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Highly exfoliated eco-friendly thermoplastic starch (TPS)/poly (lactic acid)(PLA)/clay nanocomposites using unmodified nanoclay

Ayana B., Supratim Suin, B.B. Khatua*

Materials Science Centre, Indian Institute of Technology, Kharagpur, Kharagpur 721302, India

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ABSTRACT

Highly exfoliated, biodegradable thermoplastic starch (TPS)/polylactic acid (PLA)/sodium montmorillonite (NaMMT) nanocomposites were prepared by an eco-friendly approach, involving in-situ gelatinization of potato starch in presence of dispersed nanoclay followed by melt mixing with PLA. The morphological analysis revealed that the NaMMT was selectively dispersed into the TPS in a highly delaminated manner. An increase in mechanical as well as thermomechanical properties was evident in the presence of PLA and more influenced in the presence of clay. The water absorption was significantly decreased in the presence of PLA (~8%) itself and both PLA and clay (~8–12%) in the nanocomposites. The improved mechanical properties along with its biodegradability might lead to a new green material in the area of packaging.

1. Introduction

The credibility of starch as an effective packaging material has been under scrutiny since late 80s. The low cost and wide availability of starch, combined with its high purity, non-toxicity and pure biodegradability/environmental compatibility has gathered the attention of the packaging industry which continues to depend on traditional synthetic non-biodegradable plastics. The use of pure biodegradable polymers seems to be restricted to limited areas of application owing to their high cost. Few analyses have reported the production of low cost biodegradable blends based on non-biodegradable plastics (Arvalo-Nio et al., 1996; Park, Lee, et al., 2002; Park, Li, et al., 2002) with the addition of starch as filler. Hence, efforts to replace some or all of the synthetic polymers by biopolymers through low cost methods has been put. This study reports starch as one of the economically viable biodegradable materials for packaging purposes.

The starch granules are partially crystalline and insoluble in cold water (Vazquez, Cyras, Alvarez, & Moran, 2012). The granules do not possess thermoplastic character in its pristine form unless they are de-structured. The usual de-structuring agent is water. Interestingly, the degradation temperature (~220 °C) and the melt temperature (T_m = 220–250 °C) of starch granules are very close. The starch granules swell when heated in the presence of water; the degree of swelling reaches a maximum, breaking the granules. The strong intermolecular forces between the starch granules get diminished to the minimum forming a starch paste and ultimately the state of gelatinized starch is being achieved. During the drying process, the gelatinized starch regains its crystalline nature, due to intramolecular hydrogen bonding. This recrystallization in gelatinized starch is prevented by the process of plasticization with the help of plasticizers.

The plasticizers diminish the inter-molecular hydrogen bonding sites in the crystalline regions of the starch granules, and thus reducing the melting temperature during thermoplastic processing. Therefore, a reasonable quantity of plasticizer must be available in the system to actuate the thermoplastic character of starch. But contradictorily, by increasing its content, the system grows more hygroscopic. Starch is commonly pre-treated with a plasticizer to build it as a thermoplastic material, thus enabling melt-processing as thermoplastic starch (TPS) (Chen & Evans, 2005). The mechanical properties and toughness of PLA/gelatinized starch are far superior to PLA/pure starch blends as the addition of glycerol enhances the interfacial adhesion. A study on the high priced PLA with native starch as filler and polyethylene glycol as plasticizer by Jacobsen and Fritz (Jacobsen & Fritz, 1996) states that the incorporation of filler to either pure PLA or to a blend of PLA/PEG doesn't negatively influence the thermal behaviour or the melt stability of the polymer itself or the blend. Glycerol has been selected as the plasticizer for plasticization in this study and its amount has been optimized to 30 wt% glycerol.

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* Corresponding author. Tel.: +91 3222 283978.
E-mail address: khatuabb@matsc.iitkgp.ernet.in (B.B. Khatua).

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However, thermoplastic starch-based materials suffers from certain drawbacks namely, relatively poor mechanical properties and poor water resistance, making it a difficult candidate for packaging applications. Most of the research, published so far involved the use of montmorillonite (MMT) clay as the nanocomponent (Ray, Quek, Easteal, & Chen, 2006) in polymer/clay nanocomposites (PCNs) intended for food packaging purposes. Montmorillonite based nanoclays are environmentally acceptable, plentiful in availability and are toxin-free, making them the potential ingredient in this application as components for food packaging. In particular, they show huge promise in providing exceptional barrier properties, due to the presence of the clay layers, which delays the diffusion of a molecule due to the formation of larger tortuous path (Alexandre & Dubois, 2000; Carvalho, Curvelo, & Agnelli, 2001; Neilsen, 1967; Sorrentino, Gorrasi, & Vittoria, 2007). Such character makes nanoclay as potential reinforcing agent for our purpose.

Addition of nanoclay helps in achieving augmented mechanical and thermal properties of the starch clay nanocomposites (Carvalho, Curvelo, & Agnelli, 2001; Chen et al., 2008; Dean, Yu, & Wu, 2007; McGlashan & Halley, 2003; Park, Lee, Park, Cho, & Ha, 2003; Wilhelm, Sierakowski, Souzab, & Wypych, 2003). The utilization of kaolin as a filler of reinforcement for thermoplastic starch in order to improve its mechanical properties (Carvalho, Curvelo, & Agnelli, 2001) has been reported in the literature. They also found out that samples with the unmodified clay gave the best results with better tensile strength and reduced water vapour transmission. Avella et al. (2005) reported starch/clay nanocomposites with completely intercalated clay morphology arising from the introduction of polymer matrix into the clay interlayer galleries, delivering a reinforcing effect of nanoclay on the modulus and the tensile strength to the starch. Park et al. (2003) reported that the tensile strength of TPS rose from 2.6 to 3.3 MPa at a 5 wt% loading of NaMMT, while the elongation at break was increased from 47 to 57%. It was also observed that the relative water vapour diffusion coefficient of TPS was lowered to about 65% of the value without MMT.

Much of these works emphasizes on the mechanical properties of the nanocomposites overlooking the critical problem of moisture sensitivity of TPS. This brought in the concept of blending with another biopolymer to achieve the desired modified properties without compromising the biodegradability.

Starch has been the most studied polysaccharide in nanocomposites systems, mainly into its plasticized state (Chen, Chen, & Evans, 2005; Chiou et al., 2007; Park, Lee, et al., 2002; Park, Li, et al., 2002). Efforts to blend starch with various biopolymers (polylactic acid) (Lee & Hanna, 2008), polycaprolactone (Pérez, Alvarez, Mondragon, & Vazquez, 2007; Jang, Shin, Lee, & Narayan, 2007), poly (vinyl alcohol) (Dean, Do, Petinakis, & Yu, 2008; Siddaramaiah, Raj, & Somashekar, 2004), Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) (Gilbert, 1985) along with the addition of nanoclay have been reported. The blends of PCL and PHBV with granular starch were found to be mechanically compatible but phase separated as reported by Koenig and Huang (1995). Averous et al. studied blends of TPS with polyesteramide (Averous, Fauconnier, Moro, & Fringant, 2000) and PCL (Averous, Moro, Dole, & Fringant, 1999) with TPS as the major phase in the blend (>50%). Reports on lactic acid based polymers (Sodergard & Stolt, 2002) and its emergence as a commodity packaging plastic (Sinclair, 1996) with reproducible properties like less hygroscopic character, reduced water permeability and also improved mechanical properties makes it a suitable choice. Chang, An, and Sur (2003) reported noticeable improvement in the oxygen gas permeability of PLA clay nanocomposites prepared through the melt intercalation method. They found that the improvement in the above property was increased with increase in clay content. The permeability of the nanocomposites at 4% clay loading was reduced by about 40%, which was further reduced to about half of the PLA permeability value for 6% clay loaded samples. This phenomenon might be explained in terms of the increase in the lengths of the tortuous paths in the nanocomposites due to the presence of high clay content.

As we approach closer to achieve better water resistance properties for the blend, the mechanical properties of blends of PLA and starch using conventional processes are reported to be very poor because of incompatibility (Ning, Jiugao, & Xiaofei, 2008). Few studies on starch added in granular form (Jacobsen & Fritz, 1996) and gelatinized form (Tako & Hizukuri, 2002) into PLA reported this inherent incompatibility between the polymers. However, the obvious immiscibility between hydrophilic starch and hydrophobic PLA giving phase separated blends with poor interfacial properties, which can be reduced by compatibilization. Besides, gelatinization of starch is also a good method to enhance the interfacial affinity between the distinct phases. Also, it is always desired to have an enhancement in the properties of the system by the addition of this compatibilizer. Arroyo, Huneault, Favis, and Bureau (2010) investigated the properties of TPS/PLA nanocomposites with the incorporation of NaMMT using a twin screw extruder. They studied the effect of water in enhancing the clay exfoliation with the results that TPS could intercalate into the clay intra-gallery and the preferential location of clay in the TPS phase or at the blend interface. They also reported an increase in the tensile strength and modulus along with a reduction in fracture toughness. The compatibilization mechanism in immiscible polymer blend systems achieved by unmodified nanoclay has recently been proposed by Iyer, Suin, Shrivastava, Maiti, and Khatua (2013). PLA/starch composites with acrylic acid grafted form of PLA (Wu, 2005) produced reports on compatibilization delivering fairly good mechanical properties.

Furthermore, no considerable attention has been put on water enhanced exfoliation by solution casting method for the preparation of thermoplastic starch. A variety of studies on blending starch with other polymers have been reported but largely by methods of extrusion. Zeppa, Gouanve, and Espuche (2009) did not find any significant influence of a plasticizer like glycerol and urea/ethanolamine in the dispersion of the montmorillonite clays into matrices. However, a study by Pandey and Singh (2005) revealed that the sequence of addition of components (starch/plasticizer (glycerol)/clay) had a significant effect on the nature and properties of composites formed. They reported that among glycerol and starch, penetration of glycerol into the clay galleries is favoured owing to its smaller molecule size and that if plasticizer is added after mixing of clay in the starch matrix, the mechanical properties can be obtained.

Here, the clay dispersion is mixed with the starch during gelatinization, followed by the addition of plasticizing agent, glycerol. The system is then melt mixed with polylactic acid to give (60/40, w/w) nanocompositess in TPS matrix. This gives us one of the most potential biodegradable nanocompositess consisting of organic polymers and layered silicates through an economically viable and effective method. To the authors' knowledge, very few publications have reported following this mode of preparation of starch/clay nanocomposites by this method (Arroyo, Huneault, Favis, & Bureau, 2010; Cyras, Manfredi, That, & Vazquez, 2008; Park, Lee, et al., 2002; Park, Li, et al., 2002; Wilhelm, Sierakowski, Souzab, & Wypych, 2003; Zeppa, Gouanve, & Espuche, 2009).

The aim of our research is to prepare biodegradable nanocomposites of TPS/PLA blends using unmodified nanoclay and to investigate the effects of nanoclay not just as a reinforcing agent but more as a compatibilizer on the properties of TPS/PLA/nanoclay nanocomposites. The nanocomposites were characterized by XRD, SEM and TEM. The thermal, mechanical, dynamic mechanical and water absorption characteristics were also studied.

2. Experimental

2.1. Materials details

Potato starch (soluble, extra pure, water content 2%) and glycerol (about 98% purified) were purchased from Merck, Germany. The unmodified nanoclay, sodium montmorillonite, (NaMMT) was supplied by Southern Clay Products, Inc. Poly (lactic acid) (PLA) with D content of 1.1–1.7% was obtained from Unitika Co. Ltd., Japan.

2.2. Preparation of TPS/PLA/nanoclay nanocomposites

The nanocomposites were prepared in aqueous media. Starch powder, PLA and NaMMT were dried in an air oven at 60 °C for 1 week prior to use.

The procedure consisted of two steps.

2.2.1. Preparation of starch suspension (gelatinization)

20 g potato starch was dispersed in 400 ml distilled water. The suspension was heated to 80 °C with continuous stirring at 100 rpm for 20 min. Thus, a suspension of starch was prepared. This process is termed as gelatinization of starch.

2.2.2. Preparation of nanoclay dispersion

The NaMMT was dispersed in 100 ml distilled water by sonication for 20 min at room temperature. The percentage of nanoclay added was 0.5 phr (0.1 g) and 1.0 (0.2 g) with respect to the dry starch.

For the preparation of thermoplasticized starch, the formally prepared starch solution was added to the NaMMT dispersion and was heated to 80 °C, under continued stirring at 100 rpm, followed by the addition of 20 wt%, 30 wt% and 40 wt% of glycerol, before casting into a Petri dish. The resulting products were left for drying overnight at room temperature followed by drying in a vacuum oven at 50 °C for 24 h. The material was then preserved in hot air oven at 50 °C for 3 weeks.

2.2.3. Melt mixing

Before melt mixing the PLA, as well as, the clay dispersed TPS were dried at 50 °C for 24 h, to minimize moisture induced thermal degradation during melt processing. The polymers were then melt mixed at a ratio (60/40, w/w) of TPS and PLA in a Sigma mixer (Brabender, capacity: 20 cm^3, S. C. Dey, Kolkata, India) at 185 °C, 40 rpm for 10 min.

In this work, we have tried to reduce the cost of a very popular biodegradable polymer PLA, through replacement of some volume of PLA by clay dispersed TPS. We started from the replacement of 90% PLA by TPS. The mechanical performance of the nanocomposites was so poor that it became difficult to let it out of the mold. A very week mechanical performances were obtained at other higher volume percent of TPS (e.g., 80%, 70%). The incorporation of 60% TPS (i.e., 60/40 TPS/PLA) in the TPS/PLA/clay nanocomposites leads to a mechanically eligible candidate, suitable for eco-friendly packaging application. Thus, the (60/40) ratio TPS/PLA leads to the most effective composition in terms of both the cost and performances.

3. Characterizations

3.1. Scanning electron microscopy (SEM) analysis

The cryo-fractured surface of the compression molded specimens was used for SEM analysis using a scanning electron microscope (VEGA II LSU, TESCAN, Czech Republic). The specimens were sputter-coated with gold prior to the experiment to avoid any charging during scanning. The diameter of the droplets was measured using the image J software and the values were averaged to obtain the D_n value.

3.2. X-ray diffraction (XRD) analysis

The XRD Xpert Pro PAN analytical (Netherlands) was used to measure the d_{001} spacing (gallery height) of the starch-nanoclay samples. Cu Kα_1 radiation, with a wavelength of 0.15404 nm, was generated at 45 kV and 30 mA for the measurements. The scan rate was 0.5°/min. The d_{001} spacing was calculated by first determining 2θ and then using the value in the Bragg's Law ($n\lambda = 2d \sin\theta$), where λ is the wavelength of the incident wave, d is the distance between the d_{001} planes, θ is the angle between the incident wave and the plane, and n is an integer.

3.3. Transmission electron microscopy (TEM) analysis

The bulk morphology of the clay silicate layers in the starch matrix was observed using HRTEM: JEM-2100, JEOL, Japan, operating at an accelerating voltage of 100 kV. The nanocomposites samples were ultramicrotomed under cryogenic conditions (at −50 °C) with a thickness of ~100 nm.

3.4. Water absorption studies

For water absorption characterization studies, the samples were dried in a vacuum oven until constant weight was obtained and then placed in desiccators to cool before water absorption testing by gravimetric methods and this weight was taken as initial weight (W_i). The samples were then soaked in deionized water for 24 h, after which they were blotted dry with a lint free cloth. The increase in weight was taken as final weight (W_f). Water absorption is expressed as the increase in weight percent. The percentage of water absorption was calculated by the formula, $(W_f - W_i)/(W_i) \times 100$.

3.5. Thermo gravimetric analysis (TGA)

The TGA was performed with a thermo gravimetric analyser (TGA 209F) from NETZSCH, Germany to compare the thermal stabilities of the prepared nanocomposites. The samples (~10 mg) were heated from room temperature to 600 °C at a heating rate 10 °C/min under nitrogen purge and atmospheric pressure.

3.6. Differential scanning calorimetry (DSC) analysis

The DSC analysis was carried out in DSC-200 PC, NETZSCH, Germany, at isothermal conditions using 5–10 mg of sample at a scanning rate of 10 °C/min, under nitrogen atmosphere. The samples were heated to 250 °C, held for 5 min for removing moisture and previous thermal history and then cooled to room temperature at a cooling rate of 10 °C/min. The second heating run was done to obtain the T_g.

3.7. Mechanical properties

The mechanical tests were performed as outlined in ASTM D638 on dumbbell shaped tensile bars. The tensile bars were prepared by compression moulding using a hot press (S. C. Dey, Kolkata, India) at a temperature of 185 °C and a moulding load of 2000 kg. The tensile specimens were preserved at room temperature in a desiccator for 14 days. The experiments were carried out with a universal tensile testing machine (Hounsfield HS 10KS, UK) at room temperature with an extension speed of 0.5 mm/min and a gauge length of

35 mm. The average value determined from the results of 5 samples chosen as the tensile value for the nanocomposites.

3.8. Dynamic mechanical analysis (DMA)

DMA was performed in a TA instrument DMA 2980 dynamic mechanical analyser model operating in a single cantilever bending mode with a frequency of 1 Hz and a heating rate of 10 °C/min. The temperature dependence of storage modulus (E') and tan δ was measured in the temperature range −100 °C to 140 °C.

4. Results and discussion

4.1. Optimization of glycerol content

A major hindrance that restricts the development of thermoplastic starch in the field of packaging industry is its excessive hygroscopicity and inadequate mechanical strength. As gelatinization proceeds, the starch granules get fragmented and the strong intermolecular forces between them are diminished to the minimum before mixing with other polymers (Parris, Coffin, Joubran, & Pessen, 1995). But to achieve better blending with other polymer systems, the water content in the gelatinized starch need to be removed completely. During the drying process, due to intramolecular hydrogen bonding, the gelatinized starch regains its crystalline nature. This recrystallization in gelatinized starch was prevented by the addition of glycerol as a plasticizer. It has been reported by Pushpadass, Marx, and Hanna (2008) that a minimum of 20% glycerol or plasticizer is required to plasticize starch effectively and De Carvalho and co-workers (Carvalho, Curvelo, & Agnelli, 2001) reported that very high amount of glycerol leads to its exudation from the material. Hence, the water absorption behaviour of TPS was considered to be a very important factor. However, the consistency in melting behaviour of TPS, the most important parameter during processing cannot be discarded.

It was observed that the water absorption of plain gelatinized starch was the highest recorded of all the samples with a value of 68.08%. This shows the susceptibility of pristine starch to water and its hygroscopic nature, when simply gelatinized with water. The glycerol-plasticized starch specimens showed an increasing trend in water absorption as the content of glycerol was increased from 20 wt% (49.20%) through 30 wt% (54.37%) to 40 wt% (57.35%). The introduction of 20 wt% glycerol into the starch leads to 18.88% decrease in water absorption. The significantly less water absorption values in the presence glycerol might be associated with the unavailability of sites since hydroxyl groups of glycerol are already bonded to pristine starch. A 5.17% and 2.98% increase in water absorption was evident on increasing 20–30% and 30–40% glycerol content, respectively. The increase in water absorption with increase in glycerol content can be explained in terms of the easy diffusion of water molecules throughout the matrix due to the availability of more hydroxyl group as a result of increase in chain mobility.

Simultaneously, the melt temperature of these same samples were monitored which helped us to fix the quantity of glycerol. It was observed that at 20 wt%, the plasticized starch did not show any reproducible results of melting temperature. Also, the same sample faced difficulty while being processed in a Sigma mixer as supported by the findings of the Park et al. (Park, Kim, Kim, & Kim, 2000). The samples with 30 wt% and 40 wt% glycerol content did not meet with these difficulties. Considering both the consistency in melting temperature and the water absorption behaviour, the content of glycerol was optimized at 30 wt%, as it possessed minimum water absorption with healthy melting behaviour.

4.2. SEM analysis

It is well known that mechanical properties of polymer blends and composites are strongly related to their morphology. The relationship between mechanical properties and morphology for the blend of starch and PLA was studied by Sun and co-workers (Wang, Sun, & Seib, 2001). Thus, control of morphology is very important in PLA/starch nanoclay nanocomposites blends. So, we observed the morphologies of 0.5 phr and 1.0 phr NaMMT loaded (60/40, w/w) TPS/PLA 7nanocomposites with each other.

As shown in Fig. 1a–d, the SEM image of pure blend TPS/PLA (60/40, w/w), a clear matrix and droplet structure can be seen between PLA and thermoplastic starch matrix. The PLA has a broad size distribution and most of them detached from the thermoplastic starch matrix. This is a characteristic matrix-droplet model with the droplets corresponding to the minor phase (PLA) distributed in the major phase (TPS matrix). This morphology is typical of immiscible blends with asymmetric compositions resulting in poor mechanical properties.

For NaMMT loaded TPS/PLA nanocomposites, SEM micrographs show reduced size distribution of the PLA in the TPS matrix. This morphology revealed that the NaMMT acts as the compatibilizer for the TPS/PLA blend. The number average domain diameter (D_n) of the nanocomposites was calculated and plotted in Fig. 1e. The addition of NaMMT to (60/40, w/w) TPS/PLA blend considerably reduced the D_n of the blend compared to the D_n of (60/40, w/w) TPS/PLA blend without any clay. The value of D_n was found to decrease gradually with increasing addition of NaMMT to (60/40, w/w) TPS/PLA blend. The D_n value for (60/40, w/w) TPS/PLA blend was found to be 21.3 μm, whereas, for 0.5 phr and 1.0 phr loaded NaMMT of (60/40, w/w) TPS/PLA demonstrated a D_n value of 17.2 μm and 13.45 μm, respectively. In the reverse composition (i.e., 40/60, w/w TPS/PLA blend) the value of D_n was appeared as 20.4 μm.

There are two types of fracture morphologies. One is a fracture occurring through the interface and the other is broken PLA at its centre. The fracture surface of NaMMT loaded nanocomposites shows relatively many interfacial fractures. This morphology implied that crack initiation took place near the poles and these could possibly be delayed due to the torturous path provided by the well dispersed NaMMT layers. It is possible that this improved adhesion of the nanocomposites is due to the exfoliation of NaMMT in the TPS matrix, leading to a good compatibilization between TPS and PLA (mechanism has been discussed in Section 4.9). But definitely, we cannot exclude the chances of other interactions rising between the blend components, such as hydrogen bonding and wetting because of low surface tension.

4.3. XRD analysis

The XRD study provides information about the mode of dispersion (stacked, intercalation or exfoliation) of the clay silicate layers in the matrix. In general, during the intercalation process, the polymer enters into the clay galleries and forces apart the platelets, thus, increasing the gallery spacing (d-spacing). According to Bragg's law, this would cause a shift of the diffraction peak toward a lower angle. As more polymers enter the gallery, the platelets become disordered and some platelets are even pushed apart from the stacks of clay particles (partially exfoliated). This will cause XRD peaks with a wider distribution or even further shift to the left side. The diffraction results for NaMMT as well as the (60/40, w/w) TPS/PLA/NaMMT nanocomposites containing different nanoclay concentrations as a function of 2θ are shown in Fig. 2. As a comparison, pristine NaMMT has a peak 2θ value at 7.21°, corresponding to a clay interlayer spacing (d_{001}) value of 1.251 nm. The (0 0 1) peak was not detected in any of the nanocomposites samples and thus indicated the exfoliation of clay in the matrix polymer. The nanocomposites showed high

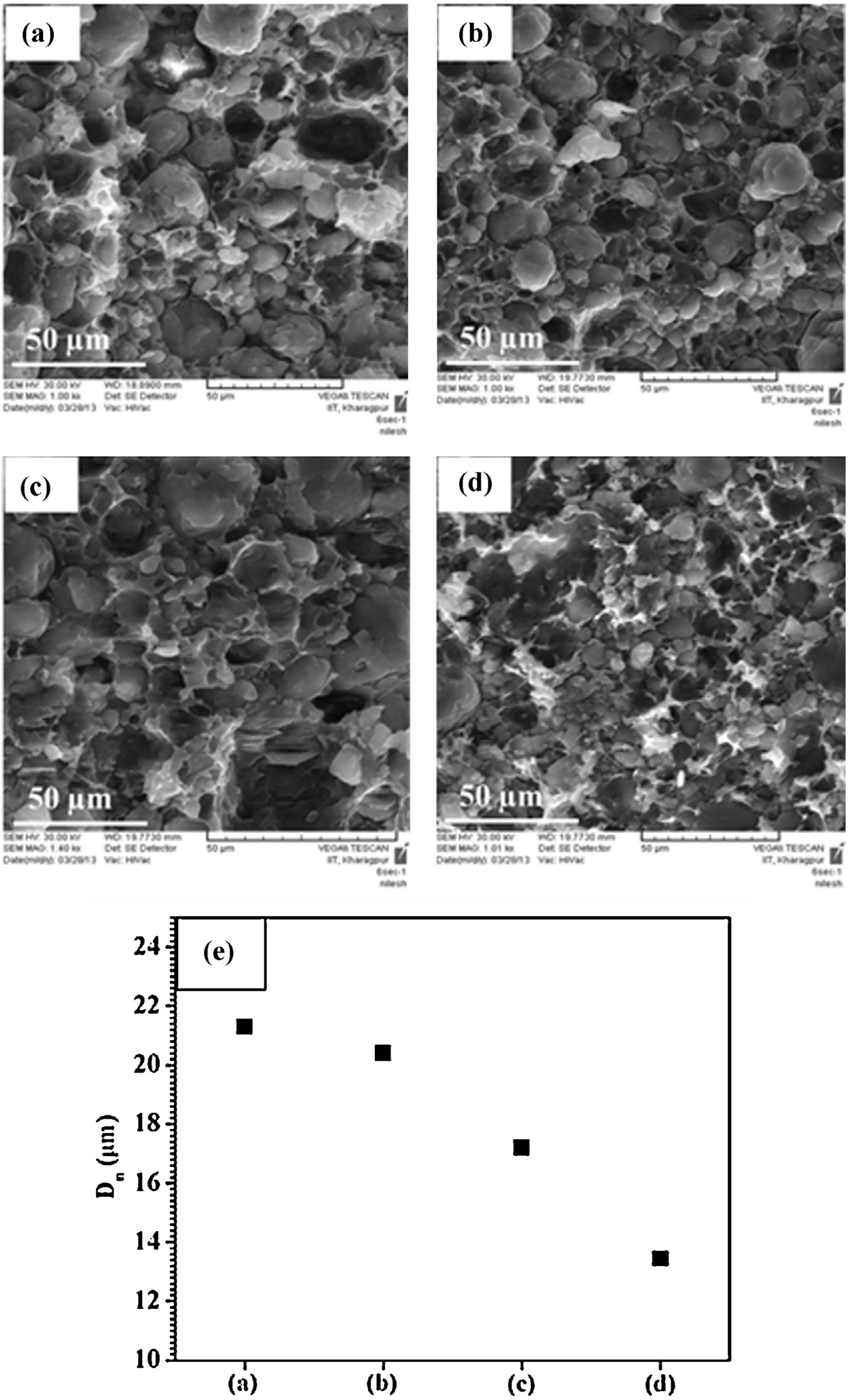

Fig. 1. SEM images of (a) (60/40, w/w) TPS/PLA blend, (b) (40/60, w/w) TPS/PLA blend, and (60/40, w/w) TPS/PLA NaMMT nanocomposites (c) with 0.5 phr NaMMT (d) 1.0 phr NaMMT; (e) Variation of D_n for the respective samples.

extent of exfoliation, i.e., extensive diffusion of polymer chains into the clay galleries. When more polymers enter and push these galleries apart, the XRD peak becomes wider and ultimately broadens into the baseline as a complete exfoliated nanocomposite structure is formed. The complete exfoliation results in high dispersion of filler throughout the matrix. Such high degree exfoliation of the unmodified clay is due to its earlier dispersion in water before its addition to the gelatinized starch followed by the addition of the plasticizer. In this case, the water and hydrophilic starch components, amylose and amylopectin, were able to penetrate into the

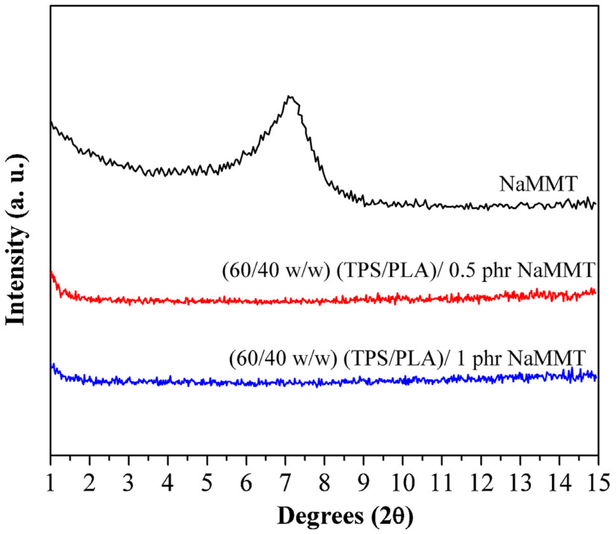

Fig. 2. XRD diffractograms of NaMMT and TPS/PLA/NaMMT nanocomposites.

hydrophilic NaMMT interlayer and exfoliate the nanoclays. Moreover, the glycerol added as plasticizer can interpenetrate between the nanoclay platelets and help in better exfoliation. During plasticization, glycerol, like water, forms hydrogen bonds with native starch and as this association would have mattered if the addition of clay was after the process of plasticization. The study (Pandey & Singh, 2005) has proven that the sequence of addition of components especially the plasticizer during the preparation of nanocomposites had a significant effect on the nature of composites formed. The exfoliated NaMMT layers present in the TPS matrix of the TPS/PLA/NaMMT nanocomposites is responsible for enhanced mechanical properties as it can be inferred that they must have acted as barriers to the incoming mechanical strains applied.

4.4. TEM analysis

The findings of XRD were further confirmed via TEM imaging in which the nanocomposites samples with NaMMT showed excellent exfoliation. TEM was used to examine the nanoclay dispersion in the (60/40, w/w) TPS/PLA blend with 0.5 phr and 1.0 phr nanoclay and both were found to be having complete exfoliation (Fig. 3). The TEM micrograph shows 0.5 phr nanoclay loading (Fig. 3a), and this complete exfoliation of the clay platelets can be attributed to the earlier preparation of clay dispersion in water. This was added to the starch suspension and the procedure allowed the preparation of a well dispersion of the nanoclay in the matrix. The delayed addition of the plasticizer promoted the penetration of starch chains into the clay galleries resulting in complete exfoliation. The same explanation stands for 1.0 phr nanoclay loaded TPS/PLA/clay nanocomposites specimen, as shown in Fig. 3b. It was noteworthy that, the simultaneous addition of clay and glycerol into the starch solution leads to an ordered geometry of clay (Fig. 3c) in the nanocomposites. The appearance of such ordered geometry in this process might be resulted from the difficulty in exfoliating clay layers in more viscous glycerol gelatinized starch.

4.5. Compatibilization mechanism of NaMMT in the (60/40, w/w) TPS/PLA blend

This work involved the preparation of bio-degradable (60/40, w/w) TPS/PLA/NaMMT nanocomposites via the melt mixing of in-situ gelatinized clay dispersed TPS and PLA. The SEM micrographs revealed matrix-droplet morphology of TPS/PLA in the asymmetric composition (60/40) of the TPS and PLA. It was also found that the droplet size of PLA was decreased on incorporating NaMMT into the TPS/PLA blend. The XRD results revealed an extensive dispersion of NaMMT in the TPS/PLA blend. The NaMMT was preferentially dispersed in the major TPS phase, as was evident from the TEM micrographs.

Table 1
Water absorption data for filled and unfilled (60/40, w/w) TPS/PLA blends in comparison to the 30 wt% glycerol containing TPS.

No.	Sample (optimized glycerol content of 30 wt%)	Water absorption (%)
1	30 wt% glycerol TPS	54.37
2	(60/40, w/w) TPS/PLA blend	48.63
3	(60/40, w/w) TPS/PLA blend with 0.5 phr clay	44.49
4	(60/40, w/w) TPS/PLA blend with 1.0 phr clay	42.83

Based on the morphological analysis of the TPS/PLA/MWCNT nanocomposites it can be concluded that the NaMMT was first dispersed into the TPS during gelatinization. The melt mixing of clay dispersed TPS and PLA did not favour the migration of clay to the minor PLA phase, as NaMMT did not feel any special attraction towards PLA.

The NaMMT played the role of compatibilzer to lead a reduction in droplet size on increasing in the amount of clay into the TPS/PLA/NaMMT nanocomposites. The reduction in droplet size on increasing the clay loading can be explained in terms of the stabilization of smaller droplets of PLA through the barrier effect of clay originating from the selective dispersion of clay into the TPS phase. Thus, the barrier effect of NaMMT can be assumed to play the prime role in the compatibilization of TPS/PLA blend.

4.6. Water absorption studies

From Table 1, it can be seen that blend samples of (60/40, w/w) TPS/PLA blend with 30 wt% optimized amount of glycerol showed a drastic decrease in the water absorption with a value of 48.63%. The blending of TPS with more water repellent (WA 0.136%) PLA can be assumed to play the prime role in the water absorption of the blend. (60/40, w/w) TPS/PLA blend samples with 30 wt% glycerol plasticized starch and 0.5 phr and 1.0 phr nanoclay were also studied. The blends with nanoclay also revealed reduced water absorption values which were much lower than that observed for 30 wt% glycerol plasticized starch without nanoclay loading. Samples with 0.5 phr nanoclay loading demonstrated remarkably low water absorption values of 44.49%. It also showed that addition of higher amount (1 phr) of nanoclay marginally reduced (42.83%) the water uptake value of the nanocomposites.

After soaking the samples in deionized water for water absorption test according to ASTM D570, it was observed that the TPS samples became soft and tender. This can be attributed to the partial dissolution followed by swelling of starch, leading to a dispersion of the material in water. As reported by Chen and Evans (2005), the presence of nanoclay enhanced the water resistance of TPS and this could be validated by the data obtained for NaMMT filled TPS/PLA nanocomposites samples. Under the immersion conditions, the nanoclay filled TPS/PLA samples continued to be dimensionally stable and intact in shape. So, after incorporation of the clay, the dispersed clay platelets, would act as barriers, thereby providing protracted pathways for the water molecules, hence reducing the hydrophilicity.

4.7. Thermal analysis

The thermal stabilities of the TPS/PLA/NaMMT nanocomposites nanocomposites were analysed by TGA and are shown in Fig. 4a.

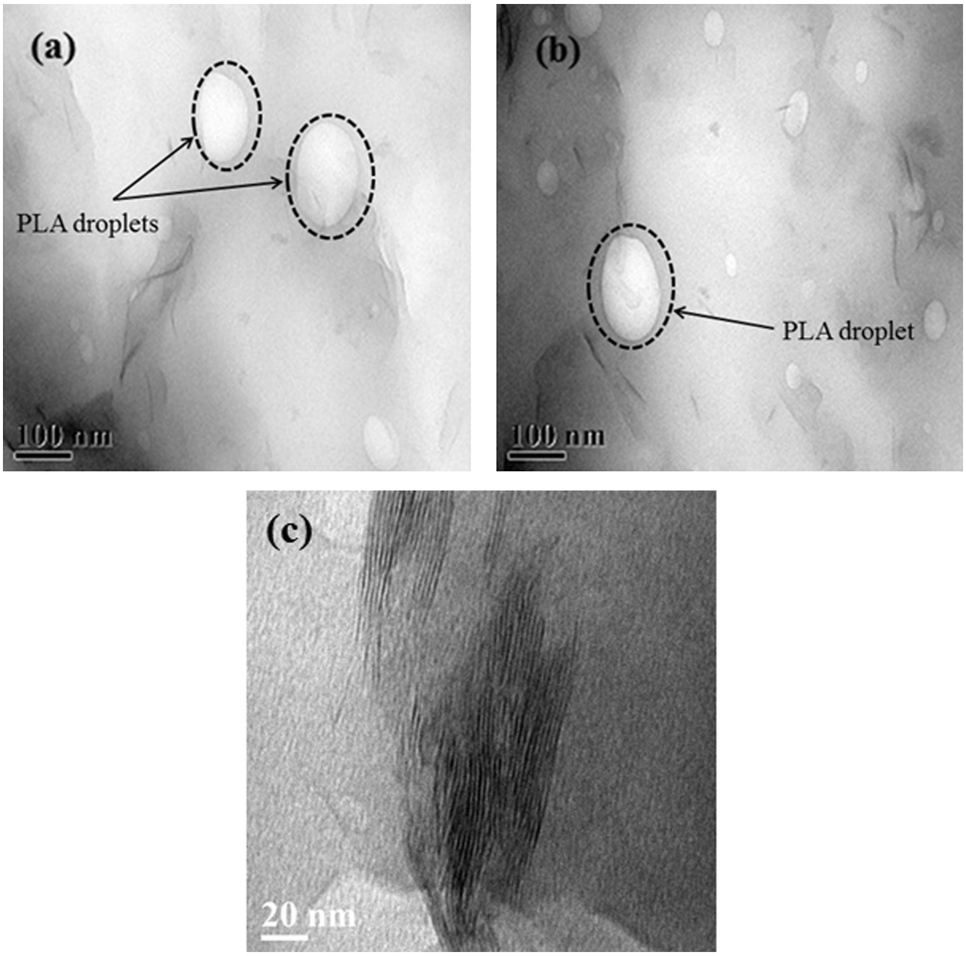

Fig. 3. HRTEM images of (60/40, w/w) TPS/PLA nanocomposites with (a) 0.5 phr NaMMT, (b) 1.0 phr NaMMT prepared by following delayed addition of glycerol. (c) HRTEM images of (60/40, w/w) TPS/PLA nanocomposites with 0.5 phr NaMMT prepared by simultaneous addition of glycerol.

Pure TPS possessed the lowest thermal stability among all the systems. The initial step in the thermogram for pristine TPS between 50 and 180 °C corresponds to water loss and volatilization of the plasticizer and the next step observed at ~300 °C, indicating starch decomposition. Blending with PLA increased the thermal stability of the (60/40, w/w) TPS/PLA blend, though not very significantly. However, the NaMMT loaded blend systems showed increased thermal stability than the blend as expected. This could be due to the restricted mobility of the polymer chains in the vicinity of the exfoliated nanoclay in the matrix phase, which needs higher energy for the degradation process.

DSC analysis was carried out to evaluate the effect of clay platelets on the T_g of the (60/40, w/w) TPS/PLA/NaMMT nanocomposites as well as their preference towards blend constituents. Fig. 4b represents the DSC thermograms of pure TPS, (60/40, w/w) TPS/PLA blend and (60/40, w/w) TPS/PLA blend/NaMMT

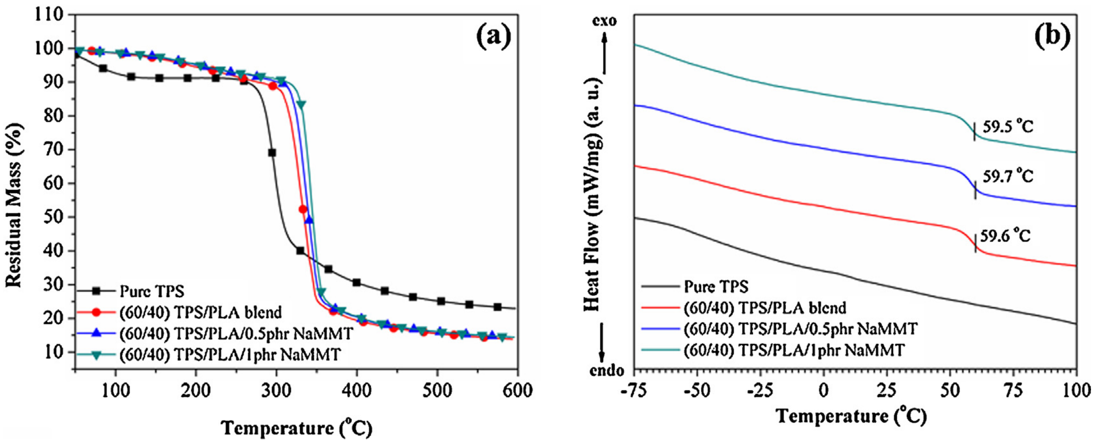

Fig. 4. (a) TGA, (b) DSC thermograms of TPS, TPS/PLA blend and TPS/PLA/NaMMT nanocomposites.

Table 2
Mechanical test data for filled and unfilled (60/40, w/w) TPS/PLA nanocomposites in comparison to pure TPS.

No.	Sample	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
1	Pure TPS	1.82 ± 0.23	146 ± 6.2	3.61 ± 0.84
2	Pure PLA	16.4 ± 0.56	542 ± 16.3	2.12 ± 0.68
3	(60/40, w/w)TPS/PLA	5.63 ± 0.32	305 ± 14.6	4.32 ± 0.87
4	(60/40, w/w) TPS/PLA + 0.5 phr clay	7.29 ± 0.48	325 ± 17.2	6.68 ± 0.98
5	(60/40, w/w) TPS/PLA + 1 phr clay	7.95 ± 0.33	329 ± 13.8	6.05 ± 1.24

nanocomposites at two different loadings of the incorporated nanoclay. As observed, the T_g of pure PLA (~60.6 °C) remained almost unaltered in all the samples under investigation consequent with the affinity of the clay platelets selectively towards TPS. However, a trivial decrease in T_g was evident in case of the (60/40, w/w) TPS/PLA blend/NaMMT nanocomposites. This sort of decrease in T_g in the TPS/PLA blend as well as in the TPS/PLA blend/Na-MMT nanocomposites might be associated with the plasticizing effect of the glycerol used for the gelatinization of starch. The T_g appearing in the range −60 °C to −50 °C might be associated with the glass transition of glycerol, as was found previously in various studies (Averous et al., 2000; Lourdin, Bizot, & Colonna, 1997). As the T_g at lower temperature involves none of the polymer (TPS & PLA), no major remarks regarding the distribution of clay can be concluded. However, the absence clay in the PLA phase can be assumed, as the T_g of PLA did not involve significant change on clay incorporation.

4.8. Mechanical properties

The mechanical properties recorded for pristine TPS samples were not very substantial as can be seen from Table 2. The limitations in mechanical properties of TPS for packaging applications can be improved by the process of blending with other polymers or by the incorporation of reinforcing agents like MMT (Carvalho, Curvelo, & Agnelli, 2001; Chang, An, & Sur, 2003). The samples were blended with PLA and tensile test procedures were carried out and the results have been depicted in Table 2. As observed, the mechanical properties were increased as a result of blending the thermoplastic starch with PLA. The tensile strength recorded for the blend is 5.63 MPa which was significantly raised (7.29 MPa and 7.95 MPa for 0.5 phr and 1.0 phr, respectively) due to the addition of nanoclay. This is in tune with the reports by Carvalho, Curvelo, and Agnelli (2001) and Wilhelm, Sierakowski, Souzab, and Wypych (2003) that the addition of nanoclays to TPS matrix shows an increase in the tensile properties. The strength and modulus of TPS were increased on blending with much stronger PLA and were increased with increase in clay loading. The improved mechanical properties in the presence of clay in the nanocomposites might be associated with the enhanced compatibility between TPS and PLA. However, the occurrence of more mechanical performances in the presence of stiffer clay layers in the nanocomposites cannot be discarded.

The pure glycerol-plasticized starch shows ~3.61% strain at break. The strain at break is slightly increased (4.32%) in the case of the blend implying the immiscibility of the components. The incorporation of nanoclay to this immiscible blend gave a maximum strain break of 6.68% in the case of 0.5 phr NaMMT loaded nanocomposites and this enhancement supporting the compatibilizing action of NaMMT in the nanocomposites. But, addition of more nanoclay decreased the strain at break (Dean, Yu, & Wu, 2007; Wilhelm, Sierakowski, Souzab, & Wypych, 2003). This indicates that addition of more inorganic filler into a polymeric matrix resulted in increase in brittleness in the nanocomposites.

Table 3 compares the mechanical property data of nanocomposites consisting of TPS as well as PLA. The PLA used by Park et al. was mechanically far superior compared to that used in our study. If we consider only into the alternation in mechanical property we can found that the replacement of 30% PLA by TPS reduced tensile strength and elongation at break by ~50%, whereas, our nanocomposites revealed such decrease after replacement of 60% PLA by TPS. In terms of elongation our results are satisfactory enough compared to the results found by Park et al. The elongation at break was decreased from 10.7 to 5.7 on replacing PLA by 30% TPS, whereas, the elongation was increased on replacing 60% PLA by TPS in our system. In another study by Yu et al. revealed a ~15% increase in tensile strength and Young modulus, whereas, our prepared nanocomposites with 1phr clay resulted >300% increase in tensile strength and >100% increase in Young modulus compared to that of pure TPS. Comparing the mechanical results reported in the literature with that of our result we can conclude that our method is good enough to prepare potential biodegradable plastics.

4.9. DMA analysis

DMA analysis was carried out to follow the temperature dependence of storage modulus and tan δ behaviours of the TPS/PLA/clay nanocomposites. Fig. 5a and b shows the respective temperature dependence of storage modulus (E') and tan δ curves for pristine TPS, (60/40, w/w) TPS/PLA blend and the (60/40, w/w) TPS/PLA/NaMMT nanocomposites. It can be observed that in the entire range of temperature (−100 °C to 140 °C), the moduli of the TPS/PLA samples are higher than those of the pristine TPS. The addition of nanoclay to the blend system extensively increased the storage modulus in both the glassy and rubbery region. Among the NaMMT loaded nanocomposites, the one with higher loading of NaMMT exhibited larger modulus than the other, due to the greater reinforcing effect of the stiffer clay silicate layers in the nanocomposites. The T_g of the amorphous phase of TPS can be determined

Table 3
Previously reported mechanical property data for various systems consisting of TPS.

Composition of matrix	Glycerol (%)	Filler	Tensile strength (MPa)	Young modulus (MPa)	Elongation at break (%)	Reference
100 PLA	0	0	58.8	1217	10.7	Park, Kim, Kim, and Kim (2000)
30/70 TPS/PLA	20	0	26.6	1059	4.1	
30/70 TPS/PLA	40	0	27.8	747	5.7	
100 TPS	0	1% clay	32.2	–	7	Dean, Yu, and Wu (2007)
100 TPS	0	1.5% clay	42.3	–	4.7	
100 TPS	0	0% clay	30.0	3090	8.7	Dean, Do, Petinakis, and Yu (2008)
100 TPS	0	1% clay	34.2	3570	9.1	

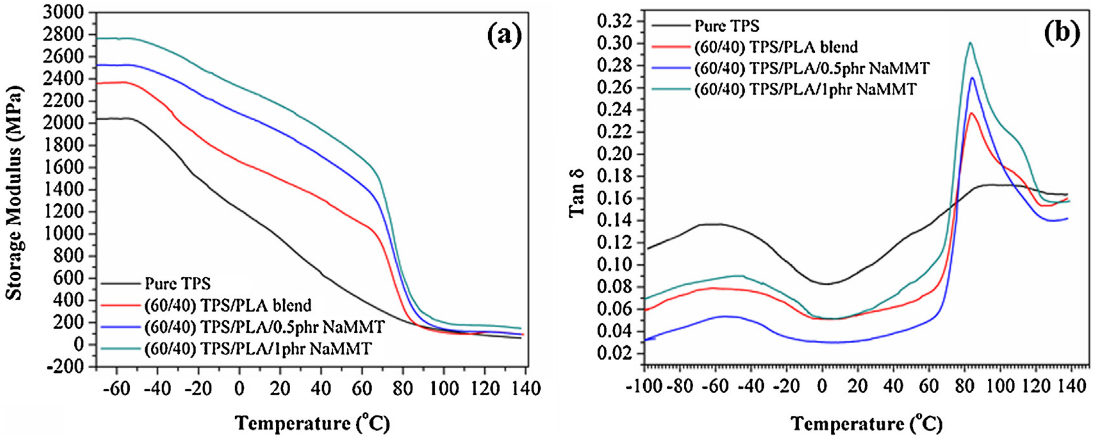

Fig. 5. (a) Storage modulus, (b) tan δ vs. temperature plots of TPS, TPS/PLA blend and TPS/PLA/NaMMT nanocomposites.

from the relaxation temperatures obtained from tan δ curves. The maximum of the respective tan δ peaks in Fig. 5b resembles the T_g of polymers. The tan δ curve for pristine TPS shows a transition peak at $\sim -52.8^{\circ}$ and a broad hump centred near $\sim 91.2\,^{\circ}$C, due to the α-relaxation of starch (T_{α}) and the β-relaxation (T_{β}) of glycerol, respectively (Park, Lee, et al., 2002; Park, Li, et al., 2002).

The blend (60/40, w/w) TPS/PLA showed similar transitions but a stronger peak at $\sim 85\,^{\circ}$C indicating the T_g of the PLA phase in the blend. The unchanged PLA peak might be resulted from the absence of clay in the PLA phase.

5. Conclusions

New biodegradable TPS/PLA/NaMMT nanocomposites with highly exfoliated clay morphology were prepared of the in an economically viable method. In spite of the inherent immiscibility of the blend constituents the blend/clay nanocomposites was appeared as mechanically improved material, due to the action of nanoclay. The effect of nanoclay on the blend system was interpreted as compatibilization; because of its extensive exfoliation, the dispersed clay platelets could reinforce the system successfully. Better resistance towards water absorption could be achieved due to the blending of hydrophobic PLA to TPS. The increased thermal characteristics were because of the exfoliation as the NaMMT layers, which acted as barriers to heat transfer. Because of its renewability, biodegradability and low cost, starch seems to be nowadays an important challenger for the development of future agro-based products, when petroleum resources are fast decreasing. They are in tune with the concept of sustainable development.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.04.024.

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