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DOI
10.1016/j.colsurfa.2022.130120

Publication date
2022

Document Version
Final published version

Published in
Colloids and Surfaces A: Physicochemical and Engineering Aspects

Citation (APA)
Shakeel, A., Ali, W., Chassagne, C., & Kirichek, A. (2022). Tuning the rheological properties of kaolin suspensions using biopolymers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *654*, Article 130120. https://doi.org/10.1016/j.colsurfa.2022.130120

Colloids and Surfaces A: Physicochemical and Engineering Aspects 654 (2022) 130120

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Tuning the rheological properties of kaolin suspensions using biopolymers

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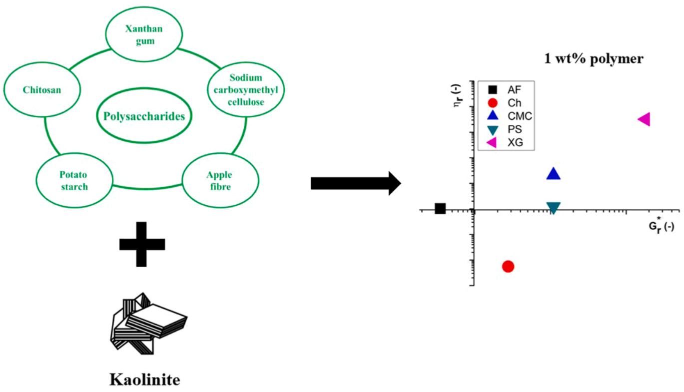
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Two-step yielding
Kaolin
Suspension
Biopolymers
Rheology

ABSTRACT

Kaolin based suspensions have wide range of applications such as slurry wall, drilling fluids, adhesives, cosmetics, refractories and pharmaceuticals, due to their abundance in nature, low cost and non-swelling nature. On the other hand, the unique properties (i.e., biodegradability) of biopolymers make them suitable candidate for variety of applications including modification of clay suspensions. In this study, the rheological properties of kaolin suspensions modified with different biopolymers (xanthan gum (XG), sodium carboxymethyl cellulose (CMC), potato starch (PS), chitosan (Ch) and apple fibre (AF)) have been investigated by varying the biopolymer type, content and clay content. The main objective of the present study is to propose a substitute for the natural mud sample. Frequency sweep tests, stress ramp-up tests and time-dependent tests were performed by using the Couette geometry (coaxial cylinders) for the prepared suspensions. The rheological results showed that both viscosity and moduli were significantly influenced by adding different biopolymers into the kaolin suspensions. For instance, an increase in viscosity of modified suspensions was observed: 3 – 4 orders of magnitude by adding xanthan gum (1 wt%) or sodium carboxymethyl cellulose (5 wt%) and 6 orders of magnitude by adding apple

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https://doi.org/10.1016/j.colsurfa.2022.130120
Received 21 May 2022; Received in revised form 3 September 2022; Accepted 4 September 2022

fibre (5 wt%). Likewise, the incorporation of different biopolymers significantly affected the complex modulus of modified clay suspensions. For example, similar or higher values of complex modulus than the pure kaolin suspension were observed at low xanthan gum or sodium carboxymethyl cellulose content (0.1 wt%). In case of chitosan, the complex modulus of the modified suspensions was higher than the complex modulus of pure kaolin suspension, even at very low polymer content (1 wt%). In the case of potato starch, a decrease in complex modulus by increasing polymer content till 10 wt% was observed followed by an increase in complex modulus with polymer content. The shear rate ramp-up and ramp-down experiments showed that the time-dependent behaviour of kaolin suspensions was not strongly influenced by adding different biopolymers. This knowledge will provide a base to choose a suitable substitute for the natural mud sample.

1. Introduction

Kaolin based suspensions have wide range of applications such as slurry wall, drilling fluids, adhesives, cosmetics, refractories and pharmaceuticals [1] due to their abundance in nature, low cost and non-swelling nature. Moreover, this clay material is also found in large amount in oil-sand tailings and natural mud present in ports and waterways [2–6]. On the other hand, rheology is one of the most important techniques to analyse the interactions between the clay particles in a suspension and even a small change in the composition of the suspension can result in a very different rheological behaviour [7,8]. Important rheological properties include yield stress, viscosity and elastic modulus. Yield stress is typically defined as a critical stress/pressure required to initiate the flow of material by disturbing the internal structure of the material. Viscosity, on the other hand, represents the resistance of a fluid to a change in shape or movement of neighbouring particles/layers relative to one another (i.e., resistant to flow). An elastic modulus is defined as a substance's resistance to being deformed elastically (i.e., non-permanently) when a sinusoidal stress/strain is applied to it. In literature, extensive research has been performed to study the rheological properties (yield stress, viscosity and modulus) of kaolin suspensions as a function of different influencing factors such as source of clay [9,10], pH [11,12], ionic concentration [13,14], additives and flocculants [15–19], type of ions [20,21], and even by mixing kaolin with bentonite [22,23]. For instance, Shakeel et al. [23] investigated the yielding transitions in mixed kaolinite/bentonite suspensions by varying the kaolinite/bentonite ratio and the total solid content. The results showed a clear transition between a single-step and two-step yielding behaviour in steady and oscillatory tests as a function of kaolinite/bentonite ratio, for a particular total solid content.

Biopolymers, of which polysaccharides, proteins, lipids, nucleic acids and other complex molecules are some examples, typically consist of long chain of monomers, which are covalently joined together [24]. The interesting properties of these biopolymers such as biodegradability, biocompatibility and renewability make them suitable candidate for a variety of applications including electronics (gas sensors) [25], medical devices (wound healing materials) [26], energy (photovoltaics) [27] and food packaging [28]. Polymer modification of clay suspensions has been performed for several applications such as soil erosion control [29], enhanced oil recovery [30], dewatering of oil-sand tailings [31], waste water treatment [32] and soil stabilisation [33]. The side groups (hydroxyl, carboxyl, ester, or amines) of the biopolymers interact with the clay particles, pore water and counter-ions. Furthermore, biopolymers have been reported to form hydrogels, which interact with clay particles, such as to lead to the formation of a network: for instance, xanthan gum and soil have been shown to form such structure [34], which exhibit large strength and lower permeability, making it suitable for geotechnical applications. However, clay-polymer interactions are quite complex and significantly dependent on clay surface characteristics, type of polymer functional groups (i.e., side groups) and water chemistry. The surface and intermolecular forces between the polymers and clay particles mainly control the floc size and microstructure of the polymer-modified clay suspensions [35].

For example, Conceiç ão et al. [36] studied the rheological properties of kaolin suspensions by adding carboxymethyl cellulose (CMC) with different molecular weights, in the presence of ammonium polycarbonate as dispersant. The results showed a significant dependence of rheological properties of modified suspensions on the polymer content, its molecular weight and the preparation procedure of suspension. Likewise, Moan et al. [37] investigated the rheological behaviour of kaolin suspensions modified with carboxymethyl cellulose (CMC) or associative polymers. The results showed higher values of viscosity and moduli (storage and loss) for the polymer-modified suspensions as compared to the pure kaolin suspensions. This enhancement in rheological properties was attributed to the steric stabilisation and also to the presence of polymer bridging and entanglements.

In addition to the modification of kaolin suspensions, biopolymers have also been reported in literature to modify the properties of other clay based suspensions. For instance, Kelessidis et al. [38] examined the rheological parameters of bentonite suspensions, at ambient conditions, modified with carboxymethyl cellulose (CMC) and carbopol. The results showed a decrease in yield stress and consistency index by adding smaller amounts of biopolymers (CMC and carbopol) followed by a plateau or an increase in yield stress and consistency index as a function of CMC content. Likewise, Benyounes et al. [39] reported the modification of bentonite suspensions using anionic polymers (sodium carboxymethyl cellulose and xanthan gum). The results displayed a decrease in yield stress along with an increase in viscosity by adding CMC in bentonite suspensions while an increase in both yield stress and viscosity was observed by adding xanthan gum in bentonite suspensions [39,40]. In addition to that, Wang et al. [41] studied the rheological and mechanical properties of red clay modified with xanthan gum. The results revealed a strong influence of xanthan gum content on the cohesiveness and shear strength of the modified suspensions, without affecting their friction properties.

The two major interaction mechanisms between biopolymers and clay particles are polymer bridging and charge neutralisation [42]. In case of polymer bridging, the polymer functional groups and attractive sites on the clay particles interact with each other through hydrogen bonding such as the hydroxide group on kaolin surface can interact via hydrogen bonding with a non-ionic polymer, i.e., polyethylene oxide [43]. For charge neutralisation, the functional groups of cationic polymers are adsorbed onto the clay surfaces through Coulomb attraction, for example, the interaction between chitosan and clay particles [44]. On the other hand, anionic polymers create an electrostatic repulsion between the negatively charged clay particles, which eventually enhance the double layer repulsion [45]. In addition to this, depletion interactions are induced by the imbalance of osmotic force between the two approaching particles created by the exclusion of small polymer molecules (i.e., non-adsorbing) [46]. These clay-polymer interaction mechanisms are significantly influenced by several factors including cation exchange capacity [47], solid concentration [48], polymer dosage and molecular weight [49]. Clay-polymer interactions define the micro-fabric of the resultant modified suspensions, which eventually influence their macroscale engineering properties such as hydraulic conductivity, compressibility, stiffness and particularly their rheological fingerprint. In literature, the microstructure (i.e., floc size and shape) and settling behaviour of polymer-modified clay suspensions have been

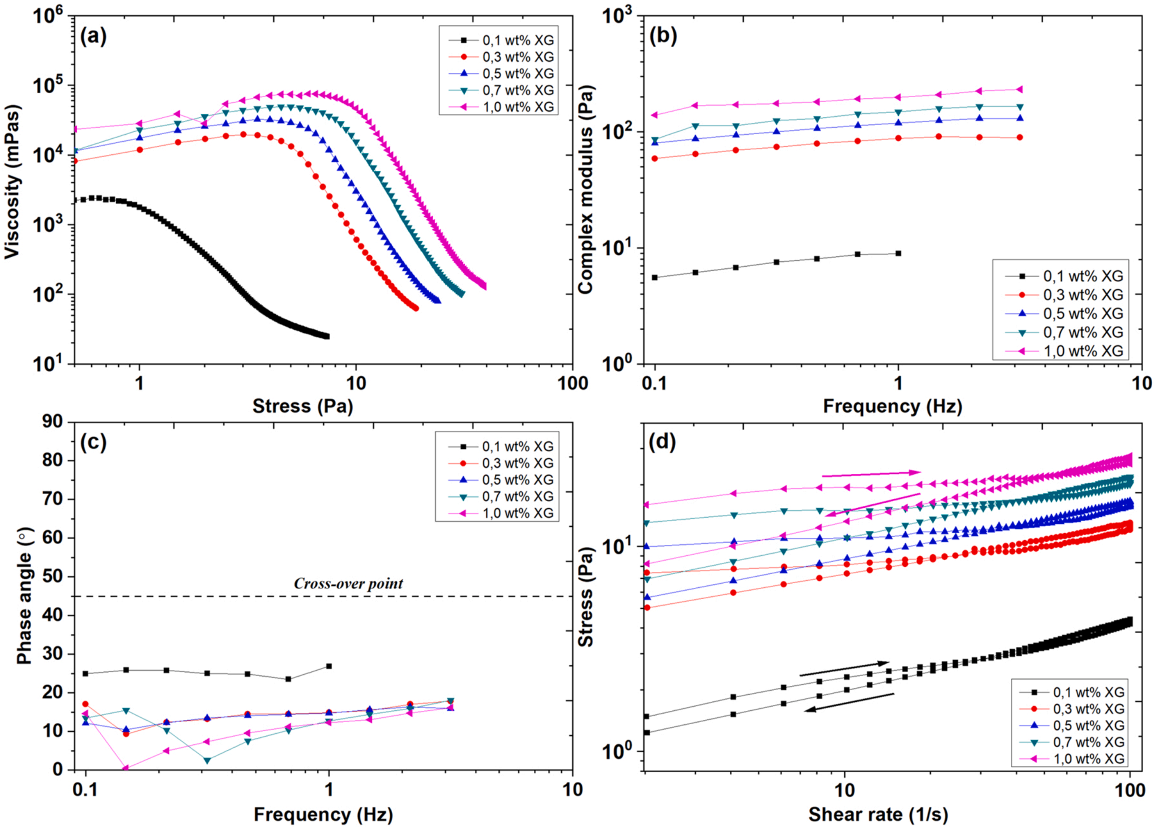

Fig. 1. (a) Apparent viscosity as a function of shear stress, (b) complex modulus (G^{*}) and (c) phase angle (δ) as a function of frequency, (d) shear stress as a function of shear rate for suspensions having 15 wt% kaolin and different xanthan gum content. Dashed line represents the crossover point between $G^{'}$ and $G^{''}$.

extensively studied, however, the comparative analysis of the rheological properties of biopolymer-amended suspensions is still lacking.

Natural mud, typically found at the bottom of rivers, lakes and in coastal areas, consist of water, clay minerals, sand, silt and organic matter (such as living microorganisms and in particular their excreted biopolymers) [50,51]. The rheological properties (i.e., yield stress, viscosity and modulus) of these mud layers are important for nautical bottom applications [52]. However, these mud deposits are quite unstable and degrade as a function of time [53,54], in addition to the costly and time consuming sampling process. Therefore, it is needed to prepare an artificial mud sample in the laboratory with controlled composition, in order to fully understand the rheological fingerprint of natural mud.

The main objective of the present article is, therefore, to investigate the rheological properties particularly the yield stress, viscosity and modulus of polymer-modified kaolin suspensions, as a function of biopolymer type (completely soluble (XG and CMC), fairly soluble (chitosan) and completely insoluble (PS and AF)), biopolymer content and clay concentration. These biopolymers were chosen on the basis of the fact that different biopolymers (with different solubility) are typically present in natural mud and to prepare a suitable substitute for natural mud, the influence of different biopolymers, having different solubility, on the rheological properties of modified system need to be understood. A detailed rheological analysis of polymer-modified clay suspensions was carried out with the help of frequency sweep tests, stress ramp-up tests and time-dependent tests. The influence of different biopolymers on the rheological properties of clay suspensions was then compared in terms of normalised viscosity, yield stress and modulus. This knowledge will provide a base to choose a suitable substitute for the natural mud sample.

2. Materials and methods

2.1. Synthesis of suspensions

Kaolin (provided by Imerys, England) and different biopolymers based suspensions were prepared by dispersing required amount of material (see Table S1) in deionized water (Merck Millipore, Darmstadt, Germany). Xanthan gum (XG), sodium carboxymethyl cellulose (CMC), potato starch (PS) and chitosan (Ch) were supplied by Sigma Aldrich while HERBACEL® AQ® Plus apple fibre (AF) was purchased from Herbafood Ingredients GmbH. These biopolymers (i.e., polysaccharides) were chosen on the basis of their solubility, i.e., XG and CMC (completely soluble), Ch (fairly soluble), PS and AF (completely insoluble). In order to prevent the aggregation of biopolymer, kaolin and biopolymer was mixed in powder form before dispersing in deionized water, followed by a high shear mixing at 1000 rpm for 5–10 min using an IKA homogeniser (RE 162, IKA-Werke GmbH & Co., Staufen, Germany). All the samples were left for 24 h at 20 °C, in order to achieve the complete dissolution of biopolymer, particularly in case of CMC and xanthan gum.

2.2. Rheological analysis

The rheological properties of kaolin suspensions modified with biopolymers were determined by using a HAAKE MARS I rheometer (Thermo Scientific, Germany). Couette geometry (diameter = 25 mm and length = 40 mm), with a gap width of 1 mm, was used to perform rheological experiments. The repeatability error was estimated by performing all the experiments in duplicate with the same suspension during the same day and its value was always lower than 2%. Peltier controller system was used to control the temperature at 20 °C during all the experiments. Yield stress of the polymer modified suspensions was

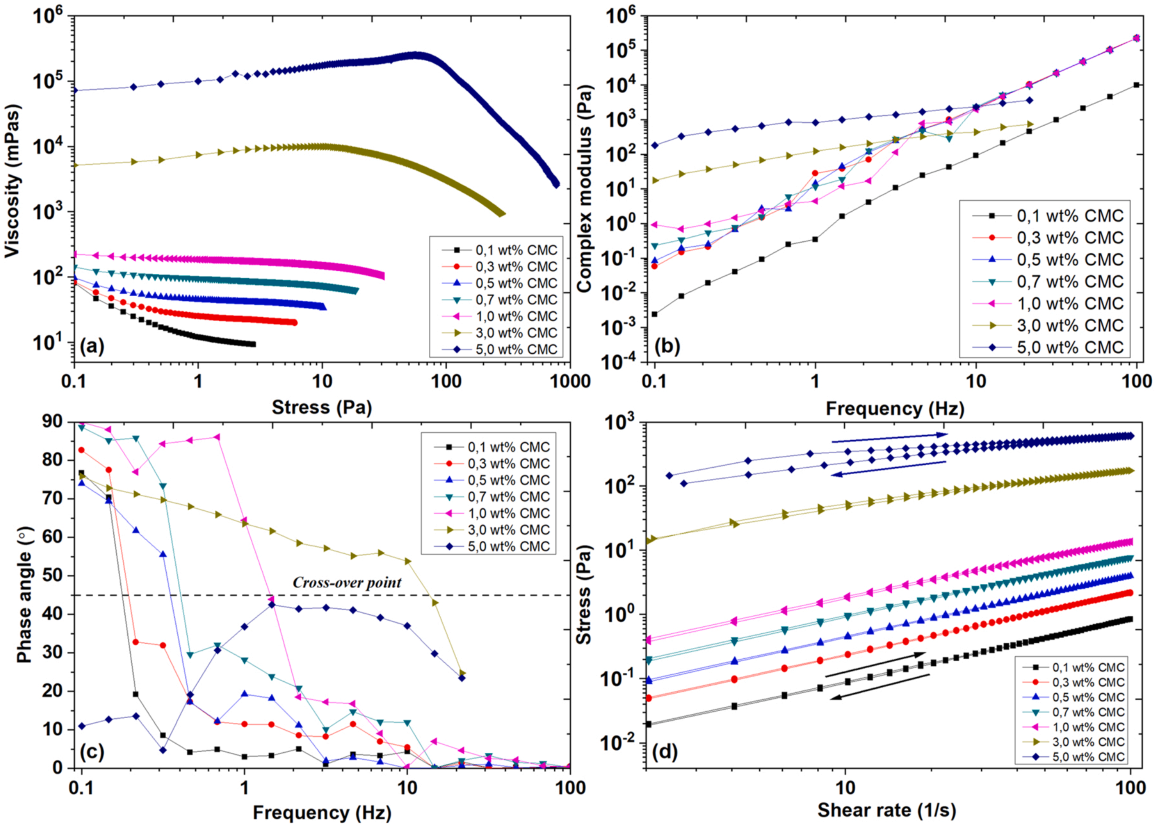

Fig. 2. (a) Apparent viscosity as a function of shear stress, (b) complex modulus (G^*) and (c) phase angle (δ) as a function of frequency, (d) shear stress as a function of shear rate for suspensions having 15 wt% kaolin and different sodium carboxymethyl cellulose content. Dashed line represents the crossover point between G' and G''.

investigated by performing the stress ramp-up tests, i.e., linear increase in stress at a rate of 0.1–1 Pa/s, until the shear rate reaches 300 s^{-1}. In order to examine the strength of the suspensions without affecting the structure, frequency sweep tests were performed within linear viscoelastic (LVE) regime. The linear viscoelastic regime (LVE) was determined by performing the preliminary amplitude sweep tests. The results of these tests were plotted in terms of storage and loss moduli as a function of stress amplitude. The initial frequency independent response of the moduli defines the LVE regime. The frequency was varied from 0.1 to 100 Hz and the results were presented in the form of complex modulus (G^*) and phase angle (δ) as a function of frequency. The experimental data at higher frequencies was removed due to the inertia caused by rheometer head. The time dependent properties of suspensions were investigated by performing a three-step protocol: (i) shear rate ramp-up from 0 to 100 s^{-1} in 50 s, (ii) constant shear rate of 100 s^{-1} for 50 s, (iii) shear rate ramp down from 100 to 0 s^{-1} in 50 s. This test is a quick and easy way of analysing the time-dependent properties (i.e., viscosity) of the suspensions. The experimental data of time-dependent tests (both ramp-up and ramp-down) was further fitted by using a Bingham model, given as:

$$\tau = \tau_B + K\dot{\gamma} \tag{1}$$

where K is the consistency index and τ_B is the Bingham yield stress.

3. Results and discussion

Yield stress values of the clay based suspensions can be easily estimated from stress ramp-up tests [55]. From the viscosity vs shear stress curve, the yield stress can be determined from the sharp decline in viscosity above the yield stress. Before analysing the biopolymer modified kaolin suspensions, pure kaolin suspensions were analysed and the results are presented in Fig. S2. These results were further used to provide a comparative analysis of the influence of different biopolymers on the rheological fingerprint of kaolin suspensions.

3.1. Kaolin/xanthan gum suspensions

The outcome of stress ramp-up tests in terms of apparent viscosity as a function of shear stress for kaolin suspensions having different amounts of XG is shown in Fig. 1a. Initially, the viscosity increases as a function of stress (except for 0.1 wt% XG), which can be attributed to the structural recovery of the sample caused by the disturbance while attaining the measurement position of the geometry (i.e., couette going inside the cup for measurement). The results clearly show a single-step yielding behaviour with increasing yield stress values from 0.95 to 9.0 Pa (estimated from viscosity decline) by increasing the XG amount from 0.1 to 1.0 wt%. This increase in yield stress/viscosity values can be attributed to the formation of a network structure or entanglements by polymeric chains, which eventually result in an increased effective macromolecular dimension [56,57]. Moreover, kaolin particles may attach to the polymeric chain in edge-to-edge manner resulting in a larger floc, which leads to the higher rheological properties [58]. A similar increase in shear strength of red clay was observed in literature as a function of increasing XG content [41].

In addition to the yield stress, the strength of XG modified kaolin suspensions was estimated by performing the frequency sweep tests within LVE regime. The results of frequency sweep tests are presented in Fig. 1b and c, in terms of complex modulus (G^*) and phase angle (δ) as a function of frequency. For all the samples, a solid-like behaviour was observed (i.e., low phase angle values and frequency independent moduli). Moreover, as for yield stress, an increase in complex modulus was found as a function of increasing XG content, which may again be

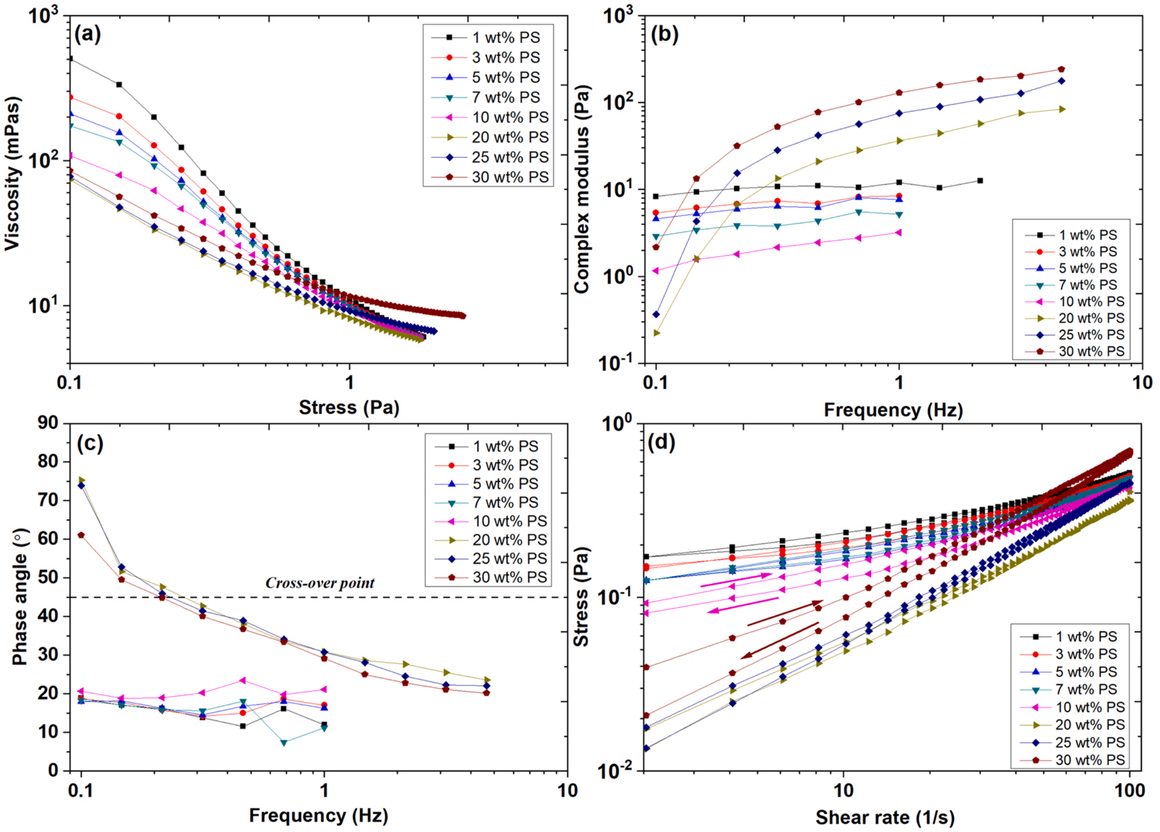

Fig. 3. (a) Apparent viscosity as a function of shear stress, (b) complex modulus (G^*) and (c) phase angle (δ) as a function of frequency, (d) shear stress as a function of shear rate for suspensions having 15 wt% kaolin and different potato starch content. Dashed line represents the crossover point between G' and G''.

attributed to the network formation due to the interacting nature of xanthan gum. On the other hand, the phase angle values were not significantly influenced by the biopolymer content (except for 0.1 wt% XG), which shows that the consistency (G^*) of the samples can be tuned by playing with the biopolymer content without affecting their degree of structuration (δ) [59]. A similar increase in moduli was observed in literature as a function of increasing XG content [60].

The time-dependent properties (i.e., viscosity or shear stress) of polymer-modified suspensions were investigated by performing shear rate ramp-up and ramp-down experiments between 0 and 100 s^{-1}. The result of this test is typically observed either in the form of clockwise or anticlockwise hysteresis loop [61,62]. The outcome of shear rate ramp-up and ramp-down experiments for XG modified kaolin suspensions show the existence of a clockwise loop at lower shear rates, however, a counter-clockwise loop was observed at higher shear rates (Fig. 1d), which may be attributed to the viscoelastic nature of xanthan gum at higher shear rate rates. The existence of counter-clockwise hysteresis loop was also observed in literature for starch pastes modified with XG, which was attributed to the network formation between starch and xanthan gum [63]. Hence, the counter-clockwise hysteresis loop for XG modified kaolin suspensions observed at higher shear rates may also be linked to the shear facilitated flocculation of biopolymer and clay particles.

3.2. Kaolin/sodium carboxymethyl cellulose suspensions

The results of stress ramp-up tests for kaolin suspensions having different amounts of CMC are shown in Fig. 2a. For low biopolymer content (i.e., ≤ 1 wt%), the suspensions show a typical shear-thinning behaviour without any yield stress value. This enhancement in shear thinning behaviour by addition of small amounts of CMC in kaolin suspensions has also been observed in literature [36,64]. However, at high biopolymer concentration (i.e., > 1 wt%), polymer modified suspensions behave as a yield stress fluid. This yield stress value was observed to increase from 13.5 to 69.5 Pa by increasing the CMC content, which may be attributed to the formation of polymer network or interaction between clay particles and polymeric chains. A similar increase in yield stress of bentonite suspensions was observed in literature after a certain critical concentration of CMC [38].

In addition to stress ramp-up tests, frequency sweep tests (within LVE regime) were also performed for kaolin suspensions modified with CMC and the results are shown in Fig. 2b and c, in terms of complex modulus (G^*) and phase angle (δ) as a function of frequency. In accordance with previous results of stress ramp-up tests, kaolin suspensions modified with lower CMC content display a liquid-like behaviour by having a strong frequency dependent modulus (Fig. 2b) and a crossover between G' and G'' at low frequencies (Fig. 2c). Moreover, an increase in complex modulus along with less dependence on frequency was found as a function of increasing CMC content, which may again be attributed to the formation of polymer network at higher biopolymer content. On the other hand, the phase angle values were also significantly influenced by the biopolymer content particularly the crossover point (i.e., $\delta = 45$), which shows that both consistency (G^*) and degree of structuration (δ) of the suspensions will be affected by changing the CMC content. In literature, an increase in moduli values was observed for kaolin suspensions as a function of increasing CMC content, which was associated to the adsorption of polymeric chains on clay particles and also to the network formation of polymeric chains [37].

The time-dependent properties of CMC-modified suspensions, in terms of shear stress vs shear rate hysteresis loops, are presented in Fig. 2d. The results showed very similar values of shear stresses for shear rate ramp-up and ramp-down cycles with almost no hysteresis area, particularly for suspensions having low CMC content. This behaviour again verifies the extremely weak nature of these suspensions. However,

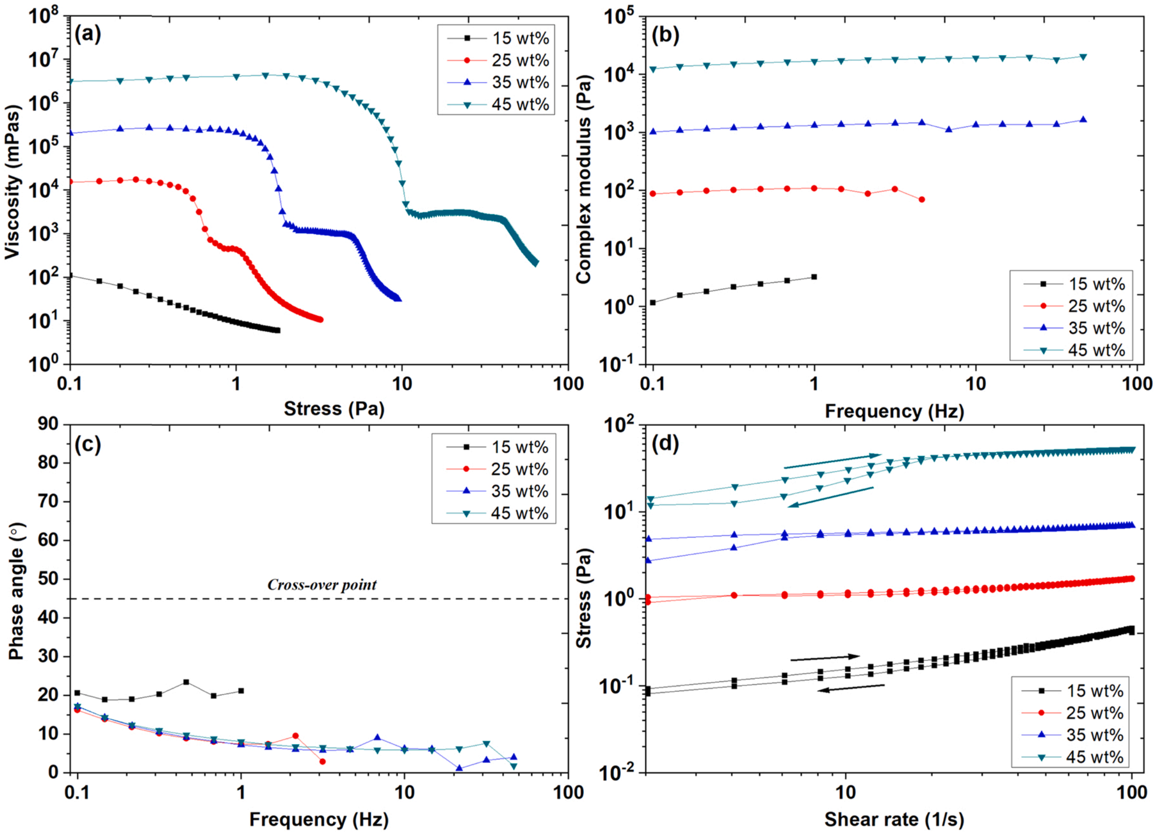

Fig. 4. (a) Apparent viscosity as a function of shear stress, (b) complex modulus (G^*) and (c) phase angle (δ) as a function of frequency, (d) shear stress as a function of shear rate for suspensions having 10 wt% potato starch and different kaolin content. Dashed line represents the crossover point between G' and G''.

at highest biopolymer content, a small clockwise hysteresis loop was observed at lower shear rates, which can be linked to the breakage of polymer network or clay-biopolymer flocs after the ramp-up cycle. Moreover, the experimental data of time-dependent experiments of biopolymer-modified suspensions is fitted with Bingham model and the values of the parameters for ramp-up and ramp-down curves are presented in Table S3. It can be clearly seen that there is a difference between yield stress values for ramp-up and ramp-down curves, however, this difference is not very significant and also not strongly dependent on biopolymer type and content, which again verifies the weak thixotropic nature of the modified suspensions.

3.3. Kaolin/potato starch suspensions

3.3.1. Effect of biopolymer content

The outcome of stress ramp-up tests for kaolin suspensions having different amounts of non-gelatinised potato starch is shown in Fig. 3a. The results clearly show a typical shear thinning behaviour for all the investigated suspensions with no yield stress. Moreover, by increasing the biopolymer content, the apparent viscosity of the suspensions was observed to decrease until 20 wt% of potato starch. After this biopolymer content, the viscosity values remained more or less constant. This decrease in apparent viscosity values can be attributed to the electrostatic charges of the kaolin particles [65], in a way similar to that of the addition of electrolytes in a clay suspension [19,66].

In addition to the viscosity, the moduli of potato starch modified kaolin suspensions was estimated by performing the frequency sweep tests within LVE regime and the results are presented in Fig. 3b and c. For the suspensions having low potato starch content (i.e., $\leq$ 10 wt%), a solid-like behaviour was observed (i.e., low phase angle values and almost frequency independent moduli). However, at higher biopolymer content (i.e., $>$ 10 wt%), the suspensions show a liquid-like behaviour by having a strong frequency dependent modulus (Fig. 3b) and a crossover between G' and G'' at lower frequencies (Fig. 3c). This result shows that at lower biopolymer content ($\leq$ 10 wt%) and fixed kaolin content (15 wt%), the suspensions behave like a clay-dominant system while at higher biopolymer content ($>$ 10 wt%) and fixed kaolin content (15 wt%), the system becomes polymer dominant, which shows the applicability of simple mixture rule.

Interestingly, this behaviour is opposite to the one observed for the CMC modified kaolin suspensions (Fig. 2b). The reason for this opposite behaviour can be attributed to the presence of interactions between polymeric chains or between clay particles and polymer chains for CMC based suspensions while in case of non-gelatinised potato starch modified kaolin suspensions, the system behaves as a non-interacting mixture of soft polymer granules and hard clay particles. Furthermore, this behaviour can also be attributed to the presence of repulsive forces at the surface of starch granules. Moreover, as for apparent viscosity, a decrease in complex modulus was found as a function of increasing potato starch content until 10 wt%, followed by an increase in complex modulus after that particular biopolymer content. The initial decrease in complex modulus/viscosity of polymer-modified suspensions can be linked to the addition of soft polymer particles into a mixture of hard clay particles. The latter increase in complex modulus values can be linked to the addition of polymer particles in a polymer dominated system, which eventually makes it more viscoelastic.

The results of shear rate ramp-up and ramp-down experiments for potato starch-modified suspensions are shown in Fig. 3d. The results show almost no hysteresis area (i.e., less time dependence), particularly for suspensions having lower potato starch content. This behaviour again verifies the extremely weak nature of these suspensions. However, at higher biopolymer content, a small clockwise hysteresis loop was observed along with the change in slope of stress vs shear rate curve, which may again be linked to the transition from clay-dominant to

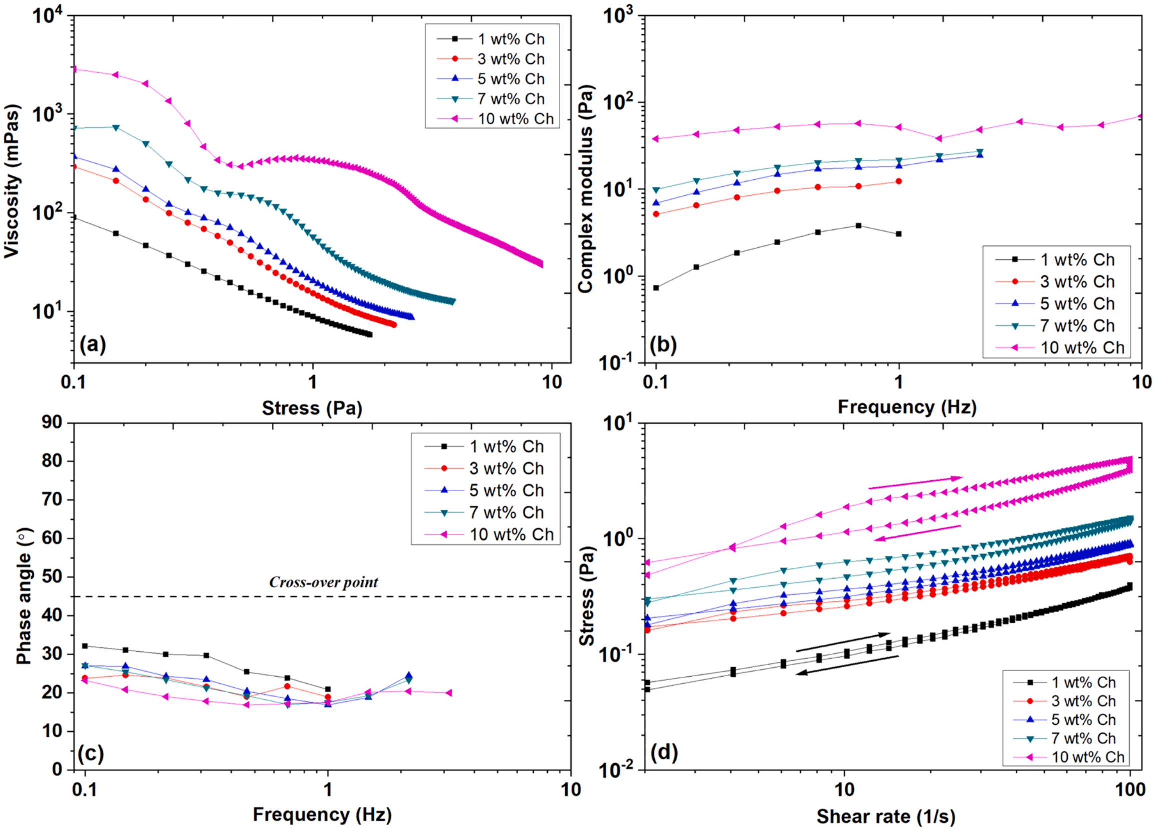

Fig. 5. (a) Apparent viscosity as a function of shear stress, (b) complex modulus (G^*) and (c) phase angle (δ) as a function of frequency, (d) shear stress as a function of shear rate for suspensions having 15 wt% kaolin and different chitosan content. Dashed line represents the crossover point between G' and G''.

polymer-dominant system.

3.3.2. *Effect of clay content*

In addition to the biopolymer content, the effect of clay content was also analysed for potato starch modified suspensions. The results of stress ramp-up tests for suspensions having different amounts of kaolin (15 – 45 wt%) and fixed amount of potato starch (10 wt%) are shown in Fig. 4a. For lowest clay content (i.e., 15 wt%), the suspensions showed a typical shear-thinning behaviour without any yield stress value, which can be attributed to the low total solid content. However, at higher clay concentrations (i.e., > 15 wt%), polymer modified suspensions display a two-step yielding behaviour, with two distinct yield points stated as static and fluidic yield stress [4,55]. This transition from shear thinning to two-step yielding behaviour may be attributed to the fact that at low concentrations, only diffusive dynamics were dominant while at higher clay content both diffusive and trapped dynamics play their role for the observed rheological fingerprints [67,68], as already observed in literature [23]. This two-step yielding behaviour is typically linked to three different dynamical regimes: (i) Reversible dynamics: particle trajectories at sufficiently small strain/stress are reversible and particles trace out ellipses in space consistent with a strictly linear response. (ii) Trapped dynamics: at intermediate strain/stress the particle trajectories are trapped. The particle trajectories do not form closed orbits but remain bounded. (iii) Diffusive dynamics: for high strain/stress, the particle motion becomes diffusive [67]. Moreover, this two-step yielding behaviour may also be linked to the anisotropic nature of suspensions and the alignment of hydro-clusters under shearing action, which needs further research.

A similar transition between single-step and two-step yielding was found in literature as a function of solid content for cocoa/vegetable oil suspensions [69]. This two-step yielding behaviour is typically analysed by performing oscillatory amplitude (stress/strain) sweep tests [70]. Therefore, oscillatory stress sweep tests were also performed for the potato starch-modified samples having different clay content and the results are presented in Fig. S3. For higher clay content (35 and 45 wt%), a clear two-step yielding was found while for lowest clay content (25 wt %), the second yield point was not evident which may be attributed to the inertial problems after the first yield point at the selected frequency for this sample [23]. The applied and measured waveforms were sinusoidal even after the first decline, and became distorted after the second decline, due to high deformations. Therefore, this two-step yielding behaviour can still be linked to the material's characteristics, instead of incorrect estimation of moduli at higher harmonics. Likewise, an increase in yield stress (Fig. 4a) and moduli (Fig. 4b) with almost no effect on phase angle (Fig. 4c) and time-dependent properties (Fig. 4d) were observed as a function of increasing clay content, which is in line with the literature results [23,36].

3.4. *Kaolin/chitosan suspensions*

3.4.1. *Effect of biopolymer content*

The results of stress ramp-up tests for kaolin suspensions having different amounts of chitosan are shown in Fig. 5a. For low chitosan content (i.e., ≤ 3 wt%), the suspensions show a typical shear-thinning behaviour without any yield stress value. However, at higher chitosan concentration (i.e., 5 – 7 wt%), polymer-modified suspensions behave as a yield stress fluid having weak two-step yielding behaviour. At highest biopolymer content (10 wt%), a single yield point with significant shear thinning behaviour was observed. This behaviour may be attributed to the fact that at low biopolymer concentrations, charge neutralisation or polymer adsorption on the clay particles is the controlling interaction mechanism, while at intermediate concentrations, inter-particle polymer bridging start to play a role [58,71]. However, at highest polymer content, interactions between polymeric chains also started to occur,

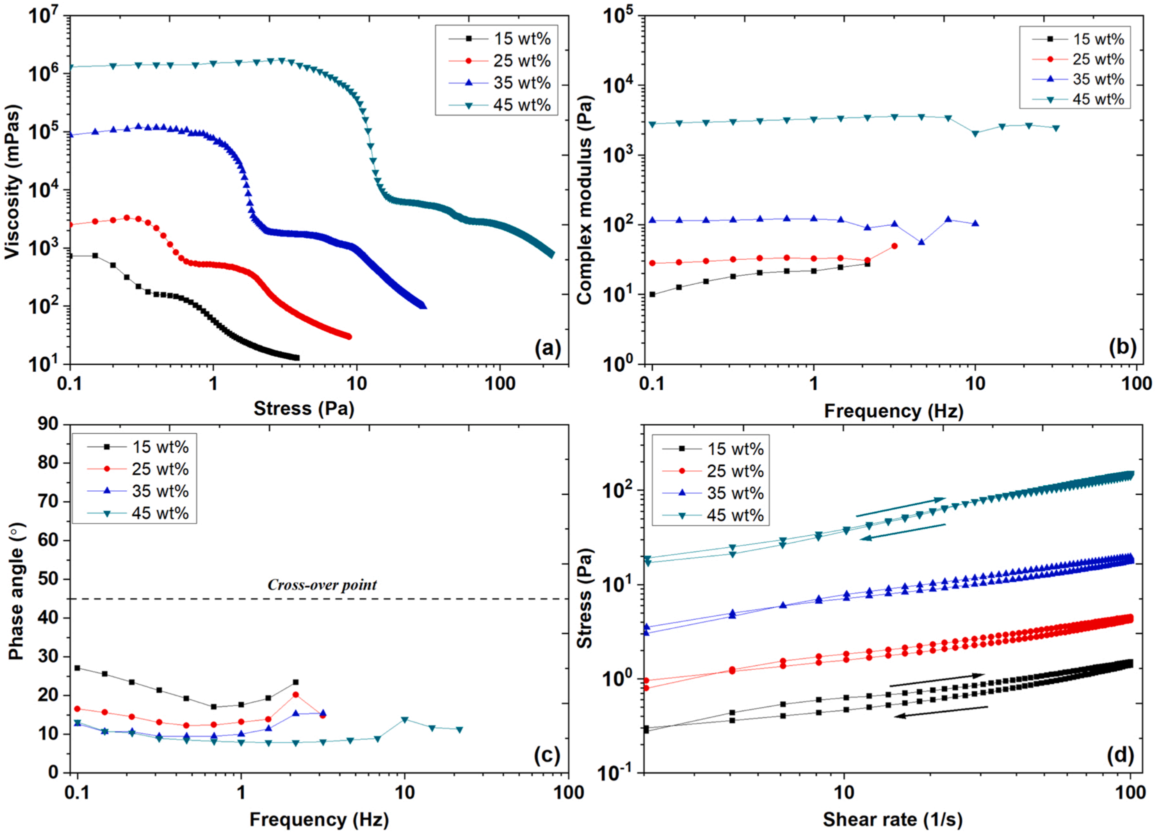

Fig. 6. (a) Apparent viscosity as a function of shear stress, (b) complex modulus (G^*) and (c) phase angle (δ) as a function of frequency, (d) shear stress as a function of shear rate for suspensions having 7 wt% chitosan and different kaolin content. Dashed line represents the crossover point between G' and G''.

which provided significant shear thinning behaviour after the first yield point. This increase in polymer content also results in an increase in apparent viscosity, which may be associated to the formation of a polymer network or interaction between clay particles and polymeric chains.

In addition to the viscosity and yield stress, the complex modulus and phase angle as a function of frequency for chitosan modified kaolin suspensions are presented in Fig. 5b and c. All the suspensions display a solid-like behaviour (i.e., low phase angle values with no crossover and almost frequency independent moduli). Moreover, an increase in complex modulus with similar phase angle values as a function of increasing chitosan content is found, which might again be attributed to the formation of polymer network or clay-biopolymer flocs [37]. The time-dependent properties of chitosan-modified kaolin suspensions are presented in Fig. 5d. The results show similar values of shear stresses for shear rate ramp-up and ramp-down cycles with almost no hysteresis area, particularly for suspensions having low chitosan content (i.e., $\leq$ 5 wt%). However, at higher biopolymer content ($>$ 5 wt%), a clockwise hysteresis loop was observed, which can be linked to the breakage of polymer network or clay-biopolymer flocs after the ramp-up cycle.

3.4.2. *Effect of clay content*

The effect of clay content on the apparent viscosity of suspensions having different amounts of kaolin (15 – 45 wt%) and fixed amount of chitosan (7 wt%) is shown in Fig. 6a. For low clay content (i.e., $\leq$ 35 wt %), the suspensions show a clear two-step yielding behaviour due to the presence of inter-particle polymer bridging, which is enhanced by increasing the clay content. However, at highest clay concentration (45 wt%), a single-step yielding along with shear thinning behaviour is observed. This behaviour shows that the first yield point originates from the clay particles while a shear thinning behaviour, instead of a second yield point, is found because polymer-to-clay ratio decreased (1:6) and polymer adsorption on the clay particles becomes the controlling mechanism (Fig. 5a). Moreover, an increase in yield stress, apparent viscosity (Fig. 6a) and moduli (Fig. 6b) with almost no effect on phase angle (Fig. 6c) and time-dependent properties (Fig. 6d) were observed as a function of increasing clay content.

3.5. *Kaolin/apple fibre suspensions*

3.5.1. *Effect of biopolymer content*

In addition to the commonly used biopolymers, kaolin-modified suspensions were also prepared by using apple fibre. The outcome of stress ramp-up tests for kaolin suspensions having different amounts of apple fibre is shown in Fig. 7a. The results clearly show a typical shear thinning behaviour for kaolin suspensions having lower fibre content (i.e., $\leq$ 2 wt%), a weak yield stress fluid behaviour for suspension with 3 wt% apple fibre and a clear single-step yielding response for suspensions having higher fibre content (4–5 wt%), which can simply be attributed to the increase in solids content. Moreover, by increasing the fibre content, the apparent viscosity and yield stress of the suspensions are observed to increase, as also reported in literature for apple fibre based suspensions [72], which can be linked to the formation of fibre network.

In addition to the yield stress and viscosity, the complex modulus and phase angle of apple fibre based kaolin suspensions are presented in Fig. 7b and c. For the suspensions having lower fibre content (i.e., $\leq$ 2 wt %), a liquid-like behaviour is observed (i.e., frequency dependent moduli and cross-over between G' and G''), which is in line with the stress ramp-up results. However, at higher fibre content (i.e., $>$ 2 wt%), the suspensions show a solid-like behaviour, with increasing modulus as a function of fibre content, which is also observed in literature for apple fibre suspensions [73]. The time-dependent properties of apple fibre-modified kaolin suspensions are presented in Fig. 7d. The results

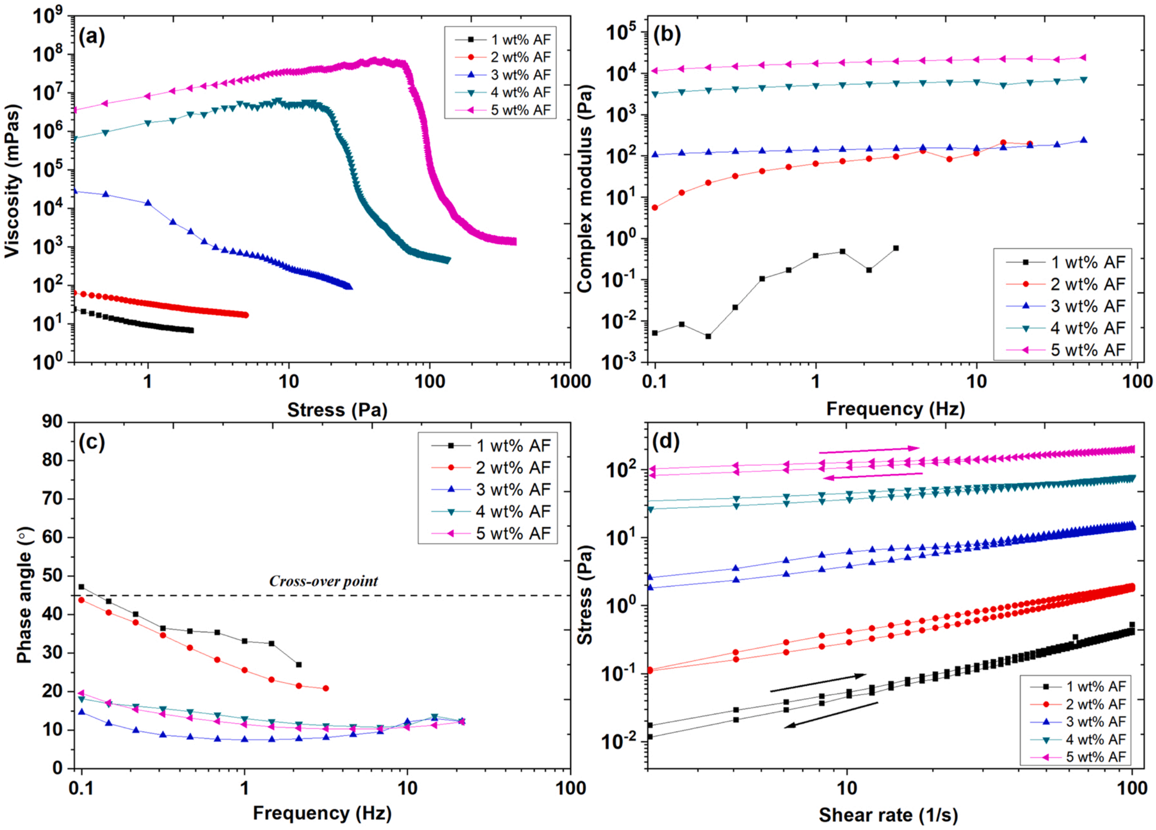

Fig. 7. (a) Apparent viscosity as a function of shear stress, (b) complex modulus (G^*) and (c) phase angle (δ) as a function of frequency, (d) shear stress as a function of shear rate for suspensions having 15 wt% kaolin and different apple fibre content. Dashed line represents the crossover point between $G^{'}$ and $G^{''}$.

show similar values of shear stresses for shear rate ramp-up and ramp-down cycles with almost no hysteresis area for all the samples, which confirms the absence of interactions between clay particles and apple fibre.

3.5.2. *Effect of clay content*

The effect of clay content on the rheological properties of suspensions having different amounts of kaolin (15 – 45 wt%) and fixed amount of apple fibre (3 wt%) is shown in Fig. 8. By increasing the clay content, the suspensions displays a clear single-step yielding with significant shear thinning behaviour at higher stresses, without any second yield point (Fig. 8a). This shear thinning behaviour can be attributed to the breakage of the fibre network and also to the rearrangement or reorientation of long fibres along the flow direction. Moreover, an increase in yield stress, apparent viscosity (Fig. 8a) and moduli (Fig. 8b) with almost no effect on phase angle (Fig. 8c) and time-dependent properties (Fig. 8d) are observed as a function of increasing clay content. However, at lower clay content, a small clockwise hysteresis loop is observed at lower shear rates, which can be linked to the randomness of apple fibres (i.e., anisotropy) during ramp-up and alignment of apple fibres during ramp down, which resulted in slightly different stress or viscosity values. This decrease in viscosity/shear stress as a function of alignment of fibres is also reported in literature for microfibrillar suspension of oxidised pulp [74].

4. Discussion

In order to compare the influence of different biopolymers on the rheological characteristics of kaolin suspensions, reduced viscosity (viscosity at 1 Pa of modified suspensions normalised by the viscosity of pure kaolin suspension) and reduced complex modulus (complex modulus at 1 Hz of modified suspensions normalised by the complex modulus of pure kaolin suspension) are plotted as a function of polymer content (Fig. 9). In case of completely soluble polymers (XG and CMC), the viscosity and complex modulus of the modified suspensions are higher than the viscosity and complex modulus of pure kaolin suspension, even at very low polymer content (0.1 wt%), which increases further as a function of increasing polymer content due to the formation of strong polymer network [75].

In case of fairly soluble polymer (like chitosan), a strong reduction in viscosity is observed as compared to the pure kaolin suspension (Fig. 9a), which can be attributed to charge neutralisation or polymer adsorption at the clay particles, which eventually facilitated the movement of particles during shearing and reduces the viscosity. However, there is still an increase in the viscosity of the modified suspensions by increasing the polymer content, which can be attributed to the formation of inter-particle polymer bridging or polymer network at highest polymer concentrations. On the other hand, the complex modulus of the chitosan modified suspensions is higher than the complex modulus of pure kaolin suspension (Fig. 9b), even at very low polymer content (1 wt %). This interesting result shows that by adding chitosan, the viscosity of modified kaolin suspensions can be reduced by almost one order of magnitude along with the enhancement in the strength of the system.

In case of completely non-soluble polymers (non-gelatinised potato starch), the viscosity of the polymer modified suspensions is almost similar to the viscosity of the pure kaolin suspension (Fig. 9a). Moreover, by increasing the polymer content, the viscosity of the modified suspensions remains more or less constant even at 30 wt% of biopolymer, which confirms the non-interacting nature of potato starch in non-gelatinised form. On the other hand, there is a decrease in complex modulus by increasing the polymer content till 10 wt% followed by an increase in complex modulus with polymer content (Fig. 9b). This decrease in the strength of the suspensions as a function of polymer content can be attributed to the addition of soft polymer granules, which

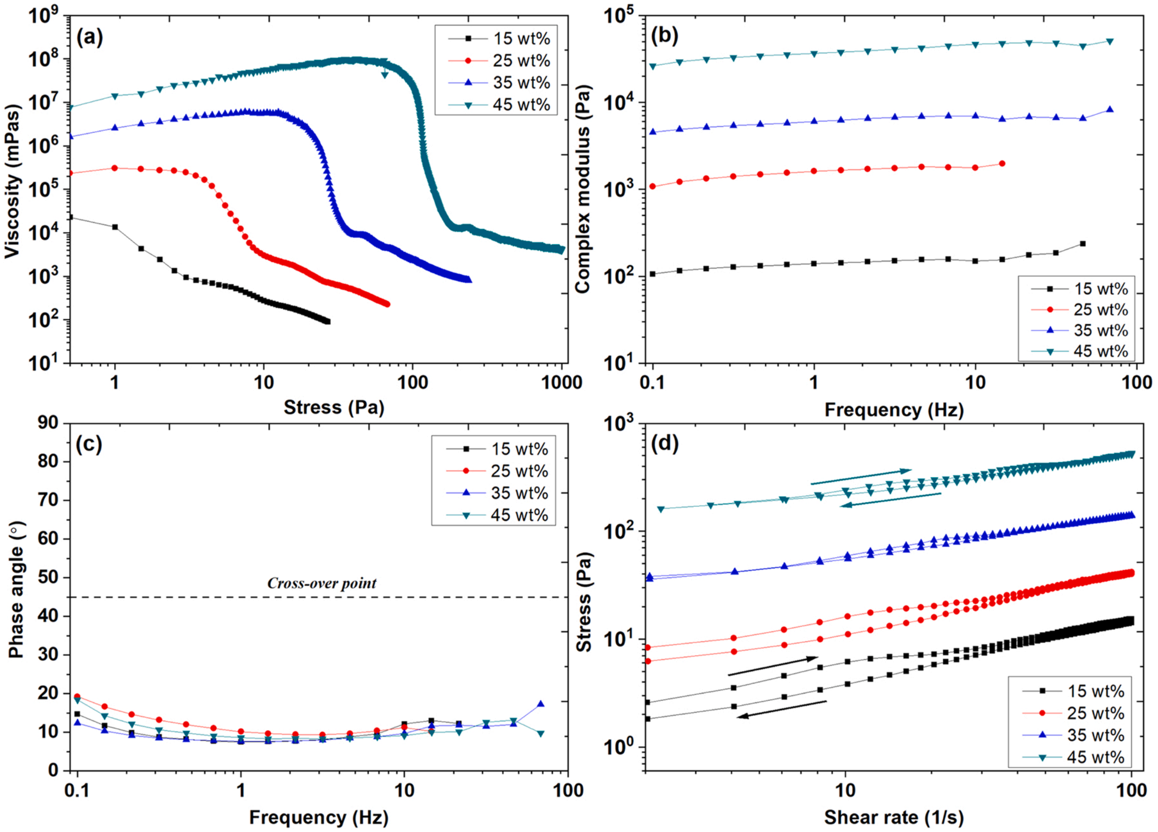

Fig. 8. (a) Apparent viscosity as a function of shear stress, (b) complex modulus (G^*) and (c) phase angle (δ) as a function of frequency, (d) shear stress as a function of shear rate for suspensions having 3 wt% apple fibre and different kaolin content. Dashed line represents the crossover point between G' and G''.

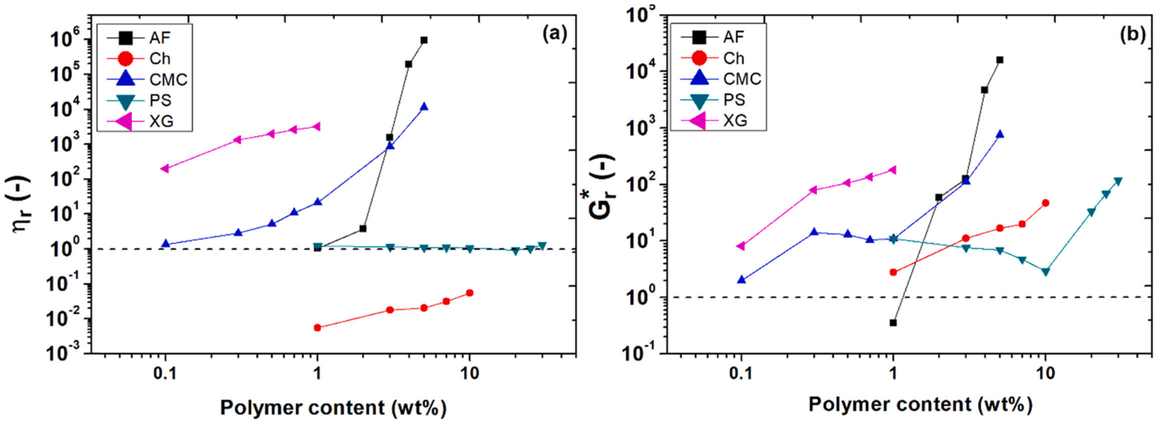

Fig. 9. (a) Reduced viscosity at 1 Pa (viscosity of polymer modified suspension / viscosity of pure kaolin suspension) and (b) reduced complex modulus at 1 Hz (complex modulus of polymer modified suspension / complex modulus of pure kaolin suspension) as a function of biopolymer content. Dashed line represents the polymer-modified system with similar value of rheological property as the pure kaolin suspension.

eventually makes the system softer. However, after certain polymer concentration, the complex modulus increases even significantly higher than the pure kaolin, which can simply be linked to the addition of polymer particles in a polymer dominated system, which eventually makes it more viscoelastic.

In case of completely non-soluble non-spherical bio-polymeric fibres (AF), the viscosity of the modified suspensions is similar to the viscosity of the pure kaolin suspension, at the lowest fibre content (1 wt%), which significantly increased (up to 6 orders of magnitude) by increasing the fibre content from 1 to 5 wt% (Fig. 9a). Likewise, a significant increase in complex modulus (up to 4 orders of magnitude) is observed by increasing the fibre content (Fig. 9b). This significant increase in rheological properties of modified suspensions by adding smaller amount of bio-polymeric fibre can be linked to the formation of a gel structure and/or randomness of the fibres, which eventually contributed towards the resistance to flow and strength of the system.

In addition to the reduced viscosity and reduced complex modulus, the Bingham yield stress is plotted as a function of polymer content (Fig. 10) for all the investigated biopolymers. This result again shows that xanthan gum, CMC and apple fibre are quite efficient in enhancing the yield stress of kaolin suspensions (two to four orders of magnitude), even by adding smaller amounts of biopolymer. On the other hand, an

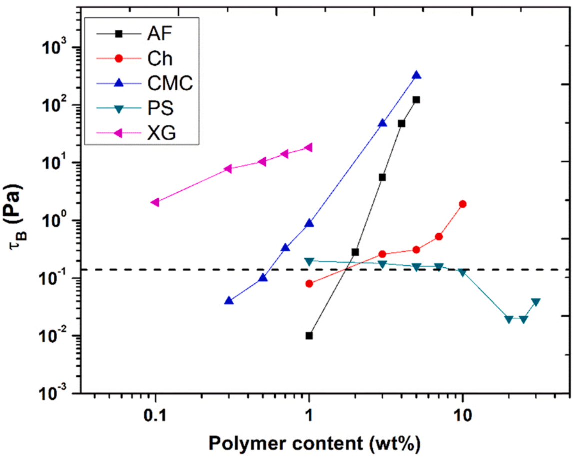

Fig. 10. Bingham yield stress (τ_B) as a function of biopolymer content for fixed kaolin content (15 wt%). Dashed line represents the yield stress of pure kaolin suspension without biopolymer.

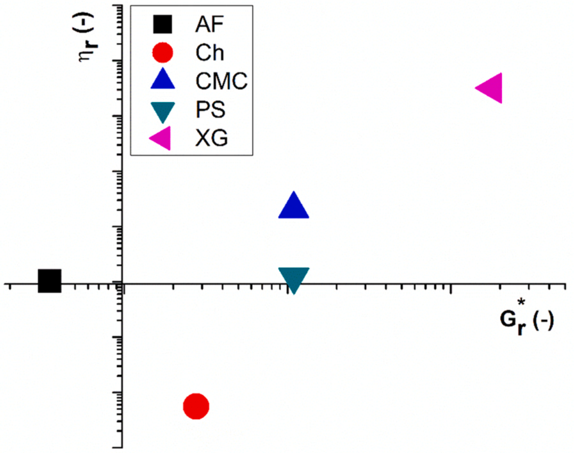

Fig. 11. Reduced viscosity at 1 Pa as a function of reduced complex modulus at 1 Hz for different biopolymers at 1 wt% biopolymer content and 15 wt% kaolin content.

increase in yield stress of kaolin suspensions by adding chitosan is relatively smaller, almost one order of magnitude. In case of potato starch, a decrease in yield stress was observed particularly at higher biopolymer content, which can be linked to the presence of repulsive forces at the surface of starch granules.

In order to qualitatively compare the influence of different biopolymers on the rheological characteristics of kaolin suspensions, reduced viscosity is plotted as a function of reduced complex modulus for different biopolymers at 1 wt% biopolymer content and 15 wt% clay content (Fig. 11). It can be seen from the graph that xanthan gum and CMC are quite suitable for enhancing the rheological properties (both modulus and viscosity) of kaolin suspensions at the selected polymer content (1 wt%). Potato starch is appropriate for enhancing the modulus of the kaolin suspension without affecting its viscosity. Chitosan is also suitable for increasing the modulus of the kaolin suspensions but with a significant decrease in viscosity of the modified suspensions. Apple fibre, on the other hand, displays a decrease in modulus of the modified kaolin suspension without affecting its viscosity.

In view of all these results, it is clear that by adding chitosan or potato starch (at higher clay content) in kaolin suspensions, a two-step yielding behaviour is obtained, which is a typical rheological fingerprint of natural mud. However, the viscosity, yield stress and moduli of kaolin suspensions modified with potato starch showed a decreasing trend as a function of biopolymer content, which is opposite to the behaviour of organic matter (biopolymer) in natural mud. On the other hand, the increase in rheological properties of polymer-modified kaolin suspensions as a function of chitosan content is relatively smaller than the increase in rheological properties as a function of organic matter (biopolymer) content in natural mud [6]. In case of apple fibre, this increase in rheological properties of polymer-modified kaolin suspensions as a function of fibre content is quite significant and comparable to the natural mud but with the absence of two-step yielding behaviour. Hence, only a single biopolymer cannot modify the kaolin suspensions, in order to make a suitable substitute for the natural mud and further research is needed.

5. Conclusions

Kaolin based suspensions have wide range of applications due to their non-swelling nature. On the other hand, the unique properties (i.e., biodegradability) of biopolymers make them suitable candidate for variety of applications including modification of clay suspensions. Clay-polymer interactions define the micro-fabric of the resultant modified suspensions, which eventually influence their bulk properties such as rheological fingerprint. In this study, the rheological properties of kaolin suspensions modified with different biopolymers have been investigated by varying the biopolymer content and clay content. Frequency sweep tests, stress ramp-up tests and time-dependent tests were performed for the prepared suspensions. All the suspensions were prepared using deionized water (i.e., very low salinity).

The rheological results showed that the viscosity of the XG or CMC modified clay suspensions was similar or higher than the viscosity of pure kaolin suspension, even at very low polymer content (0.1 wt%), which increases further as a function of increasing polymer content. In case of chitosan, a strong reduction in viscosity was observed as compared to the pure kaolin suspension, which can be attributed to the charge neutralisation phenomenon. In case of non-interacting potato starch granules, the viscosity of the modified suspensions is similar to the pure kaolin suspension and remains more or less constant by increasing polymer content even till 30 wt%. On the other hand, by adding bio-polymeric fibres into the clay suspensions, the viscosity of the modified suspensions increases up to 6 orders of magnitude by increasing the fibre content from 1 to 5 wt%.

The complex modulus of XG or CMC modified suspensions is similar or higher than the pure kaolin suspension particularly at low polymer concentration, which further increases by increasing the polymer content. In case of chitosan, the complex modulus of the modified suspensions is higher than the complex modulus of pure kaolin suspension, even at very low polymer content (1 wt%). In case of non-interacting potato starch granules, there is a decrease in complex modulus by increasing the polymer content till 10 wt% followed by an increase in complex modulus with polymer content, which can be attributed to the incorporation of soft polymer granules into the hard particles based suspensions. In case of bio-polymeric fibres, a significant increase in complex modulus (up to 4 orders of magnitude) is observed by increasing the fibre content, which was linked to the formation of a gel structure.

The shear rate ramp-up and ramp-down experiments showed that the time-dependent behaviour of kaolin suspensions is not strongly influenced by adding different biopolymers. This result highlights that the viscosity and moduli of the clay suspensions can be tuned with the help of biopolymers without affecting the time-dependent behaviour of the suspensions. Hence, this comparative study clearly shows that the nature of biopolymers, physical interactions between polymer chains or polymer-clay particles and size/shape of the biopolymers are the key factors that can significantly influence the rheological fingerprint of modified clay suspensions. Moreover, chitosan-modified kaolin suspensions seems to mimic the rheological properties of natural mud, however, further research is needed to optimise the suspension.

CRediT authorship contribution statement

Ahmad Shakeel: Methodology, Investigation, Formal analysis, Writing – original draft. **Waqas Ali:** Formal analysis, Investigation, Writing – review & editing. **Claire Chassagne:** Funding acquisition, Supervision, Writing – review & editing. **Alex Kirichek:** Conceptualization, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This study is funded by the Hamburg Port Authority and carried out within the framework of the MUDNET academic network: https://www.tudelft.nl/mudnet/. The authors would like to acknowledge Deltares, the Netherlands for the use of HAAKE MARS I rheometer, which was made possible thanks to the Memorandum of Understanding signed between Deltares and the TU Delft.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2022.130120.

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