Components interactions controlling starch–kaolinite composite films properties

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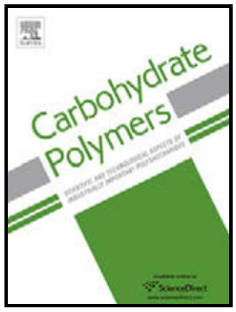

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COMPONENTS INTERACTIONS CONTROLLING STARCH-KAOLINITE COMPOSITE FILMS PROPERTIES

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Abstract

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

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

1 : Introduction

Starch and kaolinite are readily available, low cost materials that have already found uses in several domain such as composite materials (Kaewtatip and Tanrattanakul, 2012 ; Mbey et al., 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., 2000; Weissenborn et al., 1995), water treatment (Shogren, 2009 ; Bolto and Gregory, 2007 ; Krentz zt al._2006 ; Järnström et al. 1995a ; Järnström et al. 1995b). In some cases, starch 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 (Bratskaya et al., 2005 ; Chen et al., 2007 ; Wei et al., 2008).

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

composite. Also, strong interfacial adhesion between the wood particles and the starch matrix decreases the starch chains mobility and reduces the water uptake of the composite. In our previous works (Mbey et al., 2012 and 2014), unmodified or DMSO-intercalated kaolinite are used as filler in thermoplastic starch based films. The filler particle orientation and the low kaolinite dosage, together with weak kaolinite-starch interactions better account for the plasticity increase within the film. Better dispersion of the DMSO-intercalated kaolinite 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 may be useful to understand the composite properties. Hence, in the case of kaolinite-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 of starch-kaolinite composite films.

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

2 : Experimental section

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 µm, 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 $(Al_{1.94}\ Fe_{0.06})(Si_{1.98}\ Fe_{0.02})O_5(OH)_4(Mg_{0.02}\ Ca_{0.002})$. The mineralogical composition of the sample is as follows: Kaolinite 83.3 %; Illite 10.4 %; Titanium oxide 3.4 %. The fine clay fraction was collected through sedimentation after Stokes' law. The particle size distribution of the collected fraction was analysed using a Sympatec laser diffraction granulometer equipped with the HELOS optical system and the WINDOX software for data acquisition. The average particle size (D50) was found to be 4.5 µm and more than 80 % of the material has size less than 7.5 µm. The BET specific surface area, determined by nitrogen adsorption using an automatic homemade apparatus, was (25.9 ± 0.1) m^2/g. The cation exchange capacity (CEC) was measured using hexaminecobalt(III) chloride $[Co(NH_3)_6Cl_3]$. The amount of hexaminecobalt(III) sorbed by the solid phase was determined by colorimetric measurement at 472 nm using UV-vis spectroscopy and the CEC was found to be 6.0 meq/100g.

2-2: The starch material

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

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 $M\Omega\,cm^{-1}$) 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

spontaneous pH reached by the suspension (6.02) or after adjusting the pH value by adding aliquot of 0.1 M solution of either NaOH or HNO_3. The samples are left for sedimentation during 40 min after which 15 mL of the suspension supernatant was taken using a micropipette for turbidity measurements. On figure 1, are reported the results obtained. It can be noted that the turbidity is stabilized around 160 NTU. This reduction of turbidity is caused by the settling of large particles that arise from collision between the clay particles subject to Brownian motion. The acid or alkaline value of pH induced either protonation or deprotonation of edge functions (=AlO–H and =SiO–H). Given that the permanent charge of the clay is negative, hence deprotonation of the edge functions, in alkaline pH, increasing the global negative charge of the suspension which result in an increase electrostatic repulsion that prevent particles collision and hence, stabilized the suspension. Conversely, in acid pH, the edge functions are positively charge inducing then a reduction of the global electrostatic repulsion. This charge reduction favours collision that result in increase particle size that settled under their weight. This explains why, acid pH favours the sedimentation and alkaline pH slightly increases suspension stability. Intermediate pH, reached spontaneously by the kaolinite suspension (pH = 6.2), was considered as an optimal starting condition for further coagulation experiments.

The proton surface excess of both kaolinite and starch was measured by acid-base titration using a Metrohm Titrando 809 station with two dosing units Dosino 800. The system is automatically driven by the software Tiamo (version 1.2.1 light). The titration of the suspension was carried out under magnetic stirring and argon stream to avoid carbon dioxide dissolution in the suspension. Electrophoretic mobility of the kaolinite and the starch materials was measured in $NaNO_3$ background electrolyte (10^{-3} M, 10^{-2} M and 10^{-1} M) and in the presence of varying amounts of $CaCl_2$ using a Zetaphoremeter V by CAD Instrumentation (France).

For the sedimentation tests, 30 mL of the kaolinite suspensions was magnetically stirred for 5 min after addition of known dosages of starch and $CaCl_2$. The samples were then placed in vertical test tubes for sedimentation. After 40 min, 15 mL of the supernatant suspensions was taken for turbidity measurement using HACH 2100 N turbidimeter. The remaining suspensions were freeze-dried and the sediment conditioned in KBr pellets were analysed by FTIR. The FTIR spectra were recorded using a Bruker IFS 55 interferometer in transmission mode. The sedimentation tests were done in absence or in presence of calcium. A preliminary test of coagulation by calcium ions was done to determine the dosage to be used.

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

suspensions sedimentation. The measurements were done at 300 nm.

3 : Result and discussion

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 µmol/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 carboxylated residues (less than 1 % of glucose residues are bind to carboxylate group).

The titration curves at different ionic strength are virtually superimposed, which indicates a very low charge.

The titration curve of kaolinite quantifies the pH-dependent charges on the edges of the particles (=A–O– and =SiO–), resulting in a proton surface excess of about 50 µmol/g (figure 2a). This surface charge is in accordance with the commonly observed cationic exchange capacity for kaolinites, generally below 10 meq/100g (Eslinger and Pevear, 1988, after Martin and Dacy, 2004). The fact that no common intersection point is observed on the titration curves at different ionic strength indicates the presence of small amount of permanent charge due to isomorphic substitutions in the crystalline structure of the kaolinite. Similar behaviour was observed and modelled for montmorillinites and illites by Delhorme et al. (2010) and 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.

Adsorption isotherms are generally used to study the mechanism and strength of interaction between a mineral interface and an organic (macro)molecule. In the present case, such approach is ineffective for at least two reasons. Firstly, the weakness of the interactions does not allow strong amounts of organics to be adsorbed on the solid, as shown in published studies (Liu, 2007; Mpofu et al., 2003; Järnström et al. 1995a). Secondly, in the present study, cassava starch was used in the native form, therefore heterocoagulation experiments are more adapted than adsorption isotherms to study organo-mineral interactions. In figure 4, the turbidity of a kaolinite suspension is independent of the amount of added starch up to 2.5% (higher amounts would increase the turbidity due to the granular character of starch). Addition of 10^{-5} M $CaCl_2$ results in significant and rapid (40 minutes) sedimentation of the suspension, which confirms that electrostatic repulsions must be overcome to achieve attractive interactions, as also reported by Ma (2010). It is obvious that for dosage between 1 % and 1.5 %, the effect of starch on the sedimentation is maximal. In this study, the calcium ion acts as neutralizer of the kaolinite surface charge, and the screening of the kaolinite charge favours the starch adsorption on the kaolinite surface.

The increase in adsorption of starch is evidenced by the decrease in the turbidity (increase sedimentation of the clay) for the same starch concentration in presence of calcium ion (figure 4). The starch adsorption is almost maximal early at 0.33 % dosage of starch. It seems that adsorption of starch at low dosage is possible and this helps the kaolinite sedimentation. However, the adhesion forces are not strong enough and this explains the turbidity fluctuation observed around 1 %. Weak interactions take place in the system due to combine effect of hydrogen bonds between the two components and electrostatic repulsion between starch and kaolinite due to their negative surface charge. The hydrogen bonds could be beneficially increase by the reduction of the interaction sphere (that is, a reduction of the volume in which starch and kaolinite interact). Hence, the screening of the kaolinite surface charge by the calcium cations induce then an increase in starch adsorption. The effect of calcium ions on the electrostatic interactions between the clay and the starch is illustrated in figure 3 (c and d). 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 Ca^{2+}. Comparatively, the mobility of starch is less sensitive to the presence of Ca^{2+}, the complexation of which with carboxyl and eventually dissociated hydroxyls being much weaker than on dissociated surface sites on clay. The charge interaction between kaolinite and starch is hence, reduced and this results in a decrease of the interaction sphere between kaolinite and starch that favours starch adsorption. However, one can easily note that the clay

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

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 (Velraj et al., 2011) is a proof of some starch adsorption onto kaolinite particles. However, as concluded from turbidity measurements, the amount of starch adsorbed is low. The sediments 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 obtained with 2 % starch, is probably due to the loose nature of the aggregate which agree with the previously mentioned weak adhesion force between the two components. It is proposed that natural gravimetric sedimentation is dominant and the contribution of potential coagulation due to both starch and calcium is low.

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

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 starch-kaolinite 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.

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

4 : **Conclusion**

This study shows possible links between filler-polymer matrix interactions and starch-kaolinite composite films properties. Weak starch-kaolinite interactions, that result from electrostatic repulsion combined to hydrogen bonds formation, evidenced from coagulation tests corroborate the weak interfacial interactions in the composites films. These weak interactions are favourable to preferential basal orientation of clay particles within the film 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 2014). Hence, the dependency of the material properties of the starch-kaolinite film to components interactions is better evidenced. As reported in the literature, this work also

285 contributes to evidence the fact that composite material properties are dependent on the
286 interactions between the constituents of the composites.
287

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289

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376 interactions related to starch-kaolinite composite films properties
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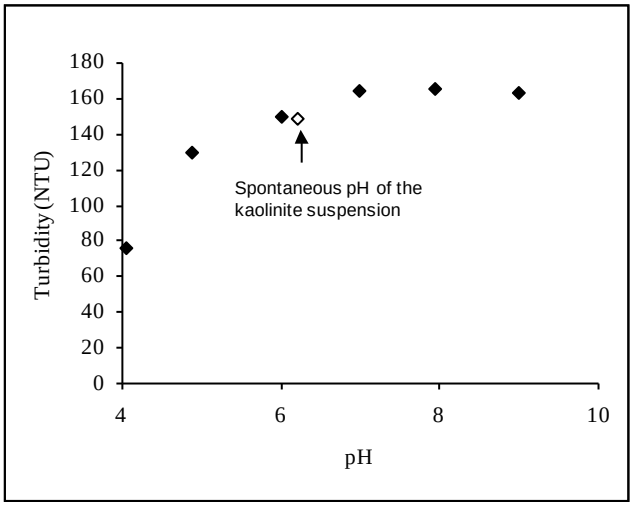

Figure 1: Analysis of the pH effect on the sedimentation of the kaolinite suspension

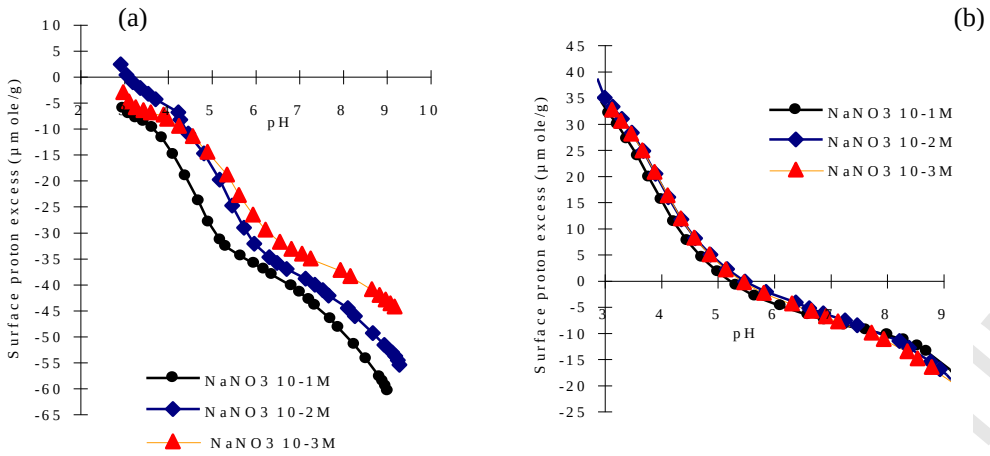

Figure 2: Surface proton excess for the kaolinite (~50 µmol/g) (a) and the cassava starch (~43µmol/g) (b) as a function of pH and ionic strength

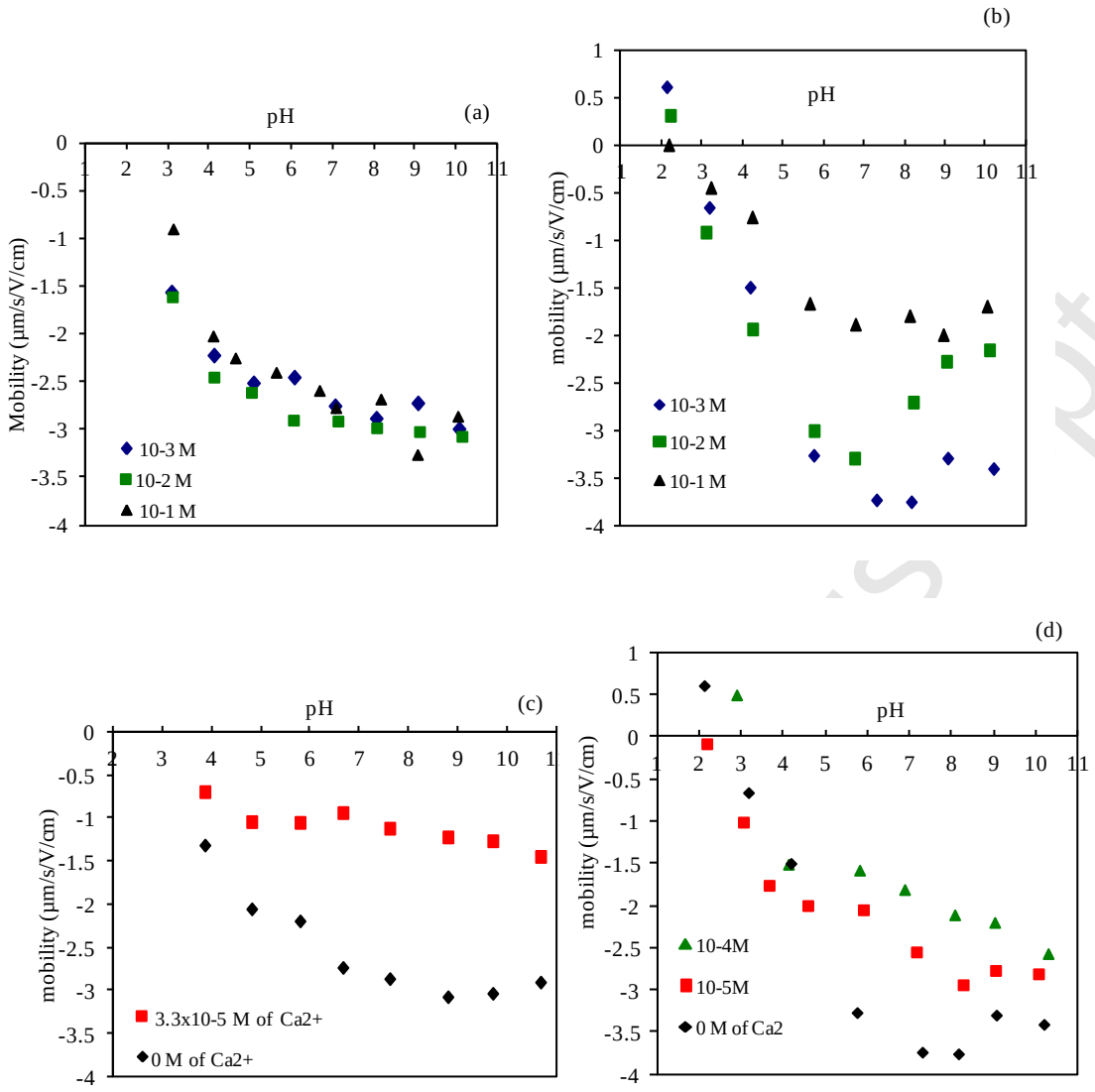

Figure 3: Electrophoretic mobility of the kaolinite (a) and the starch (b) in $NaNO_3$ background and mobility of kaolinite (c) and starch (d) in presence of calcium cations

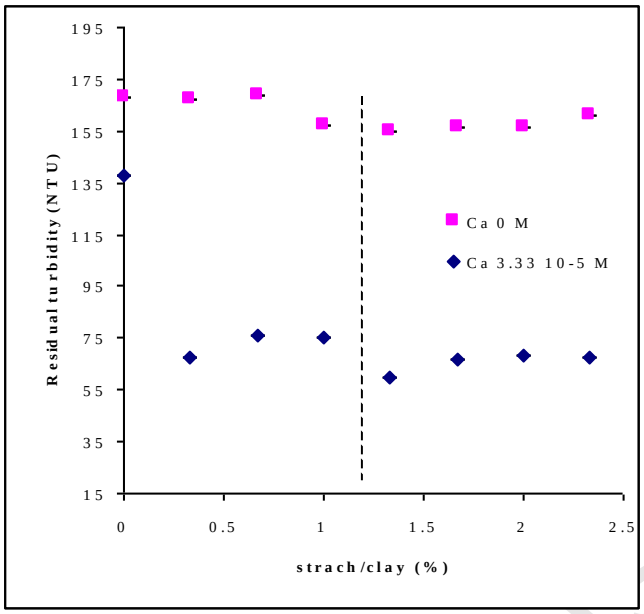

Figure 4: Turbidity measurements after 40 min sedimentation of kaolinite suspension (starting turbidity of the kaolinite suspension 235 NTU)

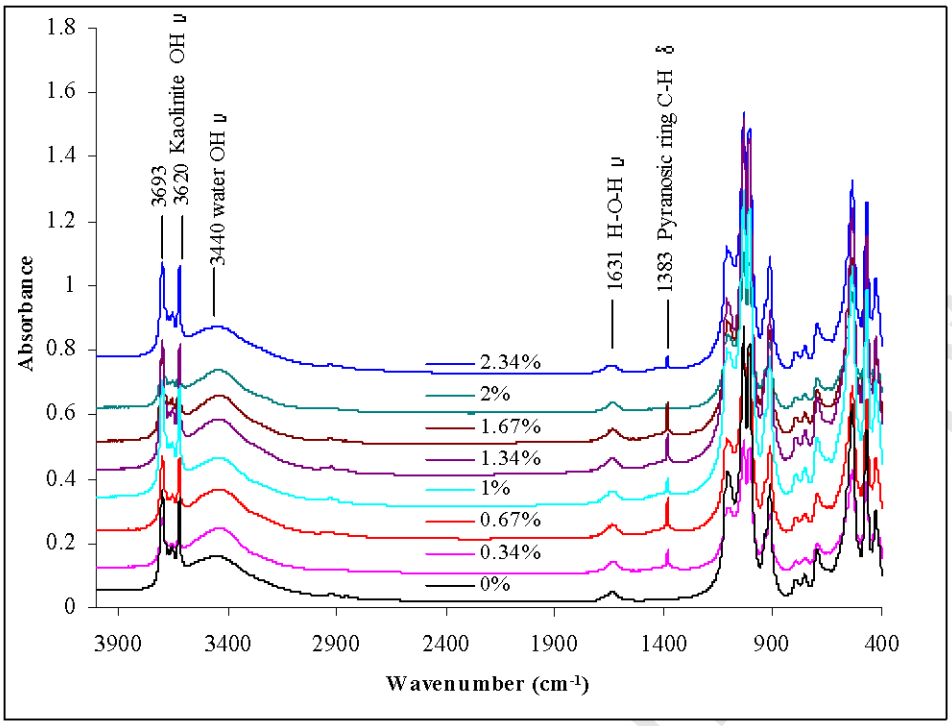

Figure 5: Infrared spectra of the kaolin-starch sediments (υ: stretching; δ: bending)

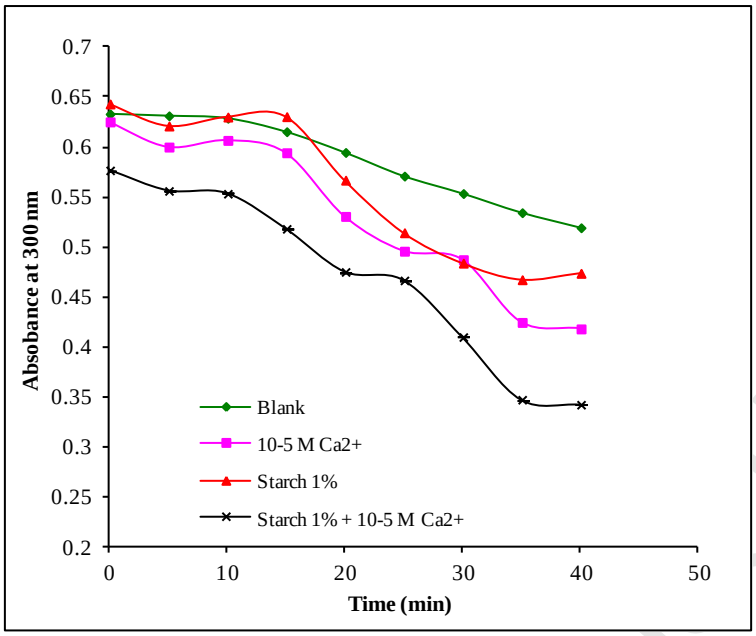

Figure 6: Uv-vis kinetic profile during kaolinite sedimentation

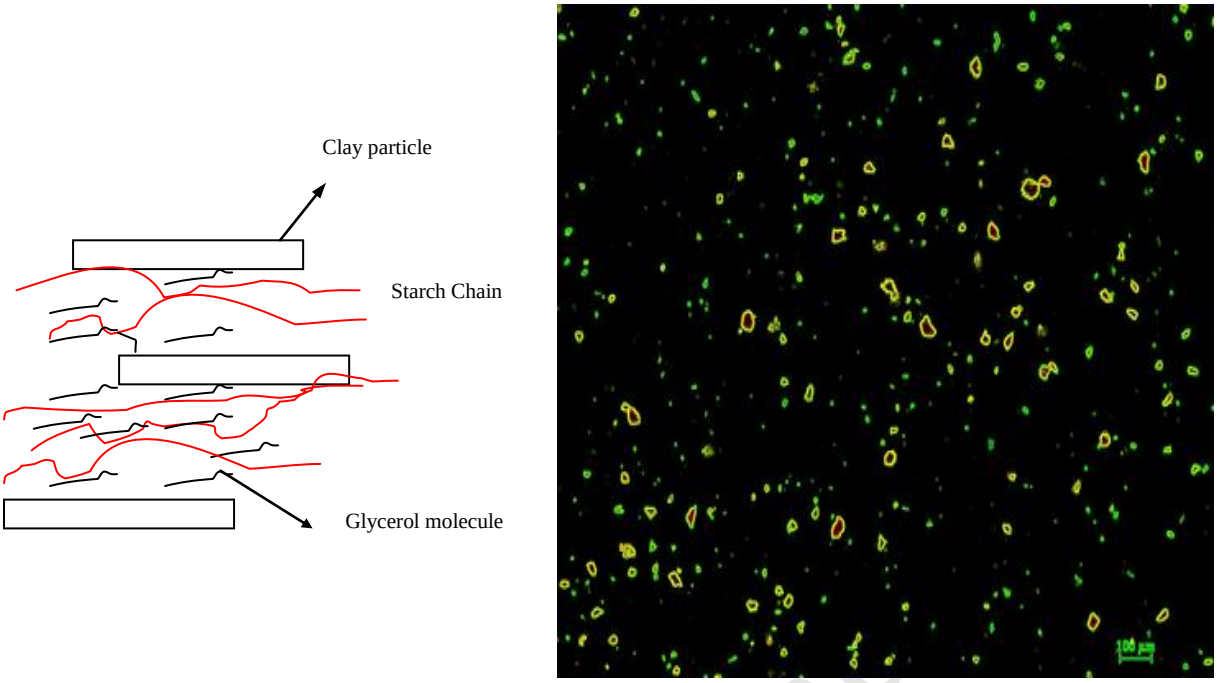

Figure 7: (a) Illustration of clay-starch interface in the composite film (b) optical micrograph of 10 % loaded kaolinite cassava starch composite film analyzed for form enhancement using image J.

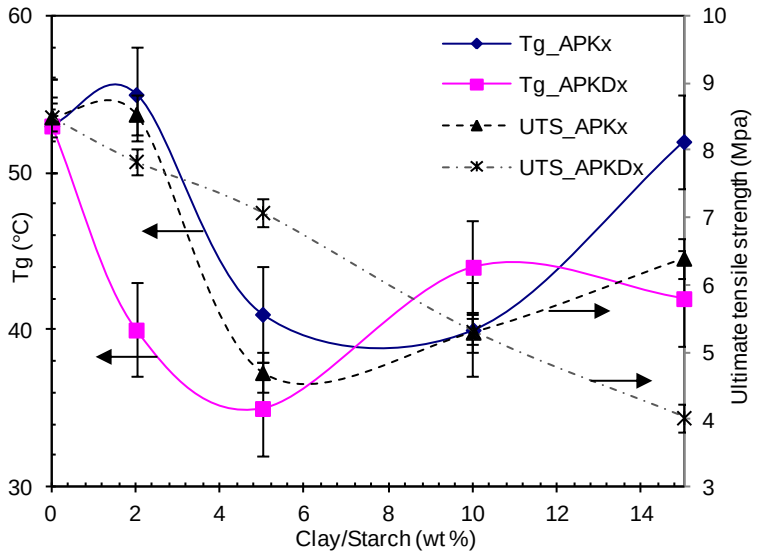

Figure 8: Variation of glass transition temperature (Tg) and ultimate tensile strength (UTS) with clay content.

APKx: films loaded with raw kaolinite and APKDx: films loaded with DMSO intercalated kaolinite