

Starch Esters with Improved Mechanical Properties Through Melt Compounding with Nanoclays

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ABSTRACT: Biobased nanocomposites were manufactured through the melt intercalation of nanoclays and starch esters synthesized at the Fraunhofer Institute for Applied Polymer Research (IAP) from high amylose starch. Starch acetates (SAs) and starch propionates (SPs) were tested in combination with glycerol triacetate (triacetin) as a plasticizer for concentrations up to 30 and 20 wt %, respectively, with different types of organomodified and unmodified montmorillonites (MMTs). The mechanical properties of injection-molded test bars were determined by a tensile experiment giving the strength, modulus, and elongation of the composites. X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM) were used to study clay dispersion and intercalation/exfoliation. Dynamic mechanical analysis was used to track the temperature dependence of the storage modulus and $\tan \delta$ behavior of the starch/clay hybrid. Because they were the best performing compositions, SP with 5 wt % plasticizer and SA with 20 wt % plasticizer were filled with 5 wt % nanoclay. For SP, a

certain increase in modulus was observed for all clays. However, the strength was practically unchanged, and the elongation decreased in most cases. One exception was found for the 2.5 wt % organomodified clay composition, where the elongation increased. For SA, the addition of 5 wt % nanoclay always increased the strength and modulus, in one case up to 60 and 75%, respectively. In the particular case with 5 wt % unmodified clay, the strength, modulus, and elongation increased by 30, 40, and 1000%, respectively. This was a dramatic improvement in the ductility of the material without losses in the strength and stiffness. XRD and TEM revealed the existence of exfoliated modified clay throughout the starch matrix, whereas for the unmodified case (with the exceptional increase in the elongation), no intercalation was observed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 503–510, 2010

Key words: biopolymers; mechanical properties; nanocomposites

INTRODUCTION

In recent years, there has been strong interest in biobased polymers in general and biobased thermoplastics in particular. On the one hand, researchers intend to reduce our dependency on nonrenewable resources (oil and natural gas). On the other hand, they also hope to reduce the carbon footprint for these kinds of materials. Prominent examples for these so-called bioplastics are cellulose esters, which are mainly used in the fiber, film, and filter tow industries; thermoplastic starch, which is used in film and packaging materials; poly(lactic acid) for bottle applications and woven shirts; and polyhydroxyalkanoates for packaging materials.

There is a growing interest in the use of starch because it is cheap, available in abundant quantities, produced from renewable resources, and completely

biodegradable. However, starch has these advantages but suffers from some drawbacks: it lacks moisture resistance and shows brittleness, its processing is difficult, and its properties are inferior to commodity polymers. To solve the mentioned defects of starch, a considerable effort has gone into the development of thermoplastic starch. Prior developments in this area have involved the use of high-amylose starch,¹ the use of nonvolatile plasticizers (at the processing temperature), such as glycerol,^{2–4} triacetin (TA),^{5,6} and sorbitol;⁷ the use of fillers,^{8,9} the alkylation of the hydroxyl groups of starch,¹⁰ and recently, the use of nanoreinforcements.

Although various types of nanoreinforcements are currently being developed, the main focus in this field is on the use of layered silicate clay for its easy availability, low cost, and most important, environmentally friendliness. There have been several attempts to improve the properties of starch with layered silicate clay.^{11–22}

The intercalation of a polymer in layered silicates has proven to be a successful approach to preparing polymer nanocomposites. The preparation methods are divided into three main groups according to the materials and processing techniques:²³ the intercalation of a polymer or prepolymer from solution,

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the *in situ* intercalative polymerization method, and the melt intercalation method.

Among the mentioned techniques, the melt intercalation technique has become the standard for the preparation of polymer/layered silicate nanocomposites. The absence of solvent not only makes the process simple and easy but also makes the process more environmentally friendly and economically favorable for industries from a waste perspective.

With a low filler concentration of a few percent, this new family of composites frequently exhibits remarkable improvements in the mechanical and materials properties compared with polymers or conventional microcomposites and macrocomposites. Improvements can be in the form of a high storage modulus, higher tensile and flexural properties, higher heat distortion temperature (HDT) and thermal stability, increased gas barrier properties, and decreased flammability. Nanoreinforcements of biodegradable polymers have a strong promise in the design of ecofriendly, "green" nanocomposites for several applications.

Esterification gradually converts starch from a hydrophilic to a hydrophobic material. This process removes the greater part of the water sensitivity problem. However, one drawback of starch derivatives is that its melt processing temperature exceeds its decomposition temperature, and also, its processing is difficult. This requires starch esters to be plasticized. Even after plasticizing, some properties of starch derivatives, especially starch acetate (SA), are still low.

To our knowledge, so far, there have not been many reports on the preparation of plasticized starch derivatives/clay hybrid nanocomposites.^{24,25} In this study on starch propionate (SP) and SA/layered silicate clay nanocomposites, we chose TA as a plasticizer. We adopted melt processing through kneading, extruding, and injection molding to fabricate the nanocomposites. By compounding organo-modified montmorillonites (MMTs) and unmodified MMTs with plasticized SP and SA via melt extrusion, we hoped to improve the properties. In this article, we report the results of optimized processing conditions with various amounts of plasticizer and different types of organomodified and unmodified MMTs. The tensile properties, transmission electron microscopy (TEM), X-ray diffraction (XRD), and dynamic mechanical analysis (DMA) of the resulting plasticized starch derivatives and nanocomposites were used to evaluate the successful preparation.

EXPERIMENTAL

Materials

SP with a degree of substitution (DS) of 2.45 and SA with a DS of 2.60 were synthesized at the Fraunhofer

TABLE I

Different Types of Used Layered Silicates–Nanoclays

Type of clay	Organic modifier
Dellite LVF	Inorganic MMT (CEC = 105 mequiv/100 g)
Dellite HPS	Inorganic MMT (CEC = 128 mequiv/100 g)
Dellite 43B	DMBHT
Dellite 67G	DMDHT (high modifier content)
Dellite 72T	DMDHT (high modifier content)

DMDHT = dimethyl dihydrogenated tallow ammonium; DMBHT = dimethyl benzyl dihydrogenated tallow ammonium.

Institute for Applied Polymer Research from high-amylose (50 wt %) maize starch.²⁶ The SA was prepared with the method described by Kakuschke and Rappthel²⁷ via the refluxing of the starch in a mixture of acetic acid and acetic acid anhydride for 24 h. SP was synthesized according the method of Mark and Mehlretter²⁸ by the refluxing of the starch in propionic acid anhydride in the presence of an aqueous sodium hydroxide solution for 5 h. 1,2,3-Triacetoxyp propane (TA or glycerin triacetate) was used as the plasticizer and was purchased from Sigma Aldrich, Taufkirchen, Germany with a 99% purity. LAVIOSA S.p. A. supplied five kinds of MMTs; three were organically modified, as shown in Table I.

Melt compounding and injection molding

The SP, SA, and clays were dried *in vacuo* at 80°C for at least 24 h before use. Certain amounts of different kinds of clays were immersed into the TA corresponding to the weight of the starch derivatives for 24 h. The starch derivatives and a mixture of TA and the clays were mixed mechanically with a high-speed mixer for about 5 min and then stored in sealed polyethylene bags for 24 h before further processing. The preplasticized mixture was then homogenized in a HAAKE (Karlsruhe, Germany) kneader at a temperature of 120–150°C and a speed of 50–100 rpm. The mixtures (SP or SA/TA/nanoclay) were then melt-compounded in a HAAKE Minilab twin-screw extruder at a temperature of 160–170°C and a speed of 250 rpm. Finally, dumbbell-shaped standard test specimens were injection molded with a HAAKE Minijet according to ISO 527, type 5 A. Prepared dumbbell specimens were put in a climate room with a temperature of 23°C and a relative humidity of 50% for 24 h before tensile testing.

Characterization

The tensile properties of the samples were measured with a Zwick 1445 universal testing machine (Zwick Roell AG, Ulm, Germany) at 23°C and 50% relative

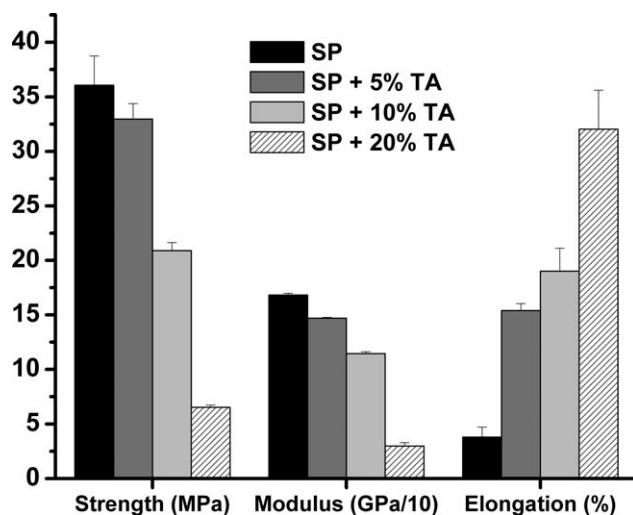


Figure 1 Effect of the TA concentration on the tensile properties of SP.

humidity. Initial clamp separation and crosshead speed were 44 and 22 mm/min, respectively. All measurements were performed at least for six replicated dumbbell-shaped specimens and averaged.

TEM images were taken from cryogenically microtomed ultrathin sections (60 nm) with a Phillips CM 200 at an acceleration voltage of 120 kV. XRD studies of the samples were carried out with a Bruker AXS two-circle diffractometer D 5000 (46 kV, 30 mA) equipped with Cu K α radiation ($\lambda = 0.15418$ nm) and a curved graphite crystal monochromator at a scanning rate of 0.1°/50 s. DMA was carried out with a TA Instrument DMA 2980 in a single-cantilever mode from -30 to 200°C at a frequency of 1 Hz and a heating rate of 2 K/min. During testing, the dynamic mechanical property parameters of the storage modulus and loss factor ($\tan \delta$) were recorded as a function of temperature.

RESULTS AND DISCUSSION

Effect of the plasticizer

Figures 1 and 2 show the tensile properties of the SP/TA and SA/TA compositions with different plasticizer contents, up to 20 and 30 wt % TA corresponding to the starch derivative weight. The extruding temperature for unplasticized SP and plasticized SP were optimized to give 190 and 170°C, respectively. The extruding temperature for unplasticized SA and plasticized SA were optimized to give 200 and 160°C, respectively. It was clear that, when the plasticizer was incorporated into the starch derivatives, the processability was facilitated, and the extruding temperature decreased.

As shown in Figure 1, increasing the amount of plasticizer in SP resulted in decreases in the tensile

strength and modulus and an increase in the elongation. The tensile strength and modulus for unplasticized SP decreased from 36.0 MPa and 1.6 GPa to 6.5 MPa and 0.3 GPa, respectively, and the elongation increased from 3 to 32% for SP with 20 wt % plasticizer, respectively. It turned out that SP (in contrast to SA), because of the longer side chain of the propionate substitute even without plasticizer, was not excessively brittle in terms of removing the test bar from the mold. The most pronounced effect visible in Figure 1 is the 400% increase in elongation to 15% by the addition of just 5 wt % TA, although the tensile strength and modulus decreased only slightly.

The effect of the plasticizer on the mechanical properties of SA was different from that on SP. The addition of up to 15 wt % TA to SA increased the tensile strength from 22 MPa to about 26 MPa. The modulus indicated a little improvement with 5% TA up to 2.2 GPa and then decreased monotonously to 1 GPa for plasticized SA with 20 wt % TA. The elongation did not change up to 20 wt % TA. Increasing the amount of plasticizer to 30 wt % resulted in a significant improvement in the elongation to higher than 30%, yet the tensile strength and modulus decreased.

Selected systems with MMT

Because they were the best performing compositions, SP with 5 wt % TA and SA with 20 wt % TA were selected to produce the nanocomposites.

As shown previously, the addition of 5 wt % TA to SP gave very good mechanical properties. For this reason, plasticized SP with 5 wt % TA was selected to be compounded with organomodified and unmodified MMTs. Figure 3 shows the mechanical

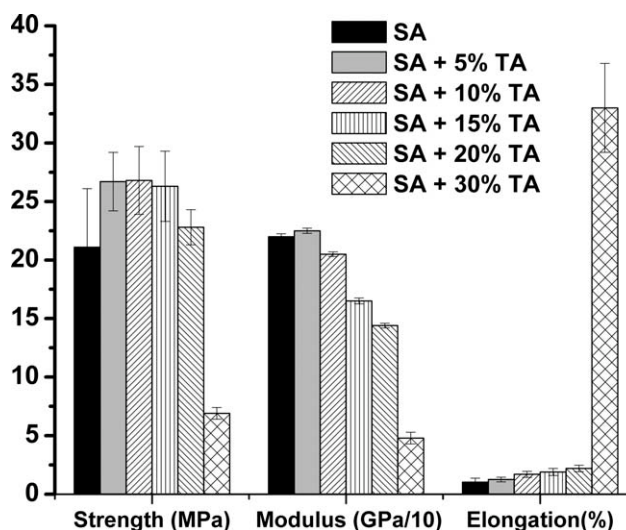


Figure 2 Effect of the TA concentration on the tensile properties of SA.

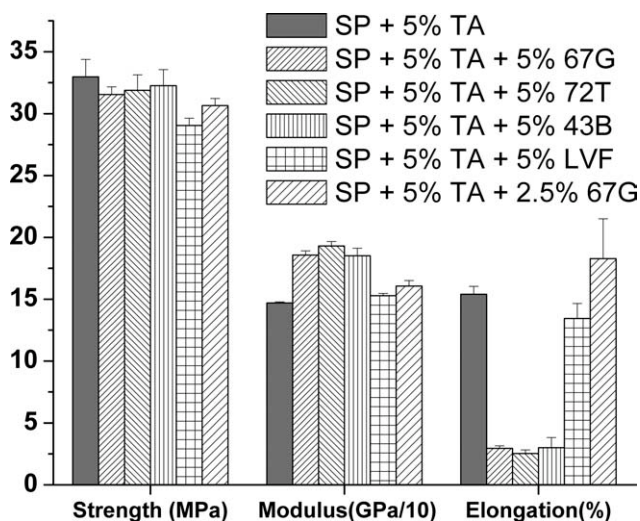


Figure 3 Effect of different types of MMT on the tensile properties of plasticized SP.

properties of SP/5 wt % TA/MMT (5 wt % Dellite 67G, Dellite 72T, Dellite 43B, and Dellite LVF and 2.5 wt % Dellite 67G). As shown in Figure 3, all of the organomodified MMTs did not show any improvement in terms of the tensile strength, whereas a small improvement in the modulus was observed. In all cases, the elongation decreased significantly. The addition of 5 wt % unmodified Dellite LVF did not show any significant change in the properties compared to plasticized SP. Better results were achieved by the addition of 2.5 wt % Dellite 67G to plasticized SP. For this composition, the tensile strength and modulus almost remained constant, but the elongation increased by 20% to 18.3%. This corresponded to the good dispersion and partial exfoliation that was shown in the TEM micrographs (see later discussion).

Figure 4 shows the tensile properties of plasticized SA with 20 wt % TA compounded with 5 wt % Dellite 43B, Dellite 72T, Dellite 67G, Dellite HPS, and Dellite LVF. Obviously, all of the organomodified clays improved the tensile strength and modulus values. For example, when 5 wt % Dellite 43B was added, the tensile strength and modulus increased by 40% to 33.0 MPa and 2 GPa, respectively; this was in agreement with the very good dispersion and partial exfoliation that was shown in the TEM micrographs (see later discussion). However, the tensile strengths and modulus were enhanced, but the elongation remained at low values of about 3%. Dellite HPS, an unmodified MMT with a higher cation-exchange capacity (CEC), improved all of the properties a little yet did not cause a considerable improvement in the elongation at break.

The best result was achieved for the composition of SA/20 wt % TA/5 wt % Dellite LVF.

This unmodified MMT with a lower CEC indicated significant improvement, especially in the elongation at break. This clay improved the properties compared to plasticized SA with 20 wt % TA by 30, 40, and 1000% for the tensile strength, modulus, and elongation, respectively. This means that, in this composition and with this clay, not only the tensile properties were improved, but also a tougher and more ductile starch-based nanocomposite was produced. It seemed that there was a specific composition needed to achieve this unexpected behavior because the incorporation of lesser and greater amounts of TA and also lesser amounts of LVF did not show the same effect. A similar behavior was found for different compositions of starch mixed esters (unpublished results).

These results were not in agreement with the TEM micrographs, which showed no intercalation and exfoliation. A possible explanation could be that the rigid, nonexfoliated nanoparticles acted like internal mixing elements and improved the homogeneity and brought out the proper potential of the matrix material. This hypothesis was corroborated by the occasional occurrence of high elongations in the pure acetate tensile specimen.

XRD of the nanocomposites

The dispersion extent of MMT layers is typically elucidated by wide-angle XRD, which allows direct evidence of the polymer chain confinement into the MMT gallery. The XRD pattern of SA with unmodified MMT (Dellite LVF) and organomodified MMT (Dellite 43B) are shown in Figures 5 and 6, respectively.

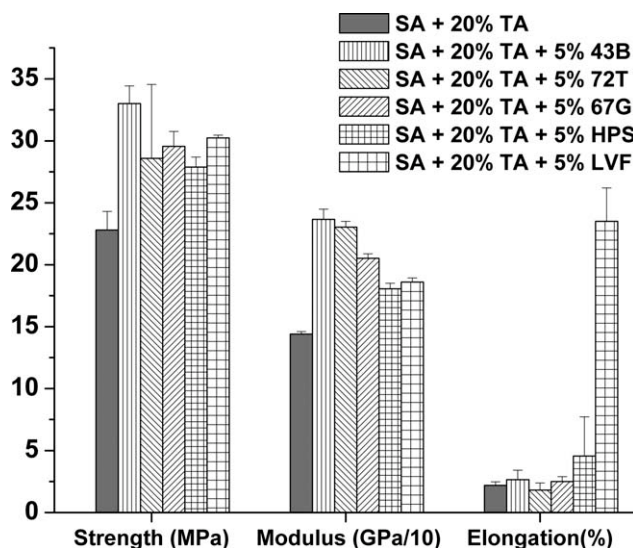


Figure 4 Effect of different types of MMT on the tensile properties of plasticized SA.

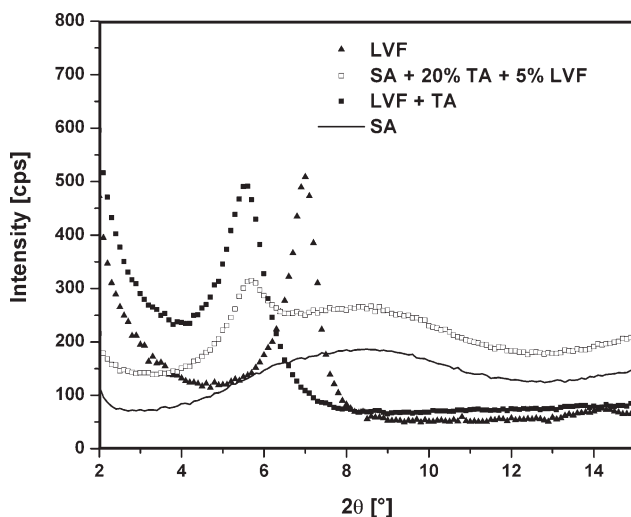


Figure 5 XRD of the SA nanocomposite with unmodified MMT.

The wide-angle XRD patterns revealed that, when unmodified MMT emerged in the TA, the diffraction peak of the MMT (001) crystal planes moved from 7.0 to 5.5°. According to the Bragg diffraction equation, the distances (d_{001}) between the silicate layers increased from 1.26 to 1.61 nm, which indicated that TA intercalated into the layers of Dellite LVF. As shown in the curve for the composition in Figure 5, compounding did not have more influence on the distance between galleries.

As shown in Figure 6, the diffraction peak of the organomodified MMT (001) crystal planes did not move much when the MMT emerged into TA. According to the Bragg diffraction equation, d_{001} between the layers of Dellite 43B was 1.96 nm. The slight peak shift, corresponding to a decrease in the distance of the silicate layers to 1.84 nm, was caused by the certain removal of modifier in favor of TA. As shown in Figure 7, Dellite 67G indicated three

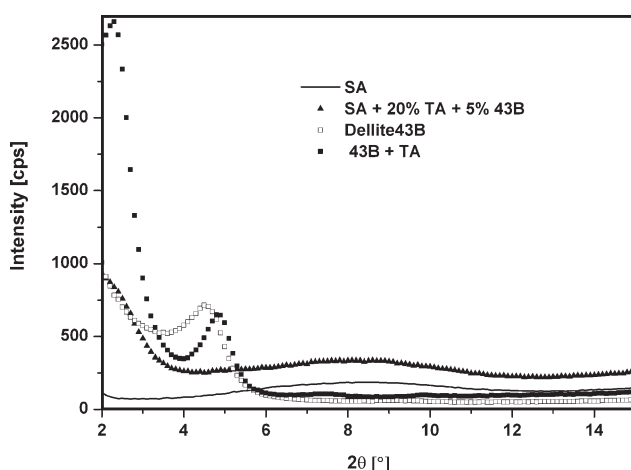


Figure 6 XRD of the SA nanocomposite with organomodified MMT.

peaks at 2.4, 4.6, and 7.1°. This means that there were layers with d_{001} spacings of 3.68, 1.92, and 1.25 nm, respectively. Obviously, this organomodified clay showed a multimodal structure. When the Dellite 67G emerged into the TA, the peaks shifted from 4.6 to 4.85° and from 7.1 to 7.4°, and the peak at 2.4° remained almost at the same position.

The X-ray patterns of the nanocomposites of SA with Dellite 43B and SP with Dellite 43B and Dellite 67G showed that the diffraction peak (d_{001}) of the nanocomposites disappeared. This indicated that the lattice structure of Dellite 43B and Dellite 67G was totally dispersed, and the slice layers were exfoliated into the SA and SP. So, exfoliated nanocomposites were formed.

TEM of the nanocomposites

To illustrate the morphology of the SP and SA/TA/nanoclay composites, TEM micrographs are presented in Figure 8. The TEM pictures showed that the SP/5 wt % TA/2.5 wt % Dellite 67G, SA/20 wt % TA/5 wt % Dellite 67G, and SA/20 wt % TA/5 wt % Dellite 43B hybrids revealed very good dispersion and partial exfoliation structures.

On the other hand, there were poor dispersion and nonbroken clay particles in the SP and SA/TA/Dellite LVF. The TEM pictures of SP and SA with unmodified MMT indicated the lack of compatibility between the starch derivatives and unmodified MMT.

The morphology of the polymer/plasticizer/clay depended on the compatibility and interaction among all of the components. Starch derivatives after derivatization changed to be more hydrophobic compared to the native hydrophilic starch material. Therefore, the polarity of hydrophilic Dellite LVF did not match the polarity of the hydrophobic SP

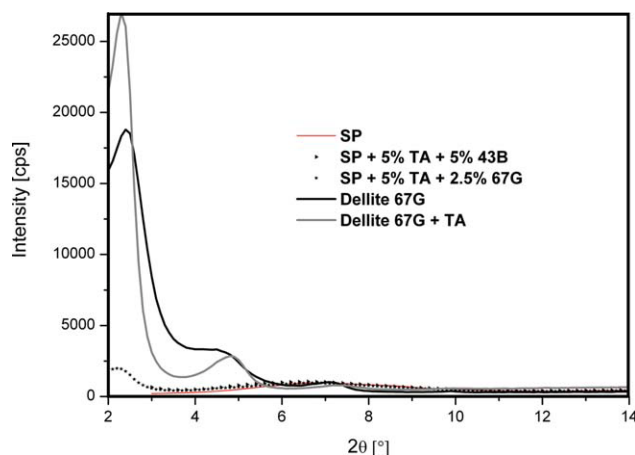


Figure 7 XRD of the SP nanocomposites with organomodified MMTs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

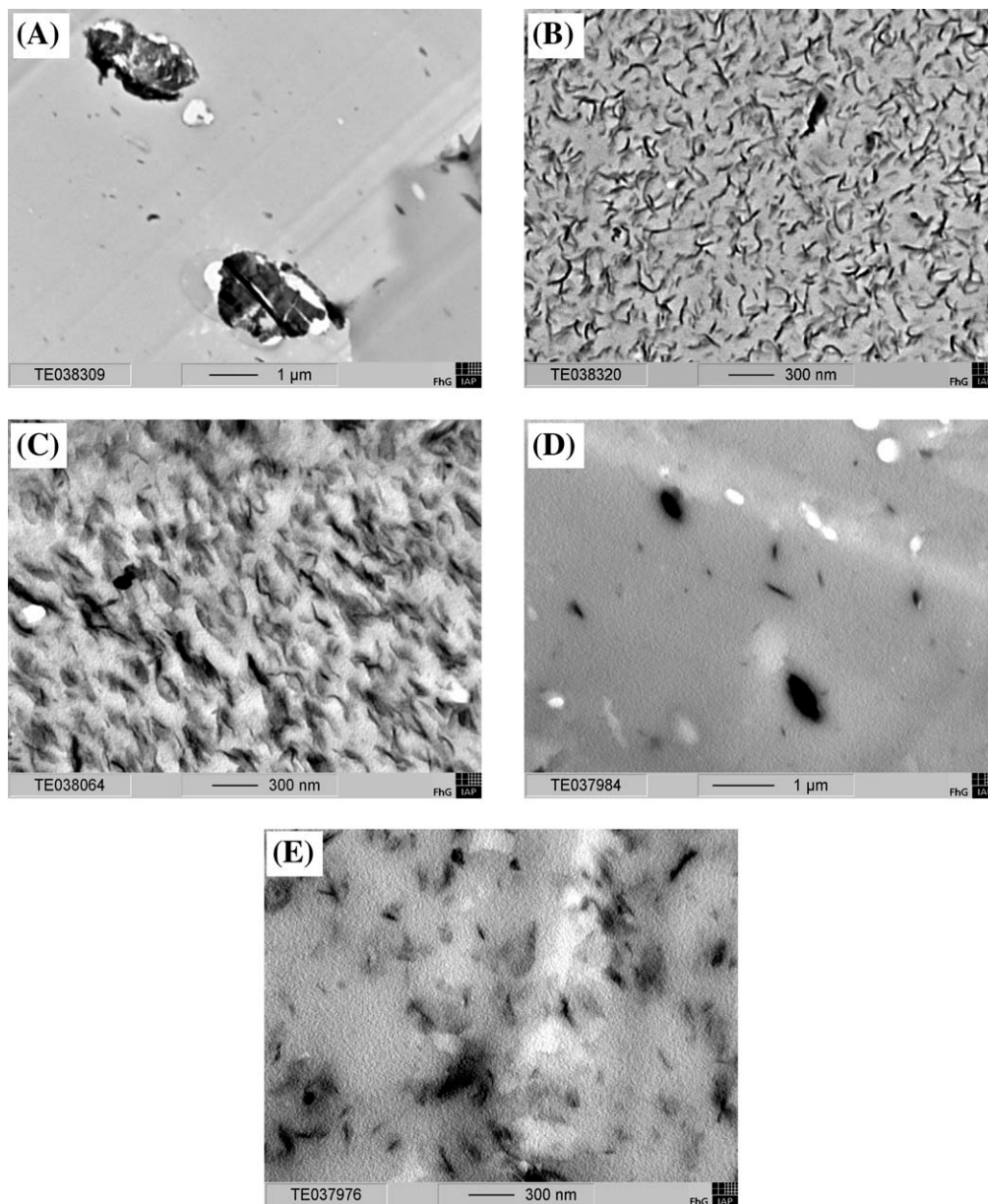


Figure 8 TEM micrographs of the nanocomposites: (A) SA/20 wt % TA/5 wt % Dellite LVF, (B) SA/20 wt % TA/5 wt % Dellite 43B, (C) SA/20 wt % TA/5 wt % Dellite 67G, (D) SP/5 wt % TA/5 wt % Dellite LVF, and (E) SP/5 wt % TA/2.5 wt % Dellite 67G.

and SA. On the other hand, the organomodified MMTs, Dellite 67G and Dellite 43B, matched well with the hydrophobic starch derivative matrix, and as a result, a very good dispersion and partially exfoliated structures were achieved. Similar interactions between the starch matrix (not starch ester) and organomodified MMT and unmodified MMT have been reported by other researchers.^{11,12}

DMA

From thermomechanical measurements based on DMA characterization, the influence of the nano-

clays on the local mobility of the chains and on the glass-transition temperature (T_g) were determined. The storage modulus and mechanical $\tan \delta$ of the plasticized starch derivatives and plasticized starch derivative nanocomposites are shown in Figures 9 and 10. The T_g values were measured through DMA as the temperature at which the $\tan \delta$ peak was located. The thermal stability or HDT was measured through DMA at a storage modulus of 1 GPa.

Figures 9 and 10 show the temperature dependence of the storage modulus of plasticized SP and SA and the nanocomposites. The incorporation of TA led to a lower T_g and HDT for both SA and SP.

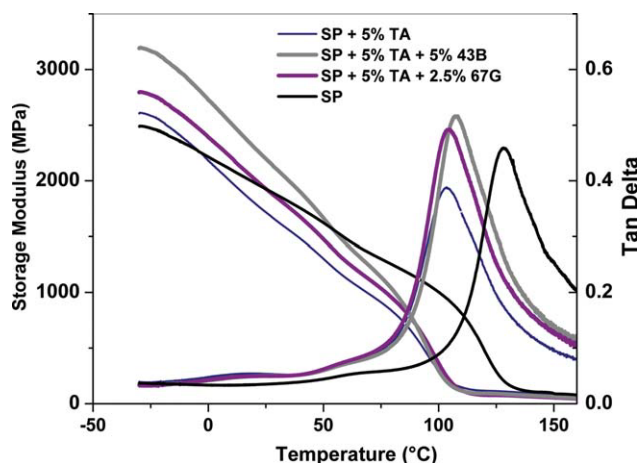


Figure 9 Storage modulus and $\tan \delta$ behavior of the plasticized SP and SP/clay hybrid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

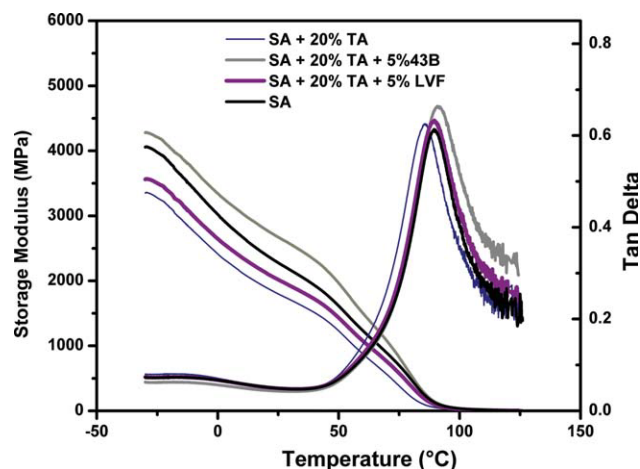


Figure 10 Storage modulus and $\tan \delta$ behavior of the plasticized SA and SA/clay hybrid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The storage modulus of the plasticized starch derivative/clay composites (especially Dellite 43B) were higher than those of plasticized SP and SA over a broad temperature range for better dispersion and partial exfoliation. In all cases, with the incorporation of organomodified clay, especially Dellite 43B, the temperatures of the relaxation peaks shifted to higher values. The addition of Dellite 43B to plasticized SA and SP increased the T_g values of the nanocomposites by 6 and 7°C, respectively. The same effect occurred with HDT; for both derivatives, HDT improved by approximately 15°C for the best clay samples. The values are given in Table II.

CONCLUSIONS

Injection-moldable, starch-based nanocomposites were successfully developed. An optimum level of plasticizer and an optimum type of nanoclay existed for each starch derivative, that is, SA and SP.

The best results were obtained for SA, where the addition of nanoclay always increased the strength and modulus, in one case up to 60 and 75%, respec-

tively. In the particular case with a particular unmodified clay (Dellite LVF), the tensile strength, modulus, and elongation increased by 30, 40, and 1000%, respectively. In this way, the combination of SA with nanoclay offers a broad range of possibilities for tailoring the mechanical properties of this biobased composite.

Future work needs to clarify whether the positive effects of nanoclay can be utilized for derivatives, especially acetates of native starch, and how the effects depend on the molecular structure of the derivatives, in particular on DS. It remains to be seen if the proposed mechanism of internal mixing by particles of unmodified clay proves valid for other DS values and starting starch types. If so, a novel processing aid has been found with implications for other polysaccharide-based thermoplastics.

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TABLE II
Thermomechanical Properties of Selected SA and SP Nanocomposites

Type of starch	TA content (%)	Type of nanoclay	Amount of nanoclay (%)	T_g (°C)	HDT (°C)
SA	—	—	—	90	70
SA	20	—	0	87	56
SA	20	LVF	5	91	62
SA	20	43B	5	93	71
SP	—	—	—	127	100
SP	5	—	0	103	67
SP	5	67G	2.5	108	77
SP	5	43B	5	110	81

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