

Preparation and Characterization of Maleated Thermoplastic Starch-Based Nanocomposites

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ABSTRACT: Biodegradable nanoscale-reinforced starch-based products were prepared from an *in situ* chemically modified thermoplastic starch and poly(butylene adipate-co-terephthalate) (PBAT) through reactive processing. Natural montmorillonite (hydrophilic Cloisite Na) and organophilic Cloisite 30B were studied. *In situ* chemically modified thermoplastic starch (MTPS) was first prepared starting from (nano)clay (previously swollen in glycerol as plasticizer), and maleic anhydride (MA) as an esterification agent. Then, these nanoscale-reinforced MTPS was reactively melt-blended with PBAT through transesterification reactions promoted by MA-derived acidic moieties grafted onto the starch backbone. The tensile and barrier properties of resulting (nano)composites were studied.

High-performance formulations with superior tensile strength (>35 MPa as compared with 16 MPa for the PBAT-g-MTPS copolymer) and break elongation (>800%) were obtained, particularly with Cloisite30B. Better water vapor and oxygen barrier properties of nanoscale-reinforced MTPS-g-PBAT were achieved rather than the PRECURSORS. Wide angle X-ray diffraction and transmission electronic microscopy analyses show that partial exfoliation of the clay platelets was observed within the PBAT-g-MTPS graft copolymer-Cloisite 30B nanocomposite. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 639–647, 2011

Key words: biodegradable; starch; polyester; nanocomposites; reactive extrusion

INTRODUCTION

Recently, polymer-layered silicate (clay) nanocomposites have emerged as a new class of materials that have shown unexpected properties such as large increase in the thermal stability, mechanical strength, and impermeability to gases such as oxygen. Such improvements in their properties achieved at low content in layered silicate (<5 wt %) are relied on the interactions between the clay nanoplatelets and polymers, which can yield intercalated and/or exfoliated nanocompositions. In the so-called exfoliated (or delaminated) nanocomposites, the silicate nanolayers are individually dispersed within the entire polymer matrix, leading to the highest improvement in the aforementioned properties.^{1–8}

Polymer-layered silicate nanocomposites have been studied within a wide range of polymer matrices^{9–14} such as polystyrene, poly(methyl methacrylate), and poly(ϵ -caprolactone). Surprisingly, very few studies have been performed on starch-based biodegradable nanocomposites, whereas recent researches have indicated that organoclays show much promise for starch-based polymer nanocomposites for improving their thermal properties.^{15–21} In the design of environmentally friendly products for short-time applications, starch represents an interesting structural platform because of its natural abundance, biodegradability, low cost, and renewability. In specific extrusion conditions, thermoplastic starch (TPS) can be readily processed in the presence of plasticizers (water and/or polyalcohol) under high shear stress.^{22–27} Park et al.¹⁷ first reported on the preparation and properties of water/glycerol-gelatinized starch/montmorillonite nanocomposites by melt-intercalation. Naturally occurring sodium clay (Cloisite Na), and three different alkyl ammonium-modified clays (Cloisites 10A, 6A, and 30B) were used as (nano)fillers. Cloisite 30B is a montmorillonite modified by methyl bis(2-hydroxyethyl)(tallow alkyl) ammonium, whereas both Cloisite 6A and

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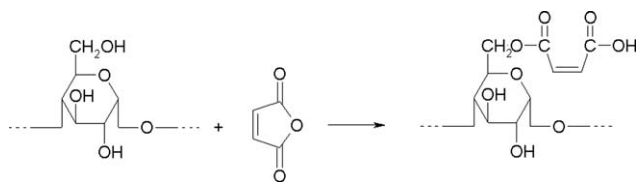


Figure 1 Esterification reactions of starch backbone with MA, occurring at the C6 position (the most preferential position).

10A are tetraalkyl ammonium and alkyl aryl ammonium-modified clays, respectively. Transmission electronic microscopy (TEM) and wide angle X-ray diffraction (WAXS) results revealed that the best dispersion was achieved with Cloisite Na-based TPS. It was also revealed that the dispersion of the organo-modified clay depends on the hydrophilicity of the organoclays, and especially the polar interaction between the (organo-) silicate layers and TPS.^{17,28} Recently, greater understanding of the relationship between structure and properties has been developed in a series of gelatinized-starch clay nanocomposites prepared by high-speed mixing and extrusion technology.²⁹ The effect of nanoclays type, plasticizer content, dispersion methodologies, and processing conditions were studied. It was shown that an optimum level of both plasticizer and nanoclay existed for each clay (which had some dependence on cationic exchange capacity) to produce a gelatinized starch film with the highest levels of exfoliation and best improvement in mechanical properties. The use of ultrasonic treatment was also advantageous to improve the clay dispersion. However, so far, most of the studies carried out on biodegradable TPS-layered silicate nanocomposites have only displayed some improvements in terms of solvent-resistance, thermal properties, and elastic modulus, whereas no substantial effect could be recorded at the level of both mechanical strength and toughness. This is due to the weak adhesion between the clay and the polymer chains even though the clay nanoplatelets could be well-dispersed within the polymer matrix. Indeed, Kalambur and Rizvi¹⁵ prepared starch-polyester blends filled with Cloisite Na (natural montmorillonite), where no significant improvement in tensile strength or ultimate properties was attained. They hypothesized that a more "hydrophilic" starch would form stronger hydrogen bonds with the clay surface, improving the adhesion between the two partners. They introduced carbonyl or carboxyl groups along the polysaccharide chains through peroxide-promoted oxidation reactions. A slight improvement in properties was accordingly gained (tensile strength of ca. 10 MPa, elongations at break from ~ 600 to 900%) although not sufficient to compete with the existing

market. The size of polymer chains to be interpenetrated into the clay gallery can also affect the structure of the resulting products. It is of prime importance since starch exhibits high melt-viscosity and poor melt-properties making it difficult to process, and products made from starch are known as brittle and water sensitive. Pandey and Singh¹⁶ reported that when TPS-based nanocomposites were prepared in solution using different addition sequences of the plasticizer and the natural clay, both glycerol and starch could penetrate into the silicate layers but the glycerol intercalation seemed easier because of its smaller molecular size.

Recently, our research group has prepared a novel chemically modified TPS through *in situ* reactive extrusion processing of starch in the presence of glycerol as plasticizer and maleic anhydride (MA) as esterification agent³⁰. The resulting "esterified" and plasticized starch materials, called maleated TPS (MTPS), was successfully recovered and proved to exhibit an enhanced reactivity (with the presence of free carboxylic groups pending along the chains) and improved processability (Fig. 1). Indeed, the MA-derived acidic moieties are capable of promoting acid-catalyzed hydrolysis and glucosidation reactions, which reduce the size of starch macromolecules. These MA functions grafted onto the starch backbone have also shown to be valuable in the preparation of biodegradable and phase-homogeneous graft copolymers *in situ* generated through acid-catalyzed transesterification reactions on melt-blending MTPS with poly(butylene adipate-co-terephthalate) (PBAT) via downstream reactive processing (Fig. 2). Because of its interesting thermal and mechanical properties, PBAT, as biodegradable aliphatic-aromatic copolyester, represents a promising candidate in the preparation of starch-based products with useful end applications, while maintaining the biodegradability of the overall composition.^{31,32} In contrast to TPS, the low melt-viscosity of MTPS, together with its increased reactivity led, by melt-blending with PBAT, to the formation of

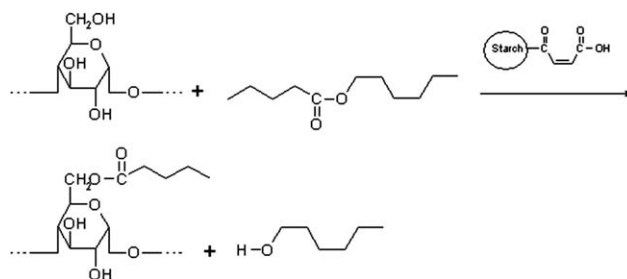


Figure 2 Proposed mechanism of transesterification reactions between MTPS and PBAT promoted by the MA-derived acidic moieties grafted onto the starch backbone.

stronger covalent bonds at the MTPS–polyester interface, and therefore a finer phase morphology for the resulting melt-blends.³⁰ However, compared with those of pristine PBAT, it was observed that the occurrence of acid-promoted hydrolysis, inter- and intramolecular transesterification reactions underwent by the polyester matrix. Their molecular weights, as well as the mechanical properties of the overall products, were therefore reduced.

This article aims at preparing layered silicate starch-based nanocomposites and their use in melt-blending with PBAT to enhance the mechanical, thermal, and barrier properties of the resulting (nano)composites. Cloisite Na and Cloisite 30B were studied as nanoclays, and their effect on the properties of the resulting composites were evaluated. Structural characterizations were carried out by TEM and WAXS analyses as well.

EXPERIMENTAL

Materials

Regular pearl silver corn starch (unmodified) was obtained from Cargill-grade SMP 1100 (MN), with equilibrium moisture content of about 12% (w/w). Anhydrous glycerol (99.9%) was supplied by J.T. Baker (NJ), and used as received. MA (99%) obtained from Sigma-Aldrich (WI) was previously grounded to a fine powder using a mortar and pestle before use. Cloisite Na is a natural montmorillonite with a cation exchange capacity of 0.93 mEq/g and with an interlayer distance of 11.7 Å (evaluated by WAXS diffraction measurement on the powder dried in vacuo at 80°C), while Cloisite 30B is a montmorillonite modified by methyl bis(2-hydroxyethyl)(tallow alkyl) ammonium with an interlayer distance of $d_{001} = 18.5$ Å and where tallow alkyl substituent comprises ~ 65% C18 chains, ~ 30% C16 chains, and ~ 5% C14 chains. Both clays were supplied by Southern Clay Products (TX). PBAT having a molecular weight of 43,510 g/mol and a polydispersity index (M_w/M_n) of 2.30 under the tradename Ecoflex FBX 7011 was purchased from BASF Corporation, and used as received.

Preparation of layered silicate-filled MTPS-g-PBAT graft copolymers

Before processing, 22.5 g of clay was mixed with 150 g of glycerol, and set for approximately 15 h at ambient temperature. Regular silver medal pearl cornstarch was reactively modified using MA in a twin-screw co-rotating CENTURY ZSK-30 extruder with a screw diameter of 30 mm and an L/D ratio of 42. The resulting slurry mixture (glycerol/clay) was hand-mixed with 450 g of starch and 48 g of MA (8

wt % by starch), and fed together into a Century ZSK-30 co-rotating twin-screw extruder. The relative ratios of the starch mixture to the glycerol were maintained at 80 : 20 (w/w). Vacuum (using water jets) was applied at the extruder vent port to remove out the unreacted MA and excess moisture. The temperature profile was 15/95/125/145/160/165/165/165/150/145 from the feed throat to the die, and the melt temperature was 153°C. The screw speed used was 120 × g. A cylindrical filament die 2.7 mm in diameter and 8.1 mm in length with a cooling sleeve was assembled to the extruder. The resulting extruded-layered silicate MTPS materials was ground to a fine powder and was stored at 50°C overnight. In the subsequent step, 300 g of the layered silicate-filled MTPS composite was hand-mixed with 700 g of PBAT (i.e., 70 wt % polyester content), and fed into a Century ZSK-30 co-rotating twin-screw extruder. This led to the formation of homogeneous PBAT-g-MTPS graft copolymers. The grafting reaction was evidenced by Soxhlet extraction in dichloromethane (Sigma-Aldrich, WI, +99%) overnight as already reported elsewhere.³⁰ The temperature profile was 15/95/125/135/150/160/160/165/150/145 from the feed throat to the die, and the melt temperature was 147°C. The screw speed used was 150 × g. The extruded strand was cooled using a water bath and pelletized in line. The pellets were dried in an oven overnight at 75°C before being blown-molded.

Blown film studies

Layered silicate PBAT-g-MTPS graft copolymers were blown-molded using a Killion single-screw blown film unit. The screw diameter was 25.4 mm with $L : D$ ratio of 25 : 1. The inner diameter of die was 50.8 mm with a die gap size of 1.5 mm. Different films with a thickness close to 100 μm were prepared using the blown film processing conditions reported in Table I.

Characterizations and analyses

A Transmission electron microscope (JEOL 100 CX) with an accelerating voltage of 120 kV was used to observe the thin cross-sections of the extruded layered silicate-filled PBAT-g-MTPS graft copolymers. The samples were prepared using a cryogenic ultramicrotome (at – 100°C) to obtain sections of a thickness of ca. 60 nm. Tensile properties were determined using UTS Mechanical Testing Equipment Model SFM-20 fitted with a 45.5 kg load cell. The crosshead speed was 50 cm/min. The tensile properties were determined in the machine direction. Tensile properties of films in the transverse direction exhibited a similar trend (not reported here).

TABLE I
Blown Film Processing Conditions for the Production of the PBAT-g-Starch Graft Copolymer-Based Films

	Die 3	Die 2	Die 1	Adaptor	Clamp Ring	Zone 3	Zone 2	Zone 1
Set (°C)	21	165	168	171	177	185	182	149
Actual (°C)	22	165	168	171	177	182	182	149
Melt (°C)	167							
Screw speed (RPM)	16.5–17							
Draw-up speed FPM (ft/min)	5–6							
Pressure (MPa)	68–117							

Rectangular film samples, $10 \times 2.5 \text{ cm}^2$ dimensions, were conditioned at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity for 48 h before being tested according to ASTM D-882 testing. WAXS diffraction analysis was performed with a Rigaku Rotaflex Ru-200BH X-ray diffractometer operated at 45 kV, 100 mA with a nickel-filtered Cu $K_{\alpha 1}$ radiation and a θ compensating slit. Data were acquired in $0.02^\circ 2\theta$, at the rate of $1^\circ/\text{min}$. The basal spacing of the silicate layer of the nanoscale clay, d , was calculated using the Bragg's equation, $\lambda = 2d \sin \theta$ ($\text{Cu } K_{\alpha 1} = 0.15406 \text{ nm}$). Samples were used in the form of a powder or a film as obtained by blown film processing. The samples were equilibrated in a constant room temperature at $23 \pm 1^\circ\text{C}$ and $50 \pm 2\%$ relative humidity for at least 72 h before testing. Water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) of nanocomposite films were determined using a Mocon Permatran – W Model 3/33 and Mocon OX – Tran Model 2/20 (Mocon, Minneapolis, MN), respectively. The films were conditioned at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity for 48 h before being tested.

RESULTS AND DISCUSSION

Table II shows the tensile properties of blown films obtained from the PBAT-g-MTPS graft copolymers reinforced with Cloisite Na and Cloisite 30B, at a final 1 wt % nanoclay composition (based on the total weight). The effect of nanoclay content in the

reactive PBAT-MTPS melt-blend was studied with Cloisite 30B. For the sake of comparison, the tensile properties for the films derived from pristine PBAT and the unfilled PBAT-g-MTPS graft copolymers were reported. Note that nanoclays were swollen overnight into glycerol (as used as starch plasticizer), and the resulting slurry mixture (20 wt % by starch) was then hand-mixed with starch and MA (8 wt % by starch) to prepare nanoscale-reinforced MTPS through reactive extrusion processing. It is worth recalling that MA was used to reduce the molecular weight of starch macromolecules through acidic-catalyzed hydrolysis and glucodisation reactions.³⁰ This facilitates the penetration of the modified/plasticized starch into the layered silicate galleries, leading to the formation of homogeneous graft copolymers as already proved by SEM analyses.³⁰ In addition, the swelling pretreatment has shown to be useful to achieve the best dispersion of the layered silicate fillers in the MTPS as well as in the MTPS-g-PBAT graft copolymer. This was supported by the tensile properties for the resulting blown films. For instance, the tensile strengths of the layered silicate-filled reactive blends were in the range of 20–25 MPa, while the break elongations were in the 600–650% range for all the investigated nanoclays, wherein the clay was not subjected to swelling in glycerol (not reported).

In the subsequent step, 30 wt % of the resulting MTPS was melt-blended with PBAT through reactive extrusion. This composition in MTPS was

TABLE II
Effect of the Clay Nature on the Tensile Strength, Modulus of Elasticity (MoE), Elongation at Break of Clay-Reinforced PBAT-g-MTPS Copolymer (PBAT : MTPS = 70 : 30 w/w) Together with Those of PBAT and Unfilled PBAT-g-MTPS Graft Copolymer (in the Machine Direction)

No	Nature	Tensile strength (MPa)	MoE (MPa)	Elongation at break (%)
1	PBAT	38.6 ± 4.0	13.8 ± 1.3	600 ± 35
2	PBAT-g-MTPS	16.2 ± 1.7	78.1 ± 7.2	735 ± 48
3	PBAT-g-MTPS (1% Cloisite Na)	26.1 ± 3.2	129.7 ± 26.7	700 ± 48
4	PBAT-g-MTPS (1% Cloisite 30B)	32.0 ± 3.9	149.7 ± 27.9	800 ± 36
5	PBAT-g-MTPS (3% Cloisite 30B)	36.7 ± 4.4	133.3 ± 16.0	840 ± 59
6	PBAT-g-MTPS (5% Cloisite 30B)	34.2 ± 4.1	144.0 ± 17.3	820 ± 49

interesting, regarding the preparation of a well-compatible and phase-homogeneous MTPS-*g*-PBAT graft copolymer as reported in a previous article.³⁰ From Table II, it could be observed that whichever the investigated clay, the mechanical properties of the MTPS-*g*-PBAT graft copolymer-based nanocomposites could be substantially improved by the introduction of the layered silicate at a content as tiny as 1 wt %. Surprisingly enough, the lowest tensile strength and elongation at break were recorded with Cloisite Na, the most hydrophilic nanoclays, respectively. In the case of hydrophilic Cloisite Na, this could rely on its high compatibility with hydrophilic MTPS,¹⁷ together with the low molecular weight MTPS (as compared with TPS). MTPS is more likely able to penetrate the clay galleries, and to specifically interact with the cations (Na^+) inside the clay. It resulted in a good dispersion of the nanoclay platelets in the MTPS phase. However, when melt-blended with PBAT, the nanoclay remained mainly in the MTPS, because of the hydrophobic character of PBAT copolyester. In other words, a medium dispersion for Cloisite Na was attained for the overall MTPS-*g*-PBAT graft copolymer. The localization and the structure of Cloisite Na in the reactive PBAT-*g*-MTPS melt-blends will be discussed in more details in the following sections. It is stressed out that the tensile strength of the Cloisite Na-filled PBAT-*g*-MTPS graft copolymer was around 26.1 MPa, much higher than that for the original PBAT-*g*-MTPS graft copolymer (ca. 16.2 MPa). Such an improvement could be attributed to the creation of a three-dimensional network of interconnected long silicate layers/MTPS, strengthening the blend through mechanical percolation.³³

Unlike Cloisite Na, the tensile strength of the PBAT-*g*-MTPS reactive blends with medium-polar Cloisite 30B increased more significantly, attaining about twice its original value (ca. 16 MPa) in the presence of only 1 wt % in Cloisite 30B. The elongation at break also improved significantly ($\sim 800\%$) on the addition of Cloisite 30B to the PBAT-*g*-MTPS graft copolymers. An increase in the modulus of elasticity (~ 150 MPa) was also observed as in the case of Cloisite Na. Usually, the tensile strength and the modulus increase with an increase in the blend crystallinity.^{26,34,35} In this case, the observed mechanical improvement was likely due to the improvement of interfacial (reactive) contact between Cloisite 30B and the surrounding matrix, leading to a nanoscale reinforcement for the blend. In addition to its moderated polarity character, such a behavior could be explained by primary hydroxyl groups from the quaternary ammonium ion present within the clay galleries of Cloisite 30B. The hydroxyl groups of Cloisite 30B would be able to make strong hydrogen interactions³⁴ with the MA-derived acidic moieties

grafted onto the starch backbone in the MTPS, and to some extent, to react with MTPS and PBAT, through (trans)esterification reactions during the melt-blending of MTPS with PBAT (Fig. 2). Such (trans)esterification reactions could allow grafting some MTPS-*g*-PBAT graft polymers onto the layered silicate organo-modified surface. However, because of the high dilution of the nanoclays within the melt-blends, we are not able to highlight such interactions between Cloisite 30B and MTPS using classical techniques as FT-IR analyses.

An addition of 3 wt % nanoclay in the composite improved the tensile strength up to 36.7 MPa, with elongation at break as high as $\sim 850\%$ (entry 5, Table II). However, higher clay content (up to 5 wt%) did not lead to better mechanical performances for the resulting materials. This was already reported in many cases, where the optimal nanofiller loading is localized around 3 wt %.³⁶ This could also be explained by the fact that at 5 wt % nanoclay, the mixture was not very well swollen in the presence of glycerol (plasticizer). This was attested by WAXS analyses (data not shown) where the interlayer distance of Cloisite Na did not change after these different reactive processes in contrast to other compositions at lower clay content. Again, this attests that the swelling pretreatment of nanoclays into the plasticizer (glycerol) is useful.

WAXS patterns of layered silicate-filled TPS, MTPS, and PBAT-*g*-MTPS

The films produced from the clay-reinforced reactive melt-blends were examined by WAXS to shed light on the extent of layered silicate intercalation and exfoliation within the polymer matrix. Figures 3 and

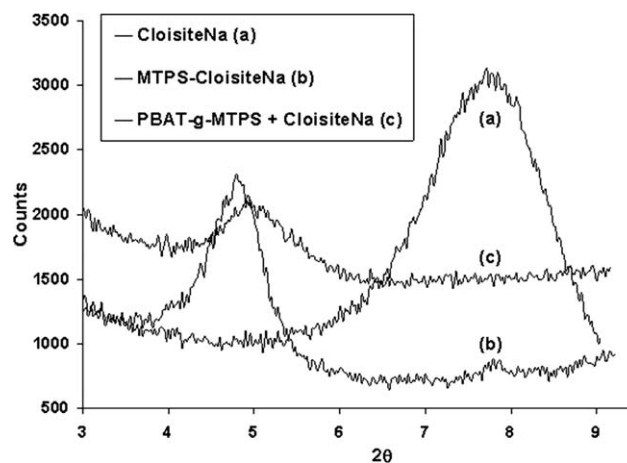


Figure 3 X-ray diffractogram (zoom on the low angle zone) of Cloisite Na alone (a), dispersed in MTPS (b), and in PBAT-*g*-MTPS graft copolymer (c) (entry 3, Table II).

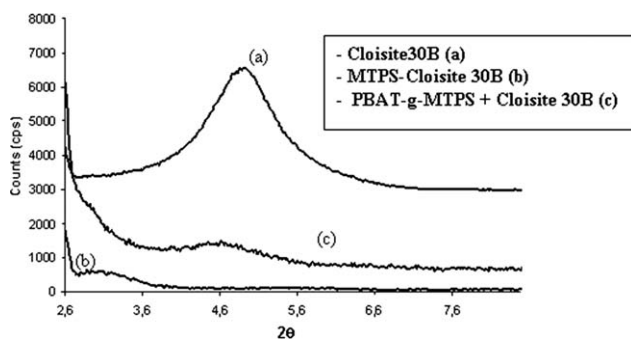


Figure 4 X-ray diffractogram (zoom on the low angle zone) of Cloisite 30B alone (a), dispersed in MTPS (b), and in PBAT-g-MTPS graft copolymer (c) (entry 4, Table II).

4 show the diffraction patterns obtained from the two investigated (organo-)clays (Cloisite Na, Cloisite 30B) at a final composition of 1 wt % clay (entries 3–4, Table II).

Figure 3 shows that the diffraction peak at ca. 8° 2θ of Cloisite Na was shifted to 4.5° 2θ within the Cloisite Na-filled MTPS nanocomposite, and to ca. 5° 2θ (much broader) in the Cloisite Na filled PBAT-g-MTPS film, attesting for the formation of intercalated nanocompositions.²⁸ However, we can observe that the diffraction peak characteristic to Cloisite Na in the graft copolymer was located at higher angles than one in MTPS. This is more likely due to the preferential localization of Cloisite Na in the graft copolymer, leading to some compaction for Cloisite Na in the graft copolymer. This is supported by the vapor properties (see the next part), showing that Cloisite Na has more affinity with the polysaccharide phase rather than the polyester phase in the graft copolymer. Figure 4 shows that the diffraction peak around 5° 2θ characteristic of Cloisite 30B was shifted to ca. 3.2° 2θ within the Cloisite 30B-filled MTPS composite, whereas only a residual peak of very low intensity could be detected at about 4.6° 2θ in the Cloisite 30B/PBAT-g-MTPS film.²⁸ This might suggest the coexistence of both structures, i.e., exfoliated and intercalated nanocompositions. In comparison with natural Cloisite Na, the organo-modified Cloisite 30B seemed to reach a higher extent of exfoliation in the presence of MTPS. The organic surfactant of Cloisite 30B functionalized by hydroxyl groups seems to be prone to interact strongly with the carboxylic acid groups present from the MTPS phase.

Park et al.¹⁷ reported WAXS results obtained from TPS added with Cloisite 30B and Cloisite Na in the presence of larger contents in plasticizer, but without any swelling pretreatment. Intercalated nanostructures were obtained in both these composites, wherein the peak at 7.8° 2θ for Cloisite Na was shifted down to 5.0° 2θ in the Cloisite Na-filled TPS

nanocomposite, whereas the peak corresponding to Cloisite 30B at 4.7° 2θ shifted to 4.3° 2θ , when dispersed within TPS. The shift to lower angles was inferior compared with our results in the MTPS-based nanocomposites, indicating a lack of dispersion of the clays in the polysaccharidic phase. Albeit the nature of starch (potato starch instead of corn starch) and the experimental conditions (larger content in plasticizer) were different, this attested for the beneficial effect of the swelling pretreatment for layered silicates, together with the reduction in molecular weight of starch (occurring during the *in situ* chemical modification of TPS) on the dispersion of nano-clays in the polysaccharidic matrix. In perfect agreement with these observations, no change in the interlayer distance of layered silicates occurred on the dispersion within the MTPS matrix when the clays were not previously swollen by the plasticizer (data not reported).

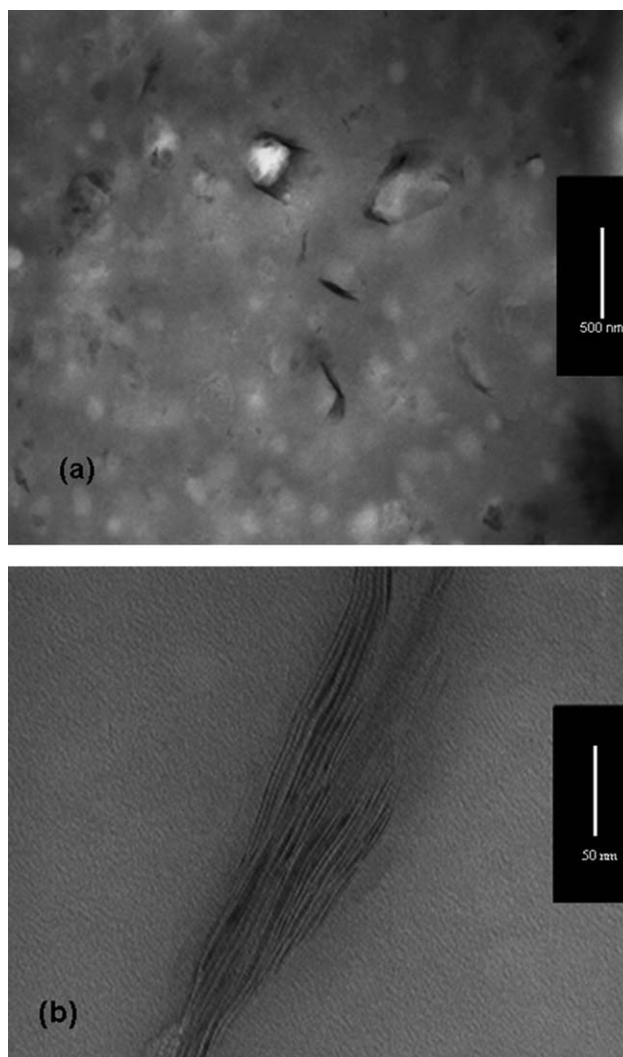


Figure 5 TEM images for Cloisite Na-filled PBAT-g-MTPS (magnitude $\times 14000$ (a) and $\times 250000$ (b)).

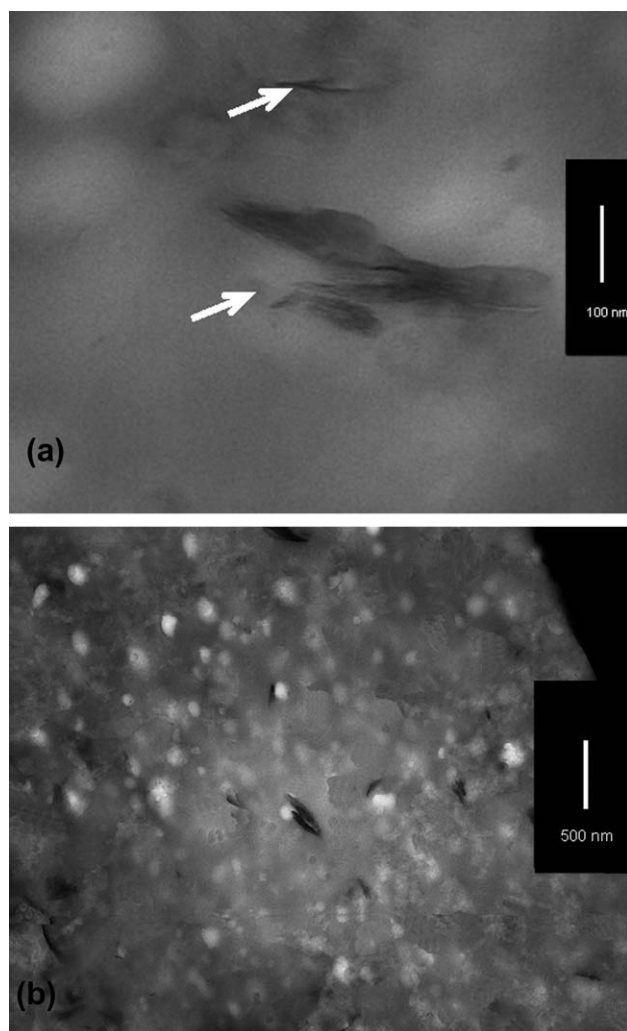


Figure 6 TEM images for Cloisite 30B-filled PBAT-g-MTPS (magnitude $\times 105000$ (a) and $\times 19000$ (b); individual exfoliated nanolayers highlighted by arrows).

To corroborate the WAXS results, TEM analyses were carried out on Cloisite Na and Cloisite 30B filled PBAT-g-MTPS composites (Figs. 5 and 6). From Figure 5(a), stacks of layered silicates were essentially observed. However, focusing onto them [Fig. 5(b)], these stacks were exclusively based on intercalated Cloisite Na in perfect agreement with the related WAXS patterns. These structures would mainly locate in the MTPS phase as supported by the gas barrier properties measurements (see hereafter). In contrast, Figure 6(a,b) exhibited some exfoliated nanolayers in Cloisite 30B-filled PBAT-g-MTPS matrix. The remaining stacks of intercalated clay platelets were however observed. As a result of their partial exfoliation together with the good dispersion of nanoclay in the reactive melt-blend, Cloisite 30B-filled PBAT-g-MTPS nanocomposites proved to exhibit good tensile properties, yielding high-performance blown films.

Water vapor barrier properties

Based on the huge interest in developing starch-based materials with improved barrier properties, the permeability to oxygen and water vapor was evaluated on blown films of MTPS-g-PBAT graft copolymers reinforced by either Cloisite 30B or Cloisite Na (Table III). Effect of Cloisite 30B content was also studied. Another purpose was to highlight the preferential localization of clay nanoparticles, i.e., the “medium hydrophobic” Cloisite 30B and the much more hydrophilic Cloisite Na, in MTPS-g-PBAT graft copolymer matrix. Indeed, PBAT-g-MTPS graft copolymer is hydrophilic in nature due to the presence of 30 wt % hydrophilic MTPS phase¹⁶ and therefore sensitive to water vapor, whereas hydrophobic PBAT is known to exhibit poor oxygen barrier properties.¹⁷ On the introduction of MTPS within the continuous PBAT matrix to form PBAT-g-MTPS, WVTR so-increased from 540 to about 1000 g/m² day. By adding the nanoclay at a loading level as tiny as 1 wt %, the water vapor permeability was reduced to 810 g/m² day for the Cloisite 30B-filled PBAT-g-MTPS nanocomposites, and more significantly to 575 g/m² day for Cloisite Na-filled PBAT-g-MTPS blown film. The lowering of the WVTR could be explained by the intercalation/partial exfoliation of the clay nanoplatelets,^{8,37} which would create a more tortuous path for the diffusion of water vapor through the PBAT-g-MTPS film. Clearly, a more significant reduction in water vapor permeability was detected for Cloisite Na-filled films. This indicated that hydrophilic Cloisite Na was preferentially located in the hydrophilic MTPS phase, which is much less resistant to water vapor than the polyester partner. Indeed, even if a much higher extent of exfoliation was reached by dispersing the more hydrophobic Cloisite 30B in PBAT-g-MTPS matrix, the beneficial effect on the WVTR values was less pronounced than for the simply

TABLE III
Water Vapor Transmission Rate (WVTR) and Oxygen Transmission Rate (OTR) of PBAT, PBAT-g-MTPS and Layered Silicate Filled PBAT-g-MTPS Blown Films Containing 30 wt % MTPS (Experimental Error = 5%)

No	Sample	WVTR (g/m ² day)	OTR (g/m ² day)
1	PBAT	540	1530
2	PBAT-g-MTPS	1000	1240
3	PBAT-g-MTPS (1% Cloisite Na)	575	750
4	PBAT-g-MTPS (1% Cloisite 30B)	810	590
5	PBAT-g-MTPS (3% Cloisite 30B)	510	520
6	PBAT-g-MTPS (5% Cloisite 30B)	760	485

intercalated structure found in Cloisite Na-filled PBAT-g-MTPS (see WAXS and TEM results). Adding 3 wt % Cloisite 30B enabled to reduce the water vapor permeability to a lower value of 510 g/m² day, attesting for the partial migration of Cloisite 30B in the MTPS phase. This can be again explained by the presence of the primary hydroxyl groups covering the Cloisite 30B surface and their possible interactions (via hydrogen bonding and/or esterification reactions) with the MA-derived acidic moieties grafted onto the starch backbone in the MTPS. Again and confirming the previously discussed mechanical properties (Table II), the dispersion of 5 wt % Cloisite 30B led to an increase in the water vapor permeability, i.e., increase in WVTR value to 760 g/m² day. This was probably due to the presence of some agglomeration or compaction of the clay platelets under extrusion conditions (shear and elongation flows) but also the lack of dispersion of Cloisite 30B in glycerol during the swelling pretreatment. This was experimentally observed by the formation of a pasty mass when 5 wt % Cloisite 30B was mixed in glycerol in contrast to the other investigated compositions.

Finally, even if both studied clays allowed reducing the OTR when dispersed in MTPS-g-PBAT copolymers, a stronger reduction in oxygen permeability was achieved with Cloisite 30B (already recorded at 1 wt % filling level). Furthermore, diffusion of the oxygen gas through the nanocomposite films was more and more hindered by increasing the Cloisite 30B content. The OTR values reached ca. 500 g/m² day at 3 to 5 wt % in nanoclay, actually a three-fold decrease as compared with the pristine PBAT. This attests perfectly that the medium hydrophobic nature of Cloisite 30B preferred being located in the hydrophobic phase, i.e., PBAT phase. It is stressed out that the introduction of the maleated starch phase (30 wt %) in the PBAT continuous phase also reduced the oxygen permeability of the PBAT-g-MTPS copolymer to 1250 g/m² day (with respect to 1550 g/m² day for the virgin PBAT films).

CONCLUSIONS

We have prepared novel MTPS-g-PBAT graft copolymers through reactive extrusion reinforced by selected (organo-)modified layered silicates. Two types of such (organo-)clays were used in this study: natural montmorillonite (hydrophilic Cloisite Na) and organophilic Cloisite 30B. The nanoscale-reinforced MTPS was first prepared in the presence of these nanoclays previously swollen in glycerol used as starch plasticizer, together with MA, and then melt-blended with PBAT in a subsequent downstream blending operation. MA was used to reduce the molecular weight of starch precursor through

acid-catalyzed hydrolysis and glucodisation reactions to facilitate the interpenetration of the modified starch (of much lower viscosity) through the layered silicate galleries. The swelling pretreatment has shown to be useful to achieve the best tensile properties for the resulting blown films. The tensile and barrier properties of resulting composites were studied, and compared with WAXS and TEM analyses. High-performance formulations having superior tensile strength (>35 MPa as compared with 16 MPa for the PBAT-g-MTPS copolymer) and elongation at break (>800%) were obtained, particularly with Cloisite 30B. In this case, the presence of a quaternary ammonium ion present within the clay galleries and bearing two hydroxyl groups enabled to create strong hydrogen bond interactions with the MA-derived acidic moieties grafted onto the starch backbone in the MTPS, and to some extent, to react with MTPS and PBAT through acid-catalyzed esterification reactions. Partially exfoliated nanostructures were achieved within the Cloisite 30B-filled PBAT-g-MTPS graft copolymers. These nanocomposites morphology is responsible for their enhanced water vapor and oxygen barrier properties.

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