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BIODEGRADATION STUDY OF SOYA PROTEIN CONCENTRATE BLENDED WITH POLY (LACTIC ACID) AND CLOISITE 30B NANOCOMPOSITES

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Abstract – In this present work, Soya Protein Concentrate, Poly (lactic acid) Cloisite 30B (SPC-PLA-C30B) blended nanocomposites were prepared by using solution cast process. The structure and properties of SPC-PLA-C30B nanocomposities were characterized by using FTIR, SEM, TEM, XRD, DSC, Impact Toughness and Tensile strength measurement. The degradation behavior of the nanocomposites were studied by enzymatic degradation and composting method. SPC-PLA-C30B films found exhibiting favourable physical properties. The results of tensile strength demonstrated the fact that tensile strength increased upto addition of 3% C30B, then the tensile strength decreases with further addition of C30B. The surface topography study of SPC-PLA-C30B was found in intercalated form with the finer distribution of particles in its microstructure. The present work suggests that solution cast method uses water as a solvent, avoids the use of halogenated organic solvent, thereby the method is environmentally benign.

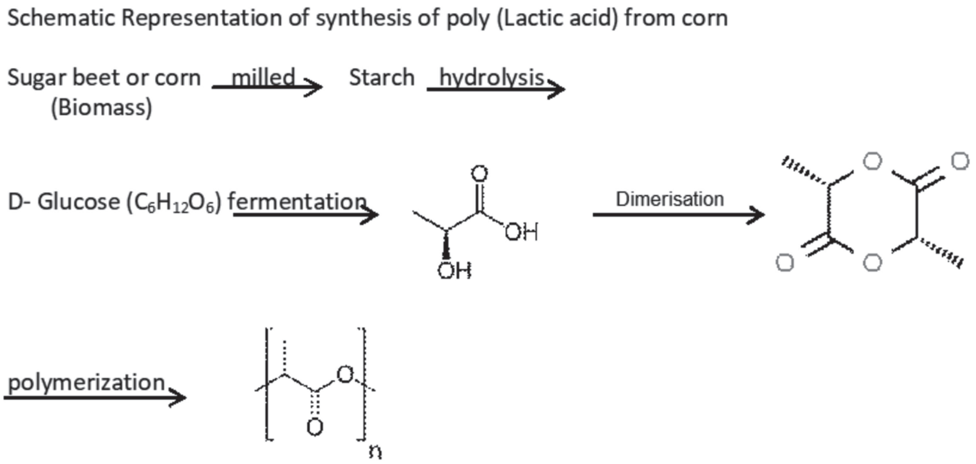
INTRODUCTION

It is well documented that synthetic polymers processed from petroleum based resources literally swamped the whole world with their astonishing variety of intricate molecular scaffolds (Arfat *et al.*, 2014; Boy *et al.*, 2015; Chang *et al.*, 2003). Plastic technology proved indispensable for contributing towards synthetic polymers, rubbers, fibers, binders, resins, lubricants, foams, gaskets, protective glass, paints and packaging materials (Ciannamea *et al.*, 2014; Dean *et al.*, 2014; Fischer, 2003). But over dependence on these synthetic polymer materials, has caused serious environmental issues around the globe. Most of the synthetic polymers, mostly single-use plastics do not undergo degradation, they remain recalcitrant in the environment thereby contribute towards solid waste pollution (Gandini *et al.*, 2015).

To address these issues, there is a burgeoning interest to develop biodegradable polymers from renewable resources. Cellulose, chitin, chitosan, starch, Levan, Zein and soyprotein, heavy weights among naturally available polymers, because of their ease of availability, show properties of polymer materials and are prone to chemical revamping. These materials have been proved to exhibit plastic properties by modification, also do have biodegradable potential (Gandini and Alessandro, 2008)

Among them Soya protein is the most suitable candidate because of its cost effectiveness, ubiquity, biodegradability and it is annually renewable. Soya protein concentrate contains about 65% protein. Therefore SPC will rapidly degrade in a wet surrounding (Gonzalez *et al.*, 2012). SPC exhibits poor mechanical properties in comparison to petroleum-based counterparts.

When a natural polymer is blended with a synthetic biodegradable polymer its material property is enhanced in addition to its biodegradability. The aim of this work is to blend SPC,a natural polymer, with Poly (lactic acid) by adding a reinforcing nanofiller like C30B. PLA is a synthetic biodegradable polymer isolated from biomass as per the following scheme (Fig. 1). PLA is a wonder commercial commodity with plethora of applications, particularly in packaging fields (Han



[Adapted from Nature Works^{TM} PLA Process]

Fig. 1. Schematic Representation of synthesis of poly (Lactic acid) from corn

et al., 2002). PLA represents the polymer of future, as it fits perfectly within the ambit of green chemistry principles.

Experimental

MATERIALS AND METHODS

Materials: Poly (Lactic acid) PLA and Soy protein Concentrate (SPC) was obtained from Hi Media. Cloisite 30B, a Southern Clay product, obtained as a gift material by the supplier through ion exchanging Sodium ion montmorillonite with bis (2-hydroxy ethyl) – methyl hydrogenated tallow alkyl) ammonium ion, this tallow contains 65% C-18.30% C-16 and 5% C-14 units. Glycerol, acetonitrile, ethanol were supplied by Sigma Aldrich. Amylase and Protease were obtained from Rajvi Enterprises. All the chemicals are of ANALAR grade.

Sample Preparation

First SPC, PLA & C30B were dried for 3 hrs at 60 °C in an oven under vacuum. SPC, PLA were taken in proper ratio as per the Table 1 below, stirred at 200 rpm, SPC was denatured at 75-90 °C in de-ionised water for 10 hrs followed by adding 1%, 3% and 5% of cloisite-30B. PLA being insoluble, is dissolved in minimum amount of acetonitrile and glycerol, the whole of the mixture solutions were subjected to reflux for two hours separately followed by ultrasonication to make sure that the modified clay

Table 1. Preparation of Sample containing SPC-PLA - C30B

Sample Code	Amount of SPC (gram)	Amount of PLA (gm)	Amount of C30B (gm)	Amount Water (gm)	Amount of glycerol (gm)	Amount of Acetonitrile (gm)
SPC - 100	4	0	0	96	0	0
SPC-PLA-(90-10)	3.6	0.4	-	91	1	4
SPC-PLA-(80/20)	3.2	0.8	-	91	1	4
SPC-PLA-(70/30)	2.8	1.2	-	91	1	4
SPC-PLA-(60-40)	2.4	1.6	-	91	1	4
SPC-PLA-(50-50)	2	2	-	91	1	4
SPC-PLA-$C_{-30}B^{-1}$ (50-50-1)	2	2	1	90	1	4
SPC-PLA-$C_{-30}B^{-2}$ (50-50-2)	2	2	3	88	1	4
SPC-PLA-$C_{-30}B^{-3}$ (50-50-3)	2	2	5	86	1	4

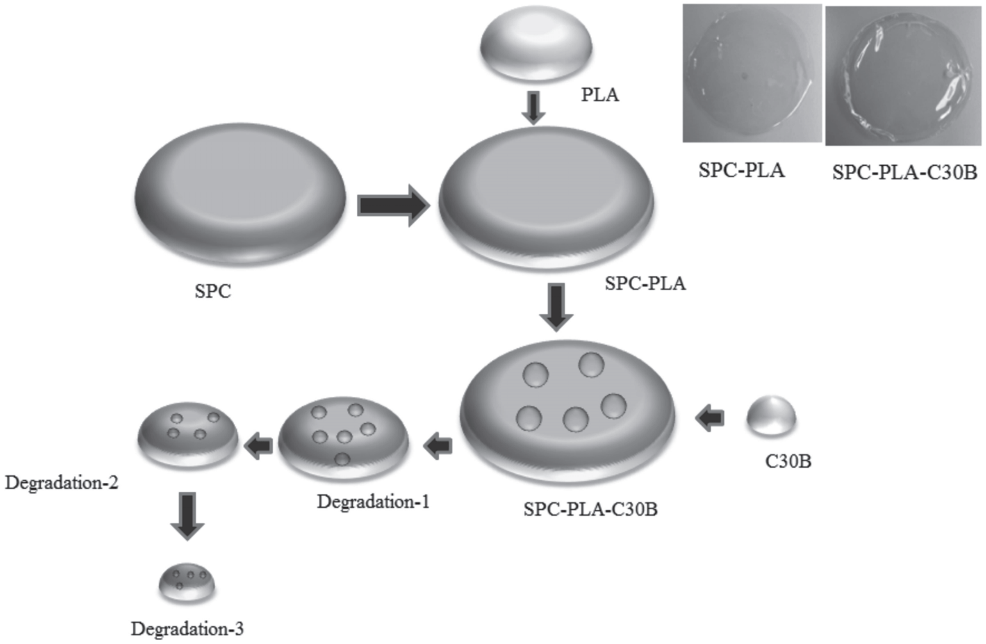


Fig. 2. Schematic representation of preparation of SPC-PLA-C30B Nanocomposites

is fully dispersed in SPC-PLA solution. The whole aqueous mixture was subjected to cast on a glass dish. The prepared films were degassed and subjected to drying in an oven at 100 ^{o}C to remove the solvents like water and acetonitrile. The samples were collected in a desiccator with silica gel uder vacuum to remove the trapped air if any before characterisation.

Characterisation

Fourier Transform infrared spectroscopy (FTIR)

Pure Soya protein, PLA and C30B were taken, then FTIR for SPC-PLA-C30B films were obtained on a Perkin-Elmer Spectrum-2000 FTIR Spectrometer, on potassium Bromide (KBr) pellets, in the range of 4000-500 cm^{-1}, with resolution of 4 cm^{-1}.

Mechanical Properties

The tensile strength of the specimen SPC-PLA-C30B samples were measured on a universal testing machine as per ASTM-D-638 protocol using UTM-20KN Machine and impact toughness was measured by Pendulum machine at CIPET. Odisha.

Scanning Electron Microscopy (SEM)

Cryo preparation of SPC-PLA-C30B nanocomposites was carried out using liquid Nitrogen, then SEM analysis was carried out by the help of a SEM instrument JEOL JSM7001F quickly, sputtered with ultrapure graphite -under voltage of 20 KV.

Transmission Electron Microscopy (TEM)

SPC-PLA-C30B samples was cut into ultrathin films by using a microtome at normal temperature, the films were directly placed on the copper grids for TEM observation. Then the structure and morphology of the nanocomposites were visualized under TEM machine HT7800 Ruti Tem under 120 KV.

XRD

D8 Advance XRD instrument(Bruker,USA) equipped with C_u-$K_{\acute{a}}$ radiation of wave length 1.54056A° was used for experiment. The data was recorded from 1^0 to 30^0 with a 0.02^0 step interval..

TGA

TGA was performed on a thermal analyser (TA Instruments, SDT Q600) from 40 ^{o}C to 700 ^{o}C heating rate of 10 ^{0} C/min under nitrogen atmosphere.

Enzymatic Testing

A Mixture containing α-amylase and β-amylase and Protease was prepared by dissolving in distilled water, It was then put into sterile Erlenmayer flask. Then the sample of Pure SPC, SPC-PLA and SPC-PLA-C30B were taken and were cut into 4x4 cm^2

from the films. The flask containing the films were incubated for 48 hrs at 58 °C. After certain period of time the enzyme mixture was removed from the film surfaces, then cleaned thoroughly, taken for drying in a desiccator under vacuum for 24 hrs before their weight was taken. The degree of enzymatic degradation was calculated using the following equation.

$$\% \text{ of DED} = \frac{W_i - W_H}{W_i} \times 100 \qquad .. (1)$$

Where W_H = dry weight of the specimen after enzyme treatment.

W_i = Initial dry weight of the specimen.

Biodegradability using Soil and compost burial method

The biodegradation properties of the SPC-PLA-C30B films was studied by soil and compost burial method as per BIS-IS/ISO-17088-2008 protocol , with slight modification as given by Thakore *et al.* The biodegradability test was carried out in different pots of 10 litre capacity filled with soil and compost. The films were cut into 2.5 x 4 cm^2 then buried under the soil and compost. Moisture content was properly maintained by sprinkling water. Compost inoculums was properly adjusted. The weight loss of the films was a direct measure of rate of degradation which was calculated as per the equation on 7 days basis.

$$\% \text{ of weight loss} = \frac{W_1 - W_2}{W_1} \times 100 \qquad .. (2)$$

Where, W_1 = Initial dry weight of the film

W_2 = Final dry weight of the film after being washed with distilled water, after seven days.

RESULTS AND DISCUSSION

Structural Analysis

From FTIR analysis, as per Fig. 3(a) and 3(b), it was noticed that SPC-PLA-C30B nanocomposites exhibit different absorption bands with respect to pure SPC, PLA,C30B and SPC-PLA as in Fig. (3a). As seen in Figure 3(b), all SPC-PLA-C30B based films showed similar types of spectra. The peaks at 1623, 1538 cm^{-1} (SPC-PLA-C30B-1), 1621 cm^{-1}, 1536 cm^{-1} (SPC-PLA-C30B-2), and 1612 cm$^{-1,}$ 1538 cm^{-1} (SPC-PLA-C30B-3), were assigned to amide-1 (C-O stretching) and a amide-II (N-H bending) of SPC structure (Arfat *et al.,* 2014; Ciannamea *et al.,* 2014).

Amide-I and II, 3(b), of the SPC-PLA-C30B films shifted to different wave number that suggested the possibility of change in bond alignments between the polymer chains.

The peaks at 2962cm^{-1}, 2951 cm^{-1} and 2956 cn^{-1} (3b) are due to C-H stretching of sp^3 hybridised C-atoms in SPC-PLA-C30B nanocomposites. The broad absorption bands observed around 3672 cm^{-1} to 3678cm^{-1} in 3b, were due to free and bound -O-H, and NH_2 groups that formed intermolecular hydrogen bonding with carbonyl and N-H group of peptide links of SPC (Zink *et al.,* 2016). The increase in vibrational wave number in SPC-PLA-C30B nanocomposites with respect to O-H and –NH vibration bands of SPC and C30B, indicative of

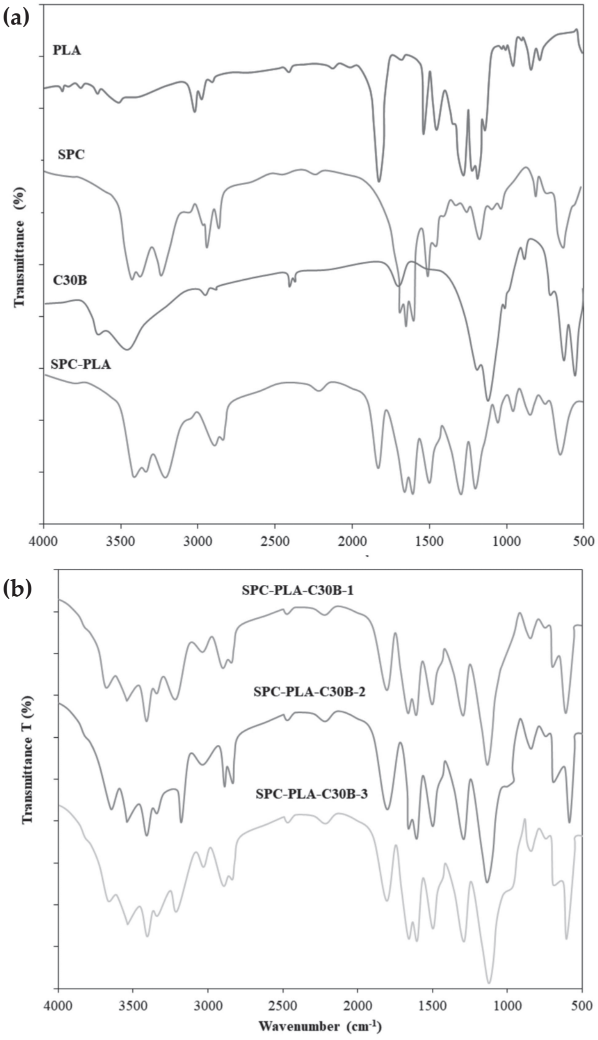


Fig. 3. FTIR of SPC, PLA, C30B SPC-PLA (a) and SPC-PLA-C30B-1, SPC-PLA-C30B-2, SPC-PLA-C30B-3(b)

intermolecular H-bonding between SPC and PLA and C30B. A strong and sharp intense band is observed in the range 1050-1250 cm^{-1} (at 1176cm^{-1}) in all the SPC-PLA-C30B nanocomposites may be due to decreased free amino group or C-O of glycerol used during processing as a solvent, or probably as a result of reaction between –OH and amine group in SPC & C30B, This changes confirmed that SPC and PLA were significantly unfolded exposing their polar groups for stronger intermolecular interactions thereby augmenting the mechanical resilience of the composites which were attributed due to the effect H-bonds or other ionic or hydrophobic interactions among SPC, PLA and C30B.

XRD

The structural properties of SPC-PLA-C30B films were studied by the X-Ray diffractograms as per Fig. 4. It is reported by (Kang *et al.*, 2008). that the basal spacing of C30B corresponding to reflection plain 001 of cloisite-30-B is 18.27 Å of 2 theta 4.83^0, but whenever nanocomposites were prepared using soy protein concentrate, polylatic acid and cloisite 30B, as per data in Table 2.

Table 2. XRD DATA of SPC-PLA-C30B composites

Sample	C30B(%)	2θ °	Basal spacing (Å)
SPC	-	12.11	-
PLA	-	19.35	-
SPC-PLA-C30B	1%	21.53	11.3 Å
SPC-PLA-C30B	3%	16.22	14.8 Å
SPC-PLA-C30B	5%	13.79	17.1 Å

From the Table 2 data and as per Fig. 4, it has been observed that the interlayer spacing is expanded from 11.3A^0 to 17.1A^0 with disappearance of characteristic peak from ordered structure to exfoliated structure beyond the detectable 2 theta range, indicative of the fact that the polymer chains of SPC containing α-helix and β-sheet structure and PLA intercalated into the galleries of cloisite 30B (Sinha Roy *et al.,* (2002). The primary reason for intercalation of the polymer into the organically modified clay (C30B) arises perhaps due to the existence of polar functional groups in SPC and ester in PLA and –OH (hydroxy)and –hydroxyl ethyl group in Cloisite 30B. These conclusions were in good agreement to SEM and TGA results. Dispersion of C30B layer in polymer matrices are confirmed in TEM studies, as per the figure 6. Darklines in Figure 6(c) refer to cross-section of the clay and the gap in between depicts adjacent clay lines in the interlayer galleries. From the TEM photographs, a very well dispersed layer of-C30B is observed in the SPC-PLA matrix for 3%.C30B but at 5% C30B discontinuity is evident due to agglomerated stacks, perhaps because of decrease of intermaterial adhesion and oxide-oxide repulsion in Si-O-Si of the nano clay as the Fig. 5.

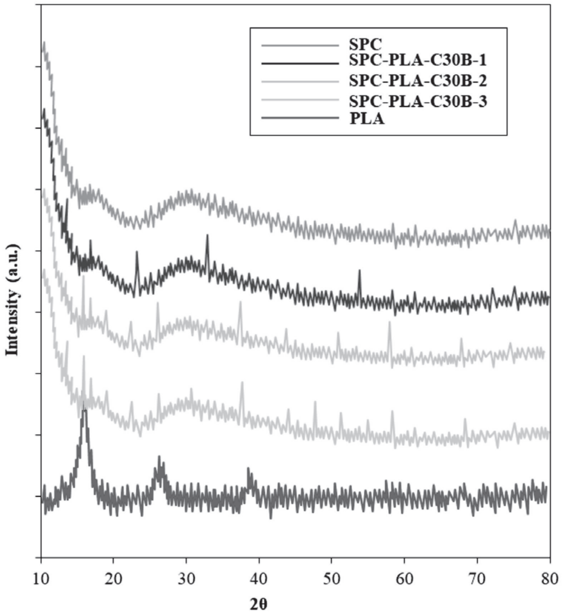
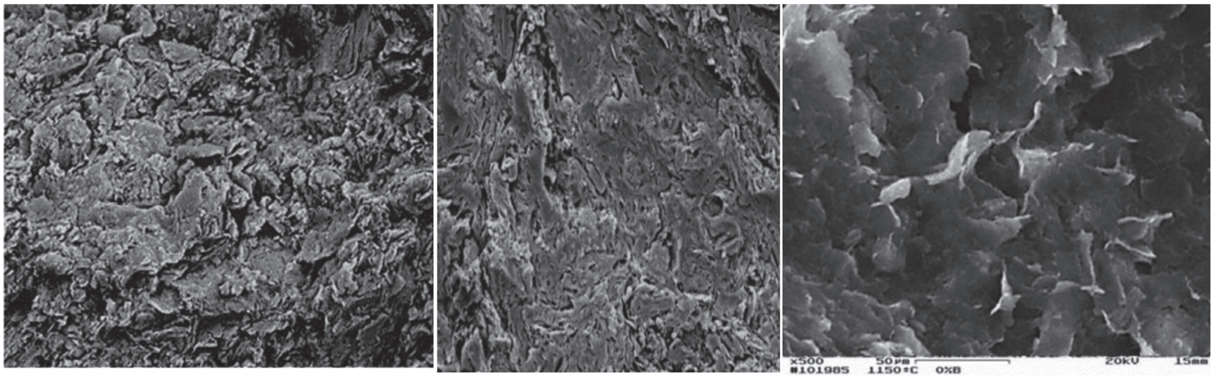


Fig. 4. XRD of SPC, PLA, SPC-PLA-C30B-1, SPC-PLA-C30B-2, SPC-PLA-C30B-3

Micromorphology of SPC-PLA-C30B films

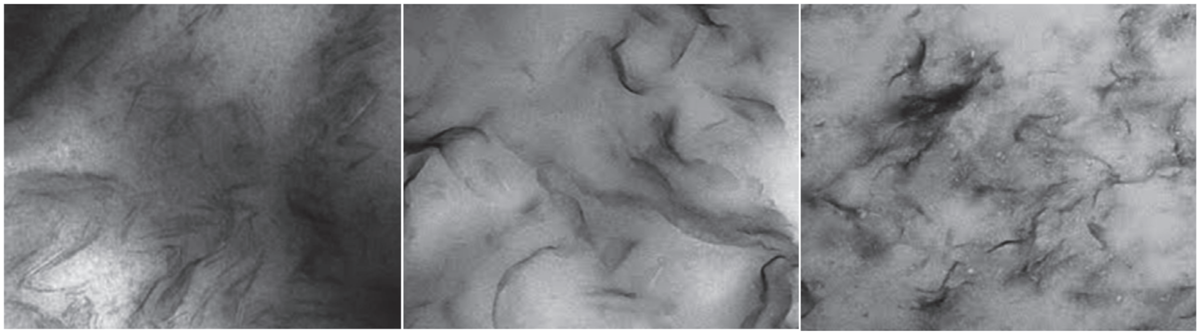
The surface topography of SPC-PLA-C30B nanocomposites was investigated by SEM analysis. As seen in figure the SPC-PLA-C30B films clearly showed a smooth, compact and clean surface, indicating the fact that SPC and PLA are associated with good film forming ability without any visible defect. However, as per Fig. 5(c), SPC-PLA-C30B with 5% C30B showed a relatively rugged surface morphology with aggregated clumps, explained the formation of heterogeneous structure.

The film with 3% C30B, as per figure 5(b), well distribution of particles observed, the agglomerates become more evenly spaced indicating better compatibility of components; it was confirmed from the TEM studies as per Fig. 6 (b) and mechanical properties of the films, as per Fig. 9. The better compatibility of SPC-PLA-C30B-2 was more likely to augment the intermolecular interaction in SPC matrix, such as H-bonding inter alia other



a b c

Fig. 5. SEM of SPC-PLA-C30B-1, SPC-PLA-C30B-2, SPC-PLA-C30B-3



a b c

Fig. 6. TEM of SPC-PLA-C30B-1 (a), SPC-PLA-C30B-2(b),SPC-PLA-C30B-3(c)

electrostatic, hydrophilic and hydrophobic interactions thereby improving the mechanical properties of the nano composite film.

Thermal Properties of SPC based films

As per the DSC data in Table 5 and Fig. 7, the melting depression occurred with SPC-PLA-C30B blends, indicating some interaction between SPC-PLA-C30B, with increasing addition of C30B(5%), The decrease of temperature to 81.78°C from 88.26 °C of pure SPC indicating damaging effect of clay content in the matrix which was associated with low mechanical properties, low TS and low impact toughness might be due to less crystallinity as reported in Table 3.

The thermal stability of SPC based nanocomposites was investigated using thermogravimetric analysis as shown in Fig. 8. Here the weight loss was measured in the range of 100-600 °C. Initially, loss of water took place above 100 °C due to vapourisation of water. In second step, the loss of glycerol took place in the range of 120 °C to 290 °C, in addition to breaking down of peptide links at 361 ⁰C of SPC chain.

The significant degradation of film observed beyond 300°C upto 470 °C, due to cleavage of intermolecular Hydrogen bond between SPC-PLA-C30B (Zhang *et al.*, 2013). In the last step from 500-600 °C, complete degradation took place leaving behind charred carbon mass. These TGA results suggested that SPC-PLA-C30B modified films with higher percentage of cloisite 30B showed higher heat resistance and higher degradation temperature

Table 4. Thermal properties SPC-based films (TGA data)

Film Sample	C30B	$T_{initial}$ °(C)	Max(°C)	T_{Final} (°C)
SPC	0	131.0	159.49	299.9
SPC-PLA-1	1%	245.27	272.7	510.29
SPC-PLA-2	3%	247.23	284.56	509.32
SPC-PLA-3	5%	247.65	284.46	513.12

Table 5. DSC thermogram data of SPC-PLA and nanocomposites

Sample	C30B	Temp(°C)
SPC		88.26
PLA		62.18
SPC-PLA-1	1%	81.23,155.23
SPC-PLA-2	3%	83.18, 124.11
SPC-PLA-3	5%	81.78, 174.28

than pure SPC as given in Table 4. Therefore more thermal stability is associated with SPC-PLA-C30B-3, with 5% of C30B in comparison to others having lesser percentage of C30B. The delaying of degradation is ascribed mainly due to incorporation of organically modified clay, that acts as a mass transport barrier to volatile products formed during thermal degradation process (Okamoto, 2005)

DSC of SPC based films

Mechanical properties of SPC based films

Mechanical properties of nanocomposite films are very much desiderative to determine their potential applications in different fields. Tensile Strength (TS) and impact toughness (R) of the nanocoposite were analysed as given in Table 6, reflected in Figure 9 that pure SPC exhibited low strength due to brittle properties of protein, however when it is modified by addition of poly lactic acid, TS values increased, which was mainly due to intermolecular adhesion between SPC and PLA (Manesa *et al.,* 2015). As per Table 6, the impact toughness decreased with increased addition of cloisite 30B into the composite. With higher percentage of C30B, perhaps intermaterial adhesion decreased due to oxide oxide repulsion in Si-O-Si of the clay, as evident inTEM photographs.

Table 6. Mechanical properties of SPC, PLA and their nanocomposites

Films	TS(MPa)	Impact Toughness (J/m)
SPC	3.41	5.27
PLA	21.92	11.29
SPC-PLA (50-50)	23.89	14.28
SPC-PLA (60-40)	21..82	13.34
SPC-PLA(70-30)	21.02	11.21
SPC-PLA (90-10)	18.28	11.18
SPC-PLA-C30B-1 (50-501%	24.38	1301
SPC-PLA-C30B-2(50-50-3%)	26.20	15.28
SPC-PLA-C30B-3(50-50-5%)	20.23	14.21

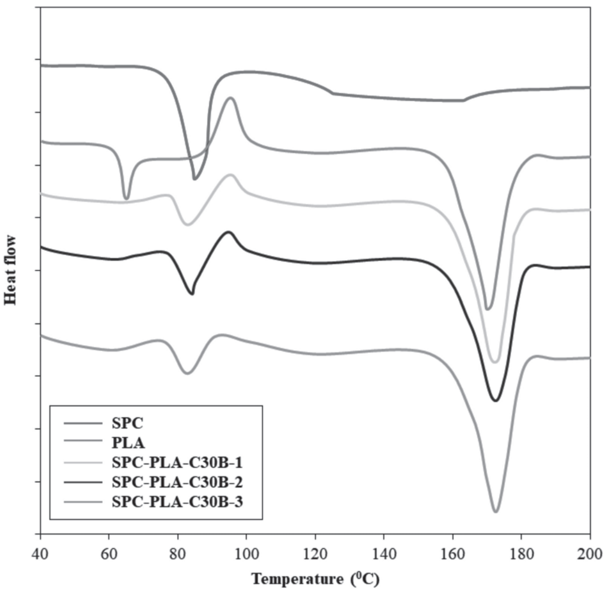


Fig. 7. DSC of SPC, PLA, SPC-PLA-C30B-1, SPC-PLA-C30B-2, SPC-PLA-C30B-3

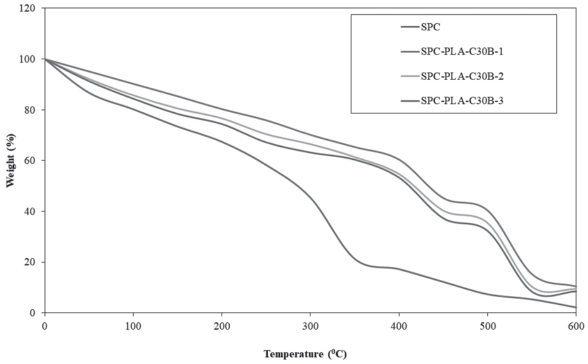


Fig. 8. TGA of SPC, SPC-PLA-C30B-1, SPC-PLA-C30B-2, SPC-PLA-C30B-3

It was reported that intermolecular interaction were most likely established in these composites, and tensile strength was maximum with SPC-PLA-C_{30}B-2, with 3% C_{30}B, but detrimental effect was observed with composites having 5% C_{30}B, which was supported by SEM and TEM analysis.

Enzymatic Testing

Figure 10 explains the weight loss of the film on enzymatic testing. By the addition of C30B, more degradation was observed. The degradation of SPC-PLA films was slower than those of SPC-PLA-C30B films. High degradation rate was observed for 50-50 weight percent SPC-PLA-C30B-3 (5% C30B) films. That underwent 91.32% weight loss after 72 hrs of immersion.

The enzymes help breaking down. SPC-PLA-C30B into smaller units amino acids and glucose.

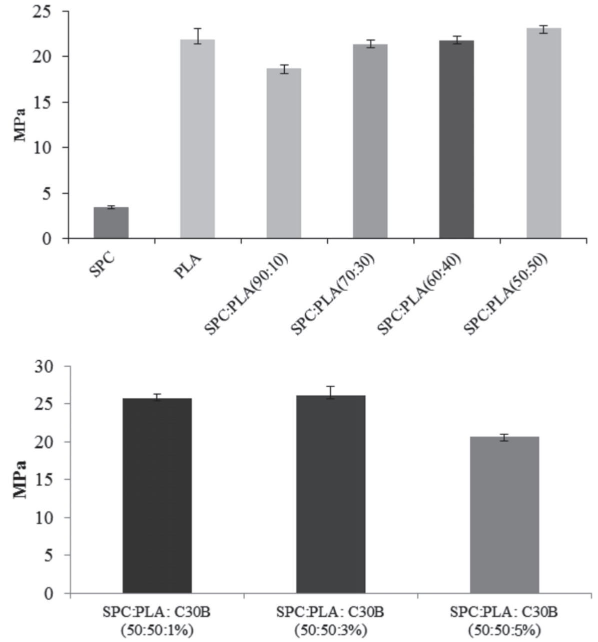


Fig. 9. Tensile strength of SPC, PLA, SPC-PLA and their nanocomposites SPC-PLA-C30B-1, SPC-PLA-C30B-2, SPC-PLA-C30B-3(a)

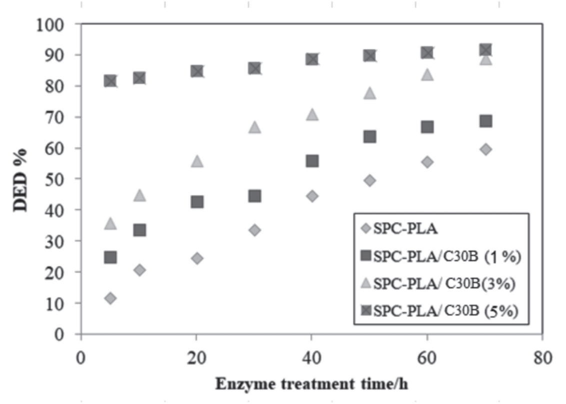


Fig. 10. Enzymatic degradation of SPC-PLA and SPC-PLA-C30B films using α-amylase and â-amylase.

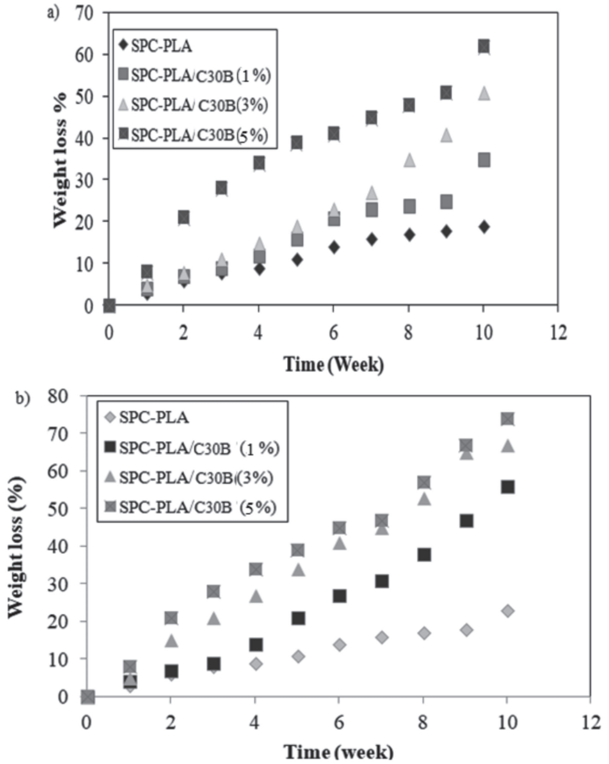


Fig. 11. Weight loss of SPC-PLA-C30B films after 10 weeks in soil (a); Weight loss of SPC-PLA-C30B films after 10 weeks in compost (b)

The hydrolysis of SPC weakens the interaction with PLA and C30B and thereby it caused significant weight loss.

Soil Burial Test

As per the Figures 11(a) and (b), it showed the weight loss of pristine SPC and SPC-PLA-C30B nanocomposites both under soil condition and compost respectively. In the figures it was observed that the biodegradation increased upto 67% as the burial time increased in both soil and about 78% in compost for 10 weeks. The degradation rate is more in compost than the soil. PLA and C30B did play a significant role in biodegradation of SPC films. The hydrolysability property of SPC films decreases with addition of C30B in soil condition. However, the rate of degradation is higher in compost burial due to higher microbial activity in biologically active environment, that is compost. Compost is enriched with nutrients that helps the films to degrade more rapidly by the microbes vis-a-vis soil condition.

CONCLUSION

SPC-PLA-C30B nanocomposite films were prepared conveniently by solution cast method. The tensile strength of SPC-PLA-C30B blend was the highest for 3% C30B. From the SEM and TEM pictures it was well understood that particles distributed in orderly manner in SPC-PLA-C30B(3%) [50-50-2] matrix. The study showed that C30B content favours degradation rate but impairs the strength of the material with greater percentage of C30B content. The tensile strength of SPC is 3.41 MPa and that of PLA is 21.92MPa but that of SPC-PLA-C30B

(50-50-2) film was about 26.2 MPa, thereby increased significantly with respect to SPC and by about 19.5% with respect to PLA which might have been attributed by the interactions among SPC matrix, PLA and C30B. The optimal improvisation of material properties of the nanocomposites would contribute to its potential application in packaging fields, and would also contribute to global sustainability because of their cost effectiveness and biodegradation properties.

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REFERENCES

Arfat, Y.A., Benzakul, S., Prodpran, T., Osako, K. 2014. Food. *Hydrocoll.* 39 : 58-67.

Boy, R., Maness, C. and Kotek, R. 2015. *Int. J. Polym.* Mater, Polym. *Biomater.* 65 : 11-17.

Chang, J.H., An, Y.U. and Sur, G.S. 2003. Poly (lactic acid) nanocomposites with various organoclays: Thermochemical properties, morphology and gas permeability. *J. Polym. Sci.* 41(1) : 94-103.

Ciannamea, E.M., Stefani, P.M., Ruseckaite, R.A. 2014. Food *Hydrocoll.* 38 : 193-204.

Dean, K., Yu, L., Wu, D.Y. 2004. Polymer blends and composites from renewable resources. *International Symposium on Engineering Plastics,* EP2, Lanzhou, China, 2004.

Fischer, H.R. 2003. Polymer nanocomposites from fundamental research to specific applications. *Meter Sci Engg.* 23 : 763-772.

Gandini, A., Lacerda, T.M., Carvalho, A.J. and Trovatti, E. 2015. Progress of polymers from renewable resources: Furans, vegetable oils, and polysaccharides. *Chem. Rev.* 116 : 1637–1669.

Gandini and Alessandro, 2008. Polymers from Renewable Resources: A challenge for the future Macromolecules materials. *(ACS).* 41(24) : 9491-9505.

Gonzalez, G., Albano, C. and Palacios, J. 2012. PLLA-HA Composites: Synthesis and Characterization; pp. 241-243.

Han, Y., Xu, K., Montay, G., Fu, T. and Lu, J. 2002. Evaluation of nanostructured carbonated hydroxyapatite coatings formed by a hybrid process of plasma spraying and hydrothermal synthesis. *J. Biomed. Mater. Res.* 60 (4) : 511-516.

Huang, X. and Netravali, A. 2009. Biodegradable green composites made using bamboo micro/nano fibrils and chemically modified soy protein resin. Compos. Sci. Technol., 69(7–8) : 1009-1015.

Kim, S.S., Utsunomiya, H., Koski, J.A., Wu, B.M., Cima M.J., Sohn, J., Mukai, K., Griffith, L.G. and Vacanti J.P. 1998. Survival and function of hepatocytes on a novel three-dimensional synthetic biodegradable polymer scaffold with an intrinsic network of channels. *Ann. Surg.* 228(1) : 8-13.

Kondo, T., Sawatari, C., Manley, R. S. J. and Gray, D. G. 1994. Characterization of hydrogen bonding in cellulose-synthetic polymer blends systems with regioselectively substituted methycellulose. *Macromol.* 27 (1) : 210-215.

Lasprilla, A.J., Martinez, G.A., Lunelli, B.H., Jardini, A.L. and Filho, R.M. 2012. Poly-lactic acid synthesis for application in biomedical devices - a review. *Biotechnol. Adv.* 30(1) : 321 328.

Nakashima, T., Xu, C., Bin, Y. and Matsuo, M. 2001. Morphology and mechanical properties of poly(vinyl alcohol) and starch blends prepared by gelation/crystallization from solutions. *Colloid Polym. Sci.* 279(7) : 646-654.

Nayak, P.L., Sasmal, A., Mishra, J.K., Sahoo, S., Nayak, P., Kang, S.C., Lee, J.W. and Chang, Y.W. 2008. Polymer. *Plastics Technology and Engineering.* 47(6) : 600-605.

Nofar, M., Sacligil, D., Carreau, P.J., Kamal, M.R., Heuzey, M.C. 2019. Poly (lactic acid) blends: Processing, properties and applications. *Int J Biol Macromol.* 25 : 307-360.

Okamoto, M. American Scientific Pub, Biodegradable Polymer Layered Silicates: A Review Vol – 1, Page – 1 -45.

Paul, M. A., Alexander, M., Degee, P., Henrist, C., Rulmont, A. and Dubois, P. 2008. New nanocomposites materials based on plasticized poly(l-lactide) and organomodifide MMT: Thermal and morphological study. *Polymer.* 44(2) : 443-450.

Potter, S.M., Pertile, J., Berber-Jimenez, M.D. 1996. Soy protein concentrate and isolated soy protein similarly lower blood serum cholesterol but differently affect thyroid hormones in hamsters. *J Nutr.* 126(8) : 2007-2011.

Raquez, J. M., Deléglise, M., Lacrampe, M. F. and Krawczak, P. 2010. Thermosetting (bio) materials derived from renewable resources: A critical review. *Prog. Polym. Sci.* 35 : 487-509.

Ray, S.S., Yamada, K., Okomato, M., Ueda, K. 2002. New poly lactide- layered silicate nanocomposites: Concurrent improvements of material properties, biodegradability and melt rheology. *Polymer*. 44(3) : 857-866.

Thakore, I. M., Desai, S., Sarawade, B. D. and Devi, S. 2001. Studies on biodegradability, morphology and thermomechanical properties of LDPE/modified starch blends. *Eur. Polym. J.* 37(1) : 151–160.

Tschan, M.J. L., Brulé, E., Haquette, P. and Thomas, C.M. 2012. Synthesis of biodegradable polymers from renewable resources. *Polym. Chem.* 3 : 8360-851.

Wang, J., Lu, Y., Yuan, H. and Dou, P. 2008. Crystallization, orientation morphology, and mechanical properties of biaxially oriented starch/polyvinyl alcohol films. *J. Appl. Polym. Sci.* 110 (1) : 523–530.

Xiong, H.G., Tang, S.W., Tang, H.L. and Zou, P. 2008. The structure and properties of a starch-based biodegradable film. *Carb. Polym.* 71(2) : 263–268.

Yu, C., Ke, Y., Hu, X., Zhao, Y., Deng, Q. and Lu, S. 2019. Effect of Bifunctional Montmorillonite on the Thermal and Tribological Properties of Polystyrene/Montmorillonite Nanocomposites. *Polymers (Basel).* 8; 11(5).

Yun, Y.H., Wee, Y.W., Byun, H.S. and Yoon, S. D. 2008. Biodegradability of chemically modified starch (RS4)/PVA blend films: Part 2. *J. Polym. Environ.* 16(1): : 12-18.

Zhang, X., Shi, J., Ye, H., Dong, Y. and Zhou, Q. Combined effect of cellulose nanocrystals and poly (butylene succinate) on poly (lactic acid) crystallization: The role of interfacial affinity. *Carbohydr Polym.* 2018 Jan 1;179:79-85.

Zou, G. X., Jin, P. Q. and Xin, L. Z. 2008. Extruded starch/PVA composites: Water resistance, thermal properties and morphology. *J. Elastomers Plas.* 40 (4) : 303-316.