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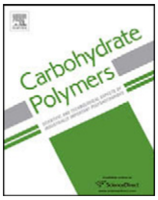

Nanocomposites of starch mixed esters and MMT: Improved strength, stiffness, and toughness for starch propionate acetate laurate

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ABSTRACT

Novel starch mixed esters were compounded with nanoclays through a melt intercalation method. Two organo-modified clays and one unmodified clay with varying percentage of plasticizer (triacetin, TA) were used. The effect of clays on the tensile, dynamic mechanical and impact properties of the nanocomposites was investigated. The dispersion and orientation of the silicate layers in the polymer matrix was characterized by using transmission electron microscopy (TEM) and wide angle X-ray scattering (WAXS).For a propionate rich system (StPrAcLau) with 10 wt% TA ductility could be improved considerably by using 2.5 wt% of organo-modified clay. Charpy impact strength was increased 5 times reaching 15 kJ/m^2. In contrast to unmodified clay, good dispersion was found with TEM for organo-modified clays while WAXS revealed the presence of tactoids consisting of 4–5 silicate layers and a preferred orientation of the platelets parallel to the sample surfaces along the injection molding direction.

1. Introduction

Shaped bodies, such as films or injection molded components from plasticized native starch suffer from brittleness and a lack of moisture resistance. Esterification of hydroxyl groups of starch to increase hydrophobicity is one approach toward increasing their water resistance. Derivatization of starch hydroxyl groups may also reduce the tendency of starch to form strongly hydrogen-bonded networks and improve the flexibility. Among different ester groups, acetate has been widely used to esterify starch. Acetylation of starch results in good thermoplastic processing and enhanced mechanical properties (Gonzalez & Perez, 2002; Volkert, Lehmann, Ganster, Hassan Nejad, & Wetzel, 2010; Xu & Hanna, 2005).

Higher esters like propionate and butyrate promise to achieve better processing and mechanical properties compared to starch acetate. For example, Rudolph and Glowaky (1978) prepared a series of starch mixed esters with total degree of substitution (DS) values in the range of 1.4–2.2. They prepared starch-acetate-phthalate, starch-propionate-phthalate and starch-butyrate-phthalate and found that by increasing the size of ester group from acetate to butyrate, glass transition temperature (T_g) and softening temperature (T_s) decreased from 147 to 74 °C and 145 to 113 °C, respectively. This kind of products follow rational structure–property trends characterized by increasing chain mobility with increasing aliphatic ester side chain length and increasing extend of side chain substitution.

Gros and Feuge (1962) also demonstrated that by changing the kind of fatty acid from acetate to laurate the mechanical properties of films prepared from amylose changed as well. They observed a big improvement in elongation at break and a reduction in Young's modulus by increasing the ester length from acetate to laurate. But because of the higher cost of pure amylose compared to native starch the uses as a commodity material is limited.

Among the bio-based polymers, starch has gotten a great interest in nano-bio-composite systems. The main focus in this field is on the use of nanoclays and essentially montmorillonite (MMT) for being environmentally friendly, easy available and of low cost. Starch has mainly been used in the plasticized state in nanocomposite formation. Most of the studies in this field are elaborated with native starch and there are just a few studies on chemically modified starch materials (starch acetate) (Qiao, Jiang, & Sun, 2005; Xu, Zhou, & Hanna, 2005).

To reach an exfoliated structure, several kinds of plasticizer and nanoclay as well as various procedures have been studied and proposed. Preferably unmodified hydrophilic MMT was incorporated into glycerol plasticized starch in solvent processes (Kampeerapappun, Aht-ong, Pentrakoon, & Srikulkit, 2007) or by melt blending (Huang, Yu, & Ma, 2004). Native starch has a hydrophilic nature and unmodified MMT-Na has the same nature as well, therefore this nanoclay was expected to give an enhanced nano-dispersion state and improve mechanical properties (Ciou, Yee, Glenn, & Orts, 2005). Starch derivatives have a

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more hydrophobic nature compared to native starch, for this reason organo-modified clay has more compatibility and better dispersion and is more effective on mechanical properties. To the authors' knowledge there is no report on the preparation of starch mixed esters nanocomposites. The objective of the current work research is to prepare the starch mixed esters nanocomposites and to investigate the effect of nanoclays on the mechanical properties and morphology of starch mixed ester/clay hybrids. For this purpose, StAcPrLau and StPrAcLau were compounded with TA as the plasticizer followed by adding organo-modified and unmodified clays to produce bio-nanocomposites through melt compounding. This paper describes the results of optimized processing conditions, tensile and impact properties, DMA, XRD and TEM of the resulting plasticized starch mixed esters and their nanocomposites were used to evaluate the resulting products.

2. Experimental

2.1. Materials

1,2,3-Triacetoxypropane (triacetin or glycerin triacetate) was used as the plasticizer purchased from Aldrich with 99% purity. Three kinds of MMT were purchased from provided by LAVIOSA S.p.A.; two organically modified MMTs (Dellite 43B and Dellite 67G) and one unmodified MMT (Dellite LVF, cation exchange capacity (CEC) = 105 milliequiv./100 g). The ammonium cations of the organo-modified clays are respectively dimethyl-dihydrogenated tallow ammonium for the Dellite 67G and dimethyl-benzyl-hydrogenated tallow ammonium for Dellite 43B.

StPrAcLau ($DS_{Prop} > DS_{Ac} \gg DS_{Lau}$) and StAcPrLau ($DS_{Ac} > DS_{Prop} \gg DS_{Lau}$) were synthesized in this institute from high amylose (50 wt%) maize starch.

To produce StPrAcLau, 2.4 mol of the air dried starch (water content 12–14%) were placed together with 5.4 mol propionic acid anhydride (2.25 moleq/AGU) in a 2 l IKA® laboratory glass reactor and the temperature was set to 95 °C. When the thermostat reached 95 °C the slurry was stirred for 45 min before 1.7 mol 1-methylimidazole (0.7 moleq/AGU) were added and the temperature of the thermostat was set to 115 °C. Having reached the set temperature of the thermostat after 10 min, 1.2 mol lauroyl chloride (0.5 moleq/AGU) was added, followed by 5.4 mol acetic acid anhydride (2.25 moleq/AGU). The reaction mixture became viscous, brownish and transparent and was stirred for further 45 min before cooling to room temperature and precipitating and washing in ethanol and finally drying at ambient temperature. The product was 834 g of a white powder with $DS_{Ac} = 0.59$, $DS_{Prop} = 2.31$ and $DS_{Lau} = 0.1$.

The degree of substitution of the acetate and propionate ester groups can be controlled by the sequence of addition. Therefore to synthesize StAcPrLau the reaction conditions were not changed. Instead, the order of the addition of the carboxylic acid anhydrides was changed. Acetic acid anhydride was used at first and after addition of 1-methylimidazole and lauroyl acid propionic acid anhydride was given to the reaction mixture. 712 g of a white powederous product was isolated through precipitation in ethanol with $DS_{Ac} = 2.27$, $DS_{Prop} = 0.63$ and $DS_{Lau} = 0.1$.

2.2. Melt compounding and injection molding

The StPrAcPrLau, StAcPrAcLau and clays were dried in an oven at 80 °C for at least 24 h before use. Predefined amounts of clays were immerged into the TA corresponding to the weight of starch mixed esters and stored for 24 h. The starch mixed esters and mixture of TA and clays were mixed mechanically with a high-speed mixer for about 5 min and then stored in sealed polyethylene bags for 24 h prior to further processing. The preplasticized mixture was then homogenized in a HAAKE kneader at a temperature of 120–140 °C and a speed of 50–100 rpm. The mixtures (StPrAcLau or StAcPrLau or StPrAcLau/TA/nanoclay) were then melt compounded in a HAAKE minilab twin-screw extruder at a temperature of 160–180 °C and a speed of 250 rpm. Finally, dumb-bell shape standard test specimens were injection molded with a HAAKE minijet according to ISO 527, type 5 A. Prepared dumb-bell specimens were put in a climate room with a temperature of 23 °C and a relative humidity of 50% for 24 h prior to tensile testing.

3. Characterization

3.1. Wide angle X-ray scattering (WAXS)

3.1.1. Sample preparation: powder samples (isotropic)

Composite samples were embrittled in liquid N_2 and milled directly in a centrifugal grinding mill (Retsch ZM100, 1 mm sieve). The powdered samples then were packed, to a reproducible density, into an appropriate sample holder of 1 mm thickness between two PET films.

Clay samples were prepared with 50 wt% cellulose powder to dilute the samples and reduce the high absorption effects in transmission mode.

3.1.2. Injection molded testing bars (non isotropic)

The testing bars were cut lengthwise into narrower pieces and then fixed parallel on the sample holder.

3.1.3. Measurement details

WAXS studies of the samples were carried out using a Bruker-AXS two-circle-diffractometer D5000 (40 kV, 30 mA) equipped with Cu-Kα_1 radiation ($\lambda = 0.15406$ nm) and a curved Ge(1 1 1) monochromator at a scanning rate of 0.1°/50 s in transmission mode. The 2θ-range from 2° to 15° was measured thrice for each sample.

3.2. Transmission electron microscopy (TEM)

TEM images were taken from cryogenically microtomed ultra-thin cross sections (60 nm) using a Phillips CM 200 at an acceleration voltage of 120 kV.

3.3. Tensile tests

Tensile properties of samples were measured using a Zwick 1445 universal testing machine at 23 °C and 50% relative humidity. Initial clamp separation and crosshead speed were 44 mm and 22 mm/min, respectively. All measurements were performed at least for six replicated dumb-bell shaped specimens and averaged.

3.4. Impact tests

Charpy impact tests were carried out on unnotched specimens with pendulum impact tester PSW 1 Joule type, from the company Wolfgang Ohst Rathenow, Germany and standard injection molded test bars with $4 \times 10 \times 80\,mm^3$.

3.5. Heat deflection temperature (HDT)

HDT-A values were determined from a DMA three point bending arrangement (same instrument) according to EN ISO 75 (without oil bath) with a temperature ramp of 2 °C/min, a stress of 1.82 MPa

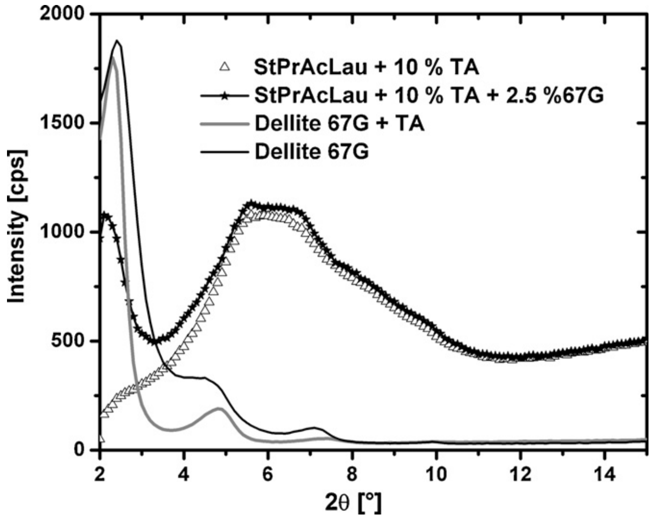

Fig. 1. X-ray diffraction of StPrAcLau nanocomposites with Dellite 67G.

and a maximum strain of 0.2% (all values taken for the tensioned outer fiber of the beam).

3.6. Dynamic mechanical analysis (DMA)

DMA was carried out by using a TA Instrument DMA 2980 in a single cantilever mode from −30 to 200 °C with a frequency of 1 Hz and a heating rate of 2 °C/min based on the ASTM D648.

During testing dynamic mechanical property parameters of storage modulus and loss factor (tan δ) were recorded as a function of temperature. T_g was determined as the temperature at the maximum of the tan δ curve.

4. Results and discussion

4.1. Orientation of clay platelets – WAXS

Wide angle X-ray scattering (WAXS) was used to study the orientation of the clay platelets in the StPrAcLau/Dellite 67G system, the most interesting one in terms of mechanical properties (see mechanical properties), in particular impact strength. Although a good dispersion and small tactoids were found with TEM (see TEM images, Fig. 3C), the first order of the clay (0 0 1) peak is clearly visible in the composite as shown in Fig. 1.

Along with the isotropized composite scattering curve (stars), the curves for the StPrAcLau matrix (triangles) alone and the pure Dellite 67G (black line) as well as TA swollen Dellite 67G (gray line), both arbitrarily down scaled, are displayed in Fig. 1. Second and third order reflections are seen for the clay samples, which are no longer detectable in the composite.

Estimating the crystallite size in the (0 0 1) direction for the pure and the swollen clay with the Scherrer equation (Klug & Alexander, 1974), gives values of 12.3 nm and 15.0 nm, respectively. In other words, what are seen by WAXS are coherent scattering entities of 12–15 nm thickness and not the much larger micron scaled clay particles themselves. With layer spacing of 3.55 nm and 3.76 nm from the peak positions of the pure and swollen clay, respectively, and using the Bragg equation, it is obvious that only 4–5 silicate layers are involved in building up a typical clay crystallite visible with WAXS. In the composite, these coherent scattering entities survive despite the good dispersion observed in TEM and the tactoids visible in TEM consist of 4–5 silicate layers on average.

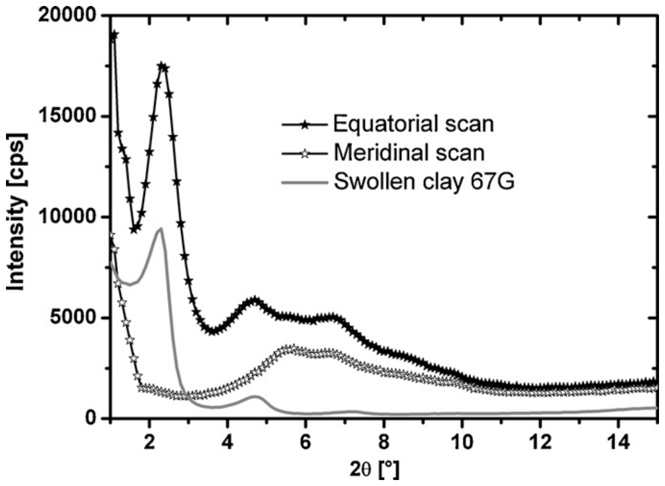

Fig. 2. Orientation of Dellite 67G in the StPrAcLau nanocomposite.

Moreover, a preferred orientation of the tactoids is seen with WAXS on the injection molded test bars. In Fig. 2, an equatorial scan of the StPrAcLau composite with 10% TA and 2.5% Dellite 67G (solid stars) is presented along with a meridinal scan (open stars) and the scattering curve of the swollen clay (gray line).

There is no peak around 2.5° along the meridian meaning that no clay platelets are laying exactly perpendicular to the injection molding direction. In contrast, a pronounced peak is detected when the sample is rotated by 90° perpendicular to the injection molding direction and the equator is scanned. In this geometry, crystallites that have their silicate layers parallel to the 4 mm wide small sides of the injection molded bar are irradiated and scatter, if present. The peak means that an appreciable amount of platelets have this orientation. By turning the sample 90° along the molding direction, platelets parallel to the 10 mm wide surface of the bar are tested and give the same scattering curve with the peak at 2.5°, not shown in Fig. 2 for clarity. This means that the clay tactoids have a clear preferred orientation parallel to the sample surfaces perpendicular to the molding direction.

4.2. Dispersion of clays in starch mixed esters matrix – TEM

Clay dispersion has been investigated by TEM and micrographs for 60 nm cuts through the injection molded composites are shown in Fig. 3 for the system StPrAcLau plus 10% TA with 2.5% Dellite LVF (A), Dellite 43B (B), and Dellite 67G (C) and in Fig. 4 for the StAcPrLau system with 15% TA and 5% Dellite LVF clay (A) and Dellite 43B clay (B).

Obviously, clay particles with dimensions in 5 the μm range remain when unmodified Dellite LVF clay is added both for the propionate rich system (Fig. 3A) and for the acetate rich one (Fig. 4A). Although a clearly positive effect of Dellite LVF on the strength of the SrPrAcLau system is seen in Table 1 (see mechanical properties), usually an indication of successful dispersion, the TEM micrographs reveal only a limited break up of the clay particles and no significant differences between the propionate rich system and the acetate rich one.

The situation is different for the organo-modified clays Dellite 43B and Dellite 67G. Here, the clay particles are broken up and a rather homogeneous structure with clay tactoids drastically reduced in size down to the nm range is revealed. Comparing the Dellite 43B and Dellite 67G systems in Fig. 3, somewhat longer platelets seem to be present in the Dellite 43B case while the clay sheets are shorter for Dellite 67G and possibly more finely dispersed.

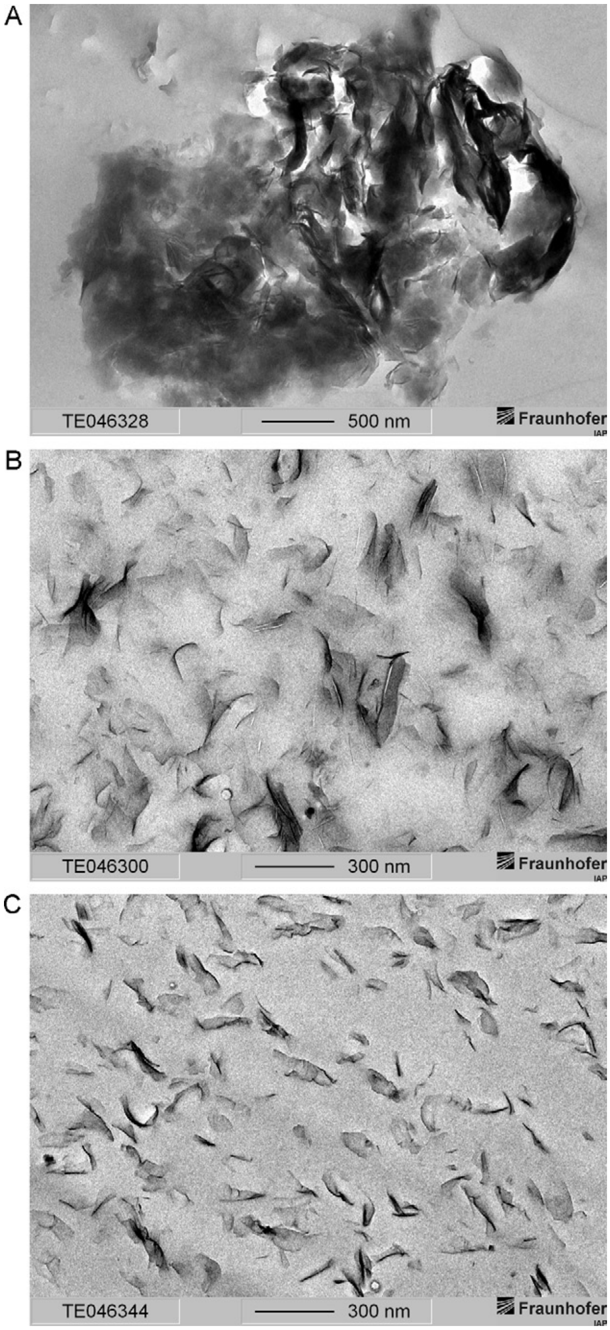

Fig. 3. TEM micrographs of nanocomposites: (A) StPrAcLau/10 wt% TA/2.5 wt% Dellite LVF, (B) StPrAcLau/10 wt% TA/2.5 wt% Dellite 43B, (C) StPrAcLau/10 wt% TA/2.5 wt% Dellite 67G.

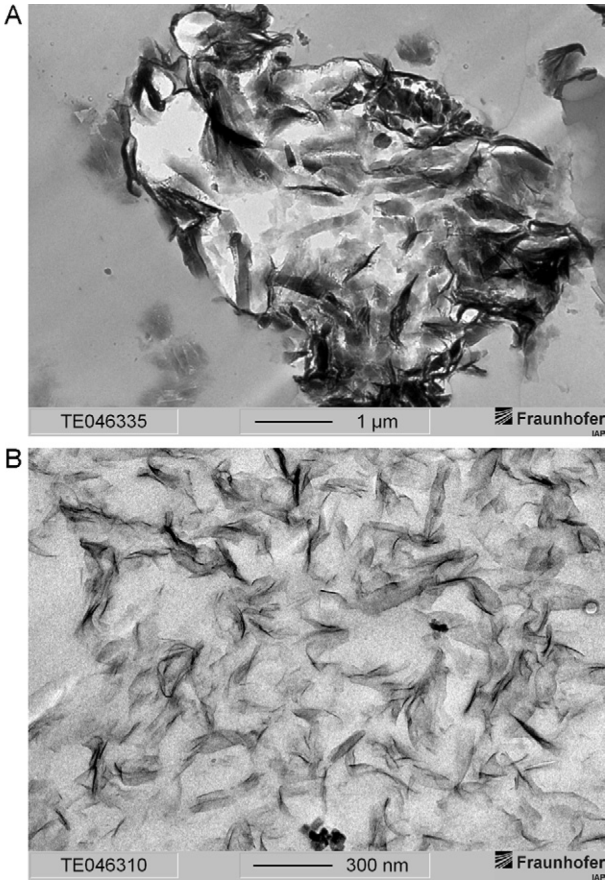

Fig. 4. TEM micrographs of nanocomposites: (A) StAcPrLau/15 wt% TA/5 wt% Dellite LVF, (B) StAcPrLau/15 wt% TA/5 wt% Dellite 43B.

4.3. Effect of plasticizer and nanoclays on the properties of StPrAcLau

Tensile properties and impact strength of plasticized StPrAcLau and their nanocomposites with unmodified clay (Dellite LVF) and organo-modified clay (Dellite 43B) are presented in Table 1.

With increasing plasticizer content, clay free systems show a systematic decrease in modulus. Within the error margins, tensile strength decreases and impact strength increases monotonously. This is the expected behavior.

The addition of clay causes a systematic increase in stiffness: the higher the amount of clay the higher the modulus. Always the organo-modified clay (Dellite 43B) is better performing than the unmodified one (Dellite LVF) for better dispersion as can be seen from TEM images. The inverse trend is seen for elongation at break: the clay always lowers this value. However, Charpy impact strength is increased with the organo-modified clay. This is an unusual behavior even more pronounced for the second organo-modified clay, Dellite 67G, as demonstrated in Fig. 5.

With this clay, considerable improvements in strength, modulus, and impact strength have been achieved. The unnotched Charpy impact value is improved from 3 kJ/m^2 to almost 15 kJ/m^2 for the system with only 2.5% Dellite 67G, i.e. a five-fold increase

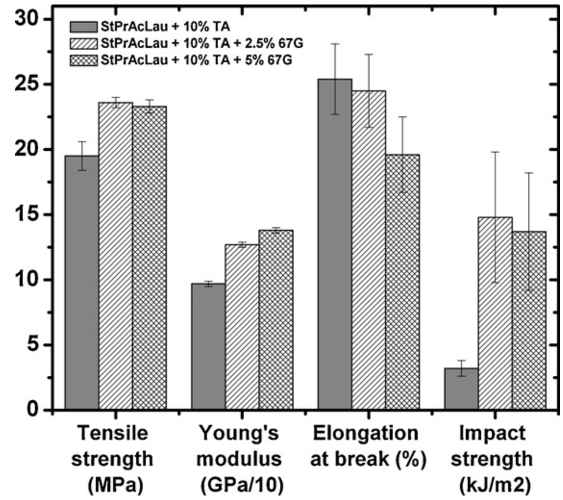

Fig. 5. Mechanical properties of plasticized StPrAcLau and StPrAcLau/clay hybrid.

Table 1
Tensile, dynamic mechanical and impact properties of plasticized StPrAcLau nanocomposites.

Type of starch	TA content (%)	Type of nanoclay	Amount of nanoclay	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	T_g (°C)	HDT (°C)	Charpy impact (KJ/m^2)
StPrAcLau	–	–	–	22.8 ± 1.3	1.55 ± 0.01	1.6 ± 0.1	130	87.9	2.1 ± 0.5
StPrAcLau	5	–	–	24.7 ± 2.6	1.40 ± 0.02	2.5 ± 0.5	108	70.5	1.8 ± 0.2
StPrAcLau	10	–	–	19.5 ± 1.1	0.97 ± 0.02	25.4 ± 2.7	88	52.5	3.2 ± 0.6
StPrAcLau	10	LVF	2.5	24.4 ± 0.2	1.26 ± 0.01	14.3 ± 2.4	94	56.5	2.7 ± 0.7
StPrAcLau	10	43B	2.5	27.1 ± 0.8	1.48 ± 0.01	12.0 ± 2.0	95	56.3	6.6 ± 2.1
StPrAcLau	10	LVF	5	25.1 ± 0.6	1.33 ± 0.02	18.2 ± 2.5	96	56.6	3.1 ± 0.6
StPrAcLau	10	43B	5	24.0 ± 0.5	1.64 ± 0.02	16.8 ± 1.1	96	56.6	7.3 ± 2.0
StPrAcLau	20	–	–	7.8 ± 0.3	0.33 ± 0.06	27.0 ± 3.0	60	29.6	n.b.
StPrAcLau	20	LVF	5	10.8 ± 0.6	0.60 ± 0.08	23.3 ± 1.4	67	36.9	n.b.
StPrAcLau	20	43B	5	13.4 ± 0.3	0.88 ± 0.01	17.0 ± 2.7	70	41.3	n.b.

Table 2
Tensile, dynamic mechanical and impact properties of plasticized StAcPrLau nanocomposites.

Type of starch	TA content (%)	Type of nanoclay	Amount of nanoclay	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	T_g (°C)	HDT (°C)	Charpy impact (KJ/m^2)
StAcPrLau	–	–	–	21.2 ± 1.9	1.94 ± 0.006	1.13 ± 0.12	148	109.2	2.1 ± 0.1
StAcPrLau	5			20.3 ± 1.2	1.88 ± 0.01	1.2 ± 0.1	124	74.9	2.2 ± 0.9
StAcPrLau	10	–	–	25.2 ± 1.2	1.51 ± 0.03	2.6 ± 1.2	108	64.4	2.1 ± 0.9
StAcPrLau	10	LVF	5	20.1 ± 1.6	1.71 ± 0.05	1.3 ± 0.1	113.5	74.4	1.5 ± 0.3
StAcPrLau	10	43B	5	27.1 ± 5.4	2.11 ± 0.02	1.7 ± 0.6	109	67.8	1.7 ± 0.6
StAcPrLau	15	–	–	21.5 ± 1.1	1.28 ± 0.03	2.8 ± 0.7	89	53.5	1.8 ± 0.4
StAcPrLau	15	LVF	5	23.7 ± 0.7	1.40 ± 0.02	13.2 ± 1.8	96	55.4	1.5 ± 0.4
StAcPrLau	15	43B	5	24.6 ± 3.0	1.76 ± 0.03	2.2 ± 0.7	98	58.9	1.5 ± 0.3
StAcPrLau	20	–	–	12.9 ± 0.3	0.80 ± 0.02	22.8 ± 2.0	72	42.3	10.5 ± 3.5
StAcPrLau	20	LVF	5	15.9 ± 0.3	1.1 ± 0.01	18.1 ± 1.8	80	50.1	4.8 ± 3.1
StAcPrLau	20	43B	5	18.7 ± 0.3	1.46 ± 0.01	13.7 ± 0.7	85	50.9	2.8 ± 1.0

was accomplished. At the same time, both stiffness and strength are increased by 20 and 30% respectively. For the system with 2.5% Dellite 43B (cf. Table 1) the increase in these latter two values is higher, namely 40 and 50%, respectively. However, Charpy impact strength is only doubled compared to the five-fold increase for Dellite 67G. One possible explanation could be the finer dispersion of Dellite 67G; as shown in TEM images.

For the highly plasticized system with 20% TA, the increase in modulus by 166% is accompanied by an increase in strength of 70%.

Thermal properties of the plasticized StPrAcLau and their composites are also listed in Table 1. Glass transition temperatures were determined from tan δ DMA curves, examples of which are shown in Fig. 6 along with the storage moduli.

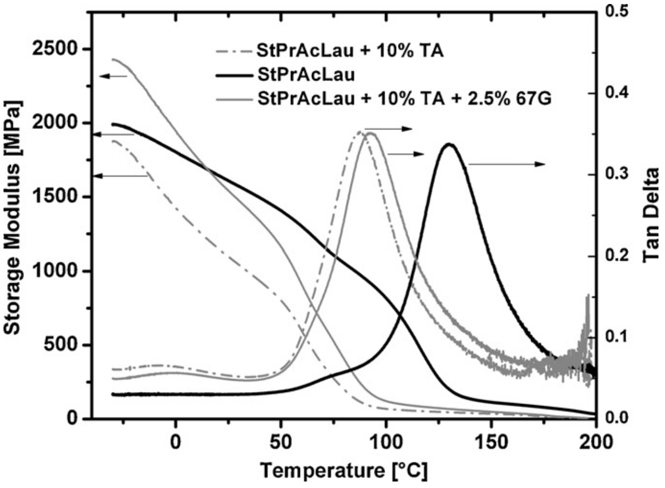

Fig. 6. Storage modulus and tan δ behavior of plasticized StPrAcLau and StPrAcLau/clays hybrid.

Obviously, the addition of plasticizer reduces T_g to an appreciable amount. This is the expected behavior. The clays, in turn, are able to increase this value only slightly. This is the case for HDT as well (see Table 1). This is true both for organo-modified and unmodified clays. The best effect is seen in HDT for the soft system with 20% plasticizer content. In particular with the organo-modified clay Dellite 43B, the HDT value is improved from 30 °C to 41 °C.

4.4. *Effect of plasticizer and nano clays on the properties of StAcPrLau*

Table 2 shows the tensile properties, DMA tan δ glass transition and HDT values as well as unnotched Charpy strength for plasticized StAcPrLau and plasticized StAcPrLau/nanoclay hybrids.

Again, for the clay free systems, a systematic decrease in modulus is observed with increasing plasticizer content. However, the stiffness is generally on a higher level compared to the StPrAcLau system owing to the lower percentage of the longer, propionate alkyl chains, which soften the StPrAcLau system ($DS_{Prop} = 0.63$ for StAcPrLau *vs.* $DS_{Prop} = 2.31$ for StPrAcLau). Accordingly, an elongation of more than a few percent is reached only with as much as 20% of plasticizer.

Up to 15% of plasticizer, the addition of clay has a positive effect only on stiffness, which is improved by approximately 40% for the modified clay Dellite 43B. The unmodified Dellite LVF is not as effective, however, one exception is observed: in the system with 15% TA, the tensile elongation is increased drastically.

The clay micron scaled particles have a plasticizing effect without, however, improving the impact properties. This tendency shows that extent of plasticization leads to greater chains mobility of starch rich acetate. This same effect has been observed before for pure starch acetate (DS = 2.6) with 20% TA plasticizer (Hassan Nejad, Ganster, & Volkert, 2010, Fig. 4).

Pandey & Singh (2005) has explained this improvement in strain happens when plasticizer was mixed after starch diffusion inside the clay gallery; it can migrate throughout the system owing to its smaller size and retaining the plasticizer efficiency. In this case the explanation cannot be accepted because this effect does not happen in lower or higher plasticizer content. A possible explanation might be that the non-exfoliated, micron sized clay particles act as internal mixing elements, improving homogeneity and bringing out the proper potential of the matrix material.

In the highly plasticized system with 20% TA, again, a modulus increase of 80% is accompanied by an increase in strength by 45%.

In contrast to the StPrAcLau system, in no case the Charpy impact value was improved by the addition of nano clay.

The thermal properties T_g and HDT behave quite similar to the StPrAcLau system. No remarkable improvements could be obtained.

5. Conclusion

Mechanical properties of novel plasticized starch mixed esters could be improved considerably by melt intercalation with commercial organo-modified nano clays. A homogeneous distribution of clay tactoids having 4–5 silicate layers on average (estimated using WAXS) was proven by TEM. Orientation of the tactoids parallel to the sample surfaces along the injection molding direction was observed for a particular system by WAXS. In all cases tensile modulus and strength was increased, in particular for soft systems with 20% plasticizer. Even for the plasticized systems without clay addition, brittleness constitutes a problem with this class of materials. With suitable types of organo modified nano clays the situation can be improved considerably. Using 2.5% of specific organo-modified clay with two aliphatic chains and two methyl groups, the Charpy impact strength could be improved 5-fold. Tailoring the modifier composition could be a means to further mitigate the brittleness of the mixed esters.

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References

Ciou, B. S., Yee, E., Glenn, G. M., & Orts, W. J. (2005). Rheology of starch-clay nanocomposites. *Carbohydrate Polymers*, *59*, 467–475.

Gonzalez, Z., & Perez, E. (2002). Effect of acetylation on some properties of rice starch. *Starch*, *54*, 148–154.

Gros, A. T., & Feuge, R. O. (1962). Properties of the fatty acid esters of amylose. *Journal of American Oil Chemist's Society*, *39*, 19–24.

Hassan Nejad, M., Ganster, J., & Volkert, B. (2010). Starch esters with improved mechanical properties through melt compounding with nanoclays. *Journal of Applied Polymer Science*, *18*(1), 503–510.

Huang, M. F., Yu, J. G., & Ma, X. F. (2004). Studies on the properties of montmorillonite-reinforced thermoplastic starch composites. *Polymer*, *45*, 7017–7023.

Kampeerapappun, P., Aht-ong, D., Pentrakoon, D., & Srikulkit, K. (2007). Preparation of cassava starch/montmorillonite composite film. *Carbohydrate Polymers*, *67*, 155–163.

Klug, H. P., & Alexander, L. E. (1974). *X-ray diffraction procedures* (2nd ed.). John Wiley & Sons Inc., ISBN 978-0471493693, pp. 687–703.

Pandey, J. K., & Singh, R. P. (2005). Green nanocomposites from renewable resources: Effect of plasticizer on the structure and material properties of clay-filled starch. *Starch*, *57*, 8–15.

Qiao, X., Jiang, W., & Sun, K. (2005). Reinforced thermoplastic acetylated starch with layered silicates. *Starch*, *57*, 581–586.

Rudolph, S. E., & Glowaky, R. C. (1978). Preparation and properties of carboxyl-functional mixed esters of hydrolyzed starch. *Journal of Polymers Science: Polymer Chemistry Edition*, *16*, 2129–2140.

Volkert, B., Lehmann, A., Ganster, J., Hassan Nejad, M., & Wetzel, H. (2010). Comparison of different synthesis routes of starch acetates and resulting thermoplastic properties. *Carbohydrate Polymers*, *79*(3), 571–577.

Xu, Y., & Hanna, M. A. (2005). Physical, mechanical and morphological characteristics of extruded starch acetate foams. *Journal of Polymers and the Environment*, *13*, 221–230.

Xu, Y., Zhou, J., & Hanna, M. A. (2005). Melt-antercalated starch acetate nanocomposite foams as affected by type of organoclay. *Cereal Chemistry*, *82*(1), 105–110.