IOP Conf. Series: Materials Science and Engineering **410** (2018) 012001 doi:10.1088/1757-899X/410/1/012001

Mechanical and biodegradation analysis of thermoplastic starch reinforced nano-biocomposites

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Abstract

The aim of the present investigation is to develop and characterize nano-filler reinforced thermoplastic starch (TPS) composites. Both montmorillonite (MMT), and Cloisite 30B are used in different weight percentages as reinforcing filler with TPS by hot compression molding to develop starch-mmt (SM) and starch-cloisite (SC) composites respectively. Fabricated composites were mechanically tested. Composite containing 3 wt% mmt showed tensile strength and tensile modulus of 2.67 MPa and 68.4 MPa respectively X-ray diffraction (XRD) and transmission electron microscopy (TEM) of nano-composites were analyzed. Biodegradation of composites were carried out in soil burial condition for certain time periods and found that the degradation rate of composites are slow and lost only on an average of 45% of their original weight after 60 days under soil burial condition. Surface topography of degraded samples was studied under scanning electron microscope. As SM and SC composites are biodegradable in nature, these can be utilized as packaging materials, molded articles and other aesthetic products to reduce the use of non degradable synthetic plastic.

Key words: Thermoplastic starch; MMT; Cloisite 30B; Nano-biocomposites

1. Introduction

Packaging with petrochemical based plastics such as polyester, polyolefins, polyamides and polyolefin halides etc. have been used largely because of their abundance and low cost. Vegetable, grocery, food packaging, etc. are growing from day to day and the materials used for packaging are concerns for preservation of all types of foods and protection from oxidative and microbial spoilage. Packaging material can be prepared from synthetic and biodegradable plastic. Better aesthetic values, durability, mechanical properties are the prime factors to choose

synthetic polymer and their composites over biodegradable polymer. But these polymers are non-biodegradable and after use creates environment, soil, water and their incineration causes air pollution. So, plastic waste management is now a great challenge due to non availability of free land for solid waste disposal [1-2].

Research on biodegradable polymer and their composite films has been increased now a day to counter the above problem. Biopolymers like starch, protein, chitosan, and cellulose are the best choices for researcher as they are renewable, cheap and abundant source. Scientifically these molecules are polar and chemically active in nature and completely biodegradable. Starch, a polymeric carbohydrate consisting of a large number of glucose units joined by glycosidic bonds and contains a number of hydroxyl groups [3-4]. Muller et al. (2012) prepared cassava starch reinforced natural and organically modified nano composites and found the use of 5% hygroscopic nanoclay increases strength and decreases the permeability to water vapor [5]. Priyada et al. (2013) studied mechanical, thermal and structural properties of rice starch films reinforced with rice starch nanocrystals and found the rice starch films containing 20% starch nanocrystals had the best mechanical properties and provided a high tensile strength and elongation at break of about 16.43 MPa and 5.76%, respectively [6]. Slavutsky et al. (2012) reported on water barrier properties of corn starch-clay nanocomposite films that addition of nanoparticles at percentages below 10% had excellent potential for their application in the technology of biopolymer based films [7].

Park et al. (2002) studied moisture and mechanical properties of starch/nanoclay composites employing an organically modified MMT and natural MMT. They reported that modified MMT reinforced composite showed higher water vapor transmission rates than samples with MMT [8]. Mohan et al. (2016) studied the effect of nanoclay fillers on the properties of corn starch polymer-based biofilm and the results reported are reduction of 22% in water absorption, 40% in moisture uptake, 30% in oxygen permeation and 31% in swelling for 2–3 wt % nanoclay-filled biofilm as compared with unfilled biopolymer [9]. Hassani and Nafchi (2014) prepared and characterized potato starch nanoclay composite and found increase in tensile strength from 7.33 to 9.82 MPa, and decrease in elongation at break from 68.0 to 44.0% [10].

Biodegradable thermoplastic starch (TPS) reinforced nano composites are a new class of hybrid engineering compounds which provides better mechanical properties, dimensional

stability, water resistance and biodegradability over non-degradable synthetic polymer [11]. In this work biodegradable polyester blended nano-composites were developed and characterized. Both natural nanoclay (montmorillonite (MMT)) and organically modified nanoclay (Cloisite 30B) of different weight percentages were utilized separately for fabrication of nano-composites. Developed bio-composites can be utilized in different sectors like packaging, decorating and automobile, etc.

2. MATERIALS AND METHODS

2.1. Materials

Thrmoplastic starch (TPS) (derived from corn starch and blended with polyester) was supplied by Bio-grade (Nanjing) Pty Ltd., China. Southern Clay Co. USA, supplied Montmorillonite (MMT) and Cloisite 30B. Glycerol (Merck, India) was procured from local market.

2.2. Fabrications of nanoclay reinforced TPS composites

Blends with various amounts (0,1, 2, 3,4 and 5 wt%) of natural nanoclay MMT, glycerol (5 wt%) and TPS were prepared by melt mixing at 100 ºC and 60 rpm for 5 min using an internal mixer having double screw extruder (Brabender mixing chamber). These different sets of TPS-MMT blends were collected and then compressed in a hot press at the temperature of 105 ºC for 10 min under 6.0 MPa pressures to prepare starch-mmt (SM) composites. Fabricated composites comprising 0-5 wt% of nanoclay are coded as SM0-5 respectively. Similarly TPS-Cloisite 30B (1, 2, 3, 4 and 5 wt%) composites (SC1-5) were prepared by following above formulation and procedure.

2.3. Characterizations

Tensile properties of SM and SC composites were characterized according to standard ASTM D638 with cross head speed of 5 mm/min using HOUNSFIELD H10K UTM instrument. From each of the composite eight specimens were tested and average value was reported. From both the sets, highest tensile strength shown composite was considered as mechanically optimized.

X-ray diffraction (XRD) study of optimized SM and SC composites was performed using a X-ray diffractometer (WAXD, ULTIMA-III, Rigaku, Japan) with nickel filtered Cu-Kα radiation (λ= 0.154nm) operated at 40 kV and 100 mA, at a scanning rate of 1 ˚/min.

Transmission electron microscope (TEM) analysis for bulk morphology study of optimized SM and SC composites were characterized using a transmission electron microscope, model JEM-1230, JEOL with an acceleration voltage of 100 kV.

Biodegradation analysis of optimized SM and SC were carried out under soil burial condition in accordance to the method specified in standard BIS 1623-1992. Field emission scanning electron micrograph (FE-SEM) analysis of optimized composites before and after degradation was taken by using a scanning electron microscope (SUPRA-40, Germany) instrument operated at an accelerating voltage of 5 kV.

3. RESULTS AND DISCUSSION

3.1. Mechanical strength analysis

Tensile strength, modulus, elongation at break values of SM and SC composites are reported in Table 1. With increase in mmt content from 0 to 5 wt%, tensile strength and tensile modulus of SM composites increased due to reinforcement of nanofiller. SM3 showed tensile strength and tensile modulus of 2.96 MPa and 66.4 MPa respectively. Elongation at break value of SM composites decreased with increase in nanoclay amount due to improvement in brittleness property [12]. Similar result obtained in case of SC composites. Tensile strength of cloisite 30B content composites enhanced from 2.54 MPa to 3.03 MPa. Tensile modulus of SC composites also increased from 58.7 MPa to 65.5 MPa. SC3 showed highest tensile strength and modulus among all SC composites and SM3 showed highest tensile properties among all SM composites, hence both are considered as mechanically optimized.

Table 1. Mechanical properties of SM and SC composites

Composite	Tensile strength (MPa)	Standard deviation (±)	Tensile modulus (MPa)	Standard deviation (±)	Elongation at break (%)	Standard deviation (±)
SM0	**1.57**	**0.13**	**56.2**	**1.42**	**6.54**	**0.04**
SM1	**2.43**	**0.15**	**58.4**	**1.42**	**6.26**	**0.04**
SM2	**2.67**	**0.12**	**61.3**	**1.42**	**6.08**	**0.04**
SM3	**2.96**	**0.11**	**66.4**	**1.42**	**5.76**	**0.04**
SM4	**2.29**	**0.18**	**55.7**	**1.42**	**5.58**	**0.04**
SM5	**1.91**	**0.12**	**51.8**	**1.42**	**5.26**	**0.04**
SC1	**2.54**	**0.16**	**58.7**	**1.42**	**6.76**	**0.04**
SC2	**2.72**	**0.14**	**60.3**	**1.42**	**6.18**	**0.04**
SC3	**3.03**	**0.13**	**65.5**	**1.42**	**5.93**	**0.04**
SC4	**2.43**	**0.12**	**55.8**	**1.42**	**5.53**	**0.04**
SC5	**2.02**	**0.12**	**50.8**	**1.42**	**5.24**	**0.04**

3.2. XRD analysis of optimized TPSM and TPSC

XRD graph of mmt, cloisite 30B, SM3, and SC3 is shown in Fig.1. Cloisite 30B nanoclay showed its characteristics peak at around 4.96° (2θ) which corresponds to interlayer clay spacing (d spacing) of 17.7 Å, consistent with the reported value [13]. In its concerned composite i.e.,

SC3 have no peak suggested exfoliation nature of nanoclay at the interphase. MMT showed its characteristic peak at around 7.17° (2θ) which is shifted to words lower angle 5.52° for SM3 composite stating intercalation of nanoclay in TPS [14].

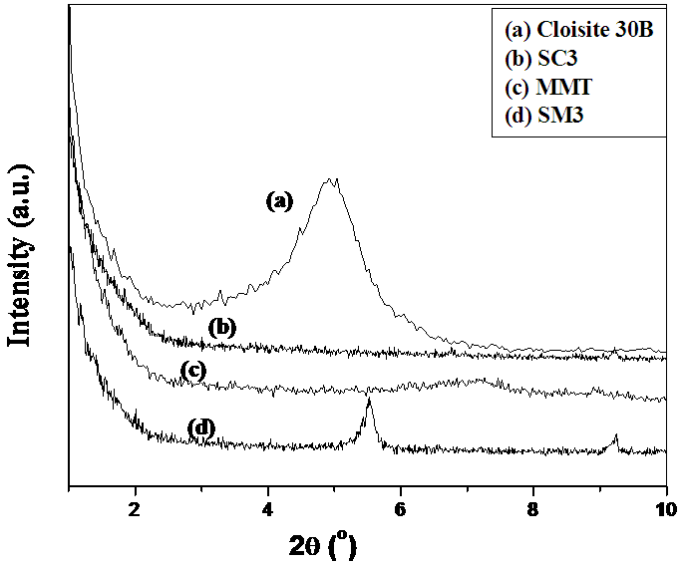

Fig.1. XRD graphs of mechanically optimized SM and SC composites

3.3. Morphology analysis of optimized SM and SC composites

TEM photographs of SM0, SM3, and SC3 is given in Fig.2. In SM0, smooth surface of thermoplastic starch is shown while in SM3 clay layers are clearly visible (marked by circle), arranged layer wise indicating intercalation of silicate layers as discussed in XRD. In SC3 composite, individual clay layers are separated from each other (marked by arrow) showing exfoliation of nanoclay in TPS. Both intercalation and exfoliation of nanoclay helps to improve the mechanical properties of TPS-nanoclay composite [14].

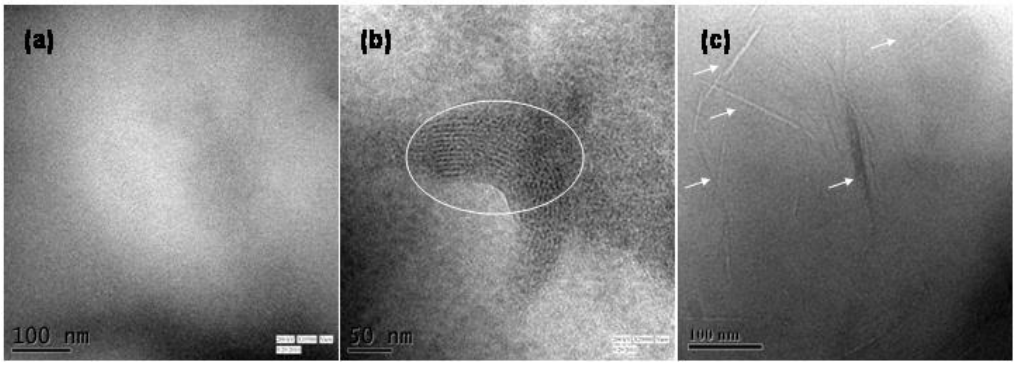

Fig.2. TEM photographs of (a) SM0, (b) SM3, and (c) SC3

3.4. Soil-burial degradation analysis of optimized SC and SM composites

Weight loss after different periods in soil burial of SM0, SM3, and SC3 are reported in Table 3. It was found SM0 without any nanoclay is less degraded initially as compared to SM3 and SC3. After 60 days under soil burial degradation SM0, SM3, and SC3 loosed 40.1%, 49.1% and 44.9% in weight respectively.

Table 2. Weight loss of SM0, SM 3, and SC3 after different biodegradation periods

Composite	After 15 days (%)	After 30 days (%)	After 45 days (%)	After 60 days (%)
SM0	**9.2**	**12.6**	**28.7**	**40.1**
SM3	**14.9**	**18.2**	**34.7**	**49.1**
SC3	**10.2**	**14.1**	**31.2**	**44.9**

3.5. FE-SEM analysis of biodegraded sample

Field-emission SEM photographs of biodegraded samples are given in Fig.3. SM3 (Fig.3(a)) and SC3 (Fig.3(c)) shows smooth surface before biodegradation. After 60 days of degradation it was found degraded SM3 (Fig.3(b)) and degraded SC3 (Fig.3(d)) has many cavities on its surface (marked by circle). Both composite surfaces were found roughed, degraded, and in maximum places some matrix has been eaten by microbes. This indicates the degradation of TPS-nanoclay composites [15].

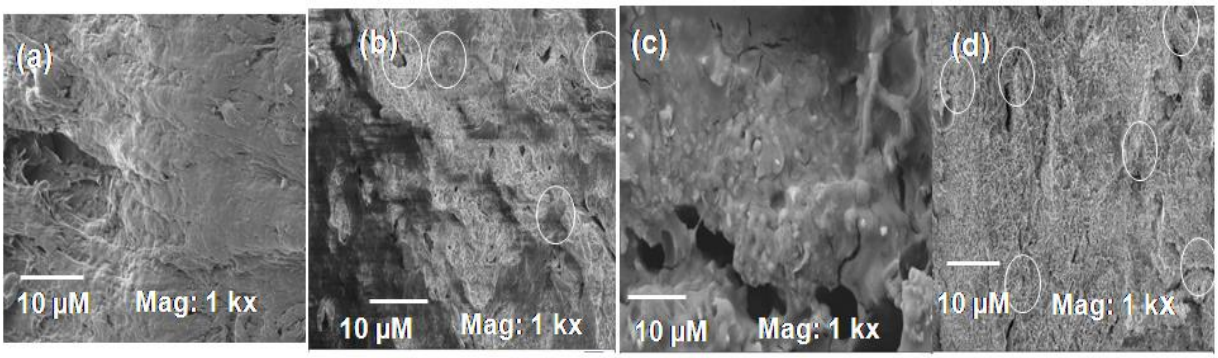

Fig.3. FE-SEM photographs of (a) SM3, (b) Degraded SM3, (c) SC3, and (d) Degraded SC3

4. CONCLUSIONS

The objective of this work was to develop and characterize biodegradable nano-bio composites. It was found with reinforcement of natural nanoclay tensile strength of composites increased upto 89%. Similarly 3 wt% organically modified nanoclay loaded composite (SC3) showed maximum tensile strength of 3.03 MPa which is nearly 93% enhancement. Both XRD

and TEM analysis of optimized composites proved formation of intercalation and exfoliation structure. Weight loss and FE-SEM photographs of degraded sample proved developed composites are biodegradable in nature. Hence these composites are eco-friendly unlike synthetic plastic and can be utilized in different sectors like packaging, decorating and automobile, etc.

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