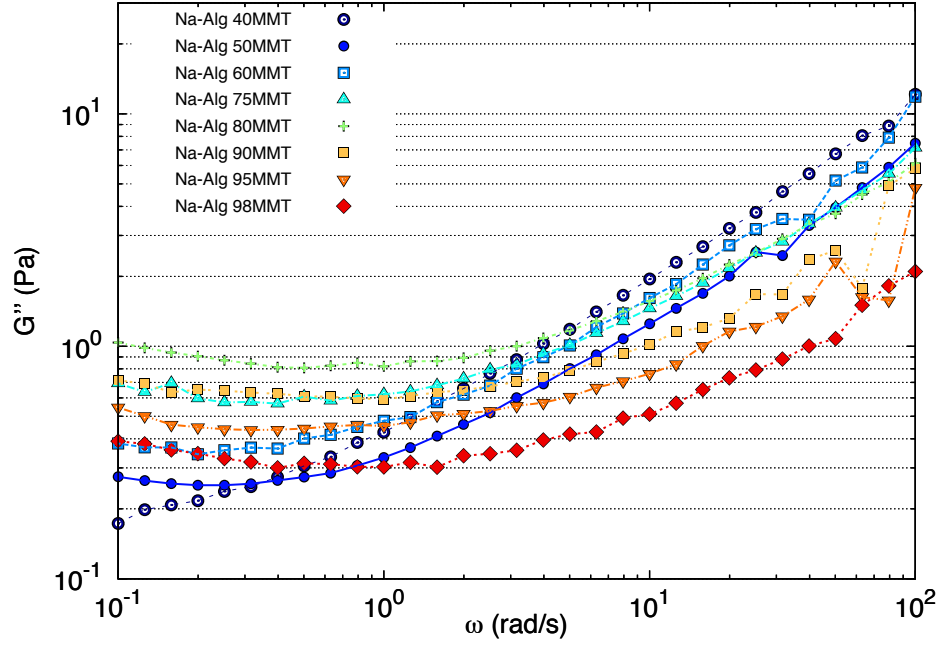


Figure 6. Loss moduli of Na-Alg with 40, 50, 60, 75, 80, 90, 95, and 98 wt.% Na-MMT as a function of angular frequency. The total solid concentration is 3 wt.%.

The measured values of plateau modulus, at 0.1259 rad/s, are presented in figure 7, where we observe that the associative network is formed at 20 wt.% Na-MMT and the measured values of the plateau modulus reach its peak at around 80 wt.% Na-MMT. Subsequently, by further addition of the Na-MMT we detect a rapid decline in the plateau modulus, which could be related to the formation of fewer bonds in the network with the decrease in concentration of Na-Alg.

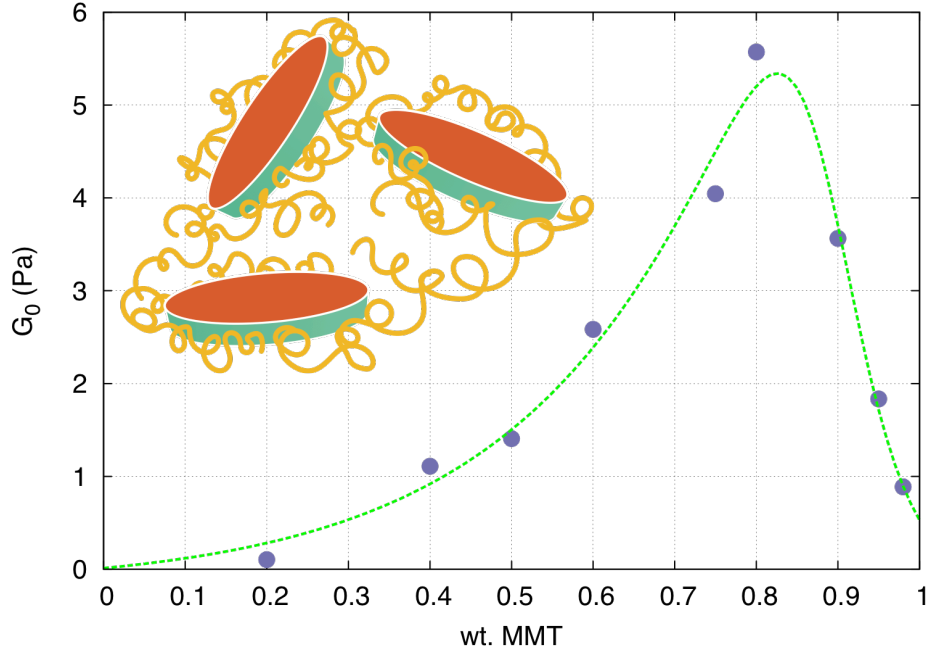


Figure 7. Plateau modulus G_0 of Na-Alg/MMT gels measured at 0.1259 rad/s as a function of Na-MMT concentration. The figure shows that above 20 wt.% Na-MMT we see an increase in plateau modulus with addition of Na-MMT until 80 wt.% Na-MMT, followed by a rapid decline. At the top left corner Na-Alg/MMT interaction is illustrated and the line connecting the points is a guide to the eye.

In figure 8 we see that the Na-Alg with 99 wt. % Na-MMT behaves similarly to pure Na-MMT suspension, as seen in figure 2. We observe that a small addition of Na-Alg increases the viscous component of the Na-MMT suspension. Such behavior might be explained by the alginate adsorption around the edges of the MMT platelets, which inhibits the face-edge interactions between the platelets. Also, as a result of the low alginate concentration no entanglement and bridging occurs that could give rise to an elastic component in the rheology of the system.

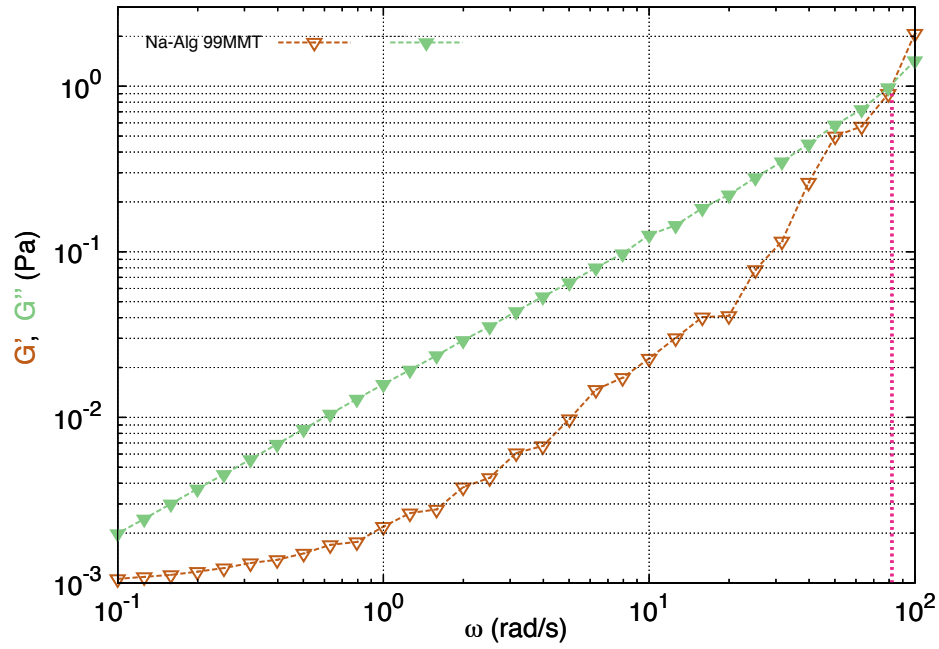


Figure 8. Storage (G') and loss (G'') moduli for Na-Alg with 99 wt.% Na-MMT as a function of angular frequency. The vertical line indicates a G' - G'' crossover.

Figure 9 shows the result of a time sweep experiment at 2 % strain amplitude and 10 rad/s angular frequency at 25 °C, during which the kinetic evolution of the network during crosslinking of alginate with MMT platelets was monitored. Time sweep oscillation experiments were used to characterize the formation of a physical network for a Na-Alg suspension with 70 wt.% Na-MMT by measuring G' and G'' recovery as a function of time. After the gel formation is complete, the G' values should reach a constant value. Initial gelation was unfortunately not measurable due the rather fast kinetics of the gel formation. Since this is a physical gel with dynamic bonds we applied a shear rate of 100 s^{-1} for 120 s to break the gel, and measured the time it needed to rebuild the network. The measured gelation time is estimated by taking the crossover point of G' and G'' at 10 rad/s, which marks a transition from liquid-like to solid-like behavior. We performed the measurement two times on the same sample and measured the

crossover point to be 43 and 49 seconds for the first and the second run, respectively. We also note that there is an orientation induced reduction in the viscous component, G'' , which has a fast recovery, while intriguingly the network recovery of the elastic component, G' , seems to be much slower.

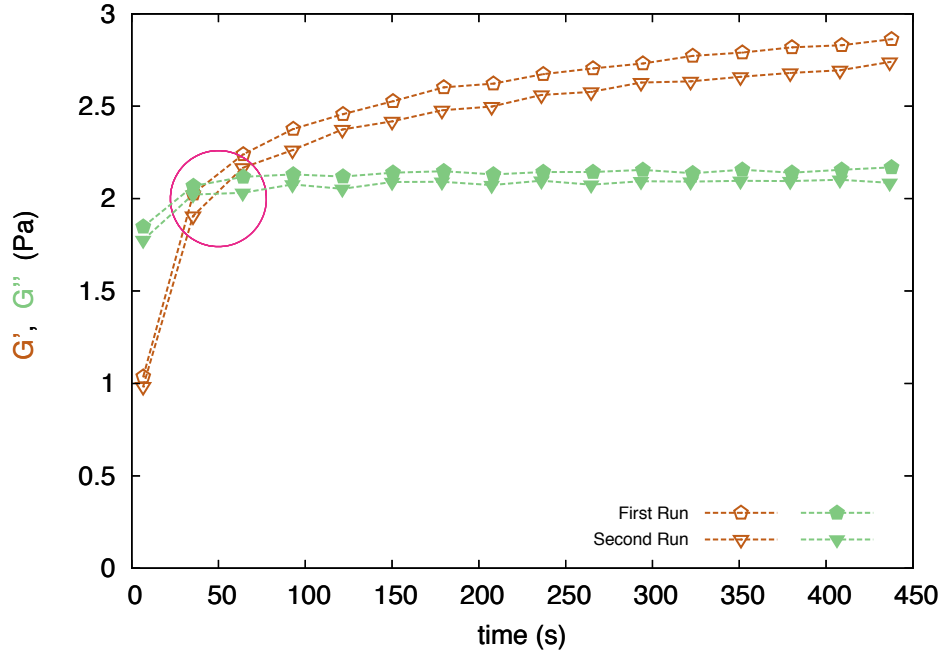


Figure 9. Evolution of storage (G') and loss (G'') moduli over time for Na-Alg with 70 wt.% Na-MMT suspension measured at 10 rad/s. Before each time sweep measurement a pre-shear of 100 s^{-1} for 120 s was performed on the suspension. Total solid concentration is 3 wt.%.

Furthermore, we measured the viscoelastic response of the bio-nanocomposite suspension at longer time-scales. In figure 10, we measured the relaxation that is characterized by a peak in viscous dissipation at a value of around $6.83\text{E-}3 \text{ rad/s}$. The storage modulus is nearly constant over a large frequency range, corresponding to an elastic, solid-like response. The $G'-G''$ crossover at very low frequencies is also visible, which implies a viscoelastic response with a

finite relaxation time. The structural implications of the relaxation observed at very low frequency (G'' maximum) is that the MMT platelets are not permanently attached to the polymer, but rather that there is a very slow dynamic (transient) cross-link.

To investigate the long relaxation times associated with interaction of the MMT platelets with the alginate backbone the frequency sweep results, of Na-Alg 70 wt.% Na-MMT, were fitted to a 2-mode Maxwell model²⁸, see Eq 1 and 2:

$$G'(\omega) = \frac{G_{P1}\omega^2\tau_{R1}^2}{1+\omega^2\tau_{R1}^2} + \frac{G_{P2}\omega^2\tau_{R2}^2}{1+\omega^2\tau_{R2}^2} \quad (1)$$

$$G''(\omega) = \frac{G_{P1}\omega\tau_{R1}}{1+\omega^2\tau_{R1}^2} + \frac{G_{P2}\omega\tau_{R2}}{1+\omega^2\tau_{R2}^2} \quad (2)$$

where, G_{P1} and G_{P2} are the shear moduli, τ_{R1} and τ_{R2} the specific times of the relaxations and ω is the angular frequency. This Maxwell-like viscoelastic model with two relaxation times fits the experimental results reasonably well.

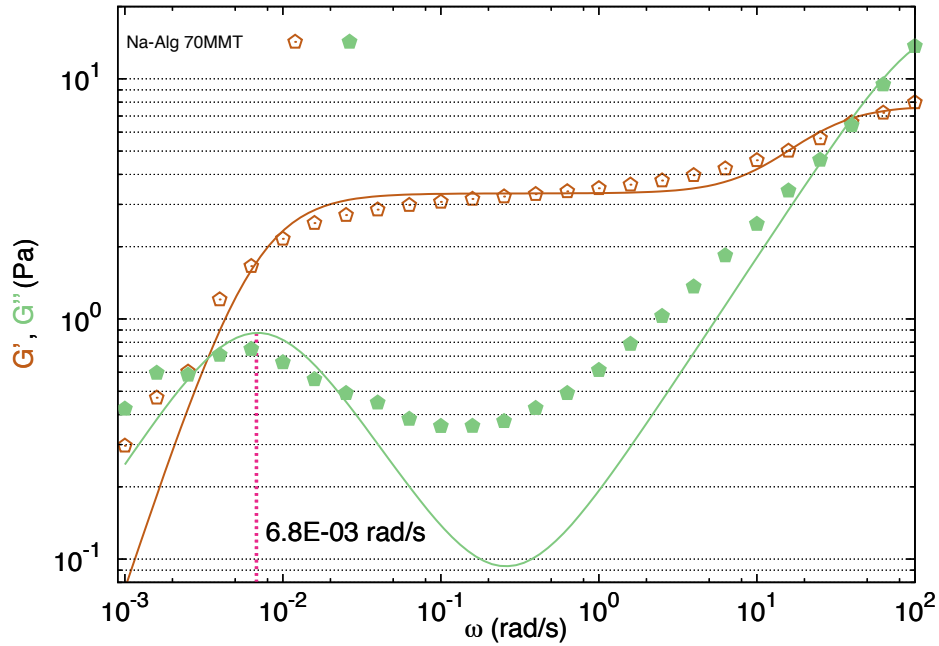


Figure 10. Storage (G') and loss (G'') moduli as a function of angular frequency for Na-Alg system with 70 wt.% Na-MMT over a longer timescale. The solid lines show the results of a dual- τ Maxwell model, see equations 1 and 2.

We also used a startup shear measurement, figure 11, to examine the nonlinear response of Na-Alg system with 70 wt.% Na-MMT. At shear rates higher than 0.01 s^{-1} , the system displays a stress overshoot at a critical strain before reaching steady state. Since we started from the same initial structure the increase in the stress overshoot with increasing shear rate reflects both the elastic response and the breakdown and rearrangement of the structure under flow. In broad terms, this is in agreement with the observed low frequency network dynamics at about $5\text{E-}3 \text{ rad/s}$, shown in figure 10.

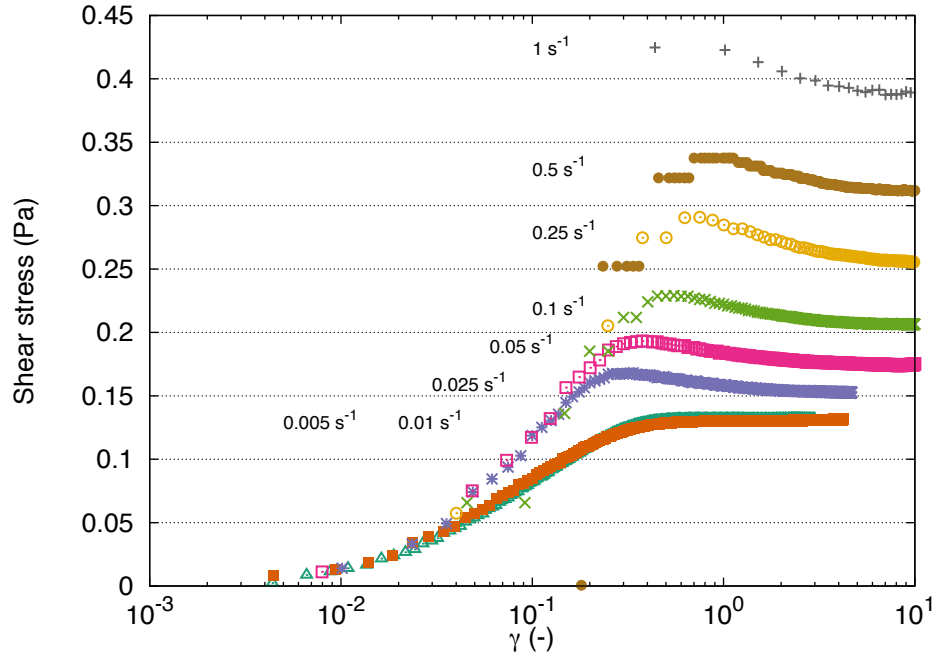


Figure 11. Stress-strain curves of a startup at various shear rates from 0.005 to 1 s^{-1} for Na-Alg with 70 wt.% Na-MMT, at 3 wt.% total solids. The stress overshoot varies with applied shear rate.

4 CONCLUSIONS

The viscoelastic properties of Na-Alg/MMT suspensions have been studied using dynamic and steady shear rheology to investigate specific interactions between the MMT platelets and the alginate polymer. The systems were observed to form a physical gel above a critical Na-MMT concentration, which in this study was 20 wt.%. The results indicate that alginate and MMT platelets form a three dimensional structure as a result of specific interactions. These interactions are a result of attraction between the negatively charged alginate backbone with the positively charged MMT edges, possibly assisted by hydrogen bonding. We find an increase in the elasticity of the gel structure by addition of the Na-MMT platelets up to 80 wt.% Na-MMT, which we believe to be due to an increased level of interaction in the gel network. This gel formation, we propose, is responsible for the later development of the highly ordered nanostructure, which is achieved during water evaporation, as reported previously⁹.

We also observed that the Na-Alg with 99 wt.% Na-MMT behaves similarly to the pure Na-MMT system, where we find an increase in the viscous component for the 99 wt.% Na-MMT. This suggests that the alginate decorates the MMT platelets and thus reduces the face-edge interactions. A dynamic oscillatory measurement was performed for Na-Alg suspension with 70 wt.% Na-MMT over longer time scales, and a relaxation time associated with the transient bonds of the physical gel occurs after which the suspension started to flow. The dual-mode Maxwell model that could be fitted to the experimental results seems to describe the relaxation of the MMT-alginate bond reasonably well.

A time sweep at fixed frequency was performed to investigate the microstructure recovery after breakdown due to high shear. We find that the structure reforms quite quickly (gel time

around 40 s) indicating a transient bonding of the suspension, in agreement with the SAOS results.

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Notes

The authors declare no competing financial interest.

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Highlights

- Alginate and montmorillonite form a dynamic physical gel with a randomly dispersed montmorillonite platelets interacting with the polymer.
- The associative network starts to be formed at 20 wt.% montmorillonite with a peak level of association at a concentration of around 80 wt.%.
- The gel formation is a crucial factor to explain the observed highly organised structure during film formation.