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ORIGINAL PAPER

Preparation and Characterization of Clay Nanocomposites of Plasticized Starch and Polypropylene Polymer Blends

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Abstract Plasticized starch (PLS) is a renewable, degradable, and inexpensive polymer, but it suffers from poor mechanical properties. The mechanical properties can be improved by blending PLS with polyolefins, nonetheless, at high PLS content, the mechanical properties remain poor. Here we show that addition of clay can greatly improve the mechanical properties of PLS/polypropylene blends at high starch content. Unmodified and organically modified montmorillonite clays, MMT and Cloisite 30B respectively, were added to blends of glycerol-plasticized starch and polypropylene, compatibilized using maleated polypropylene. TEM indicates that MMT is well dispersed in the PLS phase of the blends, while Cloisite 30B is located both within the PLS phase as well as at the interface between PLS and PP. At high PLS content, the addition of clay increased the tensile strength and tensile modulus by an order of magnitude, while reducing the ultimate elongation only slightly. Such improvements are attributable to both the addition of clay as a reinforcing component, as well as to the change in the two phase morphology due to addition of clay.

Keywords Clay nanocomposites · Thermoplastic starch · Renewable polymers · Degradable polymers

Introduction

It is becoming increasingly apparent that the use of durable, long lasting petroleum based materials for the production of short life span products is not appropriate. The resulting pollution and fears of exhausting non-renewable resources have increased interest in renewable and biodegradable polymers. One such example is plastic based on starch [1, 2]. Starch is a biodegradable, semi-crystalline polymer consisting of linear amylose chains and branched amylopectin chains, both of which have a glucose monomer unit [3]. In its naturally occurring granular form, starch cannot be processed in the same manner as traditional petroleum based thermoplastics. However, the crystallinity of granular starch can be disrupted by plasticization, creating a material called thermoplastic starch or plasticized starch (PLS). Commonly-used starch plasticizers include water and glycerol, which are often used in combination with each other [4, 5]. PLS can be processed like conventional thermoplastic polymers. Nonetheless, it is not competitive with traditional commodity polymers, such as polyethylene and polypropylene, due to its hydrophilicity and poor mechanical properties [6]. Accordingly, significant efforts have been made to improve the mechanical properties of PLS.

One approach is to blend PLS with other polymers known to have better mechanical properties. Blending PLS with renewable and biodegradable polymers such as polycaprolactone or polylactic acid can produce a fully degradable material [7], however these polyesters can be costly and full degradability is not always necessary. In contrast, blending PLS with polyolefins such as polyethylene and polypropylene, is inexpensive and can produce materials with excellent mechanical properties [1, 6, 8–13], although the blend is not fully degradable. In such cases,

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high PLS loadings are desirable, both to maximize the renewable content as well as to maximize biodegradability. Unfortunately, one may expect the mechanical properties to become poorer as the PLS content increases, and indeed the few publications that have examined blends with over 50 wt% PLS all report a decline in mechanical properties as PLS content increases [9, 10, 13, 14].

An alternative approach to improving the mechanical properties is to blend PLS with layered silicates to create PLS-clay nanocomposites [15–18]. A large literature on polymer–clay nanocomposites shows that if well-dispersed, the clay platelets act as a reinforcing agent with high aspect ratio, strength, and stiffness [19–21]. The literature on PLS-clay nanocomposites has been reviewed by Zhao et al. [22], and as expected, the clay increases the tensile strength and modulus of PLS.

This research examines the effect of clay added to two-phase blends of PLS and a polyolefin (polypropylene). Specifically we hypothesize that the clay can improve the mechanical properties of the PLS phase and therefore mitigate the decline in properties as PLS content increases. Thus, PLS/polypropylene blends that retain good mechanical properties even at a high PLS content may be realized.

Materials and Methods

Cassava starch was supplied by Copagra (Nova Londrina, Paraná, Brazil) and injection grade polypropylene was supplied by Quattor (Brazil) and has a density of 0.905 g/cm^3 and MFI of 11 g/10 min (2.16 kg, 190 °C). Maleated polypropylene (MAPP) was supplied by ExxonMobil (USA) ($\rho = 0.9$ g/cm^3 and MFI of 125 g/10 min (1.2 kg, 190 °C)) and had a maleic anhydride content of 0.5–1.0% as quoted by the manufacturer. MAPP is used as a coupling agent to increase compatibility between the PLS and PP phases [23, 24]. Glycerol was obtained from LabSynth Products (Diadema, São Paulo, Brazil). Two nanoclays were used in this research: one with an expected affinity for the PLS phase and the other with an expected affinity for the PP phase. The first is natural sodium montmorillonite (MMT), which is hydrophilic, and expected to be compatible with PLS [16]. The second, used as a control, is Cloisite 30B (30B), which is MMT that has been organically modified with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium salts. The organic modifier is known to intercalate into the clay galleries, thus greatly increasing the affinity of the clay for hydrophobic polymers. In particular, Cloisite 30B can be well-dispersed (i.e. exfoliated) into PP, particularly in the presence of a coupling agent containing polar groups, such as maleic anhydride [25, 26]. MMT and 30B were obtained from Southern Clay Products (Texas, USA).

Preparation and Processing of Materials

Modified and unmodified clays were dried for 24 h at 70 °C and then added to glycerol [5% of the total weight of Plasticized Starch (PLS)] and allowed to sit for 8 h. Wide-angle X-ray diffraction suggests that the glycerol swells the clay and intercalates into the galleries between the clay platelets (see below). To plasticize the starch, the glycerol/clay mixture was then added to dry cassava starch, mixed by hand for 20 min and allowed to sit overnight to allow the glycerol mixture to diffuse into the starch granules. The clay free samples were prepared in the same manner but without the addition of clay to the glycerol. The ratio of glycerol to starch was always 1:1.5 by weight. Sample compositions are listed in Table 1. The composites were processed in an intermeshing co-rotating twin-screw extruder (Coperion Werner-Pfleiderer, model ZSK-26 Mc, $L/D = 44$, $D = 24$ mm) with a side-feeder. The starch and glycerol were passed twice through the extruder at 150 °C to make plasticized starch (PLS) and the extrudate was pelletized. PP and MAPP were mixed by hand and passed through the extruder via the main feeder, while PLS was added in the side feeder. The PP:MAPP ratio was 75:25 and the PP and MAPP blend is referred to as the “PP phase” henceforth in this paper. The temperature profile used was 180 °C for the first three zones of the extruder and 165 °C in the remaining zones which extend from the side feeder to die. The PLS was added in the side feeder at lower temperatures to decrease its residence time in the extruder.

Morphology

The morphology of the nanocomposites was examined in a Carl Zeiss CEM 902 transmission electron microscope (Oberkochen, Germany). The microscope was operated at an acceleration voltage of 80 kV and was equipped with a Castaing-Henry energy filter spectrometer within the column. Ultrathin sections, approximately 40 nm thick, were cut perpendicular to the film plane at −120 °C, in a Leica EM FC6 cryo-ultramicrotome. The morphology was also analyzed using a JEOL JSM-6360 LV scanning electron microscope (Middleton, WI). The samples were immersed in liquid nitrogen for at least 10 min and fractured. The fractured surfaces of both groups of samples were sputter coated and observed using an acceleration voltage of 5–10 kV.

X-Ray Diffraction

The crystalline structures of the samples were examined using a Shimadzu XRD7000 X-ray Diffractometer (São Paulo, São Paulo, Brazil). The samples were exposed to the

Table 1 Sample compositions

	Starch wt%	Glycerol wt%	PP wt%	MAPP wt%	PP/MAPP vol%	MMT (%)	30B (%)
PLS50	30.0	20.0	37.5	12.5	61.0		
PLS70	42.0	28.0	22.5	7.5	40.0		
PLS80	48.0	32.0	15.0	5.0	28.0		
PLS90	54.0	36.0	7.5	2.5	15.0		
PLS100	60.0	40.0	0.0	0.0	0.0		
PLS50MMT	27.5	17.5	37.5	12.5		5.0	
PLS70MMT	39.5	25.5	22.5	7.5		5.0	
PLS80MMT	45.5	29.5	15.0	5.0		5.0	
PLS90MMT	51.5	33.5	7.5	2.5		5.0	
PLS100MMT	57.5	37.5	0.0	0.0		5.0	
PLS5030B	27.5	17.5	37.5	12.5			5.0
PLS7030B	39.5	25.5	22.5	7.5			5.0
PLS8030B	45.5	29.5	15.0	5.0			5.0
PLS9030B	51.5	33.5	7.5	2.5			5.0
PLS10030B	57.5	37.5	0.0	0.0			5.0

X-ray beam with the X-ray generator running at 40 kV and 30 mA. Scattered radiation was detected at ambient temperature in the angular region of 5°–50° at a rate of 2°min using a Cu beam ($\lambda = 1.54$ nm). The d_{001} spacing was determined by substituting the 2θ scattering peak into the Bragg's equation.

DMA

The dynamic mechanical analysis (DMA) of the extruded blends was performed in a TA Q800 DMA [New Castle, Delaware (USA)]. Pellets of the extruded blend specimens were compression molded into films and were subjected to sinusoidal deformation in tension mode analysis at a frequency of 16 Hz, strain amplitude of 0.01% and temperature rate of 5 °C/min in the temperature range from −100 to 200 °C, or until the sample broke. Typical sample dimensions were 0.65 mm × 10 mm × 5.3 mm.

Tensile Testing

The extruded materials were pelletized. Samples containing 80% PLS or more were soft and tacky and could not be injection molded. Therefore, these samples were calendared using a MH-Equipamentos double roll mill model MH-150C (Guarulhos, Brazil) at temperatures of 120–150 °C and heat pressed into films at 160 °C. The films were then cut into dumbbell shaped tensile specimens according to ASTM D-412 [27]. The prepared materials containing less than 80% PLS were injection molded into dog-bone shaped tensile specimens according to ASTM D-638 [28] using an Arburg Allrounder injection molding machine model 221 M 250–55 (Lossburg, Germany). The following temperature was kept along the barrel zones: 165, 165, 165, 170, and 175 °C. The mold temperature was kept at 40 °C. For all samples, tensile properties were characterized using an EMIC DL2000 universal testing machine (São José dos Pinhais, Brazil) with a load of 5,000 N for injection molded tensile specimens and 500 N for film specimens. Test speeds of 50 mm/min were used for both specimen types. All specimens were conditioned for at least 72 h at 23 °C and 44% relative humidity before testing. Typical specimen dimensions as well as the test conditions were chosen according to standards ASTM D-638 and D-412. At least eight specimens of the same sample were tested.

Viscosity Measurements

Rheological experiments were performed using a TA Instruments AR2000 stress-controlled rheometer with 40 mm/1° cone and plate geometry, and the sample temperature of 165 °C was maintained using a Peltier cell. Oscillatory measurements were conducted at 1% strain.

Results and Discussion

Clays are most effective as reinforcement when the clay layers are able to exfoliate [15–17]. The most important factors to consider in achieving exfoliation are the ability of the polymer matrix to intercalate the clay layers, and the possibility of promoting favorable interactions between the polymer and the silicate layers. In the present case, we have

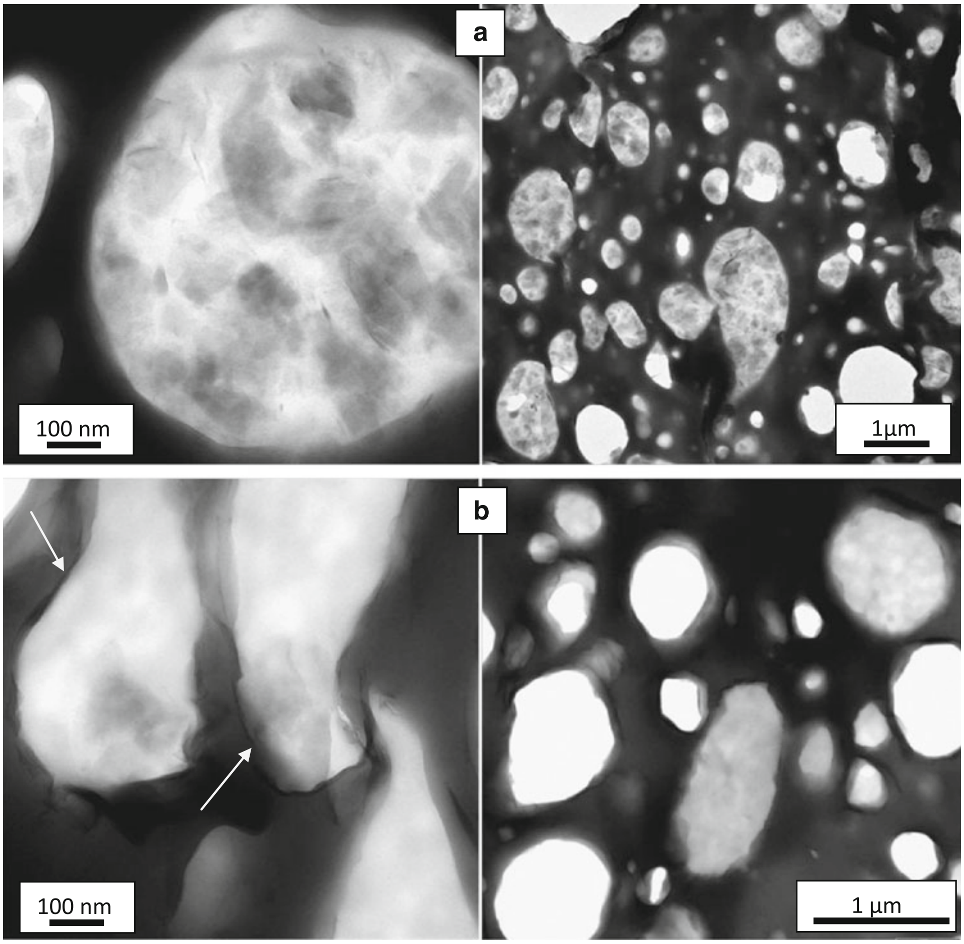

Fig. 1 TEM **a** PLS50-MMT platelet and **b** PLS50-30B showing interface distortion from the clay

chosen the unmodified, hydrophilic sodium montmorillonite for its compatibility with starch and the organically modified Cloisite 30B as a control, as it is compatible with hydrophobic polymers, especially in the presence of polar groups, such as maleic anhydride [25, 26].

Wide-angle X-ray diffraction analysis (see the "Appendix") clearly shows that glycerol increases the gallery spacing between the platelets suggesting that glycerol intercalates into the galleries in both clays, MMT as well as Cloisite 30B. Melt-extrusion with starch to prepare PLS100-MMT and PLS100-30B does not change the diffraction pattern to a great extent. These results suggest that the clays maintain a layered structure when extruded with starch and glycerol, although some exfoliation is also possible. These data do not provide a complete picture of the location or quality of dispersion of the clay, and hence we further explore the morphology using transmission electron microscopy (TEM).

The TEM images of PLS50-MMT and PLS50-30B are shown in Fig. 1. These two samples were chosen for discussion because they clearly show both the two phase morphology of the blends, as well as the location of the clay. The dark regions in Fig. 1 correspond to the polypropylene matrix phase and the gray regions correspond to the dispersed PLS phase. Due to beam sensitivity, portions of the PLS phase were destroyed by the electron beam and appear bright white. Bright white portions within the dark PP regions correspond to pores in the continuous phase. The images in Fig. 1 show that, in both MMT as well as 30B, there is good dispersion of clay (no large aggregates) and indeed, the PLS-rich regions of the MMT-containing sample show exfoliated clay platelets. The chief difference between the two samples is the location of the clay: in PLS50-MMT, the clay appears to be primarily in the PLS phase, whereas in the PLS50-30B sample, the clay appears to have migrated to the interface, presumably because its surface hydrophobicity gives it greater affinity for the PP phase. Furthermore, the migration of 30B has distorted the interface of the PLS50-30B sample, creating a jagged interface in the areas where the clay is found.

The localization of the MMT in the PLS is not surprising: MMT is known to have poor affinity for low-polarity polymers such as polypropylene, and indeed this is the reason why organically-modified clays are essential for making nanocomposites from most synthetic polymers. The case of Cloisite 30B is more complex: it has favorable interactions with the PLS phase (due to the possibility of hydrogen bonding with starch or glycerol), but it also has favorable interactions with the PP phase (the organic modification with a tallow-based surfactant makes it more compatible with polypropylene, and it can also hydrogen-bond with the anhydride groups from the maleated PP). We speculate that the interfacial localization of some of the clay is due to its favorable interactions with both the phases. It is noteworthy that similar interfacial localization of the clays has been reported in a variety of immiscible polymer blends, and several such examples have been cited in references [29, 30].

Figure 2 includes the mechanical properties of the samples obtained from tensile testing, shown as the percentage change in the samples compared to the clay free sample, i.e. PLS50-MMT and PLS50-30B are compared to PLS50. In the absence of clay, with increasing PLS content, the modulus and strength of the materials reduce significantly and the ultimate elongation increases (not shown). As mentioned in the Introduction, this was expected from the previous research in this area [9, 10, 13, 14]. Addition of either nanoclay increases the strength and modulus at all compositions, and the effects are especially large at high PLS content. Equally importantly, this improvement occurs with only a modest decrease in ultimate elongation, i.e. the clays are able to reinforce the PLS/PP blends without making them brittle. Indeed the marked improvement in mechanical properties from the addition of clay was apparent even before the tensile experiments were performed: The mechanical properties of the PLS100 samples were so poor (i.e. tacky and soft) that the tensile specimens failed during handling and loading in the EMIC tensile tester. The addition of either clay improved the properties such that the 100% PLS samples were easily handled. As a result, comparative data for PLS100 without clay are not presented in Fig. 2.

The effect of clays is not uniform at all compositions. The addition of clay at 50% PLS content does not significantly enhance the modulus or tensile strength. However, as the PLS content is increased to 70 and 80%, the modulus and tensile strength are both increased by the addition of MMT and 30B. The most significant increase was seen in PLS70-MMT, which showed increases of 1,200 and 800% in the modulus and tensile strength, respectively. The reasons for this will be discussed below. At the highest (comparable) PLS loading of 90%, the modulus and tensile strength are both increased by at least 50%. In summary, these results support the chief hypothesis that the addition of nanoclay to PLS/PP blends will mitigate the decline in mechanical properties at high PLS content.

Comparing the two different clays, there appear to be no systematic differences in the magnitude of the reinforcement in the MMT-containing samples versus the Cloisite 30B-containing samples. This is somewhat surprising for two reasons. The first is that the TEM micrographs indicate that the MMT is located in the PLS phase, whereas Cloisite 30B clay is located partly in the PLS phase, and partly at the interface. The second is that while the weight loading of the clay is the same (5 wt%) in all samples, Cloisite 30B has roughly 30 wt% organic modifier. Thus, effective volume fraction of the reinforcing agent (i.e. the silicate platelets) is about 30% lower in the Cloisite 30B. Yet, neither the difference in the location of the clay, nor the

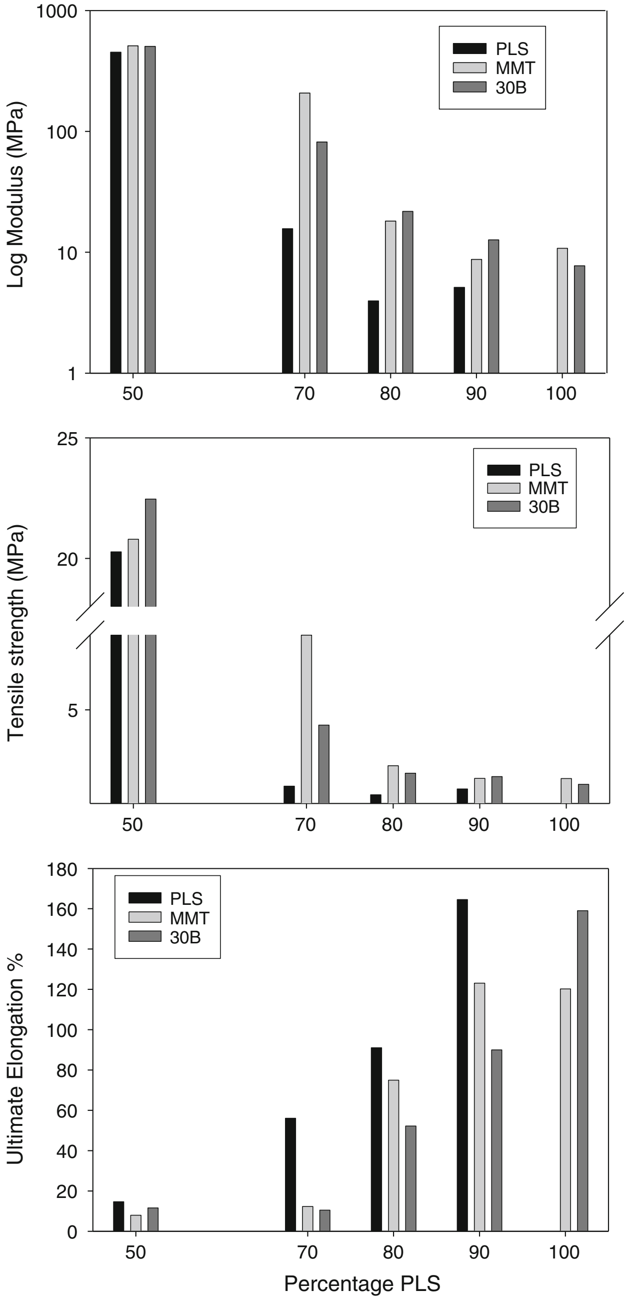

Fig. 2 Tensile properties of plasticized starch and polypropylene blends (note the *y*-axis for modulus is a log scale)

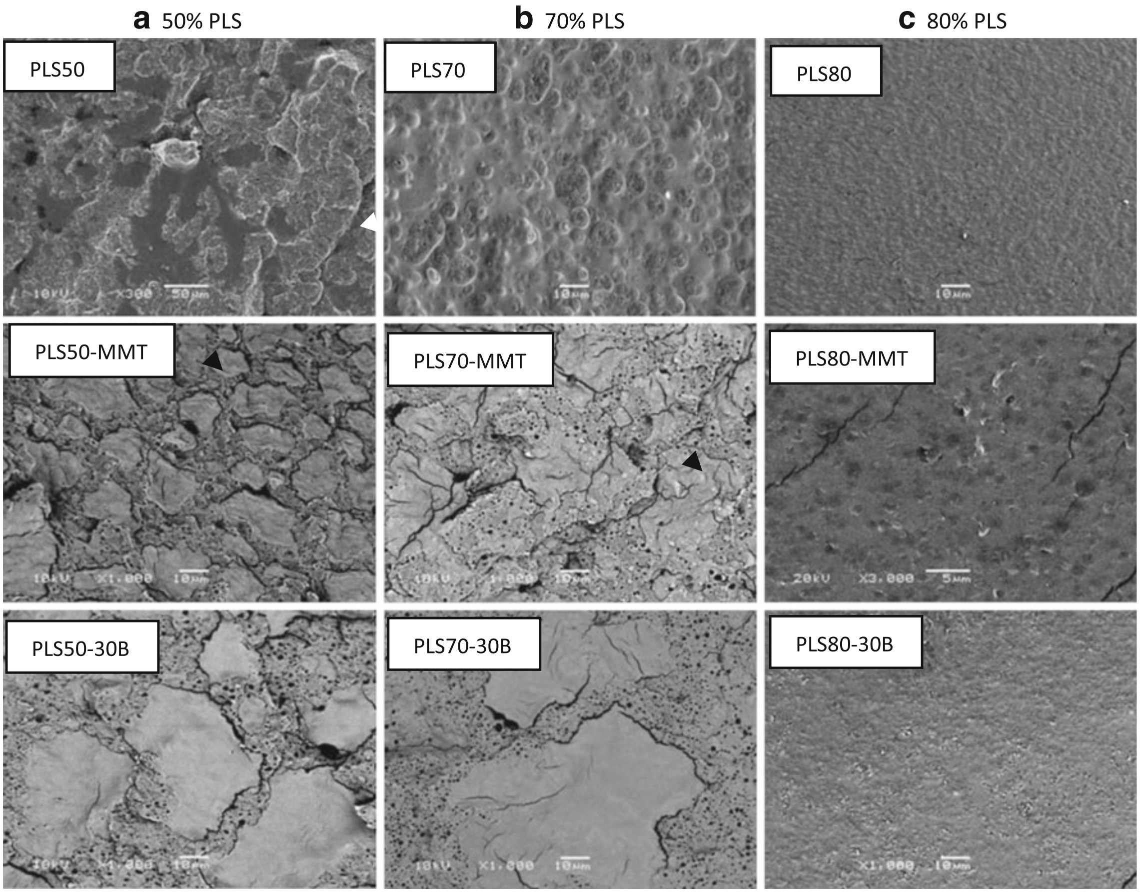

Fig. 3 SEM of PLS50, PLS70 and PLS80 blends containing **a** no clay, **b** MMT and **c** 30B. Some images were taken in electron backscattering mode, which causes some cracking of the sample. The *scale bar* in the PLS50 and PLS80-MMT images are varied

~30% difference in the clay loading seems to affect the tensile properties significantly. Although this insensitivity to organic modification of the clay is surprising, it is supported by recent publications: A recent study reported that 30B and MMT are both good choices for reinforcing plasticized corn starch [31]. A review by Averous et al. [32] also reported good dispersion when incorporating Cloisite 30B into plasticized starch, which in turn results in the improvement of mechanical properties.

Thermomechanical data of the samples is shown, and explained in greater detail in Appendix Fig. 6. Briefly, the glassy modulus and glass transition temperature were essentially unaffected by the addition of clay. Upon the addition of clay, the storage modulus increased above the glass transition temperature, with the largest increase observed in the samples containing 70% PLS.

Finally we discuss the mechanism for the improved mechanical properties with addition of clay. In homopolymer nanocomposites, the change in mechanical properties occurs because the clay acts as a reinforcing agent. In the present case of *two-phase* nanocomposites, there is potentially a second, more subtle reason, viz. the mechanical properties also depend on the two-phase morphology, and if the clay changes the two-phase structure, then the mechanical properties will be affected as well. For example, if the clays induce a change in phase continuity (changing from a dispersed PP phase to a continuous PP phase), a dramatic change in mechanical properties may be expected. Such changes in morphology are most readily examined by scanning electron microscopy (SEM). The SEM of PLS50, PLS70 and PLS80 with and without clay is presented in Fig. 3a–c and shows the two-phase structure of the composite materials. The PLS50 samples have smooth PLS domains and porous, rougher PP domains, with the PLS domains as the dispersed phase. The reason for the pores in the PP domains is not clear, but the pores were also observed in the TEM image (see the dark PP regions in Fig. 1). Furthermore, the PLS phase was identified based on its sensitivity to the electron beam. Neat PLS samples, as well as the smooth regions of the PLS/PP blended samples, both deteriorate easily under the electron beam.

At 50% PLS, the addition of clay does not have a significant effect on the domain size, shape, or phase continuity. At 70% PLS however, the clays have a significant effect on the morphology (Fig. 3b). The clay-free PLS70 sample has the PLS as the continuous phase, and has roundish PP domains with smooth borders. In contrast, both PLS70-MMT and PLS70-30B samples contain larger PP domains which do not seem to be completely separate domains, but appear continuous throughout the sample. Upon further increase in the PLS content to 80%, the clay appears to have little effect on the morphology and all 80% PLS samples appear to be PLS continuous (Fig. 3c).

The issue of phase continuity can be further examined by solvent exposure using dimethylsulfoxide (DMSO) which is a good solvent for PLS. Clay-free samples with 70% or 80% PLS were swollen significantly and separated into small fragments, while PLS90 and PLS100 completely disintegrated upon immersion in DMSO. In contrast, PLS70-MMT and PLS70-30B both remained intact in DMSO further validating the change in phase continuity. PLS80-MMT and PLS80-30B became slightly swollen by DMSO but no separation of the samples was observed. Clay-containing samples with 90 or 100% PLS disintegrated altogether.

In summary, in most of the samples, the change in mechanical properties is attributable mainly to the reinforcing effect of clays. However, at 70% PLS (and perhaps at 80% PLS) the change in morphology caused by the addition of clay may also contribute to the large change in mechanical properties.

We surmise that the large change in morphology occurs in the 70% PLS sample because this sample is susceptible to phase inversion. At this weight loading, the *volume* fraction of PP in the blend is near 40%. The clay-free sample has PLS as the continuous phase, but due to the relatively high volume fraction of PP, a modest change in the blend properties may induce phase inversion. The phase inversion composition is known to depend on the relative viscosity of the phases: the phase with lower viscosity becomes continuous even when its volume fraction is less than 50% [33]. Figure 4 shows that although the PLS is highly shear thinning, it is far more viscous than the PP/MAPP blend over the entire range of frequencies measured. With addition of either of the two clays, the viscosity of PLS100 was increased by a factor of nearly 4. Similarly, Galgali et al. [34] found that layered silicates can form network structures within a polymer matrix, increasing the viscosity of the matrix and its ability to resist deformation. This increased viscosity suggests that the clay reinforced PLS phase would have an increased resistance to deformation and breakup, and may shift the composition at which the PLS/PP blends can phase invert [33]. The effects of clay on the morphology of the sample are apparent in the samples containing 70% wt. PLS, in which the increased viscosity due to the addition of clay was able to affect the continuity of the blends since the volume fraction of each phase was near to 50%. The samples with 50 and 80 wt. % PLS, both having PLS volume fractions far from 50%, were not largely affected by the change in the PLS viscosity and have only subtle morphological differences.

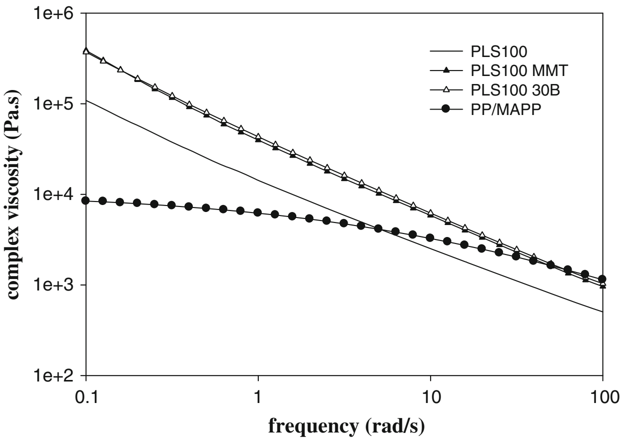

Fig. 4 Complex viscosity of PLS with and without the addition of clay compared to the complex viscosity of the PP phase, measured at 1% strain and 165 °C. The low frequency complex viscosity can be viewed as zero shear viscosity

Finally, with highly hydrophilic materials such as plasticized starch, the physical properties can be affected by moisture absorption. The effect of clay on water absorption was measured for three samples, PLS100, PLS100MMT and PLS10030B. Samples were weighed immediately after drying overnight at 70 °C in vacuum, and then again after 2 weeks at ambient temperature and humidity. The increase in mass was: PLS100 2.7%; PLS100MMT 4.7%, and PLS10030B 4.3%, i.e. the clay increases the hydrophilicity of the samples. The increase due to the clay is significant in percentage terms, but in absolute terms, all samples absorb only modest amounts of water even though they contain substantial amounts of glycerol which is known to be hygroscopic.

Conclusions

In summary, the properties of clay nanocomposites based on plasticized starch and polypropylene were investigated. X-ray diffraction and TEM revealed that both unmodified and modified clays were well-dispersed in the polymer matrix with intercalated as well as exfoliated platelets. The unmodified MMT was primarily located in the PLS phase due to its affinity and hydrogen bonding with PLS. The organically modified 30B was both dispersed in the PLS phase as well as located at the interface between PLS and PP, which is likely attributable to affinity with hydrophobic

PP and hydrogen boding with the polar maleic anhydride groups of the MAPP. The addition of clay resulted in hybrid materials with improved tensile modulus and strength in relation to PLS/PP blends alone, as observed from the DMA and tensile testing results. The improvements are greatest at high PLS content suggesting that addition of clay is a possible route to realizing starch-based plastics that have a high renewable and biodegradable content, but still possess good mechanical properties. Such improvements are the result of the addition of clay as a reinforcing component and also from the effect of clay on the morphology of the blends.

Finally, throughout this paper, the discussion has focused on reinforcing PLS/PP blends with clay. However, it is also useful to reconsider the results as blending PP with PLS/clay nanocomposites. From that point of view, a significant increase in mechanical properties of PLS nanocomposites required approximately 20–30% polypropylene. Since other polymers may be used in place of PP, this perspective expands the paths available to creating starch-based plastics.

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Appendix

The XRD patterns (Fig. 5) showed the scattering peaks for dried MMT (left) and 30B (right) were $2\theta = 8.2$ and 4.8, respectively. These values correspond to d_{001} values of 1.07 nm and 1.83 nm, respectively and agree well with the literature [35]. The larger d_{001} value for 30B arises from the organic modification. Upon swelling in glycerol, the interlayer distance increased for the both MMT ($d_{001} = 1.81$ nm) and 30B ($d_{001} = 2.32$ nm). This suggests that glycerol intercalates into the galleries of both clays. Some level of exfoliation cannot be ruled out. Upon extrusion of the glycerol-swollen clays with starch to obtain PLS100-MMT and PLS100-30B the peak position remains essentially unchanged. In summary, from the XRD experiments we can conclude that glycerol intercalates both MMT and 30B clays, and melt extrusion with PLS does not exfoliate the clay any further than glycerol.

Figure 6 shows the dynamic mechanical properties of selected blends. Strongly polar polymers, especially with hydrogen bonding have slightly higher glassy moduli [36], and accordingly, the samples containing higher concentrations of PLS, which is more polar than PP, show the highest moduli in the glassy region (−100 °C). Moreover, the effect of clay was negligible in the glassy region. The T_g of all samples (as judged by the peak in $\tan \delta$), was near −25 °C and was not significantly affected by the addition of clay. The composition of the samples (i.e. the fraction of the PP phase) also had negligible effect on T_g which likely reflects the complete immiscibility of the phases. In all samples, the modulus increased with increasing PP content in the temperature range from the glass transition temperature to 100 °C. In the PLS70-MMT sample, the addition of clay resulted in a large increase in the storage modulus as temperature is increased, presumably due to the stiffening of the material due to the restriction of chain mobility by the nanoclays. The same was observed for the PLS80-MMT sample. In contrast, the addition of 30B does not increase in the plateau modulus at high temperature significantly.

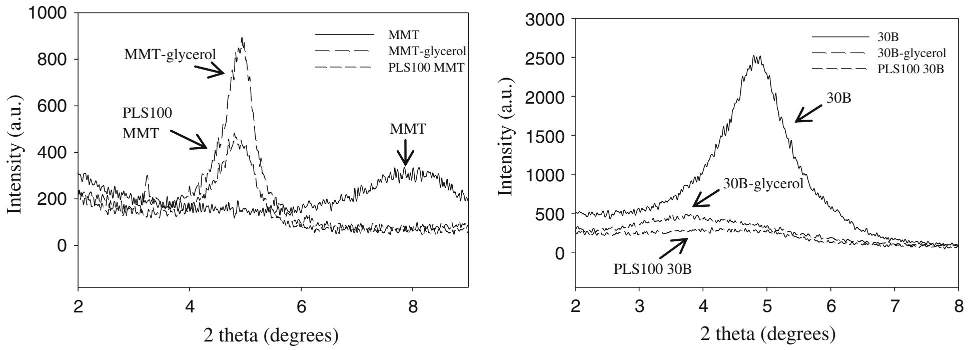

Fig. 5 The XRD patterns showed the scattering peaks for dried MMT, MMT-glycerol and PLS100-MMT (*left*) and dried 30B, 30B-glycerol and PLS100-30B (*right*)

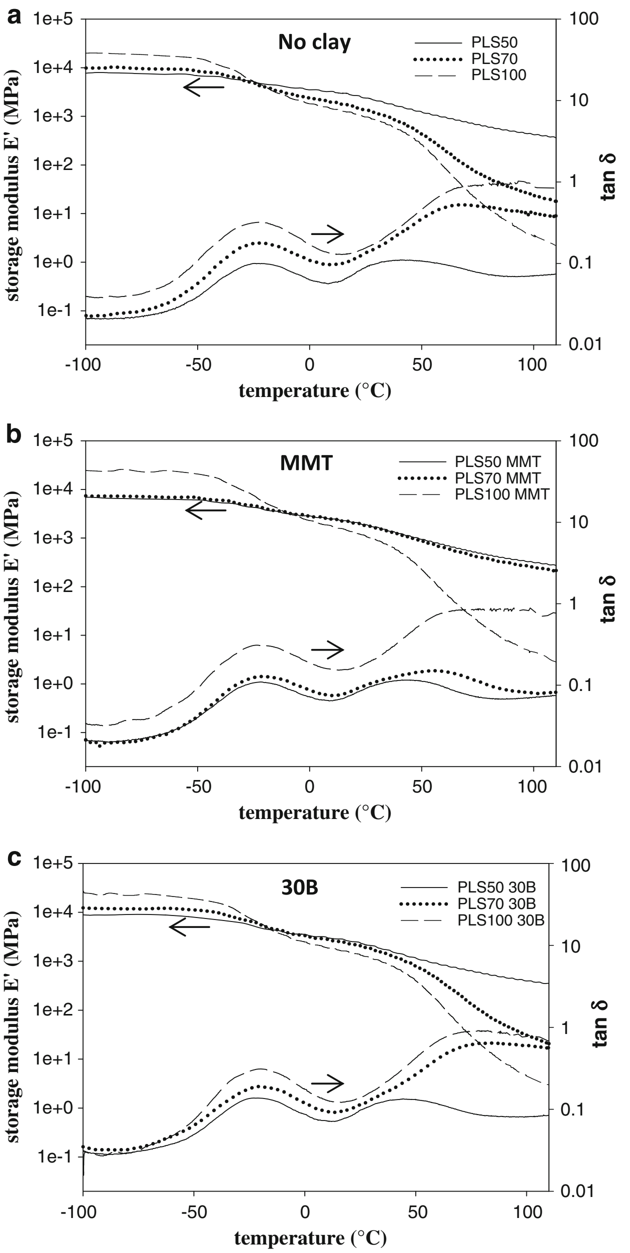

Fig. 6 DMA of (**a**) plasticized starch and polypropylene blends, (**b**) PLS/PP blends with MMT and (**c**) PLS/PP blends with 30B

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