Carbohydrate Polymers 102 (2014) 216–222

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Preparation and characterization of acetylated corn starch–(PVOH)/clay nanocomposite films

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ARTICLE INFO

Article history:
Received 30 August 2013
Received in revised form
21 November 2013
Accepted 23 November 2013
Available online 1 December 2013

Keywords:
Acetylated corn starch
PVOH
Clay nanocomposites
Properties

ABSTRACT

Acetylated corn starch (ACS)-based clay (NaMMT) nanocomposite films, with or without addition of polyvinyl alcohol (PVOH), were prepared by casting with glycerol as a plasticizer. The obtained nanocomposite structure was ascertained by XRD study for all polymer–clay nanocomposites. XRD patterns are indicative of an intercalated nanocomposite structure. Mechanical and thermomechanical properties of polymer nanocomposites were studied. The addition of clay induces significant reinforcing effects in the thermoplastic ACS systems. Replacement of glycerol with PVOH in the ACS–NaMMT system results in superior mechanical strength, due to the creation of hydrogen bonds between the ACS and the PVOH chains. Enhancement in water barrier properties was observed for all nanocomposite films, which reaches up to 67% for acetylated starch–PVOH–clay nanocomposites in comparison to acetylated thermoplastic starch, as indicated by water vapor transmission measurements.

1. Introduction

The increased application of biodegradable polymers in environmental friendly packaging and biomedical materials has drawn the attention of numerous researchers in academia and industry in recent years (Aouada, Mattoso, & Longo, 2011; Avella et al., 2005; Averous & Halley, 2009; Chen & Evans, 2005; Muller, Laurindo, & Yamashita, 2011). Starch, a natural polymer, has been considered as one of the most promising candidates especially due to its attractive combination of low price and availability.

Starch is composed of amylose (poly-α-1,4-D-glucan) and amylopectin (poly-α-1,4-D-glucan and α-1,6-D-glucan). It is based on α(1–4) (~95%) and α(1–6) linkages (~5%) constituting branching points which are localized every 22–70 glucose units and generate a type of grape branched-like structure with attached chains (Averous & Halley, 2009).

To produce thermoplastic starch (TPS), the granular structure of starch should be either completely or partially destroyed and transformed into amylose/amylopectin semicrystalline matrix under high temperature and/or pressure and in the presence of plasticizers (van Soest, Hulleman, de Wit, & Vliegenthart, 1996). Water, glycerol, sorbitol and sugars have been used as plasticizers to improve the processability and thermoplastic properties of starch (Orts et al., 2007; Muller, Yamashita, & Laurindo, 2008). However, its low water resistance due to hydrophilic character, and high T_g limit its usefulness in packaging applications.

Chemical modifications of starch including esterification are efficient methods to improve its properties. In acetylated starch, part of the hydroxyl groups in anhydroglucose units have been converted to acetyl groups. Acetylated starch (AS) is synthesized by the reaction of native starch with acetic anhydride in an aqueous medium in the presence of sodium hydroxide as catalyst. The acetyl groups introduced into the starch chains are said (Han et al., 2012) to be capable of disrupting inter- and intramolecular hydrogen bonds, thereby weakening the granular structure of starch leading to an increase in motional freedom of starch chains in amorphous regions. That is why the presence of CH_3CO— group yields starch with many unique properties, such as an increase in solubility, swelling power, clarity, reduced gelatinization temperature and decreased tendency toward retrogradation (Schlemmer, Angelica, & Sales, 2010). Heat sealing capacity of native and acetylated corn starch based films has been evaluated to develop biodegradable packages, such as bags (López, Lecot, Zaritzky, & Garcνa, 2011). For all tested films tensile strength, storage modulus (E') and height of the relaxation peak (tan δ vs. temperature curves) of the starch-rich phase, showed a similar trend: native starch < native/acetylated starch blend < acetylated starch.

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http://dx.doi.org/10.1016/j.carbpol.2013.11.030

Physical and mechanical properties of gelatinized starch can be improved by coprocessing of starch with a polar synthetic polymer (e.g. polyvinyl alcohol – PVOH) (Chiellini, Corti, D'Antone, & Solaro, 2003). Also, starch blended PVOH is reported to possess improved tensile strength. The formation of hydrogen bonds of hydroxyl functional group (—OH) between starch and PVOH tends to promote localized stability and subsequently improves miscibility of starch and PVOH (Siddaramaiah & Somashekar, 2004). However, their low water resistance and poor mechanical properties, compared to classic polymers, limit their applications.

A number of researchers have investigated ways to improve the properties of starch-based materials using nanocomposites (Chen & Evans, 2005; Dimonie, Constantin, Vasilievici, Popescu, & Garea, 2008; Fischer, 2003; Huang, Yu, & Ma, 2004; Park et al., 2002; Park, Lee, Park, Cho, & Ha, 2003). Intercalated starch/clay samples have been produced (Park et al., 2002, 2003) with a batch mixing process, using a number of different montmorillonite clays and high levels of plasticizers content. Water and glycerol were used as plasticizers. These materials exhibited particular improvements in Young modulus and barrier properties. Thermoplastic starch/clay nanocomposites prepared with reduced level of plasticizer (Huang et al., 2004) exhibited improved tensile properties. In Ref. Chen and Evans (2005) was observed good clay dispersion and a subsequent increase in modulus using both solvent casting and melt extrusion in thermoplastic starch nanocomposites. In Ref. Fischer (2003) was produced a series of thermoplastic starch/clay nanocomposites via melt extrusion and solvent casting methods. Exfoliated type structures were formed for nanocomposites with high plasticizer content.

The addition of small amounts of PVOH to the starch nanocomposite produced a very ordered intercalated structure (Dean, Do, Petinakis, & Yu, 2008; Dimonie et al., 2011). The relative concentrations of PVOH and Na-Montmorillonite (NaMMT) were directly correlated to changes in intergallery spacing. The improvement in mechanical properties was attributed to both interfacial interactions and the disruption of the retrogradation. The effect of PVOH molecular weight on the intercalation, mechanical and water barrier properties of starch nanocomposites containing glycerol has been investigated by Ali, Tang, Alani, and Faubion (2011). It was found that the higher the molecular weight, the lower the ability of the PVOH chains to intercalate within the clay galleries. Higher tensile strength and lower water vapor permeability was documented for nanocomposites with higher molecular weight PVOH, which was attributed to greater physical entanglement of the PVOH polymer chains, lower solubility and higher polymer viscosity and not to the interaction of the PVOH with the clay platelets.

The aim of the present work is the preparation and characterization of starch nanocomposites utilizing all the above-referred modifications of native starch, namely acetylation, plasticization, PVOH blending, and nanoclay addition. Therefore acetylated thermoplastic starch/NaMMT nanocomposite films with or without PVOH and/or glycerol were prepared. Two types of PVOH with different molecular weights were used in order to assess the effect of the chain length on the structure and performance of the obtained nanocomposites. X-ray diffraction (XRD) gives quantitative data on the dispersion of the clay platelets and has been used to characterize the nanocomposites structure. Mechanical and thermomechanical properties are of key importance for the applicability of polymer nanocomposites. The tensile properties of the prepared films were therefore determined. The mechanical response in a wide range of temperatures and the glass transition temperature was evaluated using dynamic mechanical analysis (DMA). Finally the water vapor transmission of the aforementioned systems was part of the current study.

2. Experimental

2.1. Materials

Acetylated corn starch (ACS) was kindly provided by New Zealand Starch Ltd. Glycerol (G), polyvinyl alcohol (PVOH) and montmorillonite clay, Nanomer® PGV (NaMMT) were purchased from Aldrich. Two different PVOHs were used, which were both 87–89% hydrolyzed and had molecular weight (M) of 13,000–23,000 (code name: PVOH1) and 31,000–50,000 (code name: PVOH2), respectively.

2.2. Preparation of starch/clay nanocomposite films

A clay suspension in distilled water with different clay contents (3 and 5 wt%) was let it stirred for 24 h in room temperature. Another suspension of starch in distilled water was heated to boil in a spherical bottle with reflux condenser and after gelatinization of starch the clay suspension was added and let it stirred for half an hour. Then the calculated amount of glycerol and/or PVOH was added to the starch/clay mixture and was stirred for 10 min. The mixture was laid to petri dishes and let it dry in an oven at 45 °C for 72 h. These composites were hot pressed in a manually operated hydraulic press, at 120 °C and 2.5 MPa, to produce films. Films were kept sealed in PE bags for further characterization. The relative humidity within the PE bags was 60% as measured using a digital hygrometer.

2.3. XRD analysis

Samples of thermoplastic acetylated starch, NaMMT, thermoplastic starch/PVOH blends, glycerol/NaMMT and acetylated starch/NaMMT for X-ray diffraction analysis were prepared by spreading about 1 mL of their water suspension (10 mg/mL) on glass slides. The water was evaporated (at RT) before the X-ray measurements. The XRD measurements were performed on a D8 Advanced Bruker diffractometer with CuK_a radiation ($\lambda = 1.5418$ Å) and the basal spacing of the samples was estimated from the d-spacing of the 0 0 1 reflection. XRD analyses of nanocomposites took place on films prepared using a hydraulic press with heated platens, in the same diffractometer.

2.4. Tensile measurements

Tensile tests were performed according to ASTM D882 using a miniature material tester with a 1000 N load cell. Three to five rectangular samples (100 mm × 10 mm × 0.4 mm) of each formulation were clamped between the grips (50 mm initial distance) and tensioned at a crosshead speed of 2 mm/min. Force (N) and deformation (mm) were recorded during the test. The results obtained from the mini-tester can only be used for comparison, because the strain values are based on the rotational movement of the drive shaft. Baseline samples (not containing nanoclays or PVOH) were tested at the beginning of each set of samples for comparison.

2.5. Dynamic mechanical analysis (DMA)

The dynamic mechanical behavior of the nanocomposites containing ACS/G/MMT and ACS/G/PVOH/MMT were selected and measured on a NETZSCH DMA 242C apparatus. Dynamic temperature spectra of the samples were obtained in tensile mode at a vibration frequency of 1 Hz, at temperatures ranging from −110 to 130 °C, at a rate of 2 °C/min. Cooling was achieved using liquid N_2. The amplitude of the deformation was 30 μm, which was small enough to ensure a linear viscoelastic response from the samples.

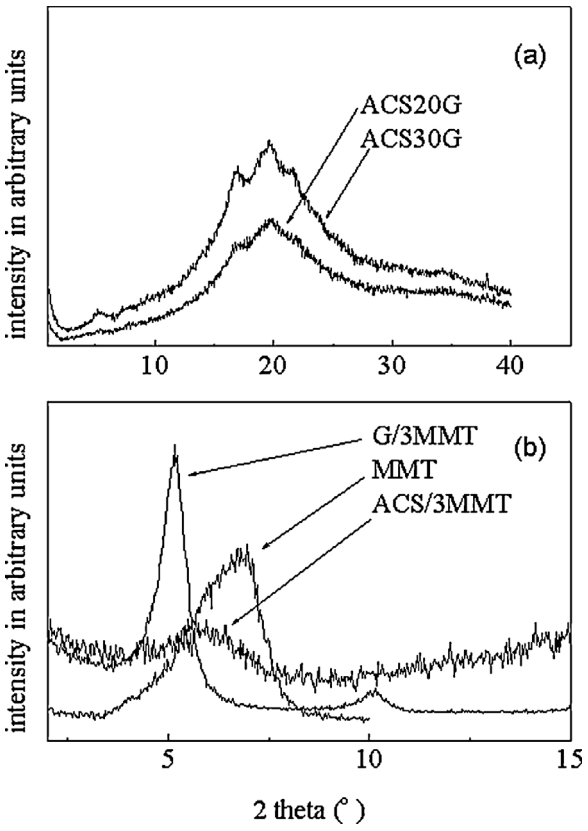

Fig. 1. XRD patterns of (a) ACS20G, ACS30G and (b) MMT, G/3MMT and ACS/3MMT.

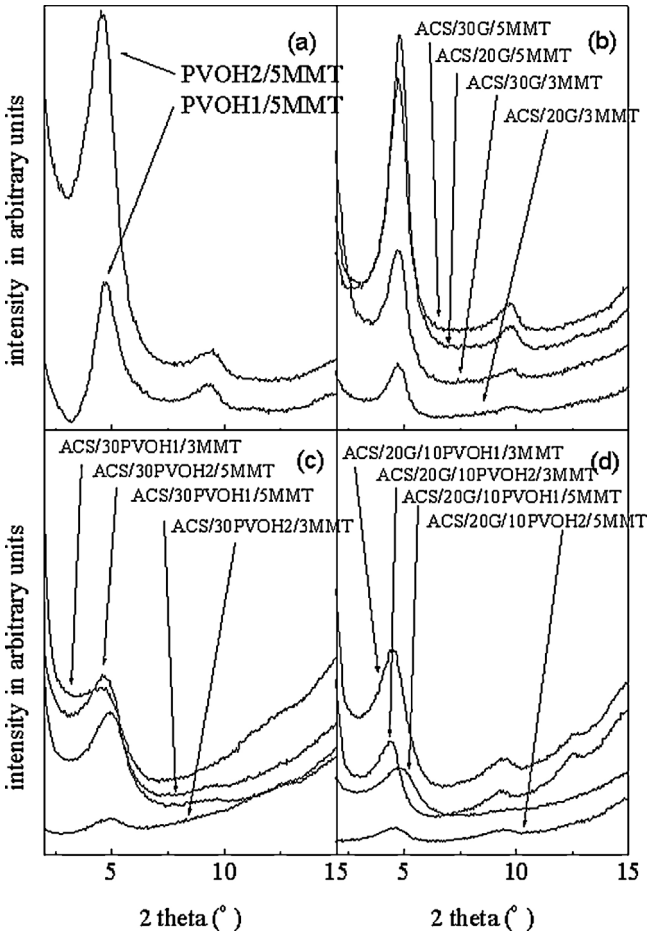

Fig. 2. XRD patterns of (a) PVOH/clay nanocomposites, (b) thermoplastic ACS/clay nanocomposites, (c) ACS/PVOH/clay nanocomposites and (d) thermoplastic ACS/PVOH/clay nanocomposites.

2.6. Water vapor transmission (WVT)

Water vapor transmission (WVT) of neat thermoplastic acetylated starch, acetylated starch/PVOH blends and thermoplastic acetylated starch based nanocomposite films was determined at 38 °C using the apparatus and methodology described in the ASTM E96/E 96M-05 and Ref. Giannakas, Spanos, Kourkoumelis, Vaimakis, and Ladavos (2008). Films with 0.1 mm thickness were sealed by a rubber O-ring on top of Plexiglas test bottles containing dried silica gel and then placed in a glass desiccators with 200 ml saturated magnesium nitrate solution (50% relative humidity (RH)). Test bottles were weighed periodically for 24 h and the WVT was calculated according to the equation:

$$\mathrm{WVT} = \frac{\Delta W/t}{A}$$

where ΔW is the weight gain of the tested bottles, t is the time during which ΔW occurred, $\Delta W/t$ is the slope of the straight line in the diagram $\Delta W = f(t)$ and A is the permeation area. Tensile strength, DMA and water vapor permeation measurements were carried out on nanocomposite films prepared using a hydraulic press with heated platens.

3. Results and discussion

3.1. XRD analysis

The XRD traces for the neat thermoplastic acetylated starch (ACS20G and ACS30G) and thermoplastic starch/PVOH blends were predominantly very broad, showing a main amorphous peak mainly due to the gelatinized starch at 19.7° spanning from 10° to 30° – see Fig. 1a. The XRD patterns of the parent NaMMT, glycerol/NaMMT (G3MMT) and acetylated corn starch/NaMMT (ACS/3MMT) are shown in Fig. 1b. An increase of the basal spacing (d_{001}) of the NaMMT is observed after the insertion of the acetylated corn starch. More specifically, the pristine montmorillonite shows a d_{001}-spacing of 1.21 nm which correspond to an interlayer space $D = 1.21 - 0.95 = 0.26$ nm, where 0.95 nm is the thickness of the individual clay sheet. In the case of the acetylated starch/NaMMT (ACS/3MMT), very broad and short diffraction beak was obtained. This indicates a non-uniform interlayer opening. The maxima of the peak correspond to basal spacing $d_{001} = 1.50$ nm, with corresponding interlayer space: $D_1 = 0.55$ nm. For the glycerol/NaMMT (G3MMT) the basal spacing was $d_{001} = 1.71$ nm, which corresponds to an interlayer space of $D_2 = 0.76$ nm. In addition to the larger interlayer space of the G3MMT compared to that of the NaMMT, a more ordered layered structure has been also identified for the former material based on the intensity and the sharpness of the XRD reflections.

The XRD patterns of the prepared nanocomposites, in film form, are shown in Fig. 2. The estimated values of basal spacing are tabulated in Table 1. In the systems containing acetylated corn starch and NaMMT (ACS/3MMT) very little order was observed in the XRD patterns giving indication that the system was probably partially exfoliated (see Fig. 1b). When 20 wt% of glycerol was added to the system distinct structural order was observed in the XRD pattern, shown as a peak at 4.8° which corresponds to basal spacing $d_{001} = 1.86$ nm – see Fig. 2b). With increase in glycerol content up to 30 wt% and in NaMMT content from 3 to 5 wt% the intensity of this peak was observed to increase further.

Table 1
The code names of the prepared samples, the w/w% nominal composition, the d_{001} in (nm) of added NaMMT, and the water vapor permeation values (in g/h m^2) of the tested films.

Code names	w/w% of ACS/G/PVOH/MMT	d_{001} (nm)	WVP (g/h m^2)
MMT	0/0/0/100	1.21	–
G/3MMT	0/97/0/3	1.71	–
ACS/3MMT	97/0/0/3	1.50	–
ACS/20G	80/20/0/0	–	28.3
ACS/30G	70/30/0/0	–	30.2
PVOH1/5MMT	0/0/95/5	1.86	–
PVOH2/5MMT	0/0/95/5	1.92	–
ACS/20G/3MMT	77/20/0/3	1.86	22.6
ACS/30G/3MMT	67/30/0/3	1.86	26.0
ACS/20G/5MMT	75/20/0/5	1.83	20.2
ACS/30G/5MMT	65/30/0/5	1.85	2.48
ACS/30PVOH1/3MMT	67/0/30/3	1.90	11.3
ACS/30PVOH2/3MMT	67/0/30/3	1.80	10.3
ACS/30PVOH1/5MMT	65/0/30/5	1.80	11.1
ACS/30PVOH2/5MMT	65/0/30/5	1.88	9.3
ACS/20G/10PVOH1/3MMT	67/20/10/3	1.96	16.1
ACS/20G/10PVOH2/3MMT	67/20/10/3	2.01	15.6
ACS/20G/10PVOH1/5MMT	65/20/10/5	1.82	16.0
ACS/20G/10PVOH2/5MMT	65/20/10/5	1.92	11.3

In the systems containing PVOH and NaMMT the basal spacing was d_{001} = 1.86 nm for PVOH1 and 1.92 nm for PVOH2 (see Fig. 2a). In the XRD patterns of the ACS/PVOH/MMT composites, in film form, peaks that correspond to clay basal spacing are present at similar 2θ angles. The basal spacing values of the clay varied from 1.80 to 1.90 nm (see Fig. 2c).

The XRD patterns of the systems containing thermoplastic acetylated starch, PVOH and NaMMT peaks that correspond to clay basal spacing are still present but are shifted to rather lower 2θ angles (i.e. higher d-spacing values). The basal spacing values of the clays varied from 1.82 to 2.01 nm (see Fig. 2d).

The XRD patterns for all polymer–clay nanocomposites are indicative of an intercalated structure where the biopolymer chains are incorporated between the silicate layers, increasing their gallery height but maintaining their layered stacking with alternating biopolymer/silicate layers.

3.2. Tensile measurements

Regarding the mechanical properties of the tested composites the average values of Young's modulus, tensile strength and elongation at break values along with those at yield point are given in Table 2. Young's modulus of the samples was determined from the slope of the initial elastic region in the stress–strain curves. The yield point is quite significant since it provides information around the formability of the obtained films. Above the yield point plastic deformation is present, which is undesirable during processing. As can be seen in Table 2 in all cases as the NaMMT content increases (from 3 to 5 wt%) Young's modulus and strength values exhibit a significant increment. The mechanical properties are in accordance with the XRD results, where a nano-composite structure was identified.

More specifically, for systems with thermoplastic acetylated starch and glycerol (ACS20G), the value of Young's modulus was 490 MPa. As the glycerol content increases from 20 to 30 wt% (ACS30G) Young's modulus values exhibit a significant decrease to 82 MPa with a parallel increase in the elongation at break from 13.4% to 30.5%. The addition of filler on the other hand induces significant reinforcing effects. For composites with 3 and 5 wt% NaMMT Young's modulus values exhibit an increase by 3–4 times, respectively, in comparison to unfilled thermoplastic acetylated starch–glycerol systems. An even more pronounced enhancement can be found in the case of the tensile strength, where the systems with 3 and 5 wt% NaMMT present an increase by app. 10 times. Elongation at break decreases with an increase in the NaMMT content. The presence of clays in an intercalated/exfoliated structure has been associated with constrained regions which enhance stiffness and strength but on the same time result in lowering the elongation properties due to the prevention of easy sliding of polymer chains against each other (Ali et al., 2011). Best results are being obtained when 20 wt% glycerol is present, in agreement with previous publications (Chiou et al., 2007; Majdzadeh-Ardakani, Navarchian, & Sadeghi, 2010). At higher glycerol contents, the interaction between the NaMMT filler and the acetylated starch becomes less effective, most probably due to higher interactions between the glycerol and starch chains.

Replacement of glycerol with PVOH in the acetylated starch (ACS–PVOH) system induces superior mechanical strength as expressed by the increased Young's modulus and strength values by 6–10 times. The significant decrease in % elongation at break (10 times lower) suggests that PVOH compared to glycerol does not offer any plasticizing effect. The stiffness of the ACS–PVOH blends is higher than that of the nano-modified systems containing glycerol indicating the creation of hydrogen bonds between the ACS and the PVOH chains. There is a distinctive difference in the mechanical performance of systems containing PVOH1 compared to those with PVOH2. A clear increase in the stiffness, strength and elongation at break has been obtained for ACS–PVOH2 blends. This is in line with data from previous publications where an increase in the mechanical performance has been achieved with higher molecular weight PVOH polymers (Ali et al., 2011). The addition of NaMMT in the thermoplastic acetylated starch–PVOH (ACS–PVOH–MMT) system leads to materials with slightly higher stiffness which is more obvious at 5 wt%. The documented properties are in the same range as those published by Majdzadeh-Ardakani and Nazari (2010). As in the case of the unfilled systems, nanocomposites with PVOH2 present superior properties compared to those with PVOH1. At the same time the tensile strength of the ACS–PVOH deteriorated after the addition of NaMMT. The observed improvement in the stiffness of the ACS–PVOH nanocomposite systems is more related to the PVOH–starch interactions which are promoted at higher PVOH molecular weights rather than clay–polymer interactions. As documented in previous studies there is a competition between PVOH–starch–clay interactions and although good clay dispersion is important, the interfacial interactions between the filler and matrix play just as important a role in the overall mechanical performance of the nanocomposite systems (Dean et al., 2008; Majdzadeh-Ardakani & Nazari, 2010).

The combined addition of glycerol and PVOH resulted in a pronounced deterioration of the mechanical performance of the ACS–G–PVOH–MMT systems with the only exception being the stiffness of the ACS/20G/10PVOH/5MMT films. The lower amount of PVOH (10 vs. 30 wt%) used in the combined systems and the presence of glycerol results in lower amount of hydrogen bonds between the PVOH and starch chains, which explains the deterioration in the mechanical performance compared to ACS/30PVOH/MMT films. ACS/20G/MMT systems presented a significant deterioration in strength and elongation at break after the addition of PVOH. Note that the addition of clays was beneficial in ACS/20G/MMT systems, which was attributed to the effective interaction between the NaMMT filler and the acetylated starch. The addition of small amount of PVOH interrupted this interaction, lowering the reinforcing ability of the NaMMT filler.

3.3. Dynamic mechanical analysis

In order to further investigate the interactions between glycerol, PVOH, NaMMT and acetylated starch, the thermomechanical

Table 2
Mechanical properties (Young's modulus, yield and tensile strength and elongation at yield and break) of the tested films.

Code names of the prepared samples	Young's modulus		Yield strength, σy		Elongation at yield		Tensile strength		Elongation at break	
	(MPa)	stdev	(MPa)	stdev	(%)	stdev	(MPa)	stdev	(%)	stdev
ACS/20G	490.57	29.03	4.17	0.10	1.54	0.02	4.65	0.33	13.40	3.17
ACS/30G	82.05	7.46	1.12	0.19	2.86	0.82	3.09	0.48	30.50	6.61
ACS/20G/3MMT	1172.33	327.36	14.33	1.61	1.81	0.50	53.08	2.52	10.67	1.15
ACS/30G/3MMT	146.07	22.64	6.25	2.37	3.67	0.71	15.60	2.08	19.10	1.01
ACS/20G/5MMT	1720.67	97.90	18.52	0.61	1.58	0.09	57.58	0.44	8.30	0.40
ACS/30G/5MMT	393.67	44.61	6.18	0.15	2.49	0.29	29.25	5.21	12.25	3.40
ACS/30PVOH1	3464.22	686.39	27.72	3.04	1.25	0.10	37.69	2.76	2.25	0.07
ACS/30PVOH2	3544.33	735.67	36.12	4.04	1.15	0.04	56.32	6.34	2.95	1.42
ACS/30PVOH1/3MMT	2940.24	1404.43	9.65	0.34	0.54	0.07	18.30	1.41	1.56	0.32
ACS/30PVOH2/3MMT	4368.65	1505.62	6.38	0.01	0.32	0.11	21.90	1.20	2.61	0.23
ACS/30PVOH1/5MMT	4237.26	595.87	12.09	4.04	0.57	0.16	18.95	0.92	1.05	0.05
ACS/30PVOH2/5MMT	6551.06	649.05	16.35	2.98	0.24	0.04	22.35	5.73	2.50	0.42
ACS/20G/10PVOH1/3MMT	641.79	356.79	4.60	0.04	1.86	0.67	8.85	0.49	6.00	1.00
ACS/20G/10PVOH2/3MMT	648.07	101.67	5.00	0.06	1.25	0.15	9.02	0.06	6.70	1.21
ACS/20G/10PVOH1/5MMT	872.47	160.42	6.00	0.06	1.12	0.21	9.47	0.33	1.90	0.60
ACS/20G/10PVOH2/5MMT	2612.05	64.89	11.86	0.03	0.61	0.10	13.22	0.32	1.40	0.30

behavior of ACS/G/MMT and ACS/G/PVOH/MMT systems was studied using the DMA technique. Fig. 3a–c illustrates the thermo-mechanical response (storage modulus (E') and loss factor, ($\tan\delta$)) of the ACS/20G/MMT and ACS/G/POVH/MMT systems at a wide range of temperatures. In Fig. 3a and b, the effect of NaMMT content is discussed in ACS/MMT systems containing PVOH and/or glycerol. Fig. 3c compares ACS/MMT systems with and without PVOH containing the same amount of NaMMT fillers and glycerol.

In Fig. 3a the storage modulus of the ACS/20G/MMT systems with 5 wt% NaMMT is significantly higher than that with 3 wt% at temperatures up to app. −60 °C. Above this temperature similar storage modulus values can be found independent to the NaMMT content. A closer observation of the storage modulus between 20 and 60 °C indicates slightly higher modulus of the system with 5 wt% NaMMT around this temperature. This is more obvious when applying a logarithmic scale in the *y*-axis (see micrograph in Fig. 3) and implies that the NaMMT at higher contents provides some reinforcing ability in line with the results from the tensile measurements.

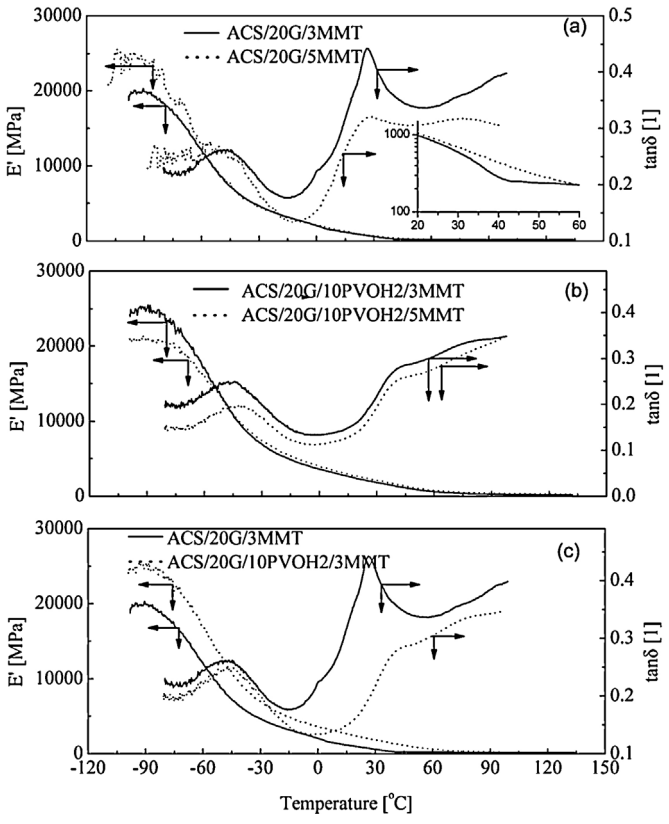

Fig. 3. Storage modulus and loss factor ($\tan\delta$) of (a) ACS/20G/MMT, (b) ACS/20G/10PVOH2/MMT systems and (c) comparison at 3 wt% MMT.

In the $\tan\delta$ curve two relaxation peaks can be observed, one at around −45 °C and a second one at app. 30 °C. The relaxation occurring at lower temperature (T_β) is being associated with the T_g of the glycerol, while the one at higher temperature (T_α) with the T_g of the ACS. The two relaxation peaks indicate the existence of phase separation between domains rich in carbohydrate chains and domains rich in plasticizer (Chivrac, Pollet, Dole, & Avérous, 2010). The systems with 5 wt% NaMMT present slightly higher T_β values and storage modulus compared to those with 3 wt%. This difference can be attributed to interactions between NaMMT and glycerol chains. As aforementioned, above the T_β relaxation, systems with 3 and 5 wt% NaMMT present very similar storage modulus. This is explained by the higher mobility of glycerol above this relaxation temperature, which reduces the reinforcing ability of the NaMMT particles. The broader peak of the $\tan\delta$ curve along with the higher stiffness around the T_α transition for systems with 5 wt% NaMMT, confirm the existence of interactions between the ACS chains and the NaMMT particles.

The effect of NaMMT content in ACS/20G/10PVOH2 systems is being illustrated in Fig. 3b. Up to temperatures of −45 °C the systems containing 3 wt% NaMMT present higher storage modulus compared to that with 5 wt%. Above this temperature the systems with 5 wt% NaMMT behave similarly to those with 3 wt%. The $\tan\delta$ curve presents two relaxation peaks, one at app. −45 °C and one at about 45 °C. The first one is associated with the T_g of the glycerol, and presents a shift from −45 °C to −40 °C for systems with 5 wt% NaMMT. This shift is due to the interaction of higher amount of NaMMT with glycerol. The transition at app. 45 °C is associated to the T_g of the ACS/PVOH blend. There is no phase separation between the two polymers ACS and PVOH. However, this transition is much broader than that of the ACS/20G/MMT systems (see Fig. 3a) due to the interaction of the PVOH with the ACS and the formation of hydrogen bonds between the two polymers. Next to that blending of the two polymers is beneficial since it results to higher T_g by 15 °C compared to the plain ACS. The peak of this transition is identical for systems with 3 and 5 wt% NaMMT. The fact that the NaMMT amount does not result in any changes in the storage

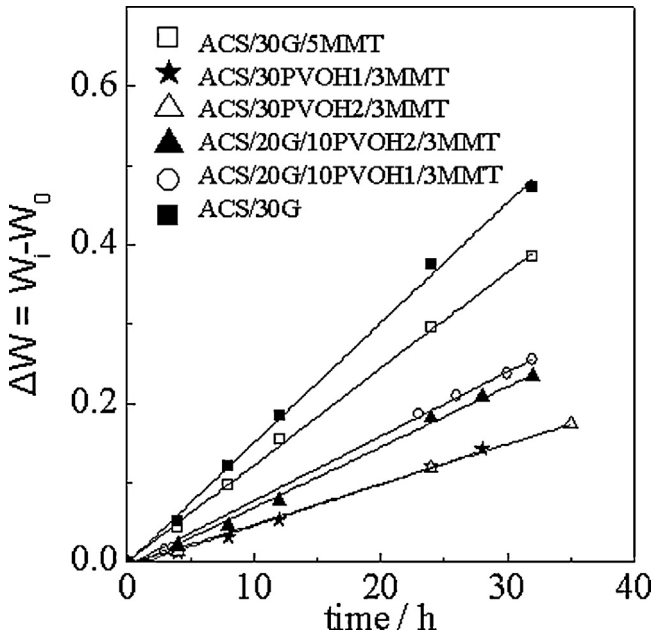

Fig. 4. Weight gain of the WVP's bottles (due to water uptake of the absorbant) as a function of time.

modulus and the T_a indicates that NaMMT interacts effectively with glycerol rather than PVOH and/or ACS, again in line with the tensile results.

A direct comparison of the ACS/20G/MMT and ACS/20G/10PVOH/MMT systems can be found in Fig. 3c for 3 wt% NaMMT content. It is obvious that the addition of PVOH resulted in an overall increase of the structural stability and reduced chain mobility over a wider temperature window, which is illustrated by the increased stiffness for temperatures up to 60 °C (up to 25% higher) and the shift in the T_g values by app. 20 °C. These observations confirm the interaction between the ACS and the PVOH chains and the benefit due to this blending.

3.4. Water vapor permeability

Representative plots of the weight gain, due to water uptake of the absorbant, as a function of time *t* are shown in Fig. 4. From these plots water vapor transmission of the films was calculated and the results are tabulated in Table 1. All nanocomposite films exhibit a significant reduction in water vapor permeability, compared to thermoplastic acetylated starch, which fluctuates between 14% and 29% for thermoplastic acetylated starch–clay nanocomposites, 43–60% for thermoplastic acetylated starch–PVOH–clay nanocomposites and 60–67% for acetylated starch–PVOH–clay nanocomposites (films without glycerol). Glycerol that used as starch plasticizer increases the WVP of tested films. This increment of WVP due to glycerol it is already referred in other studies (Muller et al., 2011; Talja, Helén, Roos, & Jouppila, 2007). The presence of inorganic clay decreases WVP of final nanocomposite films. This result attributed first of all to the fact that in nanocomposites, gas molecules have to take a long and tortuous way around the impermeable clay layers which are distributed in the polymer matrix in comparison with pristine polymer where the penetration of the film is much easier. Water vapor permeation is slightly decreased with increasing NaMMT loading from 3 to 5 wt%. Correlation between the aspect ratio of the clay and the barrier properties was shown that the best barrier properties obtained in polymer nanocomposites with fully exfoliated clay minerals (Yano, Usuki, & Okada, 1997). Therefore, the factor that affects mainly the barrier properties is the structure type of the obtained nanocomposite and not the filler content. Water vapor permeation is considerably decreased with the addition of PVOHs. The effect of PVOH and glycerol in the WVP of soy protein isolate/poly(vinylalcohol)/glycerol blend films was studied (Su et al., 2010). They concluded that WVP of final films were significantly affected by both PVOH and glycerol while WVP values decreased with increasing PVOH content.

4. Conclusions

Thermoplastic acetylated corn starch/Na-MMT nanocomposite films with or without PVOH were prepared. The XRD patterns of polymer–clay nanocomposites are indicative of an intercalated nanocomposite structure where the biopolymer chains are incorporated between the silicate layers, increasing their gallery height but maintaining their layered stacking with alternating biopolymer/silicate layers. Mechanical and thermomechanical properties are of key importance for the applicability of polymer nanocomposites. The addition of NaMMT fillers induces significant reinforcing effects in the ACS-G systems, since both stiffness and strength exhibit an increase in comparison to the unfilled systems. The higher the NaMMT content the higher the thermal stability in a wide range of temperatures as indicated by the thermomechanical results.

An excess amount of glycerol (30 wt%) reduces the reinforcing efficiency of the NaMMT filler and results in deterioration of the stiffness and strength. Replacement of glycerol with PVOH in the acetylated starch–NaMMT (ACS–PVOH–MMT) system results in superior mechanical strength, due to the creation of hydrogen bonds between the ACS and the PVOH chains.

The addition of NaMMT in the ACS–PVOH systems results in marginal improvement of the already enhanced stiffness which is more obvious at high NaMMT contents (5 wt% NaMMT). The blending of PVOH with ACS and glycerol results in a pronounced enhancement of the storage modulus and T_g, which is attributed to the creation of hydrogen bonds and the intercalation of NaMMT with the polymer chains.

All nanocomposite films exhibit significant reduction in water vapor permeability, which reaches to 67% for acetylated starch–PVOH–clay nanocomposites in comparison to thermoplastic acetylated corn starch. Glycerol addition increases the WVP of tested films. Water vapor permeation is slightly decreased with increasing NaMMT loading from 3 to 5 wt%.

Acknowledgments

The authors thank: (i) the Ring of the Laboratory Units and Centers of the U.I. for the DMA experiments and (ii) “New Zealand Starch Ltd.” for the generous donation of acetylated corn starch.

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