



# Starch-based nano-biocomposites: Plasticizer impact on the montmorillonite exfoliation process

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## ABSTRACT

The present paper analyzes the effects of the plasticizer nature on the clay exfoliation process into starch-based nano-biocomposites. The nano-hybrids have been elaborated by melt blending starch with different plasticizers, namely, glycerol, sorbitol and Polysorb®. In addition two types of nanofillers, natural montmorillonite (MMT-Na) and montmorillonite organo-modified with cationic starch (OMMT-CS) have been tested. Intercalated/aggregated and exfoliated morphologies were obtained with respectively MMT-Na and OMMT-CS as the nanofillers and glycerol as the plasticizer. Morphological analyses combined with uniaxial tensile tests have shown the negative effect of the sorbitol on the exfoliation extent into such nano-hybrid materials. Besides, thermo-mechanical analyses revealed the occurrence of a phase separation between domains rich and without nanofillers induced by the high plasticizer content of the starch formulations.

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## 1. Introduction

Nano-biocomposites are a new class of hybrid materials composed of nano-sized filler (nanofiller) incorporated into a bio-based matrix (Sinha Ray & Okamoto, 2003). Such an association between eco-friendly biopolymers and nano-objects, with the aim to obtain synergic effects, is one of the most innovating routes to enhance the properties of these bio-matrices (Alexandre & Dubois, 2000).

Depending on the geometry and the nature of the nanofiller, new and/or improved properties (gas barrier, mechanical stiffness, transparency, thermal stability...) can be obtained (Gain, Espuche, Pollet, Alexandre, & Dubois, 2005; Gorrasi et al., 2003; Sinha Ray & Okamoto, 2003). Such properties enhancements rely both on the nanofiller geometry and on its surface area, which is directly linked to the nanofiller dispersion state.

In the case of layered silicates (e.g. montmorillonite), depending on the process conditions and on the matrix/nanofiller affinity, the clay platelets can either be intercalated by macromolecules and/or exfoliated, leading to different behaviors. Intercalated structures show regularly alternating silicate layers and polymer chains compared to exfoliated structures in which the clay platelets are individually delaminated and fully dispersed into the polymer matrix. The best performances are commonly observed with the latter structure (Alexandre & Dubois, 2000; Sinha Ray & Okamoto, 2003).

At the present, it is well known that starch, which is an inherently biodegradable and renewable material, is a promising answer to develop new environmentally friendly materials especially for packaging and disposable applications. Several authors have already demonstrated the possibility to transform native starch into thermoplastic resin-like products under destructuring and plasticization conditions with low water contents and, often, higher polyols concentration (Swanson, Shogren, Fanta, & Imam, 1993; Tomka, 1991). Nevertheless, the water sensitivity and the brittleness of these materials have to be overcome to obtain suitable “green” plastics (Averous, 2004). To reduce these weaknesses, the elaboration of plasticized starch-based nano-biocomposites appears as a rising option (Park, Lee, Park, Cho, & Ha, 2003; Park et al., 2002). Since plasticized starch is hydrophilic, most of the first studies were focused on the dispersion of “natural” non organo-modified sodium montmorillonite (MMT-Na) as nanofiller (Chiou et al., 2006, 2007; Cyras, Manfredi, Ton-That, & Vazquez, 2008; Dean, Yu, & Wu, 2007; Lilichenko, Maksimov, Zicans, Merijs Meri, & Plume, 2008; Mondragon, Mancilla, & Rodriguez-Gonzalez, 2008; Park et al., 2002, 2003; Tang, Alavi, & Herald, 2008). However, it has been shown that for glycerol content higher than 10 wt.%, such systems lead to the formation of an intercalated structure with a clay inter-layer spacing ( $d_{001}$ ) of 18 Å corresponding mainly to glycerol intercalation (Pandey & Singh, 2005; Park et al., 2003; Tang et al., 2008). The same behavior has been reported by Ma, Yu, and Wang (2007) with sorbitol as the starch nano-biocomposite plasticizer. Consequently, these results have highlighted the great influence of the plasticizers on the clay inter-

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calation/exfoliation process and thus on the materials resulting properties.

To overcome the limit of the plasticizer preferential intercalation, some authors have focused their attention on the organo-modification of the clay surface. We have thus recently demonstrated that the use of cationic starch is a very efficient strategy to obtain an exfoliated morphology with highly glycerol plasticized systems (Chivrac, Pollet, Schmutz, & Averous, 2008b). However, even if this strategy is well adapted for glycerol plasticized systems, its efficiency has not been proved for other types of polyol plasticizers. Therefore, the aim of this work is the study of the montmorillonite exfoliation process into starch nano-biocomposites plasticized with sorbitol and a mixture of glycerol/sorbitol commercially named Polysorb®. The influence of these plasticizers on the exfoliation process will be highlighted thanks to morphological, water desorption, thermal and mechanical analyses.

## 2. Experimental part

### 2.1. Materials

Wheat starch (WS) was supplied by Roquette (France). The amylose and amylopectin contents are 23% and 77%, respectively. Residual protein content is less than 1%. The glycerol, Polysorb® and sorbitol used as non-volatile plasticizers were supplied by Roquette (France). Glycerol was a 99.5% purity product. The sorbitol was provided as a water/sorbitol solution (79.2/20.8 by weight) and the Polysorb® was a glycerol/sorbitol mixture (59/41 by weight). The cationic starch has also been supplied by Roquette (France). Its charge density is 944  $\mu\text{equiv. g}^{-1}$ . The cationic functions are quaternary ammonium with chloride as counter-anion. The Dellite® LVF sodium montmorillonite (MMT-Na) was supplied by Laviosa Chimica Mineraria S.p.A. (Italy) and has a cationic exchange capacity (CEC) of 1050  $\mu\text{equiv. g}^{-1}$ .

### 2.2. Samples preparation

#### 2.2.1. Starch dry-blends preparation

The formulation used in this study contained 54 wt.% of native starch, 23 wt.% of polyol plasticizer and 23 wt.% of water. The water was introduced with the clay during the nano-biocomposites elaboration, as described below. Native wheat starch granules were first dried overnight at 70 °C in a ventilated oven to remove the free water (ca. 10 wt.% of the materials depending on the atmosphere relative humidity and temperature). Then, the starch powder was introduced into a turbo-mixer and the plasticizer (glycerol, Polysorb® or sorbitol) was slowly added under stirring. After complete addition of the plasticizer, the mixture was mixed at high speed (1700 rpm) to obtain a homogeneous dispersion. The mixture was then placed in a ventilated oven at 170 °C for 40 min and occasionally stirred, allowing volatilization of the bound water and diffusion of the plasticizer into the starch granules. Such dry-blend protocol allows the preparation of plasticized starch with high plasticizer content without exudation phenomenon, mainly thanks to the stronger interactions established between the polysaccharide chains and the polyols (Averous, Fringant, & Moro, 2001). The dry-blend (powder) was then stored in polyethylene bag.

#### 2.2.2. Organo-modified montmorillonite preparation

The MMT-Na organo-modification has been carried out with the so-called Shear Induced Clay Organo-modification process (SICO) (Chivrac, Pollet, & Averous, 2009). In this organo-modification process, 11.0 g of MMT-Na, 12.3 g of cationic starch and

52 ml of distilled water were first premixed to obtain a “gel”. The cationic starch and MMT-Na proportions match the charge equivalence between these two compounds. Then, this mixture was introduced into an internal batch mixer, Rheocord 9000 (Haake, USA), at 70 °C for 40 min with a rotor speed of 100 rpm. After processing, the OMMT-CS was obtained in a swollen state as a paste and can be directly incorporated into the dry-blend to produce nano-biocomposites (the water content of this OMMT-CS/water mixture directly corresponds to the water content of the plasticized starch formulation filled with 6 wt.% of clay). To elaborate nano-biocomposites filled with 3 wt.% of clay, 56.0 g of water are added to this OMMT-CS/water paste to obtain a diluted paste (referred below as “diluted OMMT-CS/water”).

#### 2.2.3. Nano-biocomposites elaboration

In this protocol, the nano-clay was introduced into the dry-blend in a swollen state to elaborate nano-biocomposite hybrid materials filled with 3–6 wt.% of inorganic clay content (compared to the weight of starch and glycerol). For nano-hybrids elaborated with non-modified montmorillonite (MMT-Na), from 1.38 to 2.86 g of MMT-Na have been introduced into 13.5 ml of water and dispersed with an ultra-sonic bath at 60 °C for 4 h to obtain the swollen clay. Then this swollen clay is introduced into the dry-blend. For the nano-hybrid based on OMMT-CS, the nano-clay is already obtained into a swollen state after the SICO process. Thus, to elaborate the nano-biocomposites filled with 6 wt.% of clay, 19.52 g of the OMMT-CS/water mixture is added to the dry-blend. For the nano-biocomposites filled with 3 wt.% of clay, 16.37 g of the diluted OMMT-CS/water mixture are introduced into the dry-blend. Then, the dry-blend and the swollen clay were introduced together into a counter-rotating internal batch mixer. The starch nano-biocomposites were prepared by mechanical kneading with a residence time of 20 min and with a rotor speed of 150 rpm. After melt processing, molded specimens and films were obtained by hot-pressing at 110 °C, applying 20 MPa pressure for 15 min. The samples of starch-based nano-biocomposites were then stored at 23 °C and 33, 57 or 75 %RH (relative humidity percentage) for 1 month to reach stabilized properties before characterization.

Throughout this paper, the samples are designated WS/ZZZ/XXX y% where WS stands for wheat starch, ZZZ for the type of plasticizer (Gly for glycerol, Polysorb for Polysorb® or Sorb for sorbitol), XXX for the type of (organo)clay (MMT-Na or OMMT-CS) and y for the weight percentage of clay inorganic fraction.

### 2.3. Characterization

#### 2.3.1. SAXD

The small angle X-ray diffraction (SAXD) morphological analyses were performed on a powder diffractometer Siemens D5000 (Germany) using Cu ( $K\alpha$ ) radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at room temperature in the range of  $2\theta = 1.5\text{--}10^\circ$  by step of  $0.01^\circ$  of 4 s, each. The clay inter-layer spacing values ( $d_{001}$ ) were calculated from the MMT diffraction peak using the Bragg's law (Eq. (1)).

$$2d_{001} \sin \theta = n\lambda \quad (1)$$

#### 2.3.2. Water desorption analyses

The water contents of the samples were estimated on a MB45 moisture analyzer (Ohaus Corporation, USA) on films of 1.2 mm thickness considering the weight loss measured after 8 h of drying at 95 °C.

#### 2.3.3. TGA characterization

The thermogravimetric analyses (TGA) were performed on a SDT Q600 apparatus from TA Instruments (USA). For all starch/clay nano-biocomposites, the analyses were carried out under “syn-

thetic air”, which is a mixture of 75% N<sub>2</sub> and 25% O<sub>2</sub>. The clay content in inorganics (in wt.%) of each composite was assessed by the combustion residue left at 600 °C.

### 2.3.4. DMTA

Thermo-mechanical properties of the different nano-biocomposites were determined using tensile geometry with a dynamic thermo-mechanical analyzer (TA Instrument DMA 2980, USA). Samples were cut to get specimens with dimensions 0.9 × 9.5 × 24.5 mm<sup>3</sup>. The displacement amplitude was set to 15 μm. The measurements were performed at a frequency of 1 Hz. The range of temperature was from –70 to 70 °C at the scanning rate of 3 °C/min.

### 2.3.5. Tensile tests

Tensile tests were carried out with an Instron tensile testing machine (model 4204, USA), on dumbbell-shaped specimens; at 25 °C with a constant deformation rate of 5 mm/min. For each formulation five samples were tested.

## 3. Results and discussion

### 3.1. Morphology

Fig. 1 displays the typical SAXD curves recorded for MMT-Na and WS/MMT-Na 6 wt.% nano-biocomposites plasticized with glycerol, Polysorb® and sorbitol. The MMT-Na diffraction pattern displays an intense diffraction peak at 2θ angle of 7.3° corresponding to a clay inter-layer spacing value ( $d_{001}$ ) of 12 Å. As expected, all the nano-biocomposites samples display a diffraction peak located at 4.9° corresponding to a  $d_{001}$  value of 18 Å. The presence of this diffraction peak reveals that these materials are mainly intercalated, whatever the type of plasticizer, and that only few starch chains have been incorporated into the clay inter-layer spacing. This result is in agreement with the literature in which it is mentioned that both glycerol and sorbitol, by their preferential intercalation, lead to the formation of intercalated structures in highly plasticized starch nano-biocomposite hybrid materials (Ma et al., 2007; Pandey & Singh, 2005; Park et al., 2003; Tang et al., 2008).

Fig. 2 displays the typical SAXD curves recorded for OMMT-CS and WS/OMMT-CS 6 wt.% nano-biocomposites plasticized with glycerol, Polysorb® and sorbitol. The diffraction pattern of OMMT-CS displays an intense peak at 3.6° corresponding to a  $d_{001}$  value of 24.5 Å. It can be seen from these experiments that the WS/Gly/OMMT-CS 6 wt.% diffraction pattern displays no diffraction peak suggesting a completely exfoliated morphology. On the

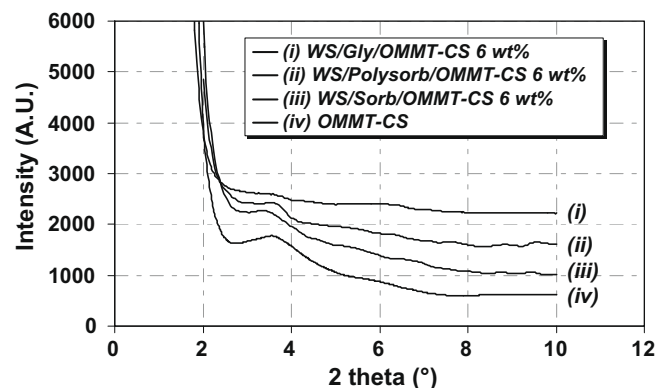


Fig. 2. SAXD patterns for OMMT-CS and WS/OMMT-CS 6 wt.% nano-biocomposites plasticized with glycerol, Polysorb® or sorbitol.

contrary, diffractograms of both the WS/Polysorb/OMMT-CS and WS/Sorb/OMMT-CS nano-biocomposites with 6 wt.% of clay display a wide and low intensity diffraction peak corresponding to a  $d_{001}$  = 25 Å. This value almost exactly corresponds to the initial OMMT-CS clay inter-layer spacing before incorporation into the starch matrix. According to these experiments, one may suppose that intercalated/exfoliated structures, with small clay tactoids remaining, are obtained with either Polysorb® or sorbitol.

### 3.2. Water content

The water content of the different unfilled matrices and nano-biocomposite hybrid materials have been determined by desorption measurements, after one month equilibration. The unfilled matrices water content variations, determined at different storage relative humidity, are presented in Fig. 3. It is seen from this graph that whatever the storage relative humidity, the water content of the glycerol plasticized nano-biocomposites is higher than those of the other plasticizers in agreement with previous results on plasticized starch (Gaudin, Lourdin, Le Botlan, Ilari, & Colonna, 1999; Lourdin, Colonna, & Ring, 2003). The lower water content is obtained with the sorbitol-based materials. These results are explained by the higher hydrophilic character of the glycerol compared to sorbitol.

These desorption experiments have been performed on nano-biocomposite materials to analyze the influence of the nanofiller content and dispersion state on the water content after equilibrium. The water contents obtained for the different starch nano-biocomposites are summarized in the Table 1. According to these

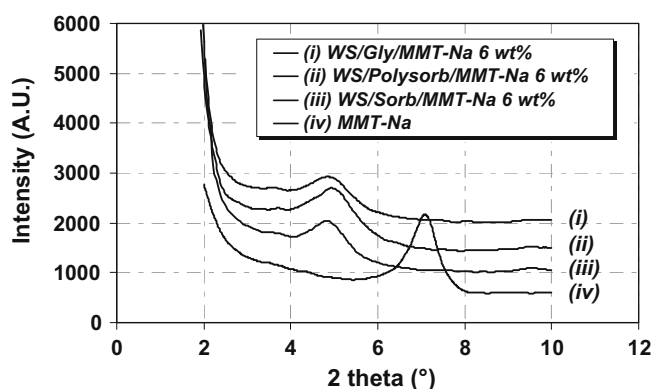


Fig. 1. SAXD patterns for MMT-Na and WS/MMT-Na 6 wt.% nano-biocomposites plasticized with glycerol, Polysorb® or sorbitol.

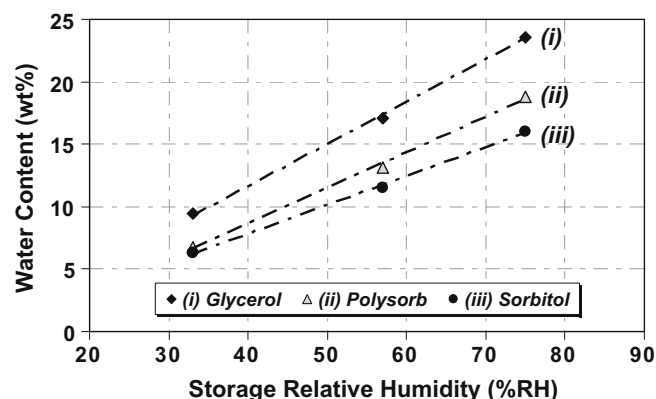


Fig. 3. Water content of wheat starch plasticized with glycerol, Polysorb® or sorbitol against storage relative humidity.

**Table 1**

Water content of starch nano-biocomposite plasticized with glycerol, Polysorb® or sorbitol at different relative humidities (%RH).

	33 %RH			57 %RH			75 %RH		
	Gly	Polysorb®	Sorb	Gly	Polysorb®	Sorb	Gly	Polysorb®	Sorb
WS/MMT-Na 3 wt.%	7.8	7.0	6.0	16.4	13.1	11.5	24.2	18.8	16.7
WS/MMT-Na 6 wt.%	8.4	7.5	6.8	16.8	13.3	11.8	25.0	19.0	16.9
WS/OMMT-CS 3 wt.%	8.9	6.9	6.4	18.5	13.1	11.8	24.4	19.1	17.1
WS/OMMT-CS 6 wt.%	9.1	6.7	6.2	19.6	14.7	12.6	24.7	19.0	17.1

data, the introduction of the nanofiller induces only small modifications of the water content without logical and marked trends. This is likely linked to the hydrophilic nature of the nanofillers that do not vary the overall hydrophilicity of the plasticized starch matrices. However, as already mentioned, the water contents measured for glycerol-plasticized materials are higher than those recorded for Polysorb® or sorbitol due to higher hydrophilicity of this plasticizer.

### 3.3. Thermo-mechanical properties

Thermo-mechanical measurements have been performed on starch nano-biocomposites to analyze the plasticizer and nanofiller impact on their thermal properties. Fig. 4 displays the  $\tan \delta$  curves recorded for the unfilled plasticized starch matrices. For each plasticizer, two relaxations peaks are observed. Such behavior is associated to the high plasticizer content of the starch formulation which leads to a phase separation between domains rich in carbohydrate chains and domains rich in plasticizer (Lourdin, Coignard, Bizot, & Colonna, 1997; Lourdin, Ring, & Colonna, 1998). The main relaxation (named  $\alpha$ ) is attributed to the plasticized starch  $T_g$ . The second relaxation (named  $\beta$ ) is consistent with the plasticizer glass transition and occurs at lower temperature. A shift of both the  $\alpha$  and  $\beta$  transition is observed and correlated to the ratio sorbitol/plasticizer. Such a behavior is related to the higher plasticizing efficiency of glycerol compared to sorbitol and to the higher water uptake at equilibrium with glycerol.

Table 2 displays the  $T_\alpha$  and  $T_\beta$  variations vs. clay content for starch nano-biocomposites plasticized with glycerol, Polysorb® and sorbitol. For  $T_\beta$ , only small variations, which are not significant, are observed. Such trend may suggest that the clay nano-platelets have no effect on the  $T_g$  of the domains rich in plasticizer. On the opposite, an increase in the  $T_\alpha$  vs. clay content is observed with all the plasticizers. At 3 wt.% of clay loading, the nano-biocomposites prepared with both OMMT-CS and MMT-Na display the same  $T_\alpha$ . For higher clay content, the  $T_\alpha$  recorded with MMT-Na as the nanofiller are slightly higher than for those elaborated with

**Table 2** $T_\alpha$  and  $T_\beta$  vs. clay inorganic content for starch nano-biocomposites plasticized with glycerol, Polysorb® or sorbitol.

	$T_\alpha$ (°C)			$T_\beta$ (°C)		
	Gly	Polysorb®	Sorb	Gly	Polysorb®	Sorb
WS	11.7	31.7	35.3	−54.6	−23.6	−6.1
WS/MMT-Na 3 wt.%	15.7	36.5	41.7	−54.9	−22.9	−6.0
WS/MMT-Na 6 wt.%	23.9	38.5	49.8	−50.56	−21.1	−6.0
WS/OMMT-CS	14.9	35.2	41.8	−53.56	−22.9	−6.7
3 wt.%						
WS/OMMT-CS	21.7	38.4	47.1	−51.6	−22.2	−4.9
6 wt.%						

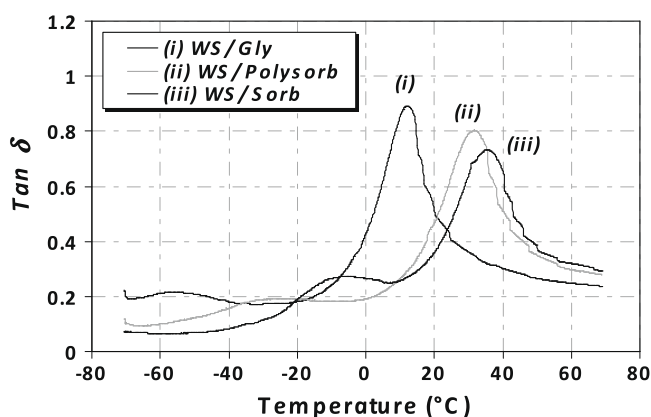
OMMT-CS. Since the better the dispersion, the higher the clay/matrix interface, a higher  $T_\alpha$  was expected for the WS/OMMT-CS samples. This unexpected behavior could be explained by the morphology of the WS/MMT-Na nano-hybrid. It has been demonstrated that such nano-biocomposites display an intercalated structure with preferential plasticizer intercalation. Consequently, a part of the plasticizer is immobilized into the galleries of clay platelets and cannot plasticize the starch matrix, explaining the higher  $T_\alpha$  obtained for the WS/MMT-Na 6 wt.% nano-biocomposites.

These results also have to be related to our previous observations from TEM analyses (Chivrac et al., 2008b) where a phase separation was observed between domains rich in clay platelets and domains without nanofiller. We supposed that this phase separation was induced by the high glycerol content of the formulation and that the nanofillers were dispersed into the glycerol-rich domains. Such assumption was based on the high affinity between the clay platelets and the polyol plasticizers. However, according to the thermo-mechanical analyses performed here, only  $T_\alpha$  is influenced by the addition of clay and shifted to higher temperature. Thus, this behavior indicates that the nanofillers are most probably localized into the plasticized starch domain. Complementary experiments, such as nanoindentation and dielectrical analyses are currently underway to better understand the mechanism of this phase separation.

### 3.4. Mechanical properties

Fig. 5 displays the Young's modulus variations of plasticized starch nano-biocomposites filled with 3–6 wt.% of MMT-Na or OMMT-CS and stabilized at 57 %RH. It is shown that the plasticizer nature greatly influences the plasticized starch stiffness. The Young's modulus of starch plasticized with Polysorb® is higher than that of the glycerol plasticized one, the highest stiffness properties being obtained with sorbitol as the plasticizer. This trend seems to be related to the sorbitol/plasticizer ratio. Since the water content of these matrices is also linked to this ratio, most of these variations are correlated to the water content of the materials which affects the starch Young's modulus properties.

For all the plasticized starch nano-biocomposites, whatever the type of plasticizer, an increase in the matrix modulus is observed and correlated to the clay content. This increase is commonly

**Fig. 4.**  $\tan \delta$  vs. temperature for WS plasticized with glycerol, Polysorb® or sorbitol.



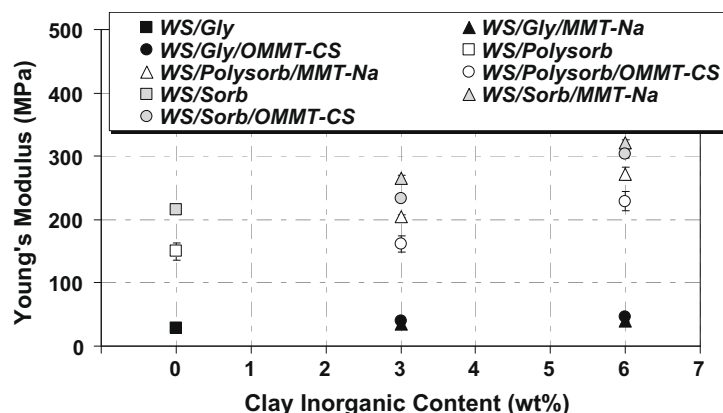


Fig. 5. Young's modulus vs. clay inorganic content for starch nano-biocomposites plasticized with glycerol, Polysorb® or sorbitol.

observed in nano-biocomposite materials and is related to the clay hardness, to its dispersion state and to the nanofiller/matrix interface (Chivrac et al., 2008a; Luo & Daniel, 2003). As expected, the WS/Gly/OMMT-CS nano-biocomposites display higher Young's modulus values compared to those of the WS/Gly/MMT-Na nano-biocomposites (Chivrac et al., 2008b). Such behavior is linked to the well exfoliated structure of the samples based on OMMT-CS compared to the intercalated/aggregated structure obtained with MMT-Na as the nanofiller. However, such a trend, namely higher modulus resulting from a better dispersion, is not observed for the sorbitol and the Polysorb®-plasticized materials. In both cases, the increase in stiffness of the MMT-Na nano-biocomposites is higher than the OMMT-CS one. As for the  $T_g$  variations recorded by DMTA, this trend may be linked to the morphology of the nano-biocomposites elaborated with MMT-Na. In these materials, a part of the plasticizer is intercalated and immobilized between the clay platelets and thus no longer acts as a plasticizer leading to slightly higher materials modulus compared to the WS/OMMT-CS nano-hybrids.

Fig. 6 displays the strains at break of plasticized starch nano-biocomposites filled with 3–6 wt.% of MMT-Na or OMMT-CS, and stabilized at 57 %RH. Like for the Young's modulus variations, the plasticizer impact on the unfilled plasticized starch matrices is significant. The strain at break properties of the glycerol plasticized starch are lower than the Polysorb® or sorbitol ones. As for the modulus, this trend is likely linked to the water content of the plasticized starch matrices. Indeed, the formulation used in this study is highly plasticized with an overall plasticizer content (polyol + water) varying from 40 to 50 wt.% and consequently, the polysaccharides chains are “swollen” and dispersed into the plasti-

cizer. Thus, a lower water content implies a decrease in the total plasticizer content (increase in starch content) and leads to a more “cohesive” material with higher strain at break properties.

The strains at break of the plasticized starch-based nano-biocomposites materials greatly depend on the plasticizer nature. For starch nano-biocomposites plasticized with glycerol, Polysorb® or sorbitol a decrease in the strain at break properties is observed with MMT-Na as the nanofiller, this decrease being more pronounced for the sorbitol-plasticized samples. At 6 wt.% of MMT-Na incorporation, the strains at break properties of these different materials are almost equivalent, suggesting that the macroscopic properties mainly depend on the nanofiller dispersion state. This trend is explained thanks to the intercalated/aggregated structure of the WS/MMT-Na nano-hybrids which creates internal stress at the filler/matrix interface and thus embrittles the nano-biocomposite materials.

The strains at break properties of the nano-biocomposites based on OMMT-CS are more dependent on the plasticizer nature. For glycerol plasticized nano-biocomposites, no variation with the OMMT-CS content is seen. This is related to the highly exfoliated structure of these materials. However, the strain at break properties of the sorbitol and Polysorb® plasticized nano-biocomposites slightly decrease with the increase in the OMMT-CS content. This trend is likely linked to the nanofiller dispersion state into the starch matrix. According to the morphological analyses performed on these materials, it was highlighted that a low intensity and wide diffraction peak remained after OMMT-CS incorporation into the matrix, such results suggesting an intercalated/exfoliated structure. Thus, the observed decreases in strain at break values are

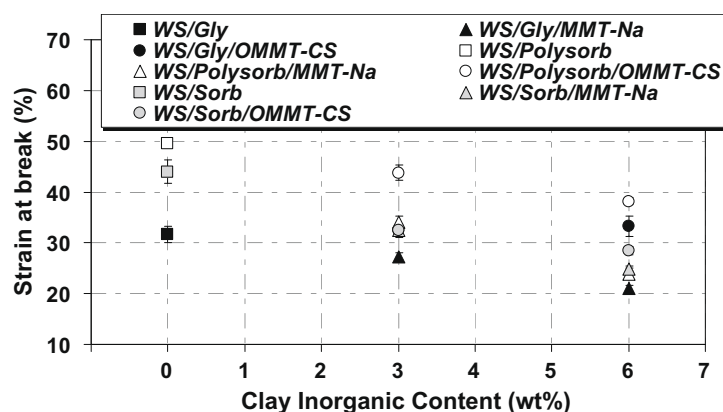


Fig. 6. Strain at break vs. clay inorganic content for starch nano-biocomposites plasticized with glycerol, Polysorb® or sorbitol.

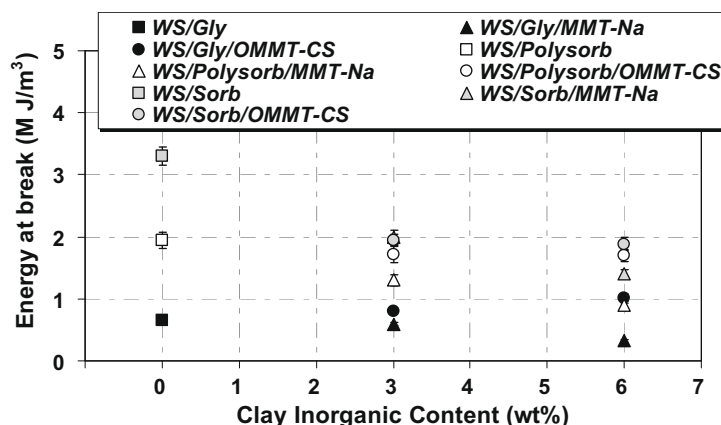


Fig. 7. Energy at break vs. clay inorganic content for starch nano-biocomposites plasticized with glycerol, Polysorb® or sorbitol.

likely due to the remaining small clay tactoids which slightly embrittle the plasticized starch matrices.

Finally, Fig. 7 displays the energy at break variations of plasticized starch nano-biocomposites filled with 3–6 wt.% of MMT-Na or OMMT-CS and stabilized at 57 %RH. This property, estimated from the area of the tensile curve, is a global parameter which depends on the stiffness, yield and break properties and thus which represents well the global mechanical properties of the materials. In direct correlation with the aforementioned results obtained on the stiffness and strain at break properties, the energy at break of the different unfilled plasticized starch matrices increases with the increase in the sorbitol/glycerol ratio.

For the nano-biocomposites elaborated with MMT-Na, a decrease in the energy at break corresponding to an embrittlement of the nano-biocomposite is observed with all the plasticizers. This decrease is more pronounced for the sorbitol-plasticized materials. As for the strain at break properties, the OMMT-CS incorporation into the plasticized starch matrix leads to different trends depending on the plasticizer. For glycerol plasticized nano-biocomposites, an overall increase in the energy at break properties related to the well exfoliated morphology of these nano-hybrid materials is observed. On the contrary, no significant variations of the energy at break are observed for the Polysorb®-plasticized materials and a decrease is observed with the sorbitol-plasticized samples. Such tendencies are related to the intercalated/exfoliated morphology, which has been previously highlighted with SAXD analyses. Thus, all these experiments have demonstrated that sorbitol perturbs the exfoliation process and then decreases the exfoliation extent into the starch matrix. This perturbation may be related to great interactions (through hydrogen bonds) taking place between the sorbitol and the nanofillers, generating a sort of tight network which hinders the large polysaccharide chains to separate and exfoliate the clay platelets.

#### 4. Conclusion

This study analyzed the impact of three kinds of polyol plasticizers (glycerol, Polysorb® and sorbitol) on the plasticized starch material properties and on the montmorillonite intercalation/exfoliation process into starch nano-hybrids.

For the starch nano-biocomposite materials, morphological analyses performed on WS/MMT-Na materials revealed an intercalated structure with preferential plasticizer intercalation whatever the plasticizer type. Such materials, with a very limited polymer chains intercalation, must rather be considered as conventional micro-biocomposites, since a huge decrease in the tensile proper-

ties, corresponding to an embrittlement of the material, has been observed.

The addition of OMMT-CS led to different dispersion state depending on the plasticizer nature. Exfoliated morphologies are obtained with glycerol as the starch nano-hybrids plasticizer. For Polysorb® and sorbitol, SAXD analyses showed an intercalated/exfoliated structure. These morphologies have been confirmed with the results of uniaxial tensile tests. Indeed, an overall enhancement of the WS/Gly/OMMT-CS nano-biocomposites tensile properties, characteristic of an exfoliated morphology, is observed. On the opposite, WS/Sorb/OMMT-CS materials display a slight decrease in mechanical properties corresponding to a more aggregated structure. Thus, these results clearly highlight a disruption of the clay exfoliation process induced by the sorbitol, likely because of the sorbitol/montmorillonite strong interactions. To overcome this limitation, further studies should be focused on the clay organo-modifier, namely the cationic starch. Special attention must be paid to the impact of the charge density and the cationic starch content adsorbed on the nano-platelets surface.

Besides, for WS/Gly/MMT-Na or WS/Gly/OMMT-CS, we previously reported a phase separation between domains rich and without nanofillers. Such heterogeneity results from the high plasticizer content of the starch formulations which leads to a phase separation between domains rich in carbohydrate chains and rich in plasticizer. The presented results of the thermo-mechanical analyses performed on these materials evidenced that the clay platelets are most likely located mainly in the starch-rich domains. Further specific experiments, such as nanoindentation and dielectric analyses will be performed to better understand and describe the mechanism of this phase separation.

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