Physico-Chemical Behavior of Glycerol-Coated Cassava Starch Gels Incorporating Kaolin and Metakaolin

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Abstract   This study aims at analyzing the physico-chemical interactions in glycerol-coated cassava starch gels incorporating clay as mineral filler during heating. The physico-chemical and structural characterization of the clay used is composed of 75% kaolinite, 14% quartz and 11% illite. A thermal treatment at 700°C for 1 hour of this kaolinitic clay has allowed strong destructuring of the crystalline structure. The suspensions of glycerol plasticized cassava starch without charge or containing 5% by weight of clay were prepared and then heated at various temperatures between 30°C and 100°C. The suspensions viscosity increases according to the temperature up to a maximum following the penetration of the water molecules inside the starch grains. This phase is followed immediately by a sharp drop in the viscosity, resulting in a granular destructuring and solubilization of the starch grains. The suspensions incorporating metakaolin have a higher viscosity than those incorporating kaolin. The gels incorporating metakaolin have a hight ability to downgrade. The infrared spectroscopy of gels taken at different temperatures show the formation of the inter and intra molecular bonds within the starch granules.

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1. Introduction

The omnipresence of plastics in daily life is undeniable (food packaging, cosmetic industries, automobiles.) [1]. The production and use of petrochemical plastics is necessarily accompanied by environmental pollution because these plastic wastes are non-biodegradable. The fight against plastic pollution requires taking into account concepts such as the recycling of petrochemical plastics and the development of biodegradable biopolymers. The starch constituted mainly of a mixture of two natural polymers (amylose and amylopectin) is considered as the most promising raw material for the production of biodegradable biopolymers. Unlike synthetic polymers, starch-based plastic films have little water resistance and low thermomechanical properties. However, these thermomechanical properties can be improved by adding mineral filler in the production of these plastics. Indeed, the introduction of mineral fillers help improving plastics their mechanical properties

without having a negative impact on their biodegradability [2].

The montmorillonite clays are in common use mainly because of their availability, versatility, high form factor (50 – 1000), nanometer thickness of their platelets and ability to disperse easily in the suspension of starch [3,4]. The kaolinitic clays are very little used because of their non-expandable character in the polymeric matrix and this despite the great abundance of kaolinitic clays deposits [5,6,7]. The less cohesive kaolinite has often been achieved by chemical treatment with dimethyl sulfoxide [8]. Another method for destructuring the crystalline edifice of kaolinite is the thermal treatment with the departure of hydroxyls in the form of water [6]. Indeed, kaolinite sheets, each constituted of a siliceous basal surface made of oxygen and an aluminous basal surface made of hydroxyl, are bonded together by hydrogen bonds. The departure of hydroxyls in the form of water leads to the layers, each constituted of a siliceous basal surface made of oxygen and an aluminous basal surface devoid of hydroxyls and side surfaces.

This present work aims at characterizing local clay and on one hand, at studying the physico-chemical interactions in glycerol-coated cassava starch gels incorporating this clay as mineral filler, during the heating by viscosity, retrogradation and infra-red spectrometry measurements on the other hand.

2. Raw Materials and Experiment Methods

2.1. Raw Materials

The starch used is extracted from Bocou 2, a cassava tuber variety grown in Côte d'Ivoire. The clay noted KB from the clay site of the region of Yaou located around the following geographical coordinates: 05°15'013"North and 03°37'485"West. The metakaolin referenced MKB was obtained after thermal treatment of this kaolinitic clay at 700°C for 1 hour with a rise speed of 5°C/min in a Nabertherm type programmable oven.

2.2. Experiment Methods

The chemical analyze was performed by Plasma Emission Spectrometry ICP-AES after a dissolution by wet path using a microwave (ANTON Paar).

X-ray diffraction diagrams were obtained using a Bruker D8 Advance type device. Measurements were carried out on non-oriented preparations in powder form using continuous scanning mode in 2θ range of 2° - 60° with a step size of 0.01° (2θ) and a counting time of 0.25 second. The phases identification was performed by comparing X-ray diffraction patterns with the International Center for Diffraction Data (ICDD) using EVA software (Brukers AXS).

Infrared spectra were obtained using a Fourier Transform Spectrometer (Tensor 27 Golden Gate Single) in Attenuated Total Reflection (ATR) mode. 1 mg of sample is deposited directly on the ATR sampling device. The spectra were recorded between 4000 to 500 cm^{-1} with a resolution of 2 cm^{-1} and 64 scans. The scanning speed is 10 kHz and the interferogram 14.22 points. The spectra are acquired with the OPUS software.

The specific area was determined using Micromeritcs Tristar II type device by BET method. The samples being previously degassed at 200 °C for 16 hours.

The starch suspensions of glycerol-coated cassava without mineral filler noted BP, with 5% of kaolin noted BPKB and with 5% of metakaolin noted BPMKB were studied. They were prepared according to the bioplastics development protocol [9]. Several heating temperatures for each suspension, between 30 °C and 100 °C, were adopted. Once the heating temperature is reached, the suspension is recovered and then placed directly into the viscometer tube for measurements.

A pH measurement of the supernatants was made using a pH meter of the inoLab pH/ION/Cond 750 type. The supernatant is obtained after centrifugation at 3000 rpm for 10 min of the prepared suspensions.

The suspensions viscosity was determined using a falling ball viscometer. The temperature of the suspension is kept constant using a water bath during measurement. The time taken by the ball to cross the suspension is determined using a stopwatch. The viscosity (mPa.s) of the suspension was calculated with the following formula: $\eta = K*(\rho_1 - \rho_2)*t$ with K: constant given by the constructor; ρ_1: density of the ball used; ρ_2: density of the suspension and t: time taken by the ball to cross the suspension in second.

The retrogradation of the starch gels was evaluated by determining the amount of water coming from the phase separation of the polymer-water type. This separation is obtained by centrifugation at 30000 rpm for 5 min of the starch gel previously stored at 4°C for 7 days.

3. Results and Discussion

3.1. Physico-Chemical Characterizations of the Clay

The physico-chemical and mineralogical characterizations of KB kaolin are recorded in the Table 1.

Table 1. Physico-chemical and mineralogical characteristics of KB clay

KB Clay	SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2	Na_2O	CaO	MgO
Chemical Composition (% wt)	64.4	29.6	3.3	1.3	0.8	0.8	-	-
Mineralogical Composition (% wt)	Kaolinite = 75;		Illite = 11;			Quartz = 14		
Specific area (m^2/g)	43.5							
Density	2.6							

Chemical analysis shows that KB clay is mainly composed of silica and alumina. The iron oxide, titanium, sodium contents are relatively low in the KB clay. The X-ray diffraction diagram of KB clay reveals the characteristics peaks of kaolinite (2θ = 12°; 25°; 35°), illite (2θ = 9°; 19.70°; 29.36°) and quartz (2θ = 20°; 26°; 36°). From the results of the chemical analysis and the ideal chemical composition of the mineralogical phases detected by X-ray diffraction, calculations based on the relationship of Njopwouo and al. [10] have allowed to evaluate the mineralogical compositions of KB clay (75% kaolinite, 11% illite and 14% quartz). The KB clay has a relatively large specific surface area (43.5 m^2/g) for a kaolinitic type clay. This could in part be due to combined action of the iron compound content and certainly to the fineness of the particles of this clay (d_{50} = 21.2 µm).

Figure 1 shows the X-ray diffraction spectra of kaolin KB and metakaolin MKB.

On the diffractogram of the MKB, the characteristics peaks of quartz are observed. The disappearance of the characteristics peaks of kaolinite and illite is related to the transformation of kaolin into metakaolin during heat treatment. Indeed, the metakaolin, product of the thermal treatment of kaolin beyond 500 °C is characterized by a lack of order at great distance in the arrangement of the constituent atoms of the main clay phases [11].

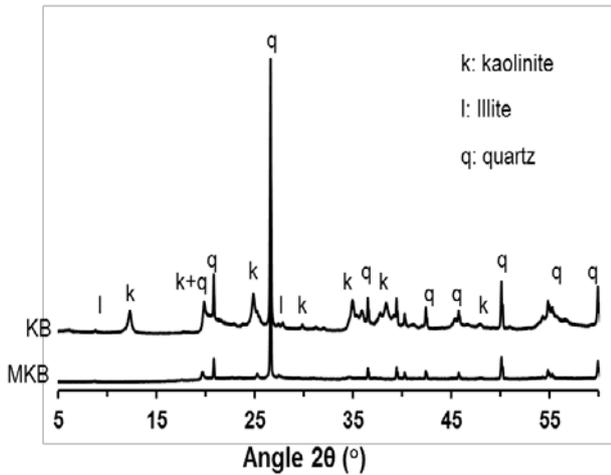Figure 2 shows the infrared spectra of raw KB kaolin and MKB metakaolin.

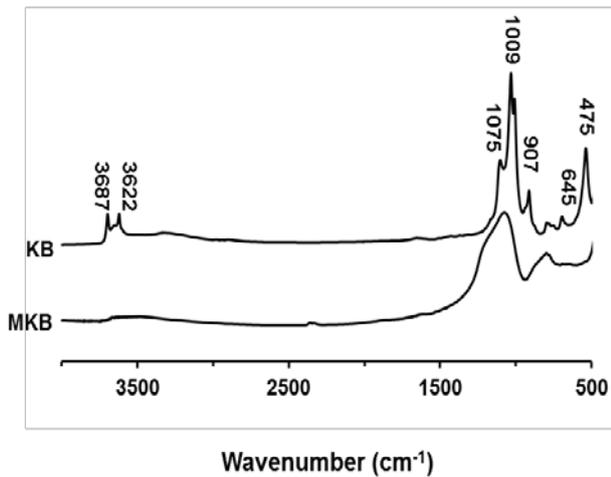**Figure 1.** X-ray diffraction spectra of the KB and MKB samples

Figure 2. Infrared spectra of the KB and MKB samples

In the 3000 – 4000 cm^{-1} range, the spectrum of raw kaolin has at 3687 cm^{-1}, 3649 cm^{-1} and 3622 cm^{-1} bands due to hydroxyls elongation vibrations. These bands have been the subject of several studies [11,12]. The band at 3687 cm^{-1} is attributed to the hydroxyls of the edges of the sheet. This located at 3649 cm^{-1} is characteristic of the surface hydroxyls of the octahedral layer in interaction with the base oxygens of the adjacent tetrahedral layer. The band at 3622 cm^{-1} is bound to the internal hydroxyls. None of these characteristics bands of the hydroxyls groups is observed on the spectrum of the heat-treated kaolin. This shows that after treatment at 700 °C for 1 hour, kaolin is totally dehydroxylated.

In the 600-1800 cm^{-1}, the spectrum of raw kaolin highlights the absorption bands at 1032 cm^{-1}, 1000 cm^{-1}, 905 cm^{-1}, 754 cm^{-1} and 698 cm^{-1}. The band at 1032 cm^{-1} is attributed to the elongation vibrations of the apical Si-O bonds while that at 1000 cm^{-1} is characteristic of the Si-O-Si bond elongation vibrations. The band at 905 cm^{-1} is due to the deformation vibrations of the hydroxyls of the aluminous Al-O-H surface.

Significant changes are observed in the intensity, shape and position of MKB absorption bands. This shows that in addition to dehydroxylation, a profound modification of the alumino-silicate structure of kaolin during the rise in temperature is observed.

3.2. Physico-Chemical Characterizations of Cassava Starch Gels

3.2.1. Hydrogen Potential (pH) of Suspensions

Figure 3 shows the evolution of the hydrogen potential of cassava starch suspensions according to the type and amount of clay used.
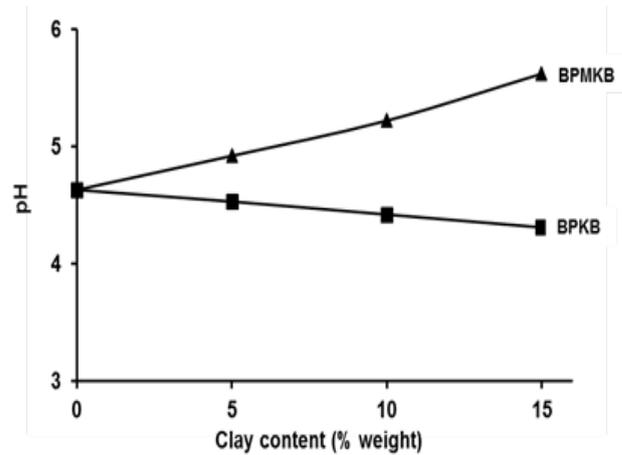

Figure 3. pH variation of suspensions according to the KB and MKB samples rate

The pH of the suspensions goes from 4.7 for BP to 4.5 for BPKB and to 5.1 for BPMKB. The decrease and increase of the suspension pH respectively for BPKB and BPMKB are amplified when the amount of mineral filler increases. This could be explained by the interactions between the surface atoms of clay platelets and the water molecules in suspension [13]. Indeed, the siliceous basal surface, through the electron pairs available on the oxygen atoms, behaves like a Lewis base. It interacts with the hydrogen of the water molecule, thus promoting the release of OH$^-$ ions in the suspension. In contrast, the aluminous basal surface through hydroxyl groups, behaves as a Bronstëd acid. It promotes the release of H$^+$ ions in the suspension. Most of the atoms on the side surface are electron deficient. These atoms tend to fix the electron donors (OH$^-$) to saturate the electronic layers. This phenomenon leads to the formation of silanols (Si-OH) and aluminols (Al-OH) on the edges of clay platelets favoring a depletion of the suspension in hydroxide ion [14]. In the case of the suspension containing the kaolin, the action of the aluminous basal surface is predominant with respect to the action of the siliceous basal surface, hence the decrease of the pH of the suspension.

In the case of the suspension containing the metakaolin, both the siliceous basal surface and the aluminous basal surface consist of oxygen atoms. These two surfaces through the electron pairs available on the oxygen atoms promote the release of OH$^-$ ions in the suspension. This phenomenon is predominant in comparison with the action of the lateral surfaces, hence the increase in the pH of the suspension.

3.2.2. Viscosity of Suspensions

The variation of the viscosity according to the heating temperature of the cassava starch suspensions with or without mineral filler is shown in Figure 4.
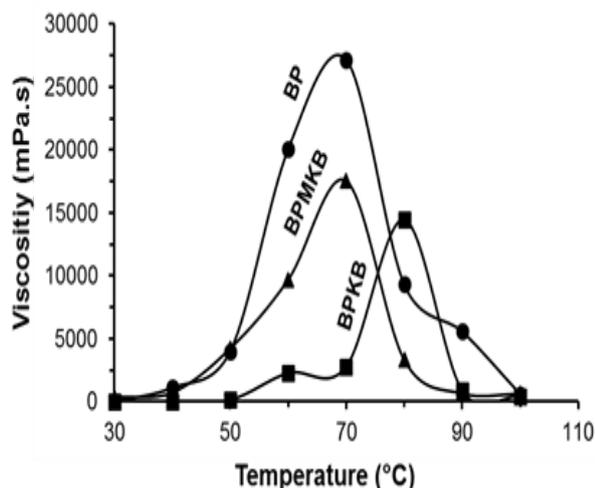
Figure 4. Variation of the viscosity of suspensions according temperature

The variation of the viscosity of the BP, BPKB and BPMKB suspensions as a function of the temperature show two distinct domains. A first zone where the viscosity of the suspensions increases gradually according to the temperature to its maximum, sign of a structuring of the suspension. This structuring would be linked to the swelling of the starch grains due to the absorption of water. A second zone characterized by a sharp drop in viscosity to the starting level. This decrease is attributed to the loss of the granular structure of the starch grains. Indeed, the large molecules (essentially amylose) go out the grain to disperse outside the grain. If the heating continues, a complete dispersion of all the macromolecules of the grain is obtained and the viscosity no longer decreases [7]. Table 2 gives the values of viscosity peaks and corresponding temperatures. The peak viscosity of the suspension of the sample BP is the highest, a sign of greater swelling of the starch grains.

The maximum viscosity of the sample BPMKB is higher than that of BPKB. This could be explained by the fact that in the BPKB suspension, the starch grains do not have the possibility to inflate sufficient because the raw kaolin absorbs part of the water available in the suspension. On the other hand, in the suspension BPMKB, the quantity of water available to penetrate inside the starch grains is important because the metakaolin absorbs very little water. The phenomenon of swelling of grains is preponderant [7].

Table 2. Values of viscosity peaks and corresponding temperatures

Suspension	BP	BPKB	BPMKB
Viscosity peaks (mPa.s)	27289	11054	17558
Temperature of viscosity peaks (°C)	70	80	70

3.2.3. Demotion of the Gels

Figure 5 gives the amount of water from the BP, BPKB and BPMKB starch gels for temperatures ranging from 50 to 90 °C.

The curves obtained show the same evolution regardless the type of gel studied. A first period of 50 to 70 °C where an increase in the amount of water from the

polymer-water phase separation for all the starch gels according to the temperature is observed. Before 70 °C, which corresponds to the temperature of the viscosity peak, the starch molecules capture the water and swell. This adsorption of water increases with temperature. During cooling, the amylose and amylopectin chains in solution pool cluster spontaneously and this water is expelled from the gels. This phenomenon is less important when the gel contains raw kaolin. A second period of 70 to 90 °C where despite the increase in the heating temperature, the amount of water from the gels varies very little. After 70 °C, the starch granules have already burst and can no longer absorb water molecules. They have lost their granular structure and the different molecules (amylose and amylopectin) are found in solution. During cooling, a more or less constant amount of water is evacuated regardless the temperature between 70 and 90 °C. The amount of water expelled from the BPMKB gels is much greater than that of the BP and BPKB gels. The high ability to retrograde gels incorporating metakaolin could be explained by the reactivity of metakaolin with the different chains of amylose and amylopectin resulting from the bursting of starch granules. The metakaolin being considered as a material with pozzolanic properties. These rearrangements would be at the origin of development of the gel texture [15].
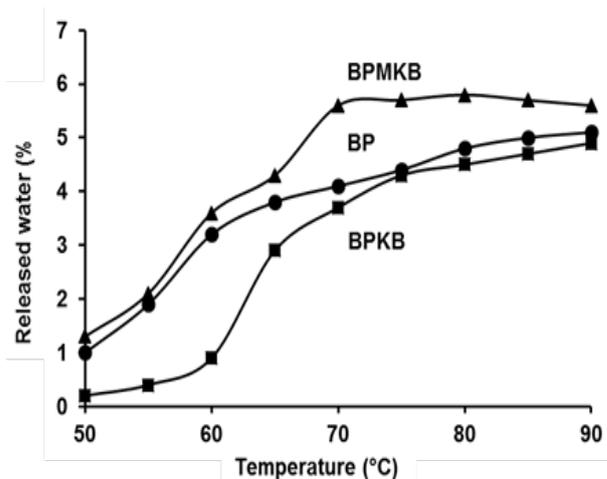

Figure 5. Variation of the quantity of water expelled from the gels according temperature

3.2.4. Structural Interactions in Gels

Figure 6 shows the infrared spectra of glycerol-plasticized cassava starch gels at different heating temperatures.

The infrared spectra relating to BP, BPKB and BPMKB gels obtained have appearance the same at 60 °C. They are characterized by the adsorption bands located between 800 cm^{-1} and 1500 cm^{-1}. This region characterizes the elongation and deformation vibration of C-C, C-O-C, C-O and C-H groups, present in amylose and amylopectin. The band at 1640 cm^{-1} corresponds to the deformation vibration of the O-H bonds of the adsorbed water [16]. The bands at 2925 cm^{-1} and 2850 cm^{-1} are associated to the C-H bonds elongation vibrations. A wide band centered around 3600 cm^{-1} corresponds to the elongation vibration of the OH groups.
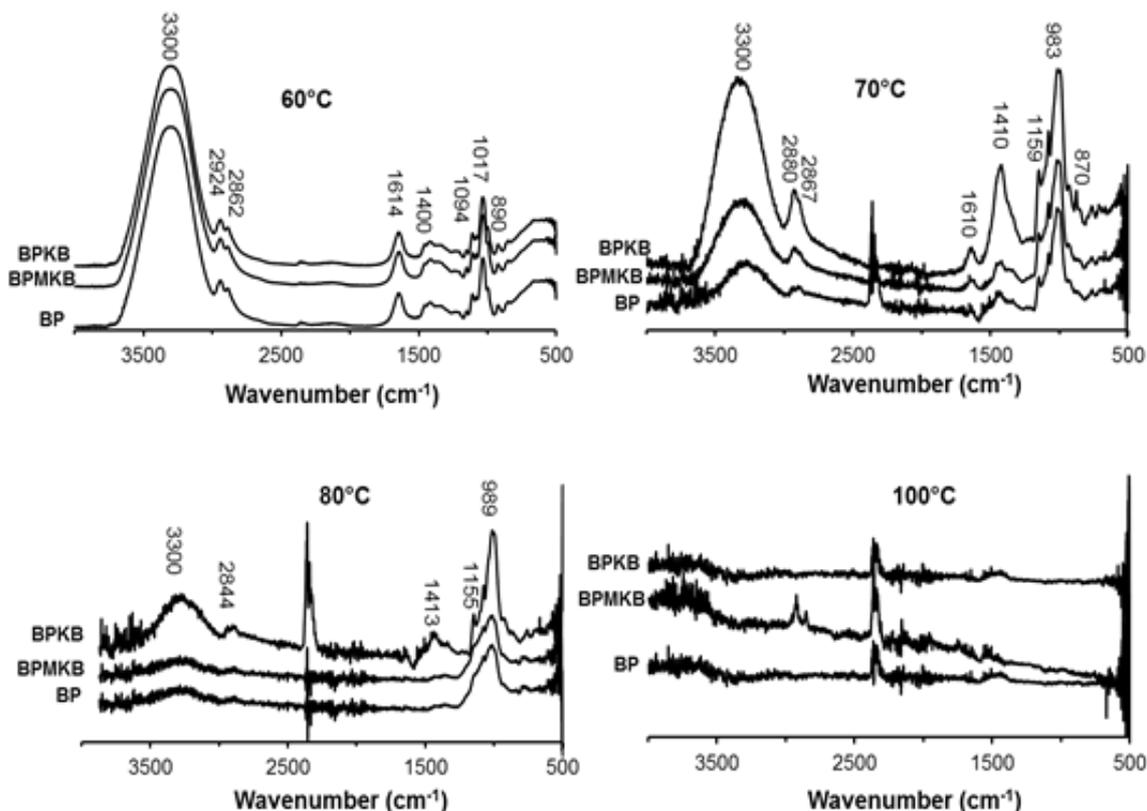
Figure 6. Infrared spectra of gels at different temperatures

The analysis of these peaks can thus account for the sorption of starch granules during heating.

At 70 °C, the intensity of peaks at 3300 cm^{-1} and 1640 cm^{-1} decreases due to penetration of adsorbed water molecules into the starch granules. Thus, the starch granules swell, which would explain the increase in viscosity before 70°C. However, the intensity of the peaks around 2925 cm^{-1} and 2850 cm^{-1} and of those located between 800 cm^{-1} and 1500 cm^{-1} increases following the fixing of these water molecules on the hydroxyl groups present in starch amylose and amylopectin by the formation of new hydrogen bonds between the chains. Water breaks weak bonds between hydroxyl groups and builds bridges through hydrogen bonds that are more energetic. This has the effect of dilating the macromolecular network.

At 80°C, the intensity of all the adsorption bands decreases due to a partial melting of the starch granules. The hydrogen bonds are broken and the macromolecular constituents of the starch granules solubilize.

At 100 °C, all the characteristic bands disappeared, a sign of a total melting of the granules soaked with water.

These structural changes in glycerol-plasticized cassava starch gels are influenced by the nature of the clay used. The raw kaolin delays and attenuates these structural changes whereas metakaolin has very little influence.

4. Conclusion

Two clays KB and MKB were used as additives in glycerol-plasticized cassava starch suspensions in order to improve the properties of use of these bioplastics. The clay KB is mainly composed of 75% kaolinite, 14% quartz and 11% illite. The sample MKB, product of the thermal treatment at 700 °C for one hour of KB clay, has a crystalline structure totally destructured and dehydroxylated. The comparative study of physico-chemical interactions in glycerol-plasticized cassava starch suspensions incorporating the KB and MKB made it possible to show that metakaolin promotes an increase in pH while raw kaolin causes a decrease. For all suspensions, the BP, BPKP and BPMKB, the viscosity increases with temperature during the heating to a maximum before decreasing. The significant increase in viscosity is due to the swelling of the starch granules while the decrease is attributed to the bursting thereof. The maximum viscosity is reached when the granules are at burst limit. The value of the viscosity peak is greater and its temperature of appearance is lower for the suspension incorporating metakaolin. The water absorbed during swelling creates local disorganization of amylose and amylopectin chains within starch granules prior to release in solution. During cooling, the spontaneous groupings of amylose and amylopectin chains are favored by the presence of metakaolin. The lowering of the viscosity peak temperature, the high demotion capacity and the structural modifications of the gels incorporating metakaolin confirm the better dispersion of the heat-treated kaolinite at 700 °C.

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