

Components interactions controlling starch–kaolinite composite films properties

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17 Abstract

In order to relate the primary filler-matrix interactions to the macroscopic properties of starch-18 19 kaolinite composite material, these interactions are monitored through homo- or heterocoagulation experiments involving both components. Turbidity measurement and Infrared 20 21 spectra confirm the extreme weakness of the interactions. The addition of calcium cations 22 shows that these weak interactions between starch and kaolinite are due to the combination of 23 the electrostatic repulsion and hydrogen bonds formation between this two negatively charge 24 components. Some possible relationships between the starch-kaolinite interactions and starch-25 kaolinite composite films properties are proposed.

26 Keys words: Kaolinite; Starch; Composite; Coagulation; Interface.

27

28 1: Introduction

29 Starch and kaolinite are readily available, low cost materials that have already found uses in 30 several domain such as composite materials (Kaewtatip and Tanrattanakul, 2012; Mbey et al., 31 2012a; Chen and Evan, 2005; de Carvalho et al., 2001; Whilem et al., 2003), paper coating (Husband, 1998), flotation of iron ore (Ma, 2011; Ma, 2010; Ma et Bruckard, 2010; Liu et al., 32 33 2000; Weissenborn et al., 1995), water treatment (Shogren, 2009; Bolto and Gregory, 2007; 34 Krentz zt al. 2006; Järnström et al. 1995a; Järnström et al. 1995b). In some cases, starch 35 undergoes some modifications prior to its use in a particular domain. Cationic starch derivatives for instance are usually of interest in flocculation of solid matter from water 36 (Bratskaya et al., 2005; Chen et al., 2007; Wei et al., 2008). 37

38 In the domain of polymer-clay composite, the filler-polymer matrix interactions are one major 39 key for properties change understanding. Those interactions are influenced by the filler-matrix 40 interface and/or interphase, the filler particles orientation, the filler dosages, the filler particles 41 anisotropy, the surface properties of the filler or the filler dispersion (Fu et al., 2008; Tran et 42 al., 2006; Wu et al., 2002; Pukansky, 1990). In those materials, the interactions between the 43 organic matrix and the inorganic filler determine structural and aging properties. Strong 44 interactions guarantee rigidity and resistance to abrasion, weak interactions are required for 45 flexibility. (Lopez et al., 2014; Müller et al., 2014; Jandas et al., 2013; Reddy et al., 2013).

Hence, the explanation of properties changes in composites are discussed on the basis of the filler-polymer matrix interactions. Lopez at al. (2014) associated the ductility conservation in starch-talc composite to low interactions between starch and talc particles. Müller et al. (2014), used wood particles to improve thermoplastic starch properties. They show that the wood particles having large aspect ratio improve the stiffness and the strength of the

51 composite. Also, strong interfacial adhesion between the wood particles and the starch matrix 52 decreases the starch chains mobility and reduces the water uptake of the composite. In our 53 previous works (Mbey et al., 2012 and 2014), unmodified or DMSO-intercalated kaolinite are 54 used as filler in thermoplastic starch based films. The filler particle orientation and the low 55 kaolinite dosage, together with weak kaolinite-starch interactions better account for the 56 plasticity increase within the film. Better dispersion of the DMSO-intercalated kaolinite 57 shows larger properties changes compared to unmodified kaolinite filled films. It is then believed that analysing the primary interactions between the components of the composite 58 59 may be useful to understand the composite properties. Hence, in the case of kaolinite-60 thermoplastic starch composite, the study of starch-kaolinite interactions is of interest.

To date, general studies on the kaolinite-starch interactions are rare (Ma, 2011; Ma, 2010; Ma et Bruckard, 2010), especially in the field of starch-clay composites. In fact, those interactions are described as very weak, since the essentially non ionic hydroxylic functions available on both starch and clay interface give rise to physical sorption through hydrogen bonds.

For this study, we will attempt to correlate the starch-kaolinite interactions to the properties ofstarch-kaolinite composite films.

67 This study aims at monitoring the adsorption of cassava starch onto kaolinite as a way to 68 understand the starch-kaolinite films properties. The dispersion or the coagulation of the 69 kaolinite phase during composite processing will largely depend on the kaolinite-starch 70 interactions. Absence of interactions could favour phase separation between the two 71 components, whereas strong interactions may induce the coagulation of the clay within the 72 polymer matrix or increase the polymers chain rigidity within the composite. On this basis, it 73 is then obvious that weak to medium interactions are preferred for viscoelastic composite 74 films making. To access the starch-kaolinite interactions, the sedimentation/flocculation test 75 of dilute kaolinite suspension in presence of natural cassava starch is used.

76

77 **2 : Experimental section**

78 2-1: The Kaolinite material

The raw kaolinite was collected from a deposit situated in Mayouom (western Cameroon) (Njoya et al., 2006). The sample used in the present study was taken at 3 m depth. The fraction < 40 μ m, labelled K3, was collected by means of wet sieving. Using inductive coupled plasma by atomic emission spectrometry (ICP-AES) to analyze the major elemental composition of the sample, an approximation of the structural formula of the kaolinite phase

was found to be $(Al_{1.94} \text{ Fe}_{0.06})(Si_{1.98} \text{ Fe}_{0.02})O_5(OH)_4(Mg_{0.02} \text{ Ca}_{0.002})$. The mineralogical 84 composition of the sample is as follows: Kaolinite 83.3 %; Illite 10.4 %; Titanium oxide 3.4 85 %. The fine clay fraction was collected through sedimentation after Stokes' law. The particle 86 size distribution of the collected fraction was analysed using a Sympatec laser diffraction 87 88 granulometer equipped with the HELOS optical system and the WINDOX software for data 89 acquisition. The average particle size (D50) was found to be 4.5 µm and more than 80 % of 90 the material has size less than 7.5 µm. The BET specific surface area, determined by nitrogen 91 adsorption using an automatic homemade apparatus, was (25.9 ± 0.1) m²/g. The cation exchange capacity (CEC) was measured using hexaminecobalt(III) chloride [Co(NH₃)₆Cl₃]. 92 93 The amount of hexaminecobalt(III) sorbed by the solid phase was determined by colorimetric 94 measurement at 472 nm using UV-vis spectroscopy and the CEC was found to be 6.0 95 meq/100g.

96

97 2-2: The starch material

98 The cassava starch was obtained by aqueous extraction from cassava tubers produced in 99 Mambando (Centre Cameroon). Starch material was manually ground and sieved at 100 µm. 100 The sieved starch was stored in high density polyethylene container at ambient temperature. 101 The moisture content, determined by drying to constant weight at 105°C, is 14 %. Content in 102 mineral ashes, determined by ignition at 550 °C in a muffle furnace, is 0.3 %. Elemental 103 analysis using the CHNS analyser Carlo Erba 1108, indicated respective contents of carbon 104 (39.1 %), hydrogen (7.5 %) and nitrogen (0.05 %). The H/C ratio, 5.2 is common for 105 polysaccharides. The very low nitrogen content, and the absence of the characteristic amine 106 band in the FTIR spectrum (not presented) indicate negligible content of proteins.

107 2-3: Experimental procedures

The kaolinite suspension was prepared by dilution of the aqueous extract of fine clay fraction
to a solid concentration of 0.5 mg/mL of turbidity 235 NTU (HACH 2100 N turbidimeter).

The starch solution was prepared by dissolving 100 mg of starch in 5 mL of analytical grade DMSO (Sigma Aldrich 99.99 %) under heating at 60 °C during 5 min. The mixture was then diluted with deionised water (18.2 M Ω cm⁻¹) to obtain 100 mL of solution (starch concentration 1 mg/mL). The dissolution with DMSO prevents alteration of the chemical functions and degradation of the carbohydrate chains (Han et Lim, 2004). The working pH was selected after analysing its effect on the sedimentation of the kaolinite suspension. Typically 30 mL of the initial suspension having 235 NTU turbidity was taken and used at the

117 spontaneous pH reached by the suspension (6.02) or after adjusting the pH value by adding 118 aliquot of 0.1 M solution of either NaOH or HNO₃. The samples are left for sedimentation 119 during 40 min after which 15 mL of the suspension supernatant was taken using a 120 micropipette for turbidity measurements. On figure 1, are reported the results obtained. It can 121 be noted that the turbidity is stabilized around 160 NTU. This reduction of turbidity is caused 122 by the settling of large particles that arise from collision between the clay particles subject to 123 Brownian motion. The acid or alkaline value of pH induced either protonation or 124 deprotonation of edge functions (=AlO–H and =SiO–H). Given that the permanent charge of 125 the clay is negative, hence deprotonation of the edge functions, in alkaline pH, increasing the 126 global negative charge of the suspension which result in an increase electrostatic repulsion 127 that prevent particles collision and hence, stabilized the suspension. Conversely, in acid pH, 128 the edge functions are positively charge inducing then a reduction of the global electrostatic 129 repulsion. This charge reduction favours collision that result in increase particle size that 130 settled under their weight. This explains why, acid pH favours the sedimentation and alkaline 131 pH slightly increases suspension stability. Intermediate pH, reached spontaneously by the 132 kaolinite suspension (pH = 6.2), was considered as an optimal starting condition for further 133 coagulation experiments.

134 The proton surface excess of both kaolinite and starch was measured by acid-base titration 135 using a Metrohm Titrando 809 station with two dosing units Dosino 800. The system is 136 automatically driven by the software Tiamo (version 1.2.1 light). The titration of the 137 suspension was carried out under magnetic stirring and argon stream to avoid carbon dioxide 138 dissolution in the suspension. Electrophoretic mobility of the kaolinite and the starch materials was measured in NaNO₃ background electrolyte (10⁻³ M, 10⁻² M and 10⁻¹ M) and in 139 the presence of varying amounts of CaCl₂ using a Zetaphoremeter V by CAD Instrumentation 140 141 (France).

142 For the sedimentation tests, 30 mL of the kaolinite suspensions was magnetically stirred for 5 143 min after addition of known dosages of starch and CaCl₂. The samples were then placed in 144 vertical test tubes for sedimentation. After 40 min, 15 mL of the supernatant suspensions was 145 taken for turbidity measurement using HACH 2100 N turbidimeter. The remaining 146 suspensions were freeze-dried and the sediment conditioned in KBr pellets were analysed by 147 FTIR. The FTIR spectra were recorded using a Bruker IFS 55 interferometer in transmission 148 mode. The sedimentation tests were done in absence or in presence of calcium. A preliminary 149 test of coagulation by calcium ions was done to determine the dosage to be used.

150 Uv-vis spectrometer, SHIMADZU UV 2101 PC, was used for kinetic monitoring of the

- 151 suspensions sedimentation. The measurements were done at 300 nm.
- 152 **3 : Result and discussion**

153 3.1: Starch-Kaolinite interactions

The titration curves presented in figure 2, show the pH-dependence of the net proton surface excess. For the starch, the specific amount of acidic groups is around 43 μ mol/g (figure 2b). In order to evaluate the spatial distribution of charges on the starch macromolecule, we can assume that the latter is composed of glucose residues of molar mass 180 g/mol. The obtained charge is then 7.7 mmol of protons per mole of glucose residue, which represents 0.77 % of

- 159 carboxylated residues (less than 1 % of glucose residues are bind to carboxylate group).
- 160 The titration curves at different ionic strength are virtually superimposed, which indicates a161 very low charge.
- 162 The titration curve of kaolinite quantifies the pH-dependent charges on the edges of the
- 163 particles (=A–O– and =SiO–), resulting in a proton surface excess of about 50 µmol/g (figure
- 164 2a). This surface charge is in accordance with the commonly observed cationic exchange 165 capacity for kaolinites, generally below 10 meq/100g (Eslinger and Pevear, 1988, after Martin 166 and Dacy, 2004). The fact that no common intersection point is observed on the titration 167 curves at different ionic strength indicates the presence of small amount of permanent charge 168 due to isomorphic substitutions in the crystalline structure of the kaolinite. Similar behaviour 169 was observed and modelled for montmorillinites and illites by Delhorme et al. (2010) and 170 could be attributed to the 10% of illite contained in the sample.
- From electrophoretic mobility measurements (figure 3), it is shown that the surface charge of both starch and kaolinite is negative in the pH range of 3 to 10. The electrophoretic mobility of the starch (figure 3b) shows positive values for pH below 2.1, which indicates the presence of cationic functions such as ammonium functions in proteins, which were detected in very low amount by elemental analysis (\$2.2). The negative values and pH dependence of the electrophoretic mobility of starch in the pH domain 2.5 – 7 is probably due to the dissociation of carboxylic groups on the starch macromolecules.
- The electrophoretic mobility of kaolinite (Figure 3a) shows very little dependence on ionic strength and also on pH in the domain above pH 6, which confirms the presence of permanent charges that were detected from the titration curves. In the domain below pH 6, strong pH dependence of the electrophoretic mobility results from the protonation of the hydroxylic functions on the edges of the clay particles.

183 Adsorption isotherms are generally used to study the mechanism and strength of interaction 184 between a mineral interface and an organic (macro)molecule. In the present case, such 185 approach is ineffective for at least two reasons. Firstly, the weakness of the interactions does 186 not allow strong amounts of organics to be adsorbed on the solid, as shown in published 187 studies (Liu, 2007; Mpofu et al., 2003; Järnström et al. 1995a). Secondly, in the present study, 188 cassava starch was used in the native form, therefore heterocoagulation experiments are more 189 adapted than adsorption isotherms to study organo-mineral interactions. In figure 4, the 190 turbidity of a kaolinite suspension is independent of the amount of added starch up to 2.5% 191 (higher amounts would increase the turbidity due to the granular character of starch). Addition of 10⁻⁵ M CaCl₂ results in significant and rapid (40 minutes) sedimentation of the suspension, 192 193 which confirms that electrostatic repulsions must be overcome to achieve attractive 194 interactions, as also reported by Ma (2010). It is obvious that for dosage between 1 % and 1.5 195 %, the effect of starch on the sedimentation is maximal. In this study, the calcium ion acts as 196 neutralizer of the kaolinite surface charge, and the screening of the kaolinite charge favours 197 the starch adsorption on the kaolinite surface.

198 The increase in adsorption of starch is evidenced by the decrease in the turbidity (increase 199 sedimentation of the clay) for the same starch concentration in presence of calcium ion (figure 200 4). The starch adsorption is almost maximal early at 0.33 % dosage of starch. It seems that 201 adsorption of starch at low dosage is possible and this helps the kaolinite sedimentation. 202 However, the adhesion forces are not strong enough and this explains the turbidity fluctuation 203 observed around 1 %. Weak interactions take place in the system due to combine effect of 204 hydrogen bonds between the two components and electrostatic repulsion between starch and 205 kaolinite due to their negative surface charge. The hydrogen bonds could be beneficially 206 increase by the reduction of the interaction sphere (that is, a reduction of the volume in which 207 starch and kaolinite interact). Hence, the screening of the kaolinite surface charge by the 208 calcium cations induce then an increase in starch adsorption. The effect of calcium ions on the 209 electrostatic interactions between the clay and the starch is illustrated in figure 3 (c and d). 210 While kaolinite showed to be relatively insensitive to monovalent cations (Na^+) (Figure 3a), its negative electrophoretic mobility dramatically decreases in the presence of 10^{-5} M Ca²⁺. 211 Comparatively, the mobility of starch is less sensitive to the presence of Ca^{2+} , the 212 213 complexation of which with carboxyl and eventually dissociated hydroxyls being much 214 weaker than on dissociated surface sites on clay. The charge interaction between kaolinite 215 and starch is hence, reduced and this results in a decrease of the interaction sphere between 216 kaolinite and starch that favours starch adsorption. However, one can easily note that the clay

217 surface charge remains negative even in the presence of calcium (figure 3c) as well as the 218 starch surface (figure 3d). The hypothesis to explain the remaining negative charge of the 219 kaolinite in the presence of calcium is that, edge-edge aggregation that leads to loose 220 aggregates takes place within the kaolinite suspension in presence of calcium. These loose 221 aggregates enclose part of the negative charge of kaolinite particles preventing then further 222 screening because of the repulsion between the calcium cation at the external shell of these 223 aggregates. Hence, even if the added calcium cations screened both starch and kaolinite 224 surface, the overall surface of both component remain negative and the electrostatic repulsion 225 between the two components is dominant and favours the stability of the system.

226 FTIR spectra of the raw kaolinite and aggregated sediments are presented in figure 5. The presence of the band at 1383 cm⁻¹ characterising the C-H bending in the pyranose ring 227 (Velraj et al., 2011) is a proof of some starch adsorption onto kaolinite particles. However, as 228 229 concluded from turbidity measurements, the amount of starch adsorbed is low. The sediments 230 are mostly made of kaolinite as shown by the similarity between the raw kaolinite spectra and that of the freezed-dried sediments. The absence of the band at 1383 cm^{-1} on the sediment 231 232 obtained with 2 % starch, is probably due to the loose nature of the aggregate which agree 233 with the previously mentioned weak adhesion force between the two components. It is 234 proposed that natural gravimetric sedimentation is dominant and the contribution of potential 235 coagulation due to both starch and calcium is low.

236 The kinetic evidence of the influence of starch on the kaolinite sedimentation is presented on 237 figure 6. The difference between the blank system and systems containing starch, calcium or 238 starch + calcium is obvious. The starting of sedimentation is effective between 10 min and 15 239 min. The kaolinite sedimentation is increase in the presence of starch. The addition of calcium 240 ameliorate the starch adsorption on the clay which better promotes the kaolinite 241 sedimentation. The increase sedimentation due to starch adsorption is rather low indicating 242 weak adhesion interactions that are clearly related to the surface state of both components 243 which are negatively charged.

244 3.2: Relating the starch-kaolinite interactions to the starch-kaolinite films properties

In the aim of understanding the properties of composite films, a global view of weak starchkaolinite interfacial interactions can explain the good dispersion of the kaolinite within the starch matrix. This view of weak interactions is regarded as a result of the predominance of the electrostatic repulsion between these two negatively charged components and the H-bonds formation due to the existence of hydroxyl groups on the surface of both components. In particular, the existence of electrostatic repulsion is favourable to the clay dispersion. The

presence of kaolinite between the starch chains with weak kaolinite-starch interactions facilitates the mobility of the starch chains, giving rise to a plasticizing effect of the clay within the starch matrix. These hypotheses correlate well with the decrease of the glass transition temperature reported in a previous work (Mbey et al., 2012). The glycerol molecules, present at the starch-kaolinite interface, may also participate in the interactions within the films network.

257 Due to the electrostatic repulsion between the two components, the clay particles are better 258 oriented in the starch matrix in the direction that minimizes the repulsion between the two 259 components. Because kaolinite charge is supposed to be more dense on edges surfaces, a 260 preferential basal orientation of the kaolinite particles is expected within the films (figure 7a). 261 Such an orientation may also contribute to an increase in starch chain mobility through an 262 increase of the plasticizer diffusion and prevention of plasticizer escape. The optical 263 micrograph presented in figure 7b, actually corroborates such an orientation. This orientation 264 also agrees well with barrier properties to water uptake, heat diffusion or UV-light 265 transmission (Mbey et al., 2012). More recently (Mbey et al., 2014), tensile test 266 measurements indicate a decrease in ultimate tensile strength and elastic modulus, in 267 accordance with the decrease of the glass transition temperature previously reported (Mbey et 268 al., 2012). These changes also corroborate the weak starch-kaolinite interactions that allows 269 better gliding of the starch chains and a basal orientation of the clay particles which are 270 consistent with the increase plasticizing effect due to the kaolinite. On figure 8, the 271 experimental evaluation of some critical films properties, namely glass transition temperature 272 and ultimate tensile strength evolution with clay content in the composite films, are given 273 (Mbey et al., 2012 and 2014) to reinforce the propose qualitative correlation of the interfacial 274 interactions with the macroscopic properties.

275 4 : Conclusion

276 This study shows possible links between filler-polymer matrix interactions and starch-277 kaolinite composite films properties. Weak starch-kaolinite interactions, that result from 278 electrostatic repulsion combined to hydrogen bonds formation, evidenced from coagulation 279 tests corroborate the weak interfacial interactions in the composites films. These weak 280 interactions are favourable to preferential basal orientation of clay particles within the film 281 and improve dispersion of the filler. All of which agree with the reported improve plasticization and water uptake, UV light and heat diffusion barrier (Mbey et al., 2012 and 282 283 2014). Hence, the dependency of the material properties of the starch-kaolinite film to 284 components interactions is better evidenced. As reported in the literature, this work also

- contributes to evidence the fact that composite material properties are dependent on theinteractions between the constituents of the composites.
- 287

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289

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Figure 1: Analysis of the pH effect on the sedimentation of the kaolinite suspension



Figure 2: Surface proton excess for the kaolinite (~50 μ mol/g) (a) and the cassava starch (~43 μ mol/g) (b) as a function of pH and ionic strength

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Figure 3: Electrophoretic mobility of the kaolinite (a) and the starch (b) in NaNO₃ background and mobility of kaolinite (c) and starch (d) in presence of calcium cations



Figure 4: Turbidity measurements after 40 min sedimentation of kaolinite suspension (starting turbidity of the kaolinite suspension 235 NTU)



Figure 5: Infrared spectra of the kaolin-starch sediments (υ : stretching; δ : bending)



Figure 6: Uv-vis kinetic profile during kaolinite sedimentation





Figure 7: (a) Illustration of clay-starch interface in the composite film (b) optical micrograph of 10 % loaded kaolinite cassava starch composite film analyzed for form enhancement using image J.

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Figure 8: Variation of glass transition temperature (Tg) and ultimate tensile strength (UTS) with clay content. APKx: films loaded with raw kaolinite and APKDx: films loaded with DMSO intercalated kaolinite

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