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Effect of thickener structure on paper-coating color properties

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Abstract Physical and chemical properties of clay-based paper-coating colors have been characterized. The "surface potential" (zeta potential) of kaolin particles used in paper-coating formulations was determined as functions of pH and sodium polyacrylate (used as a dispersant) concentration. The optimal pH and dispersant concentration have been established. The effect of adsorption of two different thickeners on the kaolinite particle potential was also investigated. The rheological properties of coating colors, thickened with an associative polymer and a commonly used thickener, have been compared. The rheological behavior of all the coating colors studied was found to be similar, except for the magnitude of the elastic modulus, which was considerably larger for the more hydrophobic thickener. The water-retention properties of the colors could be qualitatively correlated with the molecular structure of the thickeners. An interaction mechanism (e.g. formation of hydrophobic micellar domains) between kaolinite particles and the associative polymer has been proposed.

Key words Coating color · Associative thickener · Rheological properties · Surface properties · Micellar clusters

Introduction

Pigment coating is a major industrial operation used to improve the appearance and printability of paper [1, 2]. Kaolin clay and $CaCO_3$ are the most commonly used pigments for this application. In the paper-coating industry, the trend is to coat paper at high speeds with coating colors of higher and higher solid contents [2, 3] to reduce drying time and to achieve thinner coats. The process runnability is mainly governed by the flow properties of coating colors during the metering and/or the application steps [4]. Thickeners used in the formulation play a key role in controlling both the flow properties and the dewatering rate of coating colors during the application process and the subsequent film immobilisation [5]. Carboxymethyl cellulose (CMC) and starch are the most popular thickeners used in paper coating [6, 7].

Recently associative thickeners (ATs), such as hydrophobically modified ethoxylated urethane (HEUR), which is a surfactant-modified water-soluble polymer, have gained acceptance in the paint industry [8]. HEUR-thickened paints exhibit a high viscosity at low shear rates and their viscosity decreases significantly with increasing shear rate [4]. It has been demonstrated that coating colors thickened with HEUR have lower spatter and misting tendency than those thickened with cellulosic thickeners [4]. This pronounced shear-thinning characteristic is a desirable property for paper coating. However, the use of ATs in the paper-coating industry is not yet established [9]. One important issue is to ensure that the water-retention property remains acceptable while operating at commercial speed (above 1000 m/min).

The rheology of coating colors is determined by many factors, including particle concentration, particle shape, particle–particle interactions and the nature of the thickener [10, 11]. The contribution of particle–particle interactions is particularly significant. The colloidal interactions involve electrostatic, polymeric steric, dispersive and depletion forces [12]. The electrostatic and polymeric steric repulsive forces, which determine the stability of coating colors, are primarily affected by the surface charge of the particles, the dispersants and the thickeners. The rheological properties of coating colors are affected by the nature of the thickener used and depend on its chemical structure and molecular weight; however, the role of the thickener is not clearly understood yet [13]. The formation of pigment networks due to polymeric bridging between particles has been proposed as a possible mechanism for coating colors thickened with ATs [14]. Since both pigment and latex particles are negatively charged [15], it is not expected that a latex will interact with pigments strongly.

The objective of this short communication is to explore the effect of the structure of ATs on the physical and chemical properties of coating. Various measurements have been made, including the surface charge of kaolinite particles as a function of pH, the influence of both dispersant and thickener on pigment surface properties, the influence of the nature of the thickener on the rheological properties of coating colors and the water-retention property of the coating colors thickened with two different thickeners. Possible interaction mechanisms are proposed in light of the results.

Experimental

Materials

Dry kaolin pigments (TH no. 2) were obtained from Engelhard (New Jersey, USA) and the material was used as supplied. These kaolin pigments have an average particle size of about 1 μm, with a very narrow size distribution as reported by the supplier (the exact size distribution is unknown, but the size of 80% of the particle is less than 2 μm). The theoretical chemical composition of kaolin is $Al_2O_3{\cdot}2SiO_2{,}2H_2O$. Sodium polyacrylate (SP, Dispex N40V, $M_w = 3{,}000$, from Allied Colloids Canada) was used as a dispersant. Carboxylated styrene–butadiene (S/B) latex (CP 620 NA, Dow Canada) was used as a binder. The latex has an average diameter of 175 nm and the solid content of the latex mixture was approximately 50% (w/w) as determined in our laboratory. CMC ($M_w = 700{,}000$, degree of substitution of 0.75) was supplied by Omega Chemicals. Polyphobes p203 and p206 (Union Carbide Products), differing in hydrophobicity, were obtained from Dow Chemical Canada.

Preparation of coating colors

In the present study, all the formulations were based on 100 parts of dry clay pigments (pph). A typical coating color formulation consisted of 10 pph binder (S/B), 0.04 pph dispersant and 0.2 pph thickener. The total solid contents (61.5 and 66% w/w) corresponding to pigment mass fractions of 56 and 60%, and the concentrations of the S/B latex and the thickener used in the formulation are typical of those used in the paper-coating industry. Other additives, including lubricant, bactericide, etc., were not included in the formulations in order to simplify the system.

The colors were prepared by first dispersing the required amount of kaolin pigments in deionized water using a mixer. The resulted kaolin slurry was then transferred to a plastic container, followed by the addition of SP, S/B latex and a thickener under strong agitation. The final concentration of the coating colors was adjusted to 61.5 or 66% (w/w) by adding deionized water. The final pH of the colors was adjusted to 8 using 10 N NaOH. Finally the coating mixture was dispersed using a Cowles sawtooth impeller at a speed of 1000 rpm for about 1 h.

Measurement of zeta potential

All the zeta potential measurements were done on a Pen Kem model 501 Lazer Zee meter. Instead of measuring the time traveled by an individual particle, as in most zeta potential apparatus, based on electrophoresis, the Lazer Zee meter adjusts the observed image to produce a stationary frame using a patented rotating-prism technique. The prism provides a motion equal and opposite to the motion caused by the applied electric field. For measuring the zeta potential of kaolinite particles as a function of the concentration of SP added, the samples were prepared by diluting the initial kaolin slurry containing different amounts of SP with deionized water. The samples were diluted to a solid content of 0.01–0.05% (w/w). Larger particles (of size of the order of 2 μm or larger) settled to the bottom owing to gravity and the top portion was taken for the measurement. Hence, we believe that the larger particles had no significant effect on the zeta potential measurement, but the Lazer Zee meter measured a cloud of particles rather than individual particles. The final pH was around 6.7. For the measurement of the zeta potential as a function of pH, the samples were prepared by diluting kaolin slurry samples of different pH (at an optimal SP concentration) using the solution at the same pH. The measuring chamber was cleaned several times with deionized water and rinsed with a sample before starting the measurement. Similarly, the samples of coating colors thickened with different thickeners were first diluted to 0.01% using a NaOH solution of pH 8, followed by measuring their zeta potential as described previously. The zeta potential measurements are estimated to within ± 1.0 mV.

Measurement of rheological properties

The rheological properties of coating colors under shear deformation were measured using a controlled-stress rheometer (CVO, Bohlin) equipped with a Couette geometry. Typically 12 ml coating colors was transferred to a shear cell with a syringe. Then, a small coat of silicon oil was placed over the sample to eliminate evaporation. Steady-shear experiments under controlled-stress conditions were performed. Small-amplitude-oscillation shear experiments were also carried out in the linear viscoelastic region, which was predetermined by a strain-amplitude sweep at a constant frequency (1 Hz).

Measurement of the water-retention property

The water-retention property of the coating colors was measured using a gravimetric water-retention meter (Kaltec Scientific, Finland). A piece of preweighed blotting paper was first placed on a rubber supporting plate. Then, a polycarbonate-based membrane with a pore size of 5 μm (Costar Scientific, Cambridge, Mass.) was placed on the top of the blotting paper followed by a sample holder. Following this, 3 ml coating color was transferred to the sample holder. A pressure of 6.9 kPa was applied for various time periods. Finally, the blotting paper was weighed again and the weight difference of the blotting paper before and after was taken as the water loss of the sample.

Results and discussion

Effect of thickener on the physical properties of coating colors

An attempt was made to probe the effect of the chemical structure of two different thickeners on the surface, colloidal and rheological properties of coating colors. The chemical structures of the thickeners [16, 17] used in this work are illustrated in Fig. 1. CMC, a cellulose derivative, is a hydrophilic polymer which has two hydrophilic functional groups: –COONa (hydrophile–lipophile balance, HLB [18], 19.1) and –OH (HLB, 1.9). The ATs (p203 and p206) are hydrophobic. The degree of their hydrophobicity depends on the size of the hydrophobes in the macromolecules. Their main chain, $-OCH_2CH_2-$ is weakly hydrophilic (HLB, 0.33). The addition of either polymer to the coating colors significantly affects the surface properties of the pigments and the viscoelastic properties of the coating colors, as shown in the following sections.

Effect on surface properties

Kaolin pigments are platelike structures containing multilayers held together by van der Waals forces [19]. Surface atomic substitution on the basal plane (i.e. Al^{3+} to Si^{4+}) leads to a negative surface charge. Disruption of the structural continuity of kaolinite results in adsorption of aluminum ions to the edge and is responsible for a positive charge in acidic media [20]. In paper-coating applications, the final pH of the coating colors is around 8. At this pH, the surface of kaolinite particles is negatively charged, while the edge remains neutral; therefore, the dispersant, SP, is preferably adsorbed on the edge, followed by surface adsorption.

The zeta potential of kaolinite particles as a function of the concentration of SP added at pH 6.7 is reported in Fig. 2. It can be seen that the zeta potential decreases with the concentration of SP, and this decrease is followed by a plateau. This plateau reflects a maximum adsorption level. Further addition of SP to the dispersion will increase the viscosity of the solution (data not reported here) owing to dissolution of the dispersant in the aqueous phase. Consequently, the minimum in the viscosity corresponds to the maximum adsorption. Theoretically, the adsorption of SP on kaolinite particles can be treated as the adsorption of polyelectrolytes on particle surfaces with the same kind of charge [21]. The interaction forces between SP and kaolinite particles include van der Waals attractive and electrostatic repulsive forces. The former favors adsorption of SP and the latter decreases the adsorption of SP. However, the presence of electrolytes in the dispersion compresses the electrical double layer, reduces the electrostatic repulsive force and, thus, enhances the adsorption of the polymer on the kaolinite particles.

The variation of the zeta potential with pH is shown in Fig. 3. The zeta potential decreases with increasing pH to

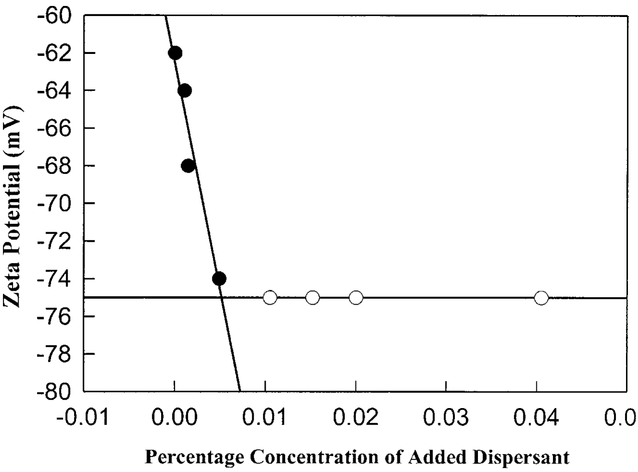

Fig. 2 Zeta potential of dilute suspensions of kaolinite particles versus concentration of sodium polyacrylate added at pH 6.8

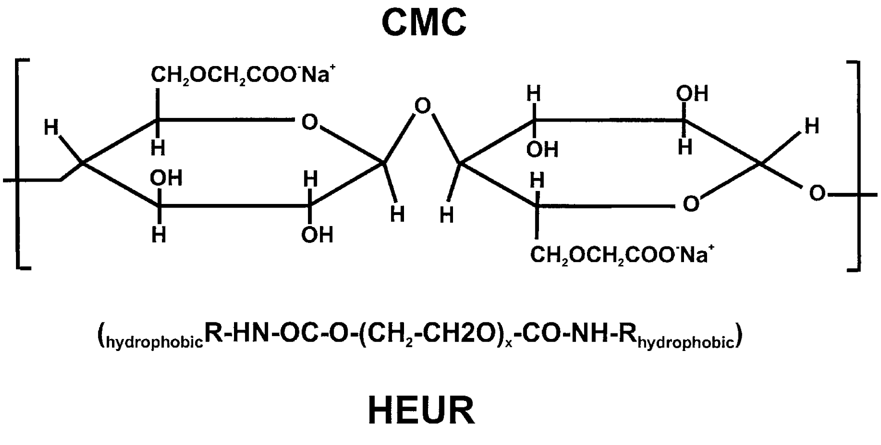

Fig. 1 The chemical structures of carboxymethyl cellulose (*CMC*) and hydrophobically modified ethoxylated urethane (*HEUR*)

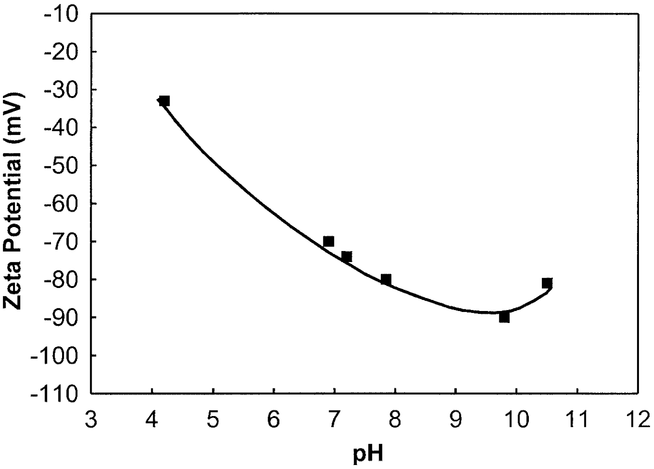

Fig. 3 Zeta potential of dilute suspensions of kaolinite particles versus dispersion pH

a minimum point. Further increase of the pH of the dispersion increases the zeta potential owing to the electrical double layer compression. Figure 3 also demonstrates that in basic media the particle surfaces are highly charged, which ensures the stability of the dispersions. The data suggest that the optimal pH and dispersant concentration for preparing coating colors are obtained by maximizing the repulsive force between pigment particles. Note, however, that these data were obtained for highly diluted suspensions. For concentrated suspensions, such as coating colors, the situation could be more complex. Following the addition of a thickener to kaolin dispersions (to make coating colors), the thickener macromolecules adsorb on the surface of the SP-treated kaolinite particles; therefore, after the addition of the thickener, the surface properties of the kaolinite particles are significantly modified, as indicated in Table 1.

Table 1 shows that, after the addition of a thickener to kaolin dispersions, the "surface potential" of the kaolinite particles increases significantly. This clearly demonstrates that there is a significant adsorption of the thickener on the particle surfaces. Moreover, the pigment particles covered with ATs have a relatively higher "surface potential" compared with those covered with CMC. Since the estimated error for the zeta potential measurements is ± 1 mV, the differences shown in Table 1 for the different thickeners are significant. It was also observed via optical microscopy that kaolinite particles aggregated and formed flocs after the addition of AT to the dispersions; p206 adsorbed particles aggregated more readily. These results can be explained as the ATs are hydrophobic and, thus, are adsorbed more readily onto the surface of kaolinite particles, as reported for modified polyacrylamides [22]. The "surface potential" is then increased and the repulsive force between particles is decreased, causing aggregation.

Table 1 Zeta potential (measured at pH 8) of pigment with different thickeners

Thickener	Carboxymethyl cellulose	p203	p206	No thickener
Zeta potential (mV)	−30	−25	−22	−80

Effect on rheological properties

The rheological response of coating colors to deformation is a result of synergistic interplay of pigments, latex and thickeners. In this study, we explore the effect of thickener on the rheological properties of coating colors and propose a thickening mechanism. The steady-shear rheograms of the coating colors (66%) thickened with CMC, p203 and p206, respectively, are shown in Fig. 4. It can be seen that all colors have about the same qualitative steady-shear behavior in the shear-rate range studied, although the coating color thickened with p206 shows a higher viscosity (about a factor of 2). The scatter in the data is typical of that observed for most kaolin-based coating colors which are thixotropic materials [23]. The decrease in viscosity with shear rate is due to the flow-induced alignment, deformation and breakdown of structured pigment domains, which depends on both the solid content and the concentration of the thickener. If aqueous solutions of associative polymers are highly shear thinning [4], no marked differences in the shear-thinning properties of the coating colors, thickened with an associative or a conventional polymer, are observed.

The elastic and loss moduli (G' and G'') of the coating colors are plotted in Fig. 5 as functions of the frequency.

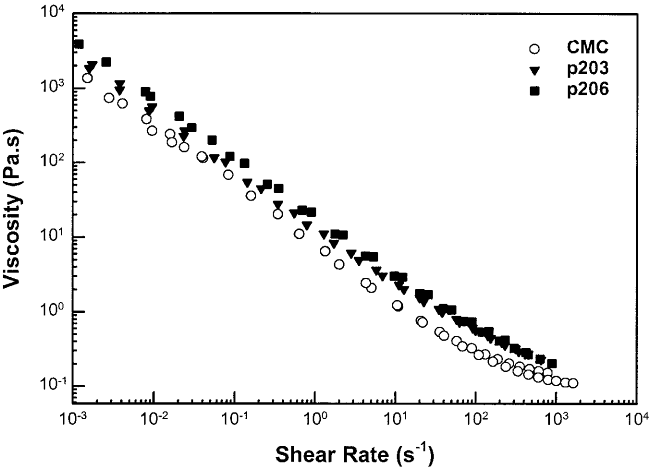

Fig. 4 Steady-shear viscosity of the coating colors (66% w/w) thickened with CMC, p203 and p206

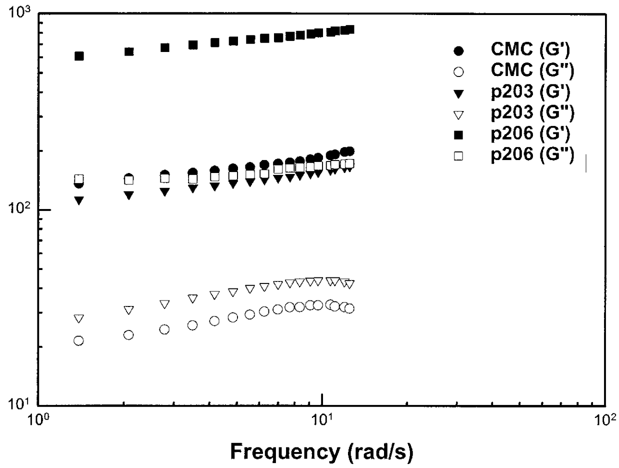

Fig. 5 Elastic and loss moduli of coating colors (66% w/w) thickened with CMC and p203 versus frequency

The coating colors thickened with CMC and p203 have a similar dynamic behavior in the frequency range investigated. Both the *G′* and *G″* increase slightly with frequency for all the samples (the slight decrease in *G″* at high frequencies for CMC and p203 suspensions is probably due to measurement inaccuracies, estimated to be of the order of 10% for such suspensions). As observed before by many authors (e.g. [23]), the *G′* is significantly larger than *G″*. The coating color thickened with p206 has a significantly higher *G′* compared with those thickened with CMC and p203. The rheological behavior of the coating colors may be explained in the light of the microstructure changes since *G′* is indicative of strong particle–particle interactions or/and microstructure buildup. In the case of the associative polymers, we may assume that the hydrophobic ends of the macromolecules are first adsorbed on the surface of kaolinite particles, followed by particle–particle interaction and network formation. ATs with both hydrophobic ends adsorbed on pigment surfaces (loop adsorption) do not interact with each other strongly because the hydrophilic portion of the polymeric chains tends to exclude them and they interact with water. AT chains with only one end adsorbed onto the pigment surface strongly interact with each other because the free ends tend to form micellar clusters in solution as suggested by Fitch [15] for latex dispersions thickened with ATs. The degree of network formation depends on both the solid content and the AT concentration. The strength of the network formed is primarily related to the micellar clusters formed. *G′* of coating colors is a function of the strength of the bonds in the network formed. p206 is more hydrophobic than p203, and the coating color thickened with p206 shows a higher *G′*. This was also demonstrated by observing more flocs in the coating color thickened with p206 under a microscope. Flocculation by polymeric chain bridging is also quite possible for the CMC-thickened color, but we had no experimental evidence of flocculation for that suspension. Detailed mechanisms are discussed later. The rheological properties of coating colors containing 61.5% solids were found to be very similar to those reported in Figs. 4 and 5, and for this reason, these data are not presented here.

Effect on water-retention property

Dewatering of coating colors during coating applications has detrimental effects on coater runnability and the final paper properties. The dewatering property is a function of the particle–particle interactions, polymeric additives used in the formulation and the base paper properties. In this work, only the effect of the polymeric thickener was studied. Figure 6 shows that the water loss of coating colors (61.5 and 66%) increases with time in a nonlinear, monotonous fashion. Water in these coating colors is not all accessible to dewatering under static conditions. Some water is trapped between pigments and in the network structure through hydrogen bonding and some remains as bulk water. Figure 6

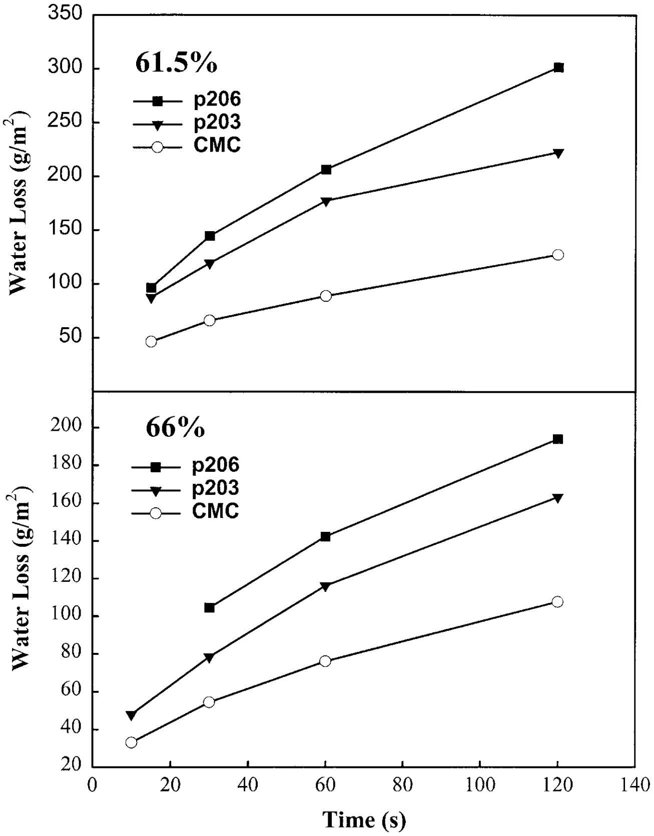

Fig. 6 Water loss of coating colors (66 and 61.5% w/w) thickened with CMC, p203 and p206 versus time

shows that the coating color thickened with CMC has the strongest water-holding capability, followed by those thickened with p203 and finally with p206. Notice that, as expected, the water losses for the coatings containing 61.5% solids are significantly larger than those containing 66.0% solids. The water retention capability of coating colors depends on the hydrophilicity of the thickener used. In general CMC is much more hydrophilic than p203 and p206 since CMC has two hydrophilic functional groups:- -COOH and –OH and p203 is more hydrophilic than p206. These results support the conclusion drawn from the rheological measurements that the coating colors thickened with p206 have higher G'' because of the presence of large hydrophobes.

Proposed interaction mechanisms

The results suggest that the interaction mechanism of kaolinite particles treated with p203 and p206 is distinctly different from that of the particles treated with CMC. CMC, a polyelectrolyte, exhibits a random-coil conformation in aqueous media. The thickness of the CMC layer adsorbed at the surface of the kaolinite particles can be considered to be of the same order as the radius of gyration of an isolated CMC chain in solution [24]: this was estimated to be 50 nm using the Flory–Fox equation [25]. The adsorption of CMC on the pigment surface stabilizes the pigment particles through polymeric–steric repulsive forces. As pointed out by Yziquel et al. [23], the high viscosity of coating color thickened with CMC is due to this repulsive interaction between pigments, not because of the increase in the viscosity of the medium. This conclusion is supported by the strong adsorption of CMC on the pigment surface as demonstrated by our zeta potential result. On the other hand, the ATs act very differently, favoring bridging flocculation as observed in optical microscopy. Their hydrophobic moieties tend to aggregate into micellar clusters in solution as well as to adsorb on the pigment particles. The viscosity is enhanced as a result of this clustering mechanism. The micellar domains are held together with weak hydrophobic interactions, and these can be easily broken down under shear as shown in Fig. 4. More significantly, the formation of micellar clusters is responsible for the large G' observed for the p206-based color. The formation of micellar domains is the most plausible mechanism for generating elasticity in the coating colors thickened with p206 and p203. As for p203, the size of the hydrophobes is too small to form strong hydrophobic micellar domains. In the case of CMC, kaolinite particles mainly interact via the adsorbed polymeric layer and this polymeric layer prevents pigment aggregation since water is a good solvent for CMC [25]. It is also conceivable that some polymer chains bridge two or more particles, since the radius of gyration is larger than the interparticle distance, estimated to be of the order of 40 nm. However, the size of the resulting aggregates would remain relatively small and, as pointed out previously, no evidence of flocculation was detected. In all cases, the thickness of the dispersant (SP) layer (~2–3 nm) is too small to have a significant effect compared to that of the thickener on the particle–particle interactions and, hence, on the rheological properties of the coating colors studied.

Conclusions

The present study aimed at exploring the effect of two different thickeners on the colloidal properties of coating colors, including surface, rheological and dewatering properties of coating colors. The "surface potential" of kaolinite particles, which is critical for the stability of coating colors, was found to depend on the pH of the colors, the concentration of SP and the chemical nature of the thickener used. The optimal pH range and the optimal concentration for the dispersant are pH 8–9 and 0.04%, respectively. The rheological properties of the different coating colors were found to exhibit similar trends. However, the coating colors thickened with p206 showed a much larger G' than that of the coating colors thickened with CMC and p203. This is believed to be due to strong particle–particle interactions through bridging between particles and hydrophobic micelles. Not surprisingly, the color thickened with CMC has the best water-retention property as the water-retention capability is directly proportional to the hydrophilicity of the thickener used. Finally, a mechanism was proposed to describe particle–particle interaction via micellar clusters.

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