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Synthesis of thermal and chemical resistant oxygen barrier starch with reinforcement of nano silicon carbide

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ABSTRACT

Starch/silicon carbide (starch/SiC) bionanocomposites were synthesized by solution method using different wt% of silicon carbide with starch matrix. The interaction between starch and silicon carbide was studied by Fourier transform infrared (FTIR) spectroscopy. The structure of the bionanocomposites was investigated by X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM). Thermal property of starch/SiC bionanocomposites was measured and a significant enhancement of thermal resistance was noticed. The oxygen barrier property of the composites was studied and a substantial reduction in permeability was observed as compared to the virgin starch. The reduction of oxygen permeability with enhancement of thermal stability of prepared bionanocomposites may enable the materials suitable for thermal resistant packaging and adhesive applications.

1. Introduction

In recent years, the development of organic–inorganic nanocomposites have attracted many researchers due to unexpected hybrid properties of these tailored materials derived from more than one components (Gangopadhyay & De, 2000; Lim, Hyun, Choi, & Jhon, 2002; Weon, Gam, Boo, Sue, & Chan, 2006). As the natural biopolymers such as starch, cellulose and chitin are cheap, abundant, biodegradable and renewable, hence, attempts have been made on blending these materials with other substances to prepare new materials with desired properties (Fischer, 2003; Huang, Roan, Kuo, & Lu, 2005; Ishiaku, Pang, Lee, & Mohd Ishak, 2002; Padalkar et al., 2010; Pandey et al., 2005; Park, Lee, Park, Cao, & Ha, 2003; Sahoo & Rana, 2006; Szepes et al., 2005; Wu, 2003).

Among the biopolymers, starch is a promising polymeric material because of its low cost, easy availability, renewability and degradability. It is composed of repeating 1,4-α-D-glocopyranosyl units; amylase and amylopectin depending upon plant resources, and stored as granules in plants. Starch has a lot of uses as thickener, water binder, emulsion stabilizer, gelling agent, coating sizing in paper and textile, adhesives, adsorbents, encapsulants and so many (Araujo-Farro, Podadera, Sobral, & Menegalli, 2010; Biswas, Willet, Gordon, Finkenstadt, & Cheng, 2006; Jasim, Karawi, Hussein, & Daraji, 2010). Starch offers a suitable substitute for petroleum-based plastics especially for short term packaging and disposable applications (Tianyi & Xiuzhi, 2000; Weber, Fastersen, & Bertelsen, 2002). Because of its sensitivity to water, starch has a severe limitation. Attempt has been made to blend starch with synthetic biodegradable polymers like, poly (glycolic acids) (PGA) (Kong, Wang, Gao, Liu, & Liu, 2011), poly (lactic acids) (PLA) (Ke & Sun, 2000), polycaprolactone (PCL) (Rosa, Guedes, & Pedroso, 2004a; Rosa, Lotto, Lopes, & Guedes, 2004b), polyhydroxybutyrate (PBH) (Rosa et al., 2004a, 2004b), and poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV) (Willett & Shogren, 2002). Among these polymers, the PLA has been studied extensively for tissue engineering (Salgado, Coutinho, & Reis, 2004), drug delivery (Tarvainen et al., 2002) and as a synthetic degradable polymers in human medicine (Vroman & Tighzert, 2009). Among the blends of starch with PCL and maleicanhydride grafted PCL, more degradability was noticed in the case of grafted PCL (Wu, 2003). Starch was blended with PHB and measured the change in glass transition temperature of the films for all proportions of PHB (Godbole, Gote, Latkar, & Chakrabarti, 2003). The immiscibility of starch with PHBV was investigated with synthesis of series of starch/PHBV blends (Reis et al., 2008). We have studied the oxygen permeability and flame retardancy properties of Polymethylmethacrylate/starch composites and suggested the composite materials for use in packaging industries (Kisku & Swain, 2012).

Carvalho et al. mixed the starch with natural rubber blends and developed a biodegradable starch-based plastic having high toughness (Carvalho, Job, Alves, Curvelo, & Gandini, 2003). A plenty of works are reported in the literatures regarding organic–inorganic based starch composites. Baczkowick et al. studied the thermal properties of Bi (III) and Bi(IV) complex materials of starch

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and found that, bismuthated starch were slightly less thermally stable than the raw starch (Baczkowicz, Wojtowicz, Anderegg, Schilling, & Tomasik, 2003). The glass transition and gas permeation properties of polyol-plasticised pullulan–starch blends were studied (Billaderis, Lazaridou, & Arvanitoyannis, 1999). Further, starch and semicarbazide hydrochloride were heated in the field of microwaves and it was noticed that the macrostructure of starch damaged on conventional heating where as degree of reaction was higher on the microwave heating (Siemion, Kapusniak, & Koziol, 2005). The porous scaffold of gelatin–starch–n hydroxyapatite composites was fabricated through microwave vacuum drying and crosslinking using trisodium citrate (Sundaram, Durance, & Wang, 2008). In another study (Vertuccio, Gorrasi, Sorrentino, & Vittoria, 2009) sodium montmorillonite was incorporated into poly (α-caprolactone)–starch blends by means of ball milling. It was observed that, the milling process not only has demonstrated to be a promising compatibilization method for immiscible PCL-starch blends, but it can also be used to improve the dispersion of nanoparticles in the polymer blends.

In recent years, the modification of properties of starch based nanocomposites have become a growing interest as a promising option for developing their thermal, mechanical and gas barrier properties (Chen & Evans, 2005; Kalambur & Rizvi, 2004; Mc Gloshan & Hally, 2003). The biodegradable starch/clay nanocomposite films were developed and referred to be used as food packaging materials (Avella et al., 2005). The improvement of thermal and mechanical properties of biopolymers due to incorporation of nano fillers has been thoroughly reviewed (Shenhar, Norsten, & Rotello, 2005; Yang, Wang, & Wang, 2007).

Fillers are particles of organic/inorganic origin that are added to modify mechanical, optical, electrical, thermal, gas barrier and flammability property of the matrix. Nano fillers having particle size between 1 to 100 nm have attracted a lot of attention world wide due to their high aspect ratio. Among nano fillers, silicon carbide is an important and non-oxide ceramic material having diversified industrial applications due to its exclusive properties such as, high melting point, oxidation resistance, high erosion resistance, high hardness, strength, chemical and thermal stability (Saravanan, Subramanian, Vishnu Kumar, & Tharanathan, 2006). Silicon carbide can occur in more than 250 crystalline forms called polytypes and has attracted much attraction these days as it has a good match of chemical, mechanical and thermal properties, that makes it a semiconductor of choice for harsh environment applications including high radiation exposure, operation in high temperature and corrosive media (Guo et al., 2008). The effect of nanometer SiC filler on Polyetheretherketone (PEEK) was studied for improvement of tribological behaviors (Wang, Xue, Liu, & Chen, 2000). Although there are numerous numbers of works are reported on starch based composites, still the synthesis of starch nanocomposites reinforced by nano SiC is limited in the literature. So it was a motivation to prepare bionanocomposites made of starch reinforced with silicon carbide in order to improve the thermal, chemical and oxygen barrier properties.

In the present study, a series of starch/SiC bionanocomposites were synthesized by low cost green solution method where water was taken as the solvent. The bionanocomposites were characterized by FTIR, XRD and FESEM. The uniform distribution of SiC was achieved in order to reduce the oxygen permeability with enhancement of thermal and chemical resistant properties.

2. Experimental

2.1. Materials

Starch powder was obtained from Merck Specialities Private Limited, Mumbai, India and used as such. The Silicon Carbide nano powder (Average Particle Size is 50 nm) was purchased from Sisco Research Laboratories Pvt. Ltd., Mumbai, India and used without modification. The other chemicals used were of analytical grade and used as such. All solutions were prepared using double distilled water to follow green chemistry.

2.2. Preparation of starch/SiC bionanocomposite

The starch/SiC bionanocomposites were synthesized by using solution technique. In this method the starch was dispersed in double distilled water by stirring continuously at 50 °C for 30 min and then treating ultrasonic cleaner (120 W/180 KHz) for 30 min (Lapshin, Swain, & Isayev, 2008; Mohanty and Swain, 2010; Swain & Isayev, 2007, 2009). Different weight percentage solution of silicon carbide was made with double distilled water by stirring SiC at 80 °C for 30 min and then passing ultra sound for 30 min using the same instrument. Then the starch solution was added to different wt% silicon carbide solutions. The solution was stirred for 3 h at 50 °C then cooled followed by addition of 6 ml of acetone as non solvent (Tan et al., 2009; Wang et al., 2012). The solution was kept for overnight. The viscous product was filtered and washed with double distilled water. The composites obtained were dried in an oven for 24 h at a temperature of 50 °C. The dried samples were grinded and marked as SSC 0, SSC 1, SSC 2, SSC 5, SSC 8, and SSC 10 for 0, 1, 2, 5, 8, 10 wt% of silicon carbide loading respectively.

2.3. Characterization of starch/SiC bionanocomposites

FTIR spectra of the synthesized samples (in form of KBr pallets) were recorded using a Shimadzu IR Affinity-1 Fourier transform infrared spectrophotometer in the range of 4000–400 cm^{-1}. X-ray diffraction patterns were obtained by using Rigaku X-ray machine operating at 40 kV and 150 mA. The surface morphology of the composites was studied with the help of Scanning Electron Microscope (SEM) from Jeol Ltd., Japan (model 5200 with magnification of 30,000×).

The thermogravimetric analysis (TGA) for the synthesized samples was performed using a TGA apparatus model DTG-60 by Shimadzu Corporation, Japan. The sample was heated under nitrogen purge and heating cycle was 10 °C/min. Oxygen permeability of the bionanocomposites was measured with ASTM F 316-86 by using Oxygen Permeation Analyzer (PMI instrument, model GP-201-A, Texas, NY, USA). For testing oxygen permeability the synthesized powdered bionanocomposites were converted into films of 5 mm thickness with the help of a polymer press at a pressure of 9 tons. The results were recorded as average of the values obtained from five same samples. The biodegradability of the bionanocomposites was studied for 180 days using sludge water. Resistance of the synthesized bionanocomposites toward dilute acid and alkali was investigated for 60 days.

3. Results and discussion

3.1. Characterization of starch/SiC bionanocomposites

The FTIR spectra of starch, SiC and starch/SiC bionanocomposites were studied to identify the functional groups present for interaction between starch and silicon carbide as in Fig. 1. The FTIR spectra of starch have a strong and broad absorption peak at 3630 cm^{-1} is the characteristic absorption peak for the stretching vibration of –OH group. The peaks at 3174 cm^{-1}, 1672 cm^{-1} and 1170–1072 cm^{-1} are assigned to the vibrational absorption of C—H bond, intramolecular hydrogen bond and C—O bond in starch respectively. The peaks at 995 cm^{-1}, 937 cm^{-1} and 867 cm^{-1} are due to vibrational absorption peaks of C—H bond of starch. Silicon

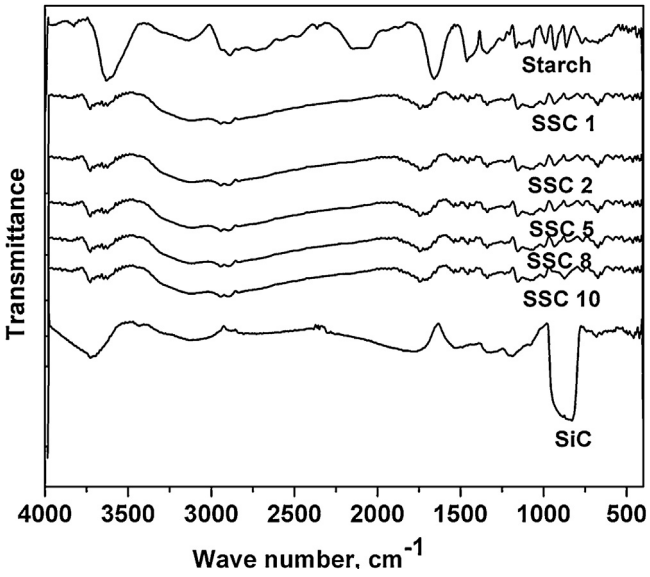

Fig. 1. FTIR spectra of starch, SiC and starch/SiC bionanocomposites at different wt% of SiC.

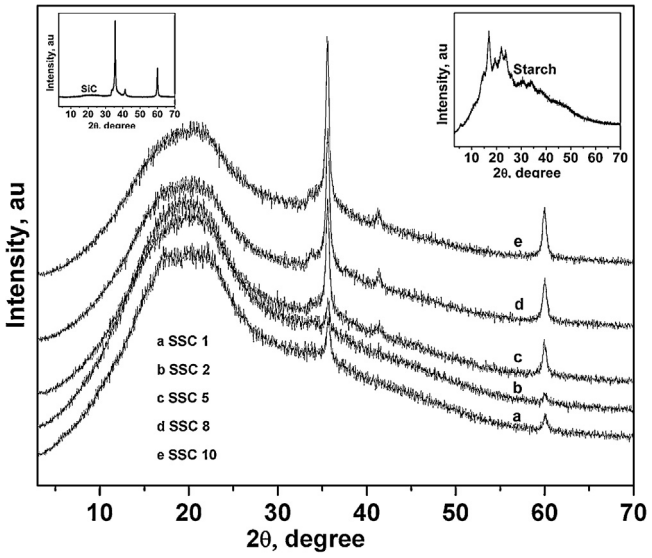

Fig. 2. XRD pattern of starch, SiC and starch/SiC bionanocomposites at different wt% of SiC.

carbide has a strong absorption peak at 860 cm^{-1} due to stretching vibration of Si—C bond. However, the peak at 860 cm^{-1} of SiC is appeared with less intensity in bionanocomposites. Similarly, the strong peak of starch at 3630 cm^{-1} becomes weak and broad in the bionanocomposites. Therefore, there is an interaction of SiC with starch during the formation bionanocomposites. The FTIR spectra of bionanocomposites are noticed to be similar at all wt% of SiC. In the synthesized bionanocomposites, the characteristic peaks of starch and silicon carbide are present at about the same position with different intensities indicating the formation of composite (Saravanan et al., 2006).

3.2. Structure of starch/SiC bionanocomposites

The structural properties of the starch, silicon carbide and starch/SiC bionanocomposites were studied by XRD (Fig. 2). The X-ray diffraction of starch shows diffraction peaks at 2θ values of 17°, 19° and 22° demonstrated good crystallinity of starch. The silicon carbide has a strong diffraction peak at 36° due to its crystalline peak whereas, other peaks are due to different phases of silicon carbide. In starch/SiC bionanocomposites, the characteristic peaks of starch and silicon carbide were found about the same region with different intensities indicating the formation of bionanocomposites. This was also evidenced by FESEM micrographs. The FESEM micrograph of starch, SiC, starch/SiC bionanocomposites of 1, 2, 5, 8, and 10 wt% filler content were studied and compared in Fig. 3. The crystal structured starch flakes were noticed from the FESEM of starch. Further, in FESEM of SiC it was found that the average diameter of SiC nanopowder was found to be about 50 nm. The bionanocomposites at lower percentage (1 and 2 wt%) of SiC, the particles were distributed and embedded in the starch matrix. However, the dispersion of SiC was improved with further increase in SiC (5, 8 and 10 wt%). It was noticed that SiC nanopowder

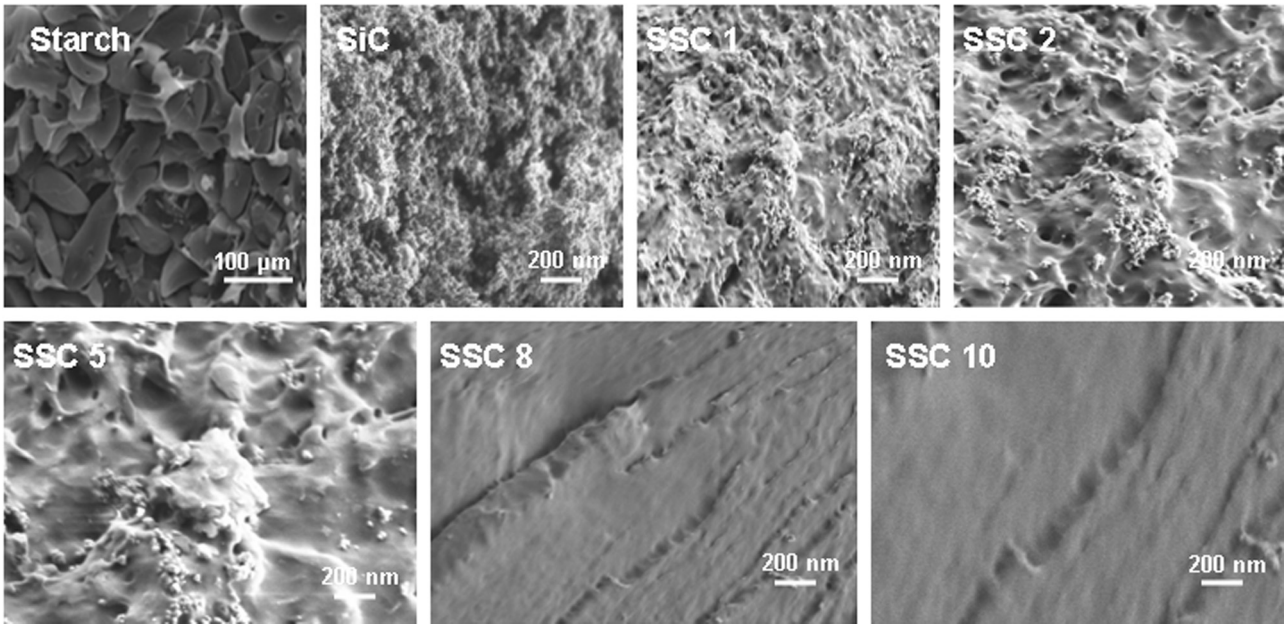

Fig. 3. FESEM images of Starch, SiC and starch/SiC bionanocomposites at different wt% of SiC (SSC1, SSC 2, SSC 5, SSC 8 and SSC 10).

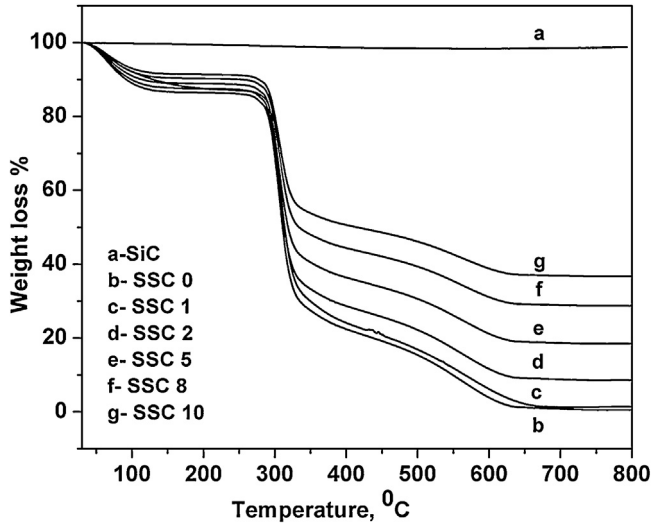

Fig. 4. TGA curves of starch, SiC and starch/SiC bionanocomposites at different wt% of SiC.

particles were completely dispersed in the starch matrix. The crystal structure of starch flakes was ruptured and partly disappeared in the FESEM picture of starch/SiC bionanocomposites having higher percentage of SiC. It may be due to better interfacial adhesion between starch and SiC during the formation of composites.

3.3. Properties of starch/SiC bionanocomposites

3.3.1. Thermal property of starch/SiC bionanocomposites

The thermal properties of starch, silicon carbide and starch/SiC bionanocomposites were studied by thermo gravimetric analysis (TGA). The thermo gravimetric analysis results of starch, silicon carbide and starch/SiC bionanocomposites in the temperature range from 30 °C to 800 °C with a heating cycle of 10 °C/min. were compared in Fig. 4. The thermal decomposition of starch is 330 °C. In the first step a maximum decomposition due to water loss was about 100 °C. In the second step decomposition of starch occurred, whereas the third step was due to the oxidation of partially decomposited starch. The degradation temperature of starch was lower than the starch/SiC bionanocomposites. The degradations of starch and starch/SiC bionanocomposites start from 250 and 275 °C respectively. The final degradation of starch starts at 330 °C where as the bionanocomposites degrade at higher temperature. The final degradation temperature of starch/SiC bionanocomposites is about 625 °C. From TGA analysis, it was noticed that the starch was decomposed completely at about 600 °C whereas a considerable amount of residue was found in the case of starch/SiC bionanocomposites. The residue left after weight loss at 800 °C was about 2%, 9%, 20%, 30% and 40% in the case of the bionanocomposites with 1, 2, 5, 8 and 10 wt% of SiC respectively. The similar result has been reported that, the thermal stability of composites becomes more than that of virgin matrix due to insertion and good dispersion of SiC nanopowder (Guo et al., 2008).

3.3.2. Gas barrier property of starch/SiC bionanocomposites

Polymer based composites which prevent oxygen permeation are studied for use in packaging industries. This thermal resistant bionanocomposite is the class of reinforced biodegradable biomaterial suitable for manufacturing packaging films. The dispersion of silicon carbide in starch matrix may provide the huddles for oxygen entrance whereas; virgin starch may have voids for oxygen permeation. The oxygen permeability of starch and starch/SiC bionanocomposites was studied in Fig. 5. The oxygen flow rate through all the bionanocomposites was observed to be less in comparison to the virgin starch at constant pressures of 2 psi (Fig. 5a). Further, the flow rate was decreased with increase in percentage of SiC loading at different pressure (Fig. 5b). The remarkable reduction in oxygen permeability may be due to dispersion of silicon carbide in the starch matrix blocking the voids. The reduction of oxygen permeation is an indication for packaging application.

3.3.3. Chemical resistance property of starch/SiC bionanocomposites

The resistance property toward chemicals like dilute acid and alkali was studied using 2 N hydrochloric acid and 2 N sodium hydroxide for 60 days in an interval of 10 days (Fig. 6). It was observed that the synthesized bionanocomposite is more stable toward these chemicals in comparison with virgin starch. Virgin starch was completely dissolved in 17 and 22 days with hydrochloric acid (Fig. 6a) and sodium hydroxide (Fig. 6b) respectively where as the synthesized bionanocomposite was stable even after 60 days. Hence the packaging films synthesized thereof may find more suitability for packing mild acidic and alkaline products.

3.3.4. Biodegradation property of starch/SiC bionanocomposites

The biodegradability of the starch and synthesized starch/SiC bionanocomposites using sludge water was studied for a period of 180 days in an interval of 30 days as in Fig. 7. The biodegradation

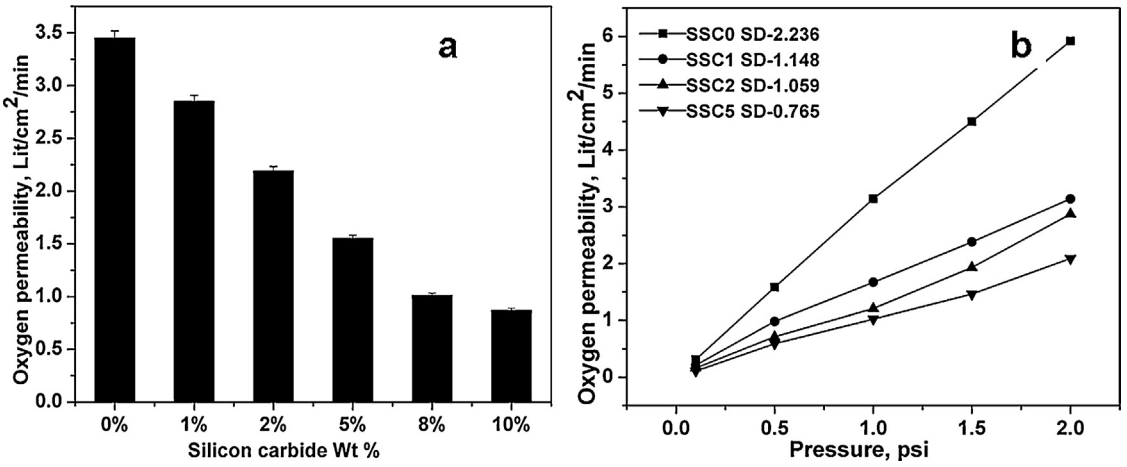

Fig. 5. Oxygen permeability of starch and starch/SiC bionanocomposites (a) at constant pressure and (b) at different pressure.

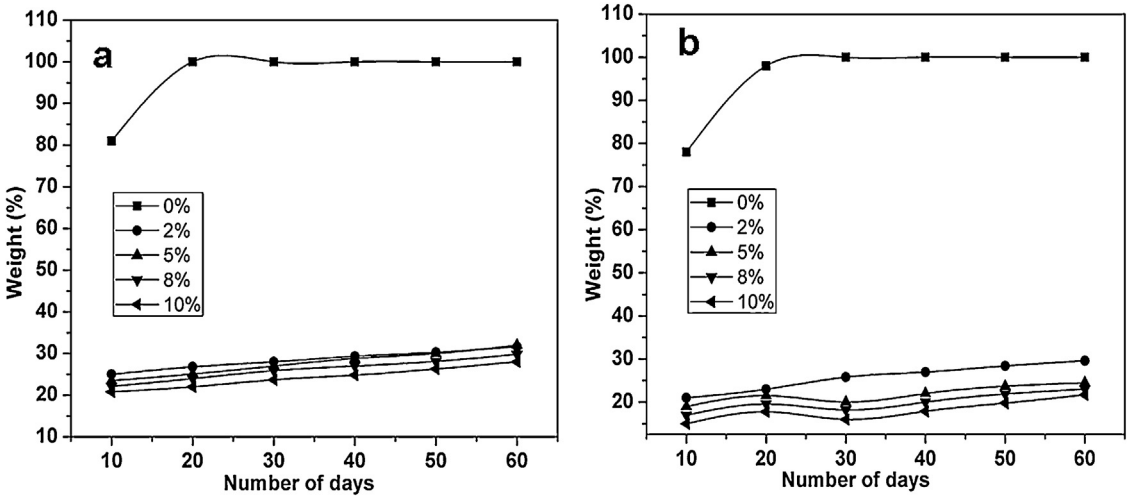

Fig. 6. Percentage weight loss of starch and starch/SiC bionanocomposites in dilute HCl and NaOH at different interval of time.

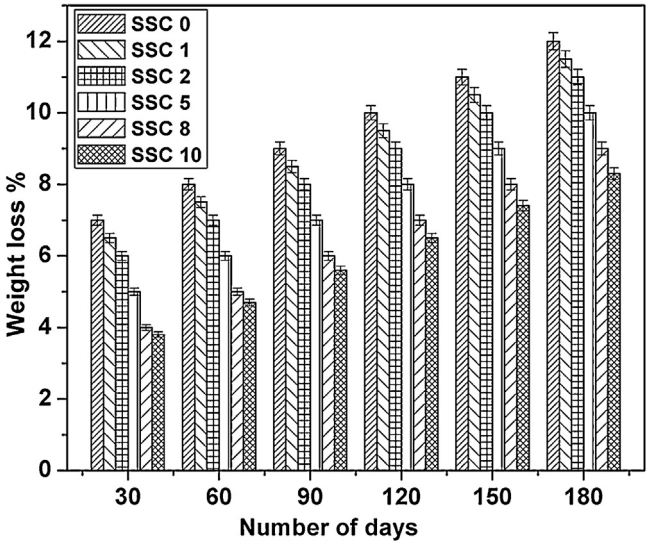

Fig. 7. Percentage weight loss of starch and starch/SiC bionanocomposites due to biodegradation in sludge water at different interval of time.

of the bionanocomposites were found to be less than that of virgin matrix due to insertion of the stable material. Further the degradation was increased with increase in time period. A similar result was noticed in our earlier study of biodegradability of albumin/clay nanocomposites (Dash, Kisku, & Swain, 2012).

4. Conclusions

Starch/SiC bionanocomposites were synthesized by low cost green technique where water was used as the solvent. The dispersion of SiC nanoparticles was achieved which has been evidenced by FESEM. The bionanocomposite was found to be crystalline from the study of XRD. The thermal stability of bionanocomposites was significantly improved as compared to virgin starch without compromising the oxygen barrier property. The synthesized bionanocomposites were resistant to mineral acid and alkali with little sacrifice in biodegradability. The chemical resistant bionanocomposites having enhanced thermal stability with substantial reduction in oxygen permeability may enable the materials for covering and protecting applications.

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References

Araujo-Farro, P. C., Podadera, G., Sobral, P. J. A., & Menegalli, F. C. (2010). Development of films based on quinoa (chenopodium quinoa willdenow) starch. *Carbohydrate Polymers*, *81*(4), 839–846.

Avella, M., Vlieger, J. D. J., Errico, M. A., Fischer, S., Vacca, P., & Volpa, M. G. (2005). Biodegradable starch/clay nanocomposites for food packaging applications. *Food Chemistry*, *93*(3), 467–474.

Baczkowicz, M., Wojtowicz, D., Anderegg, J. W., Schilling, C. H., & Tomasik, P. (2003). Starch complexes with bismuth (III) and (V). *Carbohydrate Polymers*, *52*(3), 263–268.

Billaderis, C. G., Lazaridou, A., & Arvanitoyannis, I. (1999). Glass transition and physical properties of polyol-plasticized pullulan–starch blends at low moisture. *Carbohydrate Polymers*, *40*(1), 29–47.

Biswas, A., Willet, J. L., Gordon, S. H., Finkenstadt, V. L., & Cheng, H. N. (2006). Complexation and blending of starch, poly(acrylic acid), and poly(N-vinylpyrrolidone). *Carbohydrate Polymers*, *65*(4), 397–403.

Carvalho, A. J. F., Job, A. E., Alves, N., Curvelo, A. A. S., & Gandini, A. (2003). Thermoplastic starch/natural rubber blends. *Carbohydrate Polymers*, *53*(1), 95–99.

Chen, B., & Evans, J. R. G. (2005). Thermoplastic starch–clay nanocomposites and their characteristics. *Carbohydrate Polymers*, *61*(4), 455–463.

Dash, S., Kisku, S. K., & Swain, S. K. (2012). Effect of nanoclay on morphological, thermal and barrier properties of Albumin bovine. *Polymer Composites*, *33*, 2201–2206.

Fischer, H. (2003). Polymer nanocomposites from fundamental research to specific applications. *Material Science and Engineering*, *C23*, 763–772.

Gangopadhyay, R., & De, A. (2000). Conducting polymer nanocomposites: A brief overview. *Chemistry of Materials*, *12*(3), 608–622.

Godbole, S., Gote, S., Latkar, M., & Chakrabarti, T. (2003). Preparation and characterization of biodegradable poly-3-hydroxy butyrate–starch blend films. *Bioresource Technology*, *86*(1), 33–37.

Guo, Z., Kim, T. Y., Lei, K., Pereira, T., Sugar, J. G., & Hahn, H. T. (2008). Strengthening and thermal stabilization of polyurethane nanocomposites with silicon carbide nanoparticles by a surface-initiated-polymerization approach. *Composite Science and Technology*, *68*, 164–170.

Huang, C. Y., Roan, M. L., Kuo, M. C., & Lu, W. L. (2005). Effect of compatibilizer on the biodegradation and mechanical properties of high-content starch/low-density polyethylene blends. *Polymer Degradation and Stability*, *90*(1), 95–105.

Ishiaku, U. S., Pang, K. W., Lee, W. S., & Mohd Ishak, Z. A. (2002). Mechanical properties and enzymic degradation of thermoplastic and granular sago starch filled poly (ε-caprolactone). *European Polymer Journal*, *38*(2), 393–401.

Jasim, M. A., Karawi, A. l., Hussein, R. A., & Daraji, A. l. (2010). Preparation and using of acrylamide grafted starch as polymer drug carrier. *Carbohydrate Polymers*, *79*(3), 769–774.

Kalambur, S. B., & Rizvi, S. S. H. (2004). Starch-based nanocomposites by reactive extrusion processing. *Polymer International*, *53*, 1413–1416.

Ke, T., & Sun, X. (2000). Physical properties of poly (lacticacid) and starch composites with various blending ratios. *Cereal Chemistry*, *77*(6), 761–768.
Kisku, S. K., & Swain, S. K. (2012). Study of oxygen permeability and flame retardancy properties of biodegradable polymethylmethacrylate/starch composites. *Polymer Composites*, *33*, 79–84.
Kong, W., Wang, W., Gao, J., Liu, T., & Liu, Y. (2011). Oxidised starch films reinforced with natural hallosites. *Journal of Materials Research*, *26*(23), 2938–2988.
Lapshin, S., Swain, S. K., & Isayev, A. I. (2008). Ultrasound aided extrusion process for preparation of polyolefin-clay nanocomposites. *Polymer Engineering and Science*, *48*(8), 1584–1591.
Lim, S. T., Hyun, Y. H., Choi, H. J., & Jhon, M. S. (2002). Synthetic biodegradable aliphatic polyester/montmorillonite nanocomposites. *Chemistry of Materials*, *14*(4), 1839–1844.
Mc Gloshan, S. A., & Hally, P. J. (2003). Preparation and characterization of biodegradable starch-based nanocomposite materials. *Polymer International*, *52*, 1767–1773.
Mohanty, A., & Swain, S. K. (2010). Ultrasonic and viscometric investigation of albumin proteins in aqueous solution. *Journal of Indian Chemical Society*, *87*, 461–464.
Padalkar, S., Capadonas, J. R., Rowan, S. J., Weder, C., Won, Y. H., Stanciu, L. A., et al. (2010). Natural biopolymers: Novel templates for the synthesis of nanostructurers. *Langmuir*, *26*(11), 8497–8502.
Pandey, J. K., Kumar, A. P., Mishra, M., Mohanty, A. K., Drzal, L. T., & Palsingh, R. (2005). Recent advances in biodegradable nanocomposites. *Nanoscience and Nanotechnology*, *5*(4), 497–526.
Park, H. N., Lee, W. K., Park, C. Y., Cao, W. J., & Ha, C. S. (2003). Environmentally friendly polymer hybrids Part-1 mechanical, thermal and barrier properties of thermoplastic starch/clay nanocomposites. *Journal of Material Science*, *38*, 909–915.
Reis, K. C., Pereira, J., Smith, A. C., Carvalho, C. W. P., Wellner, N., & Yakimets, I. (2008). Characterization of polyhydroxy butyrate-hydroxy valerate (PHB-HV)/maize starch blend films. *Journal of Food Engineering*, *84*(4), 361–369.
Rosa, D. S., Guedes, C. G. F., & Pedroso, A. G. (2004). Gelatinized and nongelatinized corn starch/poly(ε-caprolactone) blends: Characterization by rheological, mechanical and morphological properties. *Polimeros*, *14*(3), 181–186.
Rosa, D. S., Lotto, N. T., Lopes, D. R., & Guedes, C. G. F. (2004). The use of roughness for evaluating the biodegradation of poly-β-(hydroxybutyrate) and poly-β-(hydroxybutyrate-co-β-valerate). *Polymer Testing*, *23*(1), 3–8.
Sahoo, P. K., & Rana, P. K. (2006). Synthesis and biodegradability of starch-g-ethyl methacrylate/sodium acrylate/sodium silicate superabsorbing composite. *Journal of Material Science*, *41*(19), 6470–6475.
Salgado, A. J., Coutinho, O. P., & Reis, R. L. (2004). Bone tissue engineering: state of the art and future trends. *Macromolecular Bioscience*, *4*, 743–765.
Saravanan, L., Subramanian, S. S., Vishnu Kumar, A. B., & Tharanathan, R. N. (2006). Surface chemical studies on SiC suspension in presence of chitosan. *Ceramic International*, *32*, 637–646.
Shenhar, R., Norsten, T. B., & Rotello, V. M. (2005). Polymer-mediated nanoparticle assembly: structural control and applications. *Advanced Materials*, *17*, 657–669.
Siemion, P., Kapusniak, J., & Koziol, J. J. (2005). Solid-state thermal reactions of starch with semicarbazide hydrochloride, cataionic starches of a new generation. *Carbohydrate Polymers*, *62*(2), 182–186.
Sundaram, J., Durance, T. D., & Wang, R. (2008). Porous scaffold of gelation-starch with nanohydroxyapatite composite processed via novel microwave vacuum drying. *Acta Biomaterialia*, *4*(4), 932–942.
Swain, S. K., & Isayev, A. I. (2007). Effect of ultrasound on HDPE/Clay nanocomposites: Rheology structure and properties. *Polymer*, *48*, 281–289.
Swain, S. K., & Isayev, A. I. (2009). PA6/clay nanocomposites by continuous sonication process. *Journal of Applied Polymer Science*, *114*, 2378–2387.
Szepes, A., Hasznos-Nezdei, M., Kovacs, J., Funke, Z., Ulrich, J., & Szabo-Revesz, P. (2005). Microwave processing of natural biopolymers-studies on the properties of different starches. *International Journal of Pharmaceutics*, *302*(1–2), 166–171.
Tan, Y., Xu, K., Li, L., Liu, C., Song, C., & Wang, P. (2009). Fabrication of size-controlled starch-based nano spheres by nanoprecipitation. *Materials and Interfaces*, *1*(4), 956–959.
Tarvainen, T., Karjalainen, T., Malin, M., Pohjolainen, S., Tuominen, J., & Jarvinen, K. (2002). Degradation of and drug release from a novel 2,2-bis (2-oxazoline) linked poly(lacticacid) polymer. *Journal of Controlled Release*, *81*(3), 251–261.
Tianyi, K., & Xiuzhi, S. (2000). Physical properties of poly (lactic acid) and starch composites with various blending ratios. *Cereal Chemistry*, *77*(6), 761–768.
Vroman, I., & Tighzert, L. (2009). Biodegradable polymers. *Materials*, *2*, 307–344.
Vertuccio, L., Gorrasi, G., Sorrentino, A., & Vittoria, V. (2009). Nano clay reinforced PCL/starch blends obtained by high energy ball milling. *Carbohydrate Polymers*, *75*(1), 172–179.
Wang, Q., Hu, Y., Zhu, J., Liu, Y., Yang, X., & Bian, J. (2012). Convenient synthetic method of starch/lactic acid graft copolymer catalyzed with sodium hydroxide. *Bulletin of Material Science*, *35*(3), 415–418.
Wang, Q. H., Xue, Q. J., Liu, W. M., & Chen, J. M. (2000). Effect of nanometer SiC filler on tribological behaviour of PEEK under distilled water lubrication. *Journal of Applied Polymer Science*, *78*(3), 609–614.
Weber, C. J., Fastersen, V. H., & Bertelsen, G. (2002). Production and application of biobased packaging materials for food industry. *Food Additives and Contaminants*, *19*, 172–177.
Weon, J. I., Gam, K. T., Boo, W. J., Sue, H. T., & Chan, C. M. (2006). Impact toughening mechanisms of calcium carbonate-reinforced polypropylene nanocomposite. *Journal of Applied Polymer Science*, *99*(6), 3070–3076.
Willett, J. L., & Shogren, R. L. (2002). Process and properties of extruded starch/polymer foams. *Polymer*, *43*, 5935–5947.
Wu, C. S. (2003). Physical property and biodegradability of maleated-polycaprolactone/starch composites. *Polymer Degradation and Stability*, *80*(1), 127–134.
Yang, K. K., Wang, X. L., & Wang, Y. Z. (2007). Progress in nanocomposite of biodegradable polymer. *Journal of Industrial Engineering and Chemistry*, *13*(4), 485–500.