Impact of dispersing agents on the flow behaviour of montmorillonite-starch coating formulations

Erik Olsson[1,2], Caisa Johansson[1], and Lars Järnström[1]

[1] Karlstad University, Faculty of Health, Science and Technology, Karlstad, Sweden
[2] Present address: Danfoss Värmepumpar AB, Arvika, Sweden

ABSTRACT

Montmorillonite was incorporated into thermoplastic starch to improve the barrier properties of coating formulations. Citric acid and its sodium salt were used as dispersing agents. The state of dispersion was studied by rheology. The barrier effectiveness was related to the volume fraction of aggregates and swelling of the clay mineral.

INTRODUCTION

The replacement of synthetic petroleum-based polymers with renewable materials as barriers for consumer packages is an intense research field. The incorporation of clay minerals of various origins into polymeric matrices has been examined in numerous reports in recent years because of their potential to improve the barrier properties.

The reduction in gas permeability through the incorporation of particles into polymeric matrices has been attributed to the formation of a tortuous pathway which increases the effective distance for the gas molecules to diffuse through the material[1]. Increased particle volume fraction, increased aspect ratio, reduced aggregation and enhanced particle alignment reduces the permeability. Incorporation of clay minerals can limit the mobility of the polymeric phase close to the particle surfaces[2], which limits the mobility of penetrant molecules and hence leads to reduced diffusion through the structure.

Montmorillonite, Mt, is a swelling clay mineral consisting of thin layered silicates of thickness approximately 1 nm. It is generally accepted that polymer-based composites with Mt can form three different structures: micro-composites, intercalated nano-composites and exfoliated nano-composites and that this is dependent both on the Mt-matrix interactions and the method of preparation. Mt can form micro-composites when the individual layers are kept together in stacks and are present as aggregates which are of micrometer size range. This occurs when there is no exfoliation of the interlayer spacing and can be due to both incomplete dispersion and unfavourable interactions between the clay mineral surface and the polymer. Intercalated nano-composites have an ordered structure with alternating polymer chains and clay mineral layers and an increased interlayer distance (d-spacing) due to polymer and/or plasticizer diffusion into the clay mineral interlayer spacing. Exfoliated nano-composites form when the layers are individually delaminated and homogeneously dispersed in the matrix.

From the theory of Nielsen[1], it is clear that aggregates of particles may increase the permeability of gases or small molecules through composite films. The degree of aggregation for particles in solution can be

determined by the elastic floc model[3]. From a plot of shear stress versus shear rate of a polymer-clay mineral dispersion, it is possible to extract both the Bingham yield value and the plastic viscosity, Eq. 1.

$$\tau = \tau_B + \dot{\gamma}\eta_{PL} \qquad (1)$$

where τ is the shear stress, τ_B is the Bingham yield, $\dot{\gamma}$ is the shear rate and η_{PL} is the plastic viscosity. Both the Bingham yield value and plastic viscosity can be used to calculate the volume fraction of aggregates. For non-swelling clay minerals, such as kaolinite and illiite it is generally accepted that there will be a reduction in viscosity with improved dispersion. This is not necessarily true for swelling clay minerals such as Mt, due to the hydrated layer formed upon contact with water which substantially increases the effective volume fraction. In addition, the increased d-layer spacing will also increase the effective particle size[4].

Both the Bingham yield value, τ_B and the plastic viscosity, η_{PL} can be used to compare the volume fraction of aggregates between two dispersions of Mt of the same concentration. The ratio between aggregates and particles according to the elastic floc theory can be expressed by Eq. 2[3]:

$$\tau_B = \frac{\varphi_f \varphi_p E_L}{\pi r^3} \qquad (2)$$

where τ_B is the Bingham yield, φ_f and φ_p are the volume fractions of aggregates and particles respectively, E_L is the energy required to break up the aggregates and r is the particle radius. If φ_p, E_L and r are constant for the different systems, the Bingham yield is directly proportional to the volume fraction of the aggregates. It is not obvious to use Eq. 2 for swelling clay minerals, since the volume fraction solid phase is not easy to define. Any swelling and exfoliation would cause an increase in the effective particle volume fraction. A relation between plastic viscosity and the volume fraction solid phase is given by the Krieger-Dougherty equation[5], Eq. 3:

$$\eta_{PL} = \eta \left(1 - \frac{\varphi}{p}\right)^{-[\eta]p} \qquad (3)$$

where η_{PL} is the plastic viscosity, η is the viscosity of the dispersing medium, p is the volume fraction where viscosity goes to infinity, φ is the volume fraction solid phase and $[\eta]$ is the intrinsic viscosity. If the viscosity of the dispersing medium, the volume fraction at which the viscosity goes to infinity and the intrinsic viscosity are constant, then the lower the volume fraction of aggregates, the lower is the plastic viscosity. It has been shown previously that the Bingham yield value for 4 wt % Mt in water and the plastic viscosity both are reduced with increasing pH and this has been attributed to a reduced edge-to-face flocculation[6].

It is generally accepted that three types of aggregates can be formed, edge-to-face, EF, edge-to-edge, EE and face-to-face, FF. The degree of aggregation of Mt has been reported to be highly dependent on the pH and to decrease with increasing pH. This is due to the charge difference between the edges and the faces of the Mt particles when the pH is below the isoelectric point of the edges.

Mt can be electrostatically stabilized by the adsorption of anionic compounds to the edge and hence reduce the edge-to-face aggregation which is promoted by the charge difference[7] where the solution pH is an important factor[6]. It has been shown for low concentrations of bentonite that more aggregated dispersions of clay minerals possess a lower viscosity[8]. This can be explained by the reduction of the hydrated layer and hence the effective particle volume fraction.

Poly(ethylene glycol), PEG, can be used to intercalate Mt[9] and thereby increase the interlayer distance in the solid phase. PEG adsorbs to the Mt faces through entropic

effects and it has been shown that PEG can be used to induce the adsorption of other substances to the Mt since it can promote other molecules to intercalate the Mt interlayer spacing[10].

Citric acid, CA, has a potential to improve the barrier properties by reducing the moisture content and water vapor diffusion in starch films[11]. This has at least partly been attributed to the cross-linking ability of CA.

In paper coating there are limitations of the coating formulation viscosity that can be applied from a coater runnability perspective and this limits the effective solids content.

This paper summarizes some findings regarding the influence of dispersing agents on the flow behavior of montmorillonite-starch formulations for paper coating presented in detail in Olsson et al.[12]. Also presented is how the orientation of Mt in the dry layers is affected by the addition of citrate anions. Different starch-plasticizer-dispersant-Mt systems at high Mt content were analyzed and one formulation was used for coating on pilot scale, the details of which can be found in Olsson et al.[13]. It was found that the flow behavior could be related to volume fraction of aggregates and to swelling and exfoliation of Mt stacks, which in turn affected the barrier properties of coated paper.

MATERIALS AND METHODS

Hydroxypropylated and oxidized potato starch (Solcoat P 55 supplied by Solam, (Kristianstad Sweden), poly(ethylene glycol) with average M_n 380-420 g/mol, (tri)sodium citrate (sodium citrate tribasic hydrate) (3NaCA) and citric acid (anhydrous citric acid puriss) (CA) purchased from Sigma-Aldrich Inc., St. Louis, MO, USA was used. Cloisite Na^+, a commercial, natural Mt with Na^+ as counter ion was supplied by Southern Clay Products (Gonzales, TX, USA).

The Mt was dispersed in deionized water at 6.8 % solids content for 45 min with a saw-tooth dispersing blade at 1000 rpm. This dispersion was then divided into three parts where dispersant (CA or its sodium salt, 3NaCA) was added to one part each. CA or 3NaCA were added to the same molar concentration with respect to the dry amount of Mt[12].

The starch solutions were gelatinized by immersion in a boiling water bath under vigorous stirring. Potential plasticizers (CA or PEG) were added at 30 parts per hundred parts of dry starch, pph, after the gelatinized starch had been cooled to room temperature. When CA was investigated in its potential role as plasticizer, the pH was adjusted to 4 with NaOH. The Mt dispersion (30 parts Mt per 100 parts dry starch) was then added to the solution of starch and plasticizer and mixed under high shear, 2000 rpm, with a propeller impeller for at least 15 minutes. The formulation with CA as dispersant and PEG as plasticizer was selected for coating on a pilot coater[13].

Polarized attenuated total reflection-Fourier transform infra red, ATR-FTIR, spectra using a diamond crystal were recorded on the coated paper using a FTIR-Nexus from thermo scientific Nicolet (Resolution 4 cm^{-1}, accumulation of 32 scans) with the aim to investigate the Mt interlayer swelling.

Rheological measurements were performed at 23°C in duplicates on a controlled strain (Paar Physica, MCR 300, Graz, Austria) rheometer. Rotational flow curves were recorded with a concentric cylinder measuring system (CC17) from low to high shear in the shear rate region from 1 to 4000 s^{-1}.

At a shear rate above 400-600 s^{-1}, depending on the recipe, the plot of shear stress vs. shear rate resembled a straight line, indicating that only flocs and no permanent floc aggregates existed above that shear rate[3]. The plastic viscosity and the Bingham yield value were determined by fitting flow curves at shear rates between 1000-4000 s^{-1} to the Bingham plastic flow

model. Since the plastic viscosity was constant and no permanent floc aggregates existed in this interval of shear, the ratio of the volume fraction of aggregates to the volume fraction of dispersed particles was constant[3].

A greaseproof paper with very low porosity, Super Perga WS Parchment 50 g/m^2 (Nordic Paper Greåker Mill, Norway) was used for coating and subsequent evaluation of barrier properties. The dispersion coatings were applied to the paper substrate in two layers with a wire-wound bar using a bench coater (K202 Control Coater, RK Coat Instruments Ltd., Royston, UK) at a coating speed of 6 m/min. The coated sheets were dried in a ventilated oven for 90 s at 105 °C after each applied layer[12]. Pilot coating was performed at BillerudKorsnäs in Frövi, Sweden at a speed of 500 m/min using a bent blade for metering. The coating dispersion was applied in two layers and dried by means of infrared- and air float dryers[13].

The water vapor transmission rate, WVTR, was determined by the gravimetric dish method (ISO 2528) using silica gel as desiccant. The test conditions were 23°C and 50% RH.

RESULTS AND DISCUSSION

Rheological analysis

Table 1 shows the pH values in the aqueous Mt dispersions as well as in the final coating formulations. Addition of CA resulted in a significant reduction of pH whereas the use of 3NaCA resulted in a slightly higher pH in the final coating formulation compared to the case without dispersant. Table 1 also shows that the Bingham yield value and the plastic viscosity of the aqueous Mt dispersions decreased after addition of CA (pH 4.26) and 3NaCA (pH 8.77), indicating reduced aggregation after the addition on condition that exfoliation and swelling were unaffected by the addition of dispersants.

However, CA was more effective than 3NaCA to reduce the plastic viscosity, while the opposite was found when the Bingham yield value was investigated.

Table 1. pH, Bingham yield value and plastic viscosity for aqueous Mt dispersions and coating formulations (average and standard deviation of duplicates).

| *Dispersing agent* | Aqueous Mt dispersions | | |
	pH	τ_B (Pa)	η_{PL} (mPa s)
None	8.73	106 ± 1.9	351 ± 0.7
CA	4.26	95.3 ± 0.36	293 ± 0.7
3NaCA	8.77	86.6 ± 0.55	358 ± 0.01
	Coating formulations		
Dispersing agent/Plasticizer	pH	τ_B (Pa)	η_{PL} (mPa s)
None/None	7.60	105.3 ± 1.88	103 ± 0.6
None/CA	4.30	88.9 ± 2.07	98 ± 0.6
None/PEG	7.50	56.0 ± 2.12	46 ± 0.8
CA/PEG	4.37	46.5 ± 0.87	41 ± 0.02
3NaCA/PEG	8.06	43.1 ± 0.56	43 ± 0.4

The difference between the reduction of plastic viscosity and the Bingham yield value gives an indication that a different type of aggregate structure is present in the CA-dispersed than in the 3NaCA-dispersed Mt. The pH of Mt dispersions without dispersing agents controls the aggregation/stabilization and the type of aggregation. A higher EF aggregation or house-of-cards structure is expected at pH 4.26 than at pH 8.77, due to the charge difference between the edges and the faces. It is not unlikely that this effect to some extent is of importance in CA- or 3NaCA-containing Mt dispersions. The viscosity shown in Fig. 1, where the Mt dispersed with CA has the highest viscosity at low shear rates also supports the interpretation about formation of a house-of-cards structure when CA is used as dispersant. It has been reported that the EF aggregation can be reduced but not fully eliminated by the adsorption of anions on the edges of the particles[7]. It was seen that CA led to a higher viscosity at γ<200 s^{-1} compared to that of the Mt dispersion without added dispersant (pH 8.73). At γ>200 s^{-1} there was only minor differences in viscosity

between the three dispersions, indicating the higher importance of colloidal interactions at low shear rates. It was also seen that the addition of 3NaCA reduced the viscosity at $\dot{\gamma}$<200 s^{-1} significantly compared to that of the Mt dispersion without added dispersant.
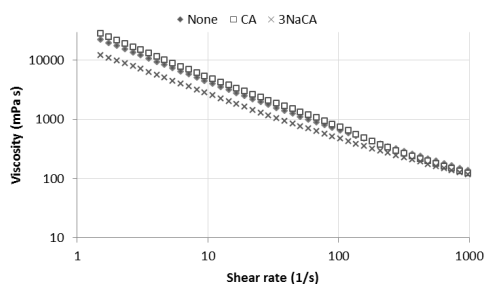

Figure 1. Viscosity vs shear rate (1-1000 s^{-1}) for aqueous Mt dispersions without dispersant (denoted None) and with CA or 3NaCA as dispersant.

One explanation why CA or 3NaCA addition can reduce the volume fraction of aggregates is that they increase the net negative charge of the Mt particles, which can be due to an adsorption of the negatively charged CA anions on the positively charged Mt edges. It is also well known that CA and its anions can be used to chelate di- and multivalent cations. Also at low concentrations, divalent cations such as Ca^{2+} have been shown to have a strong flocculating effect[7].

The reduction in both the Bingham yield and the plastic viscosity of the coating formulations (Table 1) indicated that the formulations containing PEG had a lower effective volume fraction solid phase or of aggregates. This can be due to lower basal spacing d_{001} of the Mt stacks, reduction in the exfoliation, reduction of the hydrated layer[4], or reduced aggregation compared to the two formulations without PEG.

Fig. 2 shows that the formulation where CA was used as plasticizer had significantly lower viscosity at $\dot{\gamma}$<10s^{-1} than any of the other coating formulations, indicating less

colloidal interaction when CA was used. Thus it is not likely that the main reason for the lower yield value and plastic viscosity of the PEG-containing formulations compared to the one with CA as plasticizer would be lower aggregate volume fraction in the former formulations.
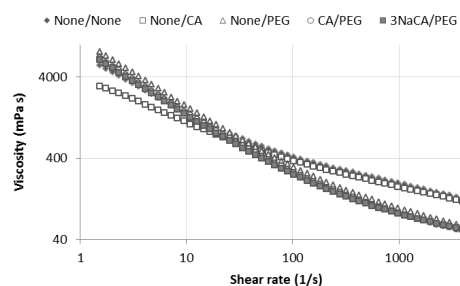

Figure 2. Viscosity vs shear rate (1-4000 s^{-1}) for coating formulations. The notations refer to Dispersant/Plasticizer respectively.

The statistically significant reduction in the Bingham yield value and in the plastic viscosity observed for the coating formulations containing CA or 3NaCA as dispersants can be explained by the same mechanisms as for the Mt dispersions. Also here there was a similar difference in the Bingham yield and the plastic viscosity reduction as observed for the Mt dispersions (Table 1).

All coating formulations possessed shear thinning behavior (Fig. 2). Comparing the coating formulation without plasticizer with those containing CA or PEG as plasticizers, it is clear that the CA-plasticized formulation and the formulation without added plasticizer exhibit much less shear thinning than the formulations containing PEG, which could be explained by lower basal spacing d_{001} for the PEG-containing containing formulations. For the PEG plasticized coating formulations, the dispersants slightly reduced the viscosity at the shear rates studied, which is important in paper coating since this indicates that the coating formulation can be prepared at a

higher solids content. A strong shear thinning behavior, resulting in a low viscosity at a high shear rate is believed to be due to enhanced particle alignment in the flow field, which is considered to be favorable for the barrier properties on condition that the aligned structure remains after consolidation.

Interlayer swelling

For layered silicates, the silicon-oxygen stretching band give rise to a complex spectra with strongly absorbing overlapping bands in the region around 1000-1100 cm^{-1} which can be studied both with transmission and reflectance FTIR[14]. There are four major peaks in this area. Peak I, Peak III and Peak IV corresponds to the basal oxygens of the Si-O tetrahedral linkages and are hence oriented in the direction of the Mt layer, whereas Peak II arises from Si-O bonds directed towards the octahedrally coordinated aluminum ions in the centre of the layer and are hence perpendicular to the layer[15]. This band has been attributed to mis-orientation between particles within stacks[14] which was shown to be due to increased swelling[14]. From the reflectance spectra (Fig. 3), it is clear that the addition of PEG leads to diminishing of Peak II, which would then be due to reduced interlayer swelling and exfoliation and a subsequent reduction of the mis-orientation within the stacks.

The ratio between Peak III and Peak IV can be used to determine the interlayer distance; when the ratio of Peak III to Peak IV increases, the interlayer distance increases[15], which was found to be due to the increase in the intensity of Peak III with higher intercalation or exfoliation or swelling. In Fig. 3, it is also shown that the Peak III to Peak IV ratio increases for the pilot coated sample compared to the laboratory coated, which indicates that it is likely to have a larger interlayer distance. Peak I was sharper for the pilot coated sample than for the laboratory coated

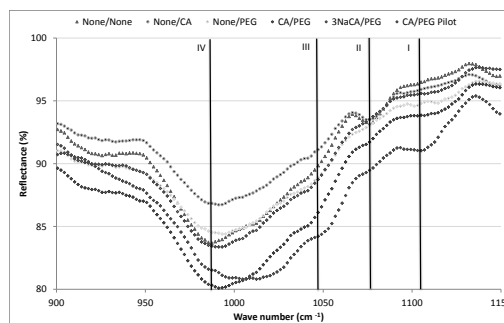sample, indicating higher degree of dispersion in the former, since thick Mt stacks tend to broaden the absorption bands[14].

Figure 3. Reflectance spectra in the 900-1150 cm^{-1} wave number range for laboratory coated paper and pilot coatings with the starch-PEG-Mt system / CA as dispersant. (notations in the legend refer to Dispersant/Plasticizer respectively).

The improved dispersion and increased interlayer distance for the pilot coated sample compared to the laboratory coated is most probably due to the higher shear rates operating in the machine coating process, compared to the laboratory bench coating. Increased shear is well known to increase the orientation of Mt particles in the wet dispersion.

Moisture barrier properties

The measured WVTR values were normalized to a coat weight of 6 g/m^2 (average coat weight obtained for coating starch-Mt formulations on laboratory scale) to facilitate comparison. Addition of a plasticizer significantly reduced the WVTR of the pure starch coating and that the addition of CA led to a substantially lower WVTR than the addition of PEG in the absence of Mt (Fig. 4). The low WVTR in the case of the CA-plasticized starch has previously been attributed to cross-linking of the starch[11]. Adjustment of pH to 4 was shown to almost completely hinder unwanted hydrolysis at moderate curing

temperatures and short curing times needed for drying of coated papers. At the same pH, the moisture barrier properties were shown to be most effective.[16] The starch plasticized by CA was shown to achieve almost the same barrier properties as the starch-Mt composites (Fig. 4).

The incorporation of Mt into the starch gave substantially different effect depending on the plasticizer and dispersant for the starch matrix. Expressed in terms of a calculated tortuosity factor, Eq. 4[1,12], it was concluded that Mt incorporation did not improve the barrier properties further when CA was used as plasticizer.

$$T = \frac{\varphi_M P_M}{P_C} \qquad (4)$$

where P_M and P_C are the normalized WVTR (assuming constant density upon Mt addition) of polymer matrix and polymer composite, respectively, φ_M is the volume fraction of the polymeric matrix in the composites (set constant to 0.9 for all composites) and T is the tortuosity factor.

This indicates that too high degree of swelling and exfoliation of Mt stacks will increase the WVTR value, since the coatings without plasticizer or with CA as plasticizer had higher degree of swelling/exfoliation than the PEG-containing samples. For the starch without added plasticizer, the tortuosity factor was about 1.6 and for the PEG–starch-Mt composite, there was a fairly high tortuosity factor of 4.4-5.4 depending on the dispersant, which could be explained by the reduction in the aggregate volume fraction and/or reduction in the interlayer swelling. It is likely that adsorption of CA-anions on the edges of the particles contributes to a more aligned structure in the dry coatings.

When comparing WVTR values normalized to a coat weight of 6 g/m^2 for double layer coating, it is evident that WVTR values achieved by pilot coating (actual coat weight ca 3.0 g/m^2) were comparable to those obtained on laboratory scale (Fig. 4).
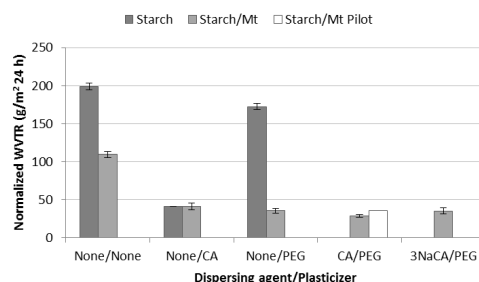

Figure 4. Normalized WVTR for starch and for starch-Mt formulations. The notations on the x-axis refer to Dispersant/Plasticizer respectively. Also shown is the value for pilot coated material using the formulation starch-PEG-Mt with CA as dispersant.

CONCLUSIONS

Starch containing 30 pph CA adjusted to pH 4 gave the lowest WVTR for the non-filled starch-matrix, which can be attributed to a cross-linking reaction resulting in the same low WVTR as the Mt filled composites. The incorporation of Mt was found to be effective in reducing the WVTR of coated paper. The improvement in barrier properties was affected by the aggregate volume fraction and swelling of the Mt. The incorporation of Mt improved the barrier properties of the PEG-plasticized starch formulations substantially, whereas the CA-plasticized starch formulations showed no further improvement. The PEG plasticized starch showed much less interlayer swelling compared to the 30 pph CA containing and the non-plasticized starch composites. Small amount of dispersant, CA anions could be used to slightly reduce the aggregate volume fraction and the viscosity of the PEG-plasticized starch Mt coating formulations.

ACKNOWLEDGMENTS

industrial companies taking part in the project for financial and intellectual support.

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