



A Comparison on Biodegradation Behaviour of Polylactic Acid (PLA) Based Blown Films by Incorporating Thermoplasticized Starch (TPS) and Poly (Butylene Succinate-co-Adipate) (PBSA) Biopolymer in Soil

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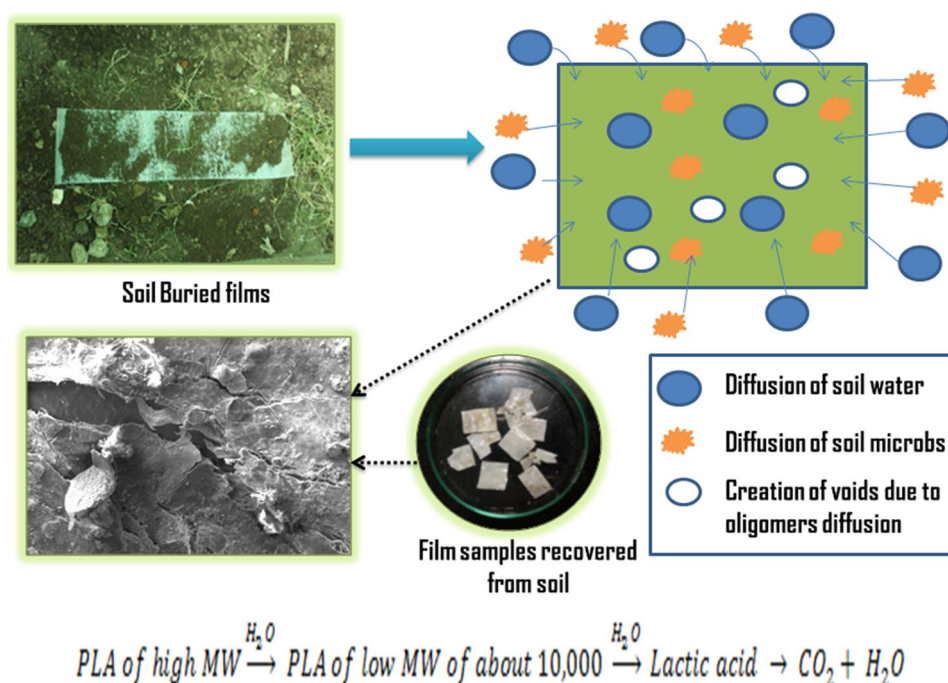
Abstract

The comparative study of biodegradation of various blown films obtained from Poly (lactic) acid (PLA) has been studied via soil burial method. A total of 3-different types of films prepared from neat PLA and the reactive blends containing poly butylenes succinate-co-adipate (PBSA), and thermoplasticized starch (TPS); namely VPLA, PLA/PBSA, PLA/TPS respectively were the subjects of investigation. Several analytical techniques including weight loss method and analysis of mechanical properties were performed in each seven days interval until ninety days to elucidate the biodegradation in soil. The tensile modulus of VPLA and PLA/PBSA blown films were deteriorated to the tune of 60.32% and 71.28% respectively within 28 days, while PLA/TPS blown films recorded a significant reduction of 75.31% in the modulus value within 21 days of soil exposure compared to unexposed blown film samples. Similarly, blown films of PLA/TPS reported the highest rate of weight loss in the order of 40.06% in 90 days of soil burial with an estimated half-life of 103 days in soil environment compared to its counterparts. The depletion in both mechanical properties and weight of the film samples suggesting the occurrence of biodegradation in the real soil environment. Scanning electron microscopy (SEM) revealed the formation of coarse morphology for all three types of soil buried samples which trace of microbial action appeared on PLA/TPS films. Fourier transform infrared microscope (FTIR) showed the decrease in carbonyl index and variation in the intensities of carbonyl and hydroxyl peaks irrespective of the film samples after 90 days of soil exposure. Gel permeation chromatography (GPC) documented reduction in molecular weight and variation in polydispersity index (PDI) of post-exposed soil samples. The elemental analysis exhibited that the percentage of organic carbon and hydrogen content of all the films decreased while the oxygen percentage increased after soil burial due to the biodegradation of film specimens. Both Differential scanning calorimetry (DSC) and X-ray diffraction analysis (XRD) reported increase in crystallinity for soil exposed samples indicating the initiation of degradation kinetics preferably at the amorphous region of film composition. It has also been inferred that the biodegradation mechanism of VPLA and PLA/PBSA blown films predominantly driven by hydrolysis of ester bond. Contrastingly, the biodegradation kinetics in case of PLA/TPS film has been proceeded with microbial assimilation of TPS component which further thrived on hydrolysis of PLA component of the blown film system.

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Graphic Abstract



Keywords PLA · Biodegradation · Soil burial · Hydrolysis

Introduction

Plastics have become materials of choice for packaging applications owing to its low cost, good environmental resistance, durability, and safety and hygiene aspects of materials to be packed and moved from one place to another. Most of the plastic materials used in packaging are single use; nonbiodegradable petroleum-derived and directly disposed of to the environment after its first application. As per the “Our world in data” agency, the packaging industry has been responsible for the maximum plastic waste generation in the year 2015–2016 marked with 141 million tons [1]. The vicinity of “white pollution” has spreaded out geographically from high altitude mountainous region of Himalayas to the deep sea of Pacific Ocean, to the terrestrial land; endangered the habitat of animals, plants, aquatic and marine ecosystems. In order to counter the severity of plastic pollution and to reduce dependency on depleting petroleum resources, the study on bio based-biodegradable and renewable resource derived polymers has found promising as contemplated by researchers, industrialists, and environmentalists across the globe [2].

Among many biopolymers such as poly(β -hydroxybutyrate) (PHB), poly(ϵ -caprolactone) (PCL) [3]; poly (lactic acid) PLA, produced via bacterial fermentation of annually renewable sources such as starch, sugar

and other biomasses [4, 5] has favourable properties like transparency, good tensile modulus and ease of processibility to convert into single-use disposable cups, cutlery items and packaging films [6, 7]. PLA also is inherently biodegradable under suitable environmental conditions which in turn could potentially prevent plastic littering in the environment [8–10]. The degradation mechanism of PLA proceeds through two steps (a) chemical hydrolysis of ester bond of PLA at elevated temperature (58 °C) (b) mineralization of broken hydrolysed products into carbon dioxide and water by microorganisms under aerobic conditions in compostable atmosphere [11–15]. In which hydrolysis of ester bond can be regarded as abiotic process and the second step consists of biotic degradation activity catalysed by microorganisms. The ester bond of PLA main chain backbone is readily hydrolysable in presence water at elevated temperature as it sustains random chain scission due to the lower pKa (approx = 3) value of carboxylic acid group of PLA compared to other available carboxylic acid counterparts (pKa = 4 to 5). This lower dissociation factor is mainly responsible for further hydrolytic degradation called autocatalysis, thereby producing low molecular weight species of PLA oligomers. It has also been observed that hydrolytic degradation by products of PLA whose molecular weight falls below 10,000 Da can easily be metabolised by microorganisms available in natural

environment. However, the comparison of rate of degradation of PLA in three different media viz. in microorganism rich compost medium, in abiotic media lacking of compost and in sterile aqueous medium showed no difference, evinced the fact that participation of microorganism have no effect on the rate of degradation of PLA [16].

Further, to understand the biodegradation behavior of PLA based materials, various authors have elucidated several studies. The biodegradation behavior of PLA films in a solid substrate (compost) environment was investigated. The study was carried out in all three types of conditions such as biotic, abiotic, and sterile water environment which discerned that the degradation occurred primarily due to the hydrolysis of the ester bond [17]. The degradation rate of PLA in microorganism-rich compost and soil was found to be faster than sterile compost and soil at elevated temperature [11]. On the other hand, PLA showed a lower biodegradation rate in a real soil environment tested in Mediterranean field condition [18]. Similarly, blend films of PLA with other biopolymers such as polybutylene adipate-co-terephthalate (PBAT) exhibited different degradation behavior which resembled to individual polymers in the soil environment [19]. The tensile test specimen prepared from PLA blended with corn starch and Poly hydroxylester-ether (PHEE) showed that degradation occurred only due to incorporation of starch and PHEE at higher percentage whereas pure PLA did not degrade significantly [20]. The biodegradation nature of PLA would complex [18] and complete disappearance might also take several years [3]. Moreover, the degradation behaviour of PLA and its composite with other bio-based materials were evaluated and found to be selectively degrading in specific environmental condition in presence of certain microbial colony [21–26]. Albeit PLA is biodegradable the observations in the real soil environment is inconclusive.

In the current study, the biodegradation behavior of PLA based blown films was investigated in the real soil environment. The test encompassed the degradation study of pristine PLA films along with PLA based starch mulch films and PLA based PBSA transparent films for flexible packaging applications. The biodegradation was characterized in terms of loss of transparency, percentage (%) of weight loss, deterioration in tensile strength, modulus, and elongation. The chemical and morphological analysis of biodegradation was carried out in terms of FTIR and SEM respectively of soil buried blown film samples. Similarly, variation in molecular weight, PDI and elemental compositions of the films were traced by using GPC and elemental analyser. DSC and XRD techniques were also employed to study the biodegradation kinetics of the blown films. Furthermore, a comprehensive biodegradation mechanism of the blown films was stipulated in the soil environments.

Experimental

Materials

Poly(lactic acid (PLA) (PLA-4044D) with melt Flow Index (MFI) of 11.3 g/10 min (at 190 °C/2.16 kg), density of 1.2 g/cc, molecular weight ($M_n = 195$ kDA and $M_w/M_n = 2$) and melting temperature in the range of 150–170 °C was procured from M/s Nature Works LLC, USA. Cassava starch was collected from M/s Suvam Starch, India with 15% moisture content, 30-wt% amylose and 70-wt% of amylopectin. Poly (butylene succinate-co-adipate) (PBSA) polymer was purchased from M/S Showa Denko K.K, Japan melting temperature range (140–180 °C), MFI of 1.4 g/10 min (at 190 °C/2.16 kg), molecular weight ($M_n = 12.1$ kDA, $M_w/M_n = 2.8$) and density 1.3 g/cc. The chain extender, epoxy functionalized styrene acrylate (ESA) was provided by BASF, India under the trade name Joncryl® ADR 4368 to produce PLA/PBSA film.

Preparation of Films

The details of the film preparation process have been discussed in our previous studies [1, 2]. Briefly, PLA/TPS film was prepared by melt blending of PLA with thermoplasticised starch (TPS) in presence of glycidyl methacrylate (GMA) (1 wt%) as grafting agent and benzoyl peroxide BPO (0.1 wt%) as initiator in a twin screw extruder (M/S Steer, India, Omega 25, L/D = 25:1) maintained at a temperature profile of 150 °C/160 °C/170 °C from feed to die zone. Subsequently, the extrusion blown film process was carried out with a temperature profile of 155 °C/160 °C/165 °C /170 °C/175 °C, blow up ratio (BUR) of 2.1. For PLA/TPS film production, thermo plasticization of starch was carried out using a batch mixer (HAAKE™ Rheomix OS Lab Mixers, M/S ThermoFisher Scientific, Germany) at temperature 120 °C by mixing 70 wt% of starch with 25 wt% of glycerol and 5 wt% of water.

Similarly, the PLA/PBSA film was prepared from reactive blend of PLA/PBSA (95/5) in presence of ESA (3 wt%) employing a twin screw extruder at a temperature profile of 155 °C/160 °C/165 °C/170 °C/175 °C followed by extrusion blown film process at a temperature profile of 160 °C/165 °C/170 °C/175 °C, BUR of 2.5, respectively. The films with various compositions and corresponding sample codes are enumerated in Table 1.

Soil Burial Biodegradation Test

The soil burial test of VPLA, PLA/TPS and PLA/PBSA films was carried out at CIPET-IPT, Bhubaneswar campus

Table 1 Compositions and sample codes of PLA based films for soil burial test

| S. no. | Composition | Sample code |
|--------|--|-------------|
| 1 | PLA (100%) | VPLA |
| 2 | PLA (95 wt%)/PBSA (5 wt%)/Joncryl (3 wt%) | PLA/PBSA |
| 3 | PLA (80 wt%)/TPS(Cassava) (20 wt%)/GMA (1 wt%)/BPO (0.1 wt%) | PLA/TPS |

located in Odisha, India. The geographical information of the place is as follows: Longitude (85.833267°), Latitude (20.358824°), Elevation (31 m). (<https://www.latlong.net/place/patia-bhubaneswar-odisha-india-12732.html>).

Prior to the soil burial test under real soil environment, the samples were cut into (20×10) cm rectangular shape and buried in a pit of 100 mm depth from soil surface. The test was carried out for three months from August to September with average outdoor temperature of 30 ± 2 °C. The biodegradation in the soil is largely influenced by the water content present in soil. The available water content of the soil can be defined as the amount of available for the growth of the plant. It is the difference between the maximum water that can be hold by soil (soil holding capacity) and to the extent where no water is available for the extraction of plant root (wilting point). This can be determined by methods such as gravimetric soil water content or volumetric soil water content. In gravimetric soil water content method, the measurement usually considers the mass difference of moist soil and oven dried soil at 105 °C. The available water content of the soil depends upon adhesive force between soil and water, which normally controlled by the type of the soil, presence of types of mineral and organic matter in the soil, and surface tension offered by the soil. The soil water holding capacity (WHC%) can be determined by calculating mass difference of water saturated soil and over dried soil at 105 °C [27]. In this process the distilled water would be added to known weight of soil sample until saturation denoted as ‘ W_{sat} ’ by draining out excess amount of water. Further the same would be dried up in an oven and measured weight as ‘ W_{dry} ’. Hence, the WHC% can be determined as follows [27]

$$WHC\% = \frac{W_{sat} - W_{dry}}{W_{sat}} \times 100 \quad (1)$$

The soil of the burial site belongs to the sub-group of aeric tropaquepts having soil order of inceptisols. The values of available water content and pH are documented to be 0.244–0.246 cc/cc and 6.7–7.6 respectively. These characteristics have been derived from the studies of Singh and Kundu et al. [28]. In our study, we tried to establish the nature and extent of biodegradation of prepared PLA based blown films in natural soil environment which is uncontrolled. However,

the biodegradation site was watered often in order to avoid complete dryness.

Characterization Techniques

Scanning Electron Microscopy (SEM) Analysis

The surface morphology of the degraded films was studied using an EVO MA 15, Carl Zeiss SMT, Germany SEM analyser at an accelerating voltage 6.52 kV. Prior to analysis, the samples were cleaned using acetone followed by gold coating to avoid electrostatic charging.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The quantitative analysis of biodegradation of VPLA, PLA/TPS and PLA/PBSA films were carried out using a Nicolet 6700 USA spectrometer. The equipment was operated at 2 cm^{-1} resolution within the spectral range of $4000\text{--}500 \text{ cm}^{-1}$. The surface of the soil buried samples was cleaned using acetone prior to the analysis in order to avoid damage of the equipment.

Gel Permeation Chromatography (GPC)

The variation in molecular weight of the film samples before and after degradation has been investigated using GPC (Waters Corporation, USA) as per ASTM-D-6474-12. The samples were dissolved in tetrahydrofuran (THF) (HPLC grade, Sigma Aldrich) at a concentration of 0.1 (w/v). The filtration of the solution was accomplished through 0.45 mm filter in order to prevent blockage of HPLC channels. A solution volume of 10.00 µl was injected into the columns and elution flow rate and run time was fixed at 1 ml/min and 60 min respectively. The instrument was equipped with UV visible and refractive index detector; was calibrated as per polystyrene (PS) standard. However, it may be noted that due to the insolubility of starch in THF, only PLA content was determined in PLA/TPS system [29].

Elemental Analysis

The elemental analysis of film samples of about 2–3 mg for each composition (before and after soil burial) was conducted using CHNS/O analyser (Flash-200, Thermo Scientific, USA) as per ASTM-D-5291. The oxidation tube and the restoration tube were maintained at 1200 °C and 900 °C respectively. The recovered film samples were cleaned thoroughly using acetone prior to the analysis to yield error free results.

Weight Loss Percentage

The percentage of weight loss was calculated using Eq. (2)

$$\%WL = (m_i - m_o)/m_o \times 100 \quad (2)$$

where m_o is the initial mass of the samples, m_i is the residual mass at an interval of different burial period. The samples were manually cleaned using tissue paper and kept in vacuum oven at 50 °C for 4 h to remove moisture and soil dirt for accuracy prior to weighing via weighing balance machine (Mettler Toledo, USA) with a least count of 0.001 mg.

Thermal Analysis

The determination of glass and melt transition temperature of blend films during prior and later phase of soil burial was carried out using a differential scanning calorimetry (DSC) analysis by a DSC Q 20, M/S TA Instruments, USA. A total of 3 to 4 mg of sample was fed in the DSC pan from room temperature to 300 °C at heating rate of 10 °C/min with a cooling rate of 2 °C/min. The T_g and T_m were reported from the second heating scan of DSC cycle. The percentage of crystallinity (X_c) for PLA/TPS films was calculated using formula $X_c(\%) = (\Delta H_m / \Delta H_{m0}) \times 100$, where ΔH_m is melting enthalpy of the sample, ΔH_{m0} is melting enthalpy of 100% crystalline PLA (93.0 J/g) [2, 30]. On the other hand, the same was calculated for PLA/PBSA as well as VPLA films using formula $X_c = \Delta H_m - \Delta H_{cc} / W_{PBSA} \times \Delta H_m^0$, Where ΔH_m is the sample melting enthalpy, ΔH_{cc} is the cold crystallization enthalpy of the sample, W_{PBSA} is the mass fraction of PBSA in the blend and ΔH_m^0 is the melting enthalpy of 100% crystalline PBSA, 110.3 J/g. [1, 31, 32].

X-ray Diffraction (XRD) Analysis

The XRD analysis has been carried out to study the variation in percentage crystallinity of film samples due to biodegradation in soil environment. It has been accomplished by using a X-ray diffractometer (Philips X Pert MPD, Japan) having a graphite monochromatic beam at a variable diffraction angle 2θ from 5° to 80°. The machine is equipped with Copper K- α radiation source emitting x-ray of wavelength ($\lambda = 0.154 \text{ nm}$) operated at 40 kV and 30 mA. The percentage of crystallinity ($X_c\%$) has been calculated using the formula $\frac{\sum A_{Crystalline}}{\sum A_{Crystalline} + \sum A_{Amorphous}}$ [33].

Mechanical Properties

The tensile tests of the soil buried film samples were characterized in terms of modulus, strength and elongation at

break using a Universal testing machine (Instron, UK) as per ASTM D-882-18 in both machine and transverse directions at a cross head speed of 50 mm/min. The testing was carried out in each 7 days of interval by taking minimum of five numbers of samples having dimension of (100 × 25) mm, from each composition and the corresponding standard deviation was calculated. It has been elucidated in our previous work. [1, 2]

Statistical Analysis

The consistency of data obtained from weight loss percentage has been estimated by using one way ANOVA in origin pro-8.5 software. The significantly different group in weight loss data has been identified by employing Tukey's (HSD) test at 95% confidence level.

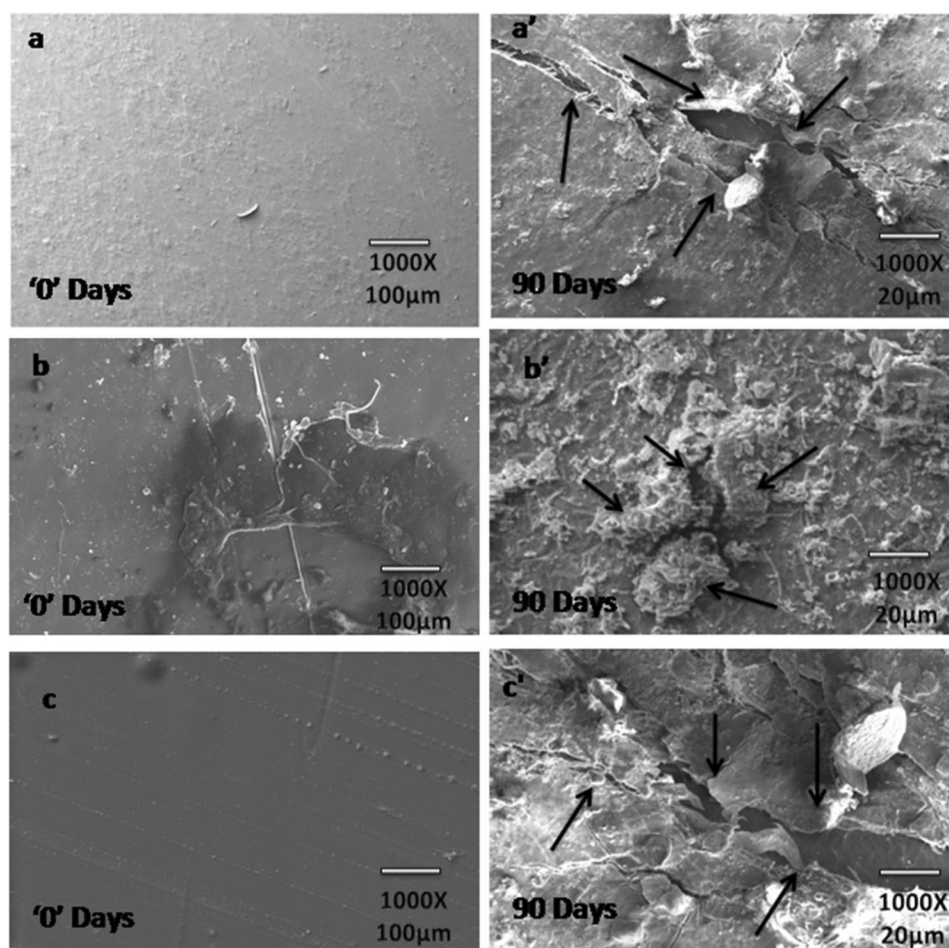
Results and Discussion

Scanning Electron Microscopy (SEM) Analysis of Soil Buried Films

The surface morphology of soil buried samples before and after soil exposure for 90 days is depicted in Fig. 1. The SEM micrograph of VPLA before degradation (Fig. 1a) was traced to be relatively featureless than the sample exposed to soil for 90 days. A number of cracks and coarse structure were observed along with large corrosive holes as indicated by arrow marks in Fig. 1a' [19]. This type of coarse morphology has been resulted from hydrolytic degradation of PLA molecules in real soil environment. The moisture from the soil would have been penetrated the PLA matrix, which further hydrolyses the ester group present in the PLA main chain. It can be substantiated from the findings of Weng et al. [19] where similar phenomena of degradation have been observed of PLA extrusion casted films buried in soil for 4 months. The same can be corroborated from FTIR and GPC analysis of PLA explained in the respective sections.

In case of PLA/PBSA film (Fig. 1c) a smooth surface devoid of any cracks or fragmentation was observed. However, the blend film post soil burial after 90 days (Fig. 1c') was exhibited significant fragmentation of surface layer with large corrosive holes similar to the VPLA system as highlighted with arrow marks. It is assumed that since the PLA/PBSA blend films constitutes of 95 wt% of PLA and 5 wt% of PBSA, compatibilized with 3 wt% of Joncryl, the behavioural pattern of degradation after soil burial was similar to that of VPLA films. However, presence of PBSA which is microbial synthesised polymer the surface fracture was higher in the latter [29]. Similar observations have been incurred in the findings of Ratto et al. 1999 [29], in which the biodegradability of PBSA films was characterised by

Fig. 1 SEM micrographs of before (a, b, c) and after (a', b', c') exposure to soil. VPLA (a, a'), PLA/TPS films (b, b') and PLA/PBSA films (c, c')



holes, cracks and surface fragmentations while tested by soil burial method for 6 months. There was no evidence of any microbial activity in PLA/PBSA films. Moreover, the conversion of PLA/PBSA films into opaque and brittle after 30 days of exposure in soil environment may be characterised by hydrolytic degradation of individual polymers PLA and PBSA [18]. This can be substantiated from the findings of Rudnik et al. 2011 [18], in which they have observed that microbes responsible for degradation of PLA is not available abundantly in real soil environment. The same can be corroborated from FTIR and GPC analysis explained in the later section. Considering the PLA/TPS film, the SEM image (Fig. 1b) was seemed to have a smooth surface in comparison to, SEM image (Fig. 1b') of soil buried sample recovered after 90 days. There was evidence of traces of growth of different bacterial micro colonies indicated with arrow marks that would have been present in the soil. The growth of one type of bacteria or fungus onto the substrate of other groups of micro-organisms stimulate more extensive destruction of PLA/TPS films morphology by assimilation of starch. This microbial action resulted in formation of cracks thereby promoting the deterioration of PLA matrix under these conditions [34]. Similar results have been

reported by Rogovina et al. 2018 [34], where the experiment was conducted upon the pressed film samples prepared from the blends of PLA, potato starch and polyethylene glycol (PEG). The films were tested in soil burial condition for 6 months and growth of fungus and other microbes were significantly observed.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra of VPLA system before and after soil burial of 90 days duration are presented in Fig. 2.

The peaks at 2918 cm^{-1} and 2818 cm^{-1} corresponds to characteristics stretching vibration of $-\text{CH}_2$, peaks at 1750 cm^{-1} and 1180 cm^{-1} related to stretching vibration of carbonyl group ($-\text{C}=\text{O}$). The bending vibration peak of $\text{C}=\text{C}$ of PLA main chain appeared at 730 cm^{-1} [35]. Similarly peaks at 1456 cm^{-1} and 1360 cm^{-1} assigned to bending of $-\text{CH}_3$ group and 1075 cm^{-1} related to $-\text{CH}_3$ rocking of VPLA [36]. While considering the FTIR spectrum of VPLA blown films after 90 days of soil burial, there was not much difference observed. Moreover, the shifting of peaks towards higher values, drop in intensities of FTIR spectra

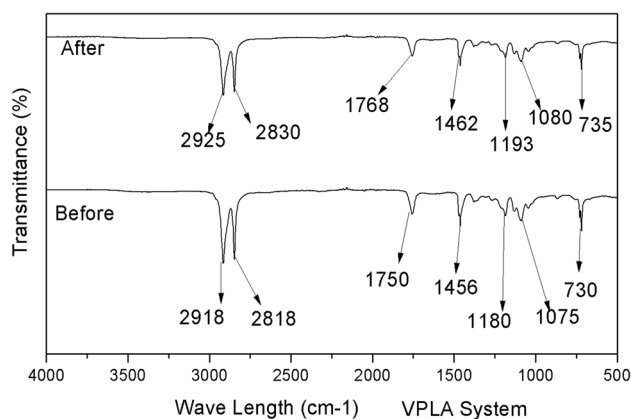


Fig. 2 FTIR spectra of VPLA film

was observed. The shifting of peak corresponds to carbonyl group from 1750 to 1768 cm^{-1} might suggest the degradation of PLA predominantly due to hydrolysis of ester linkage in presence or absence of micro-organisms [17]. This is in consistent with the findings of Agarwal et al. 1998 [17], where they observed the variation in carbonyl group of PLA film tested under biotic, abiotic, and sterile water environment.

The FTIR spectra of PLA/PBSA film systems (Fig. 3) showed peaks at 2918 cm^{-1} and 2818 cm^{-1} is related to $-\text{CH}_2$ stretching, 1744 cm^{-1} and 1181 cm^{-1} corresponds to characteristics stretching of $-\text{C}=\text{O}$ and $\text{C}-\text{O}$ respectively. Likewise, peaks at 1450 cm^{-1} may arise due to bending of 'OH' bond of PBSA. The peak at 867 cm^{-1} might be in tune with chain extension reaction of PLA and PBSA in presence of chain extender Joncryl. The peaks at 2900 , 2800 and 1700 cm^{-1} representing the characteristics peaks of PLA/PBSA blend systems [35].

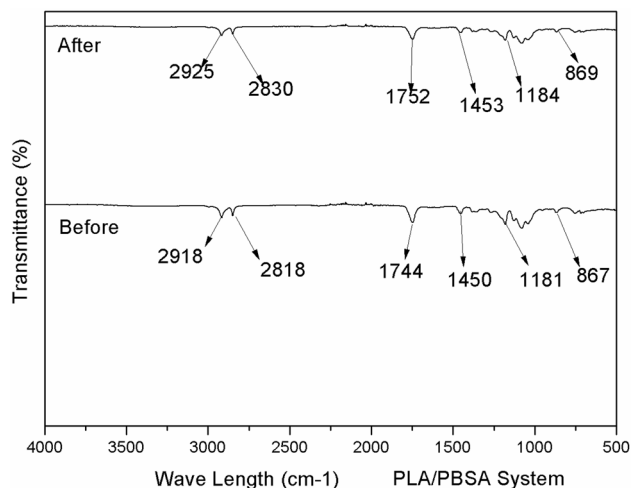


Fig. 3 FTIR spectra of PLA/PBSA blend film

On the other hand, the FTIR spectra of soil burial sample of PLA/PBSA film showed shifting of characteristics peaks of $-\text{CH}_2$ stretching from 2918 and 2818 cm^{-1} to 2925 and 2830 cm^{-1} respectively. The stretching of $-\text{C}=\text{O}$ and $\text{C}-\text{O}$ changed from 1744 and 1181 cm^{-1} to 1752 and 1184 cm^{-1} respectively. The bending vibration of 'OH' group of PBSA shifted its position from 1450 to 1453 cm^{-1} and the peak at 867 cm^{-1} representing the interaction of PLA/PBSA reactive blend switched to 869 cm^{-1} . However, the peaks did not change significantly before and after soil burial for the period of 90 days. But migration of peaks and drop in intensities might suggest the occurrence of degradation of PLA/PBSA films under real soil environment [19]. Weng et al. 2013 [19] also noticed similar degradation behavior of PLA/PBAT blends in real soil environment which characterized with the migration of carbonyl and methyl group as compared to undegraded sample.

The FTIR spectra of PLA/TPS film system in Fig. 4 depicted interesting phenomena. The PLA/TPS film before degradation showed peaks ranging from 3300 to 3280 cm^{-1} related to 'OH' stretching of starch during thermo plasticization. Also, peaks ranged from 2918 to 2848 cm^{-1} correspond to $-\text{CH}$ stretching in both starch and PLA. The peak at 1747 cm^{-1} related to carbonyl stretching of PLA and TPS in PLA/TPS film system. The peak at 1648 cm^{-1} correlated to absorbed water molecules during thermo plasticization. The peak at 1022 cm^{-1} exhibited the presence of anhydrous glucose units of starch molecule [37–39]. On the contrary, the FTIR spectra of PLA/TPS film after degradation showed complete absence of peaks in the range of 3300 cm^{-1} to 3280 cm^{-1} of hydroxyl (OH) group of starch, representing the degradation of starch portion of the PLA/TPS films. The carbonyl stretching at 1747 cm^{-1} did not change significantly, affirming that the

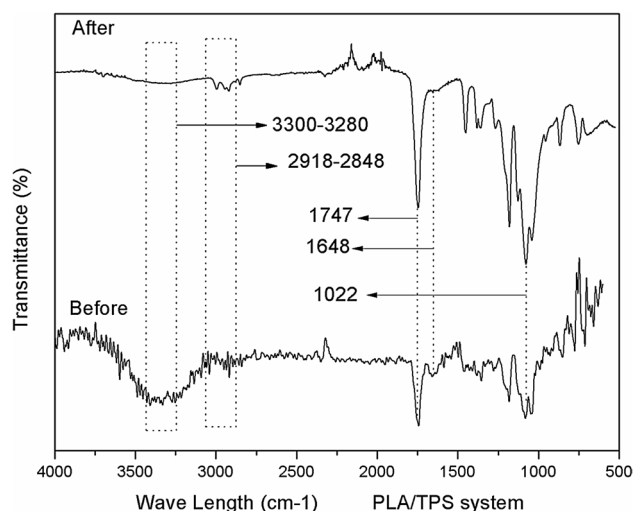


Fig. 4 FTIR Spectra of PLA/TPS blend films

degradation occurred only for starch not the PLA content within 90 days of soil exposure [40]. This can be substantiated from the findings of Akrami et al. 2016 [40], the biodegradation pattern of PLA and corn starch compression molded sample has been analysis through soil burial method for 90 days of time period, where the FTIR graph showed complete absence of hydroxyl peak along with unchanged carbonyl peak.

The quantitative analysis of degradation can be accomplished through the determination of carbonyl index with respect to exposure time represented in Fig. 5 [41]. It can be calculated by Eq. (3) [18]

$$\text{Carbonyl Index (CI)} = \frac{\text{Intensity of the carbonyl band around } 1700 \text{ to } 1750 \text{ cm}^{-1}}{\text{Intensity of the reference peak around } 1450 \text{ cm}^{-1}} \quad (3)$$

The carbonyl index of VPLA system prior to the soil exposure was found to be 0.68 and later at 90 days of exposure to be 0.49. For PLA/PBSA film system carbonyl index before and after soil degradation was 0.95 and 0.82, respectively. This small change in carbonyl index suggested a lesser rate of biodegradation as PLA is not readily degradable in natural environment within short time period [18] because micro-organisms responsible for degradation of PLA not available abundantly [42] and it preferably degrades at 60 °C due to increased hydrolysis at its glass transition temperature. Moreover, the degradation of PLA is abiotic, caused by hydrolysis of ester bonds present in its molecular architecture. This is consistent with the observations of Rudnik et al. 2011a [18] in which the carbonyl index of soil buried PLA films in Mediterranean

filed did not decreased significantly, attributed to the slow hydrolysis of carbonyl group of PLA yielding no degradation by product.

Contrastingly, the carbonyl index for PLA/TPS film system prior to the exposure was found to be 2.16 and on later stage of 90 days of soil degradation it tuned to 0.25, a significant reduction in carbonyl index value suggesting a notable biodegradation in soil environment which in fact occurred due to rapid degradation of starch portion of the bio films [40]. Additionally, incorporation of starch would stimulate the biodegradation process in natural environment [21, 29]. Moreover, Ratto et al. 1999 [29] observed that the

degradation kinetics of PBSA and corn starch blend in soil environment accelerated due to the incorporation of starch.

Gel Permeation Chromatography

The determination of variation in molecular weight of all three film systems before and after soil burial for the period of 90 days has shown in Fig. 6. The molecular weight of VPLA system was found to be 195.4 kDa and 173.2 kDa whereas the PLA/PBSA film system showed to be 205.3 kDa and 168.2 kDa prior and later phase of soil exposure for 90 days respectively. The molecular weight for PLA/TPS film systems was 156 kDa before degradation and 117 kDa after degradation. Similarly, poly dispersity index (PDI) of all three film systems is represented in Fig. 7. The PDI of VPLA was 1.8 before soil burial and ascent to 2.3 after 90 days of soil burial, whereas for PLA/PBSA film

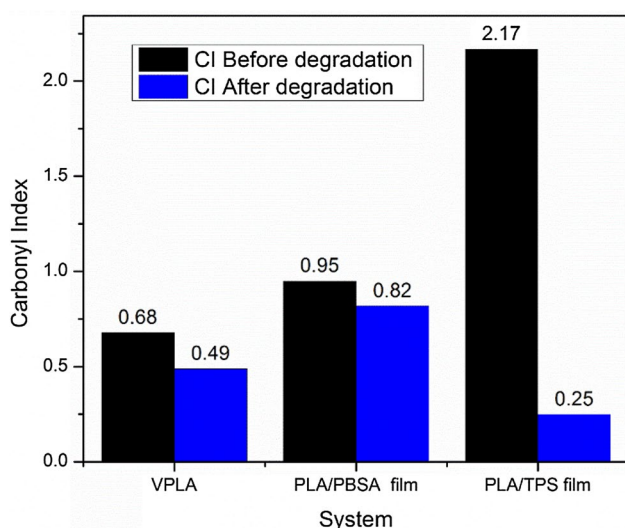


Fig. 5 Carbonyl index of blend films

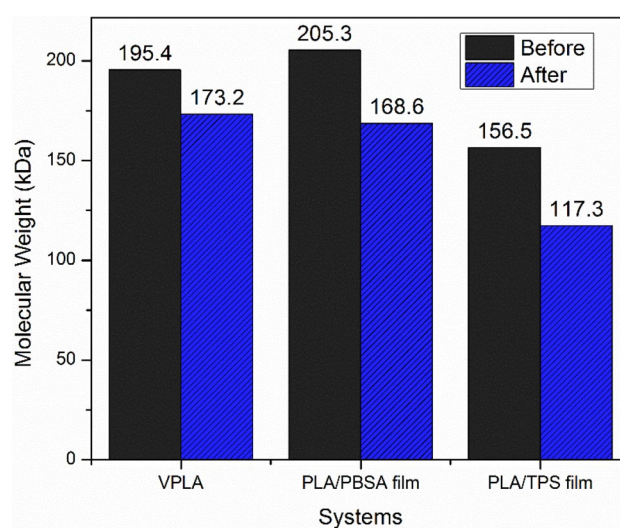


Fig. 6 Molecular weight of film systems

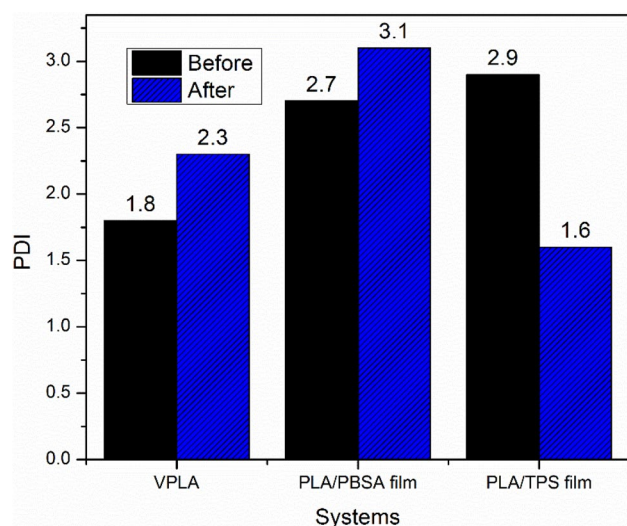


Fig. 7 Poly dispersity index (PDI) of films

system showed 2.7 and 3.1 before and after soil exposure for 90 days, respectively. On the contrary, PDI of PLA/TPS film system was found to be 2.9 and 1.6 for both before and after soil burial.

The molecular weight of the all the blend films prior to the soil exposure was found to be high in comparison to soil buried samples recovered after 90 days. This variation in molecular weight may be ascribed to occurrence of degradation of films in soil environment [17, 43]. On the contrary an ascending pattern in case of poly dispersity index (PDI) values was observed in case of VPLA and PLA/PBSA blend films. This discerned the fact that, the biodegradation of both the films occurred due to random scission of polymeric chain due to autocatalysis of hydrolytic degradation of carbonyl group of PLA which resulted from penetration of soil moisture in the films subsequently accelerating the degradation process [44]. Further it may be noted that PLA/PBSA film comprised of 95 wt% of PLA for which degradation mechanism was quite similar with VPLA. Moreover, it pointed towards the absence of participation microorganism in the degradation process which may be corroborated from SEM analysis of both the films [45]. However, in case of PLA/TPS blend films both molecular weight and PDI decreased concomitantly, which ascribed to the etching of starch particles due to their enzymatic assimilation as evident from SEM

analysis. The synergism of abated rate of hydrolysis of high molecular weight and crystalline portion of polymer; and accelerated rate of microbial assimilation of oligomers and amorphous fraction of polymer would result in decrease of both molecular weight and PDI [46]. Both VPLA and PLA/PBSA blown films sustains abiotic hydrolytic degradation due to the soil water ingress into the films, while in case of PLA/TPS film both abiotic and biotic factor facilitates the biodegradation. TPS being hydrophilic in nature ought to enhance the penetration of soil water into the film surface thereby improving the rate of hydrolysis compared to its counterparts. Furthermore, it is evident that TPS can support enzymatic degradation as being easily assimilated by soil microbes which can be corroborated from SEM and FTIR studies. Therefore, the biodegradation of the films initiated with hydrolysis due to absorption of water in soil, fragmented the larger molecule into oligomers which further assimilated by microbial colony available in soil. Puchalski et al. 2018 [45] studied the biodegradation behaviour of PBSA and PBS in both compost and artificial weathering condition. In both the cases molecular weight has been found to be decreasing while PDI increased only in the sample tested under compost. Decreasing in molecular weight was ascribed to the hydrolysis of macro molecules whereas increasing in PDI evinced to the occurrence of enzymatic assimilation of oligomeric species produced as a by-product of hydrolysis. Moreover, the study reported the reluctance of PBSA towards enzymatic degradation which has also been observed in this study.

Elemental Analysis

The percentage of organic carbon–hydrogen–oxygen (CHO) obtained from elemental analysis of all three film samples before and after soil burial is enumerated in Table 2.

As per the tabulated values in Table 2, the percentage of elemental carbon of VPLA prior to soil burial was found to be 49.5%, hydrogen 6% and oxygen 44.5%. In the later phase of soil exposure for the period of 90 days the organic carbon percentage in the VPLA remained at 48.2%, hydrogen at 5.8% but elemental oxygen percentage increased to 46%. Similarly, the percentage of organic carbon content of PLA/PBSA film was detected to be 51.6%, hydrogen 6.1% and oxygen 42.3% prior to the soil contact. After the exposure films to soil environment, the organic carbon and hydrogen

Table 2 CHO elemental percentage of film systems

| Sample code | Carbon (%) | | Hydrogen (%) | | Oxygen (%) | |
|----------------------|------------|-------|--------------|-------|------------|-------|
| | Before | After | Before | After | Before | After |
| VPLA system | 49.5 | 48.2 | 6 | 5.8 | 44.5 | 46 |
| PLA/PBSA film system | 51.6 | 49.9 | 6.1 | 5.9 | 42.3 | 44.2 |
| PLA/TPS film System | 50.5 | 46.3 | 5.3 | 5.1 | 44.2 | 48.6 |

decreased to 49.9% and 5.9% respectively, in contrast the elemental oxygen tuned to 44.2%. Likewise, the organic carbon, hydrogen and oxygen of PLA/TPS films were determined to be 50.5%, 5.3%, and 44.2% preceding to the soil burial while these values changed to 46.3%, 5.1% and 48.6 for organic carbon, hydrogen and oxygen respectively succeeding to the soil burial. The depletion in percentage of elemental carbon content and the augmentation in oxygen content for all the films analysed and compared for prior and later phase of soil exposure signifies the occurrence of biodegradation in real soil environment. The enhancement in oxygen percentage in soil degraded samples may be ascribed to the increment in carboxyl group concentration in the molecular architecture [19]. These results can be substantiated from the findings of Weng et al. 2013 [19], in which PLA, PBAT and PLA/PBAT blend films were tested for biodegradation in real soil environment buried for four months. They reported the decrement in organic carbon content and increment in oxygen content as the symptoms of biodegradation in soil buried samples. Further it may be noted that PLA/TPS film system exhibited highest fluctuation of carbon and oxygen content in case of prior and later phase of degradation compared to VPLA and PLA/PBSA film systems, which would be attributed to the readily bio assimilation nature of starch in real soil proximity rather than PLA and PBSA. Moreover, the enzymatic degradation caused by action of soil microbes seemed to be more prominent on starch surface corroborated from SEM analysis of the film surfaces [40] (Table 3).

Weight Loss Percentage

The weight loss percentage of VPLA, PLA/PBSA film and PLA/TPS film buried in soil is depicted in Fig. 8. The loss of weight percentage was measured using Eq. (2) and recorded in each 7 days interval. The kinetics of the soil degradation of all three films can be divided into three phases (a) initial phase of decay, (b) growth phase of decay, (c) plateau phase. The initial phase of degradation was characterized with negligible mass loss percentage which continued till the period of 14 days for all the three types of films. The growth phase of decay was observed after 14 days, sustained till 70 days in which the decomposition escalated exponentially, and maximum decomposition was achieved. Further in the period of 70 to 90 days the decay seemed to be constantly growing

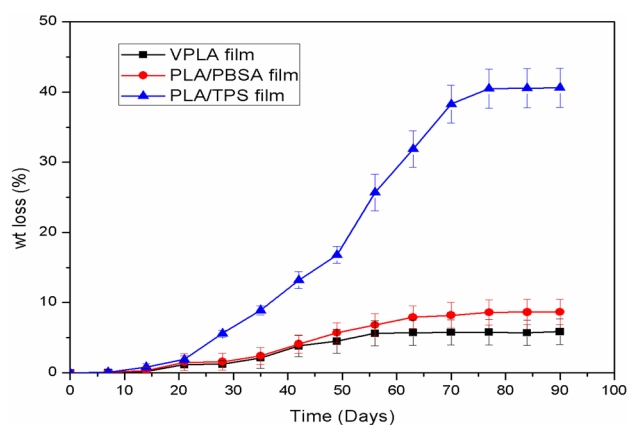


Fig. 8 Percentage of weight loss of film systems

with a becalmed growth rate, defined with plateau phase. Both VPLA and PLA/PBSA film systems exhibited a very low rate of degradation kinetics in comparison to PLA/TPS film systems. The degradation mechanism of PLA is predominantly hydrolysis promoted by the penetration of water from the soil which can be corroborated from FTIR and GPC analysis. That is the reason, both VPLA and PLA/PBSA film systems, composed of larger portion of PLA owing to the degradation behaviour of PLA with optimum degradation of 5.8% and 8.6% respectively for both VPLA and PLA/PBSA film systems in 90 days of soil burial test. However, addition of biodegradable PBSA improved the degradability of PLA/PBSA films [47]. It has also been evident that due to the compact structure of PLA, it remained impermeable to the soil water [48]. Therefore, both VPLA and PLA/PBSA films showed lower rate hydrolytic degradation, presented as relatively flattened curve (Fig. 8) compared to PLA/TPS films. On the other hand, PLA/TPS films with 20 wt% of thermoplasticized starch exhibited an excellent degradation pattern in real soil environment. The degradation of the films proceeded through assimilation of readily degradable starch particles by soil micro-organisms followed by hydrolysis of PLA content synergistically assisted by soil microbes. This behaviour was observed in SEM and FTIR analysis. The optimum degradation of PLA/TPS film was reported to be 40.6% in the period of 90 days [40]. Moreover, incorporation of starch in PLA reduced its molecular weight, crystallinity, and increased hydrophilicity which in turn catalysed the degradation of PLA/TPS films in soil environment [49], given that starch has a stark biodegradability higher than PLA, thus recording higher rate of biodegradability for PLA/TPS films [48]. Furthermore, the early degradation of starch component in PLA/TPS film increases the contact area of water and microorganisms for PLA component resulting higher rate of mass loss in soil environment [48]. The phenomena have been explained in the study of Jandas et al. 2013 [49], in which the study of biodegradability of PLA/PHB/

Table 3 Regression analysis data of film systems

| Sample code | $t_{1/2}$ (days) | R^2 | a | b |
|---------------|------------------|---------|-----------|---------|
| VPLA | 835 | 0.90259 | 100.31406 | 0.99917 |
| PLA/PBSA film | 559 | 0.94816 | 100.88236 | 0.99872 |
| PLA/TPS film | 103 | 0.91764 | 108.08664 | 0.91764 |

nanoclay compatibilized extrusion blown films in compost, fungi and bacterial medium was conducted. The biodegradability of the films was found to be enhanced due to the reduction in molecular weight, crystallinity, and increment in hydrophilicity of the blend films compared with pristine PLA film. Due to the enhancement in hydrophilicity the moisture from the soil can easily penetrate the PLA molecules, leads to disrupt the molecular architecture promoted by hydrolysis of ester group of PLA main chain. This creates severe structural fragmentation as evident from surface morphology analysed by SEM. Subsequently, it reduces the molecular weight thereby formation of low molecular weight oligomer which can easily assimilated by micro-organisms as corroborated from GPC analysis.

The weight loss percentage data obtained for VPLA, PLA/PBSA and PLA/TPS blown films are significantly different ($p > 0.5$) from each other. However, they are not significantly different ($p < 0.5$) within the group. The population mean of the obtained data are reported to be different from each other as per Tukey's (HSD) test at 95% confidence level, whereas the population variation found not to be significantly different statically in terms of Levene homogeneity of variance test.

The estimation of half-life period ($t_{1/2}$) was calculated from exponential decay function, carried out by calculating weight/mass retention percentage from the experimentally obtained mass loss data (Fig. 3).

The calculated mass/weight retention was fit to exponential decay Eq. (3) and regression analysis out comes were enumerated in Table 4 [44].

$$y = ab^x \quad (4)$$

where 'y' is the weight or mass retention percentage, 'a' and 'b' are constants determined from the regression analysis and 'x' is the time period and presented in Fig. 9. The half-life of VPLA film was found to be 835 days suggesting a very slow rate of degradation, whereas the estimated $t_{1/2}$ of PLA/PBSA film was reported to be 559 days demonstrated a substantially high rate of degradation in real soil environment compared to VPLA films.

Although both PLA and PBSA undergoes hydrolytic degradation, the degradation rate of PBSA is higher than that of PLA and the blend of PLA and PBSA exhibited higher rate

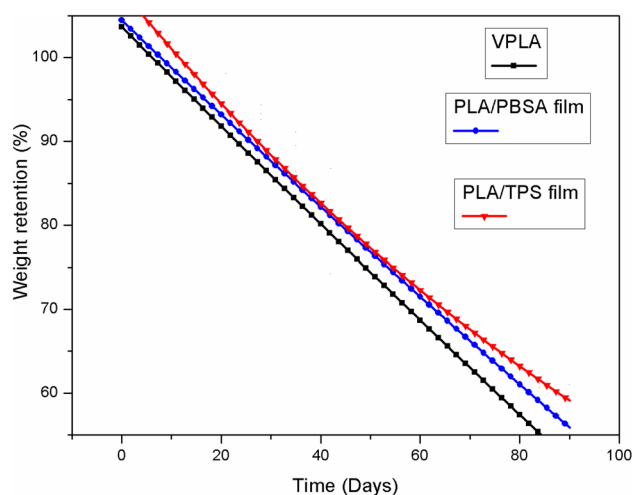


Fig. 9 Regression curve of VPLA, PLA/PBSA, PLA/TPS films

of degradation compared to individual polymers [47]. This observation is in consistent with Malewela et al. 2015 [47], in which the degradation behaviour of PLA/PBSA blend along with individual polymers was studied and higher rate of biodegradation was reported for PBSA. This might be the reason of comparatively high rate of decay of PLA/PBSA films than VPLA films. Further the PLA/TPS films with $t_{1/2}$ of 103 days depicted the optimum rate of degradation, which can be attributed to the incorporation of biodegradable starch resulted in decreasing the sustenance of films in real soil environment. The highest values of adjacent R^2 closes to 1 suggesting the goodness of fit of the regression analysis.

Thermal Analysis

The glass transition (T_g), melt transition (T_m) and percentage of crystallinity (X_c) of all the blend films during prior and later phase of soil exposure have been determined using DSC analysis and the corresponding data obtained from second heating are enumerated in Table 4. The T_g and T_m of all the soil exposed blend films were found to be decreasing concomitantly as compared with unexposed samples. It is also evident from the DSC thermogram in Fig. 10 that, the intensity of glass transition seemed to be decreasing in case

Table 4 DSC analysis of films before and after soil burial

| Composition | Before | | | | | After | | | | |
|-------------|------------|---------------|------------|--------------------|-----------|------------|---------------|------------|--------------------|-----------|
| | T_g (°C) | T_{cc} (°C) | T_m (°C) | ΔH_m (J/g) | X_c (%) | T_g (°C) | T_{cc} (°C) | T_m (°C) | ΔH_m (J/g) | X_c (%) |
| VPLA | 66.5 | 114.2 | 148.6 | 32.56 | 5.02 | 58.4 | 110.3 | 144.3 | 45.9 | 48.3 |
| PLA/PBSA | 66.2 | 106.4 | 151.1 | 11.75 | 15.4 | 57.8 | 102.1 | 143.5 | 13.1 | 37.5 |
| PLA/TPS | 59.7 | 110.0 | 150.7 | 26.5 | 28.3 | 55.6 | 106.8 | 141.7 | 43.2 | 46.5 |

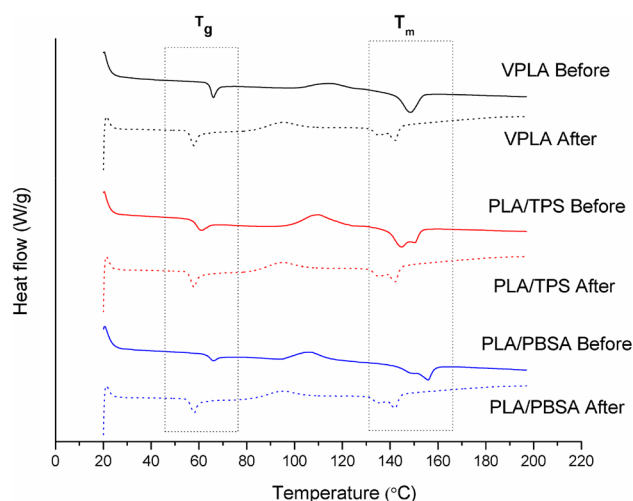


Fig. 10 DSC curve of films before and after of soil burial

of all the soil buried samples. Further the bimodal T_m curve in case of PLA/TPS and PLA/PBSA films appeared due to different lamellar structure of PLA, subsequently found to be decreasing in its intensity along with the broadening of peaks in case of all the soil exposed films. This is attributed to the reduction in molecular weight due to hydrolytic degradation of PLA as corroborated from GPC analysis [50]. In the investigation of Way et al. 2012 [50], it was found that the depression of T_g and T_m intensity along with reduction in their values of DSC curve of aerobically biodegraded PLA and PLA/wood fibre composite as per ISO 14855 prepared from sequentially treated with sodium hydroxide (NaOH) solution and two other solution prepared from NaOH-acetone and NaOH-silane, predominantly due to hydrolysis.

Further the cold crystallization temperature (T_{cc}) of all the soil exposed samples were found at lower side as compared to unexposed films irrespective of their compositions. This is underlining the enhancement of cold crystallizability of PLA due to the occurrence of hydrolytic degradation of films in the soil environment. The hydrolytic degradation diminished the chain entanglement of PLA which increased the cold crystallization process, consequently responsible for the enhancement of the chain mobility and crystallinity of PLA [33]. Further, this phenomenon can be observed from the values of percentage of crystallinity enumerated in Table 4, that crystallinity of the all the degraded films is higher compared to pristine films. In general, crystallinity is an important criterion to determine the occurrence of degradation, as it is more compact and less prone towards hydrolytic degradation due to lesser tendency of moisture ingress. Therefore, it is reported that amorphous portion ought to be degraded preferentially during hydrolysis which can be substantiated from Salomez et al. 2019, where degraded PBSA films as per ISO 14855 prepared from calendaring

process showed increased crystallinity [46]. This is in turn resulted in increment in crystallinity of the soil exposed films compared to unexposed films [51, 52]. Moreover, the small endothermic transition may be attributed to the emergence of short chain species as the degradation by product in the soil environment [53].

X-ray Diffraction Analysis

The X-ray diffractograms of film samples has been depicted in Fig. 10 pertaining to prior and after soil exposure. The XRD analysis has been discussed in our previous work [1, 2].

VPLA showed diffraction amorphous halo peak (2θ) at 16° or 16.5° corresponding to (110) and (200) orthorhombic α crystal form. The broadening of the peak is enumerating the low crystallinity of the PLA [1, 33]. The interlayer d-spacing was calculated to be 0.553 nm using Bragg's equation $n\lambda = 2d\sin\theta$. PLA/TPS depicted the diffraction peak at 17.06° , 22.5° , and 32.93° with d-spacing 0.519 nm [2]. For the PLA/PBSA films, 2θ appeared at 16° and 17° as in case of VPLA film due to predominance of PLA content (95 wt%) in the film composition. The percentage of crystallinity for unexposed film samples could not be determined by XRD technique because of the superimposition of crystalline peaks in the diffractograms [1].

On the other hand, the crystalline peaks have been visibly appeared at (2θ) around 44.2° , 64.5° and 77.6° for the film sample of VPLA and PLA/PBSA recovered after 90 days of soil burial. Similarly, PLA/TPS after 90 days of soil exposure depicted the crystalline peaks at 42.3° , 61.5° , and 73.2° . In hindsight, the characteristic diffraction peaks at 17.06° and 22.5° representing TPS content in PLA/TPS film disappeared in the soil recovered sample (Fig. 11) due to the proactive degradation of TPS in the soil environment. Moreover, utterly faster degradation thereby isolation of TPS content from the PLA/TPS films, facilitated the greater surface contact of PLA with soil for hydrolytic followed by enzymatic degradation. The hydrolytic degradation of all the film samples caused evolution of distinct crystalline peaks irrespective of their compositions, as the amorphous content of the films sustained the initial phase of degradation due to ingress of water from the soil and oozing out the coalesce. The percentage of crystallinity was found to be 51.6%, 38.6% and 50.3% respectively for VPLA, PLA/TPS and PLA/PBSA after 90 days of degradation in soil. These can be substantiated from the studies of Shanshan et al. [53] and Balapa et al. [33].

Mechanical Properties

The variation in mechanical properties of soil buried VPLA, PLA/PBSA and PLA/TPS film systems has been discussed

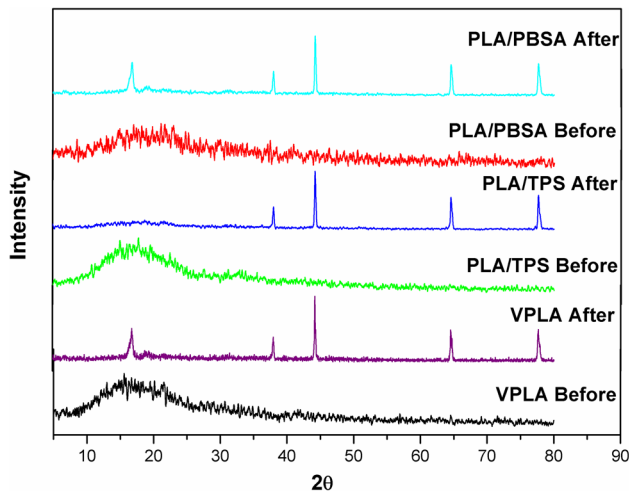


Fig. 11 X-ray diffractograms of film samples before and after soil burial

in terms of tensile modulus, strength and elongation at break percentage in both machine and transverse directions and enumerated in Table 5. The tensile modulus of VPLA at 0th day of soil exposure was 2407 MPa in MD and 2060 MPa in TD. During initial phase of decay till 14 days there was limited reduction in tensile modulus to 1950 MPa and 1720 MPa in both MD and TD until growth phase was attained. The tensile modulus during growth phase of decay at 21 days and 28 days decreased significantly and least value of modulus reported at 28 days of soil exposure decline to 60.3% in MD and 81.3% in TD, respectively. The tensile strength of VPLA at 0th day was found to be 37.4 MPa and 28.7 MPa in MD and TD, respectively. It trailed the similar trend of reduction

in values throughout the initial phase to growth phase of degradation, from 0th day to 28th day of soil burial and the value diminished to 76.73% and 84.3% compared to original tensile strength. The elongation at break percentage in MD and TD of VPLA prior to soil exposure observed to be 5.1% and 1.8%, declined gradually to 4.8% and 3% in MD, 1.5% and 1.1% in TD after 7 and 14 days of soil exposure within the initial phase of degradation. When the growth phase was arrived from 14th day onwards, the brittleness of the film increased significantly, and elongation value could not be determined.

The mechanical properties of PLA/PBSA film data showed that the tensile modulus during the soil exposure duration decreased to 71.28% in MD and 88.25% in TD in 28 days of burial period compared to modulus value before soil exposure. A clear loss of quantum was recorded in case of tensile strength from 48.7 to 9.8 MPa in MD and 43.3 to 3.5 MPa in TD within 28 days of soil burial. The drastic reduction of elongation at break percentage from 7.5 to 3.2% and 2.3 to 1.3% in both machine and transverse direction within barely 21 days resulted from rapid deterioration films owing to increase in brittleness of films in real soil environment.

Similarly, the overall momentous depletion was observed in tensile modulus of PLA/TPS films to 75.31% and 83.97% and slumping of tensile strength to 60.42% and 80% in both machine and transverse direction within 21 days of soil burial compared to unexposed film samples suggesting amicable biodegradation nature of the films. It was also observed that, the starch particles started phasing out of the film surface after 21 days and increased phenomenally during growth phase of degradation from 21 days onwards, aided

Table 5 Mechanical properties of VPLA, PLA/PBSA and PLA/TPS films

| Sample code | Modulus (MPa) | | Strength (MPa) | | Elongation (%) | |
|-------------------------------|---------------|------------|----------------|-----------|----------------|----------|
| | MD | TD | MD | TD | MD | TD |
| (VPLA) ₀ Days | 2407 ± 445 | 2060 ± 258 | 37.4 ± 4 | 28.7 ± 4 | 5.1 ± 1 | 1.8 ± 1 |
| (VPLA) ₇ Days | 2396 ± 432 | 1988 ± 238 | 35.6 ± 4 | 26.2 ± 3 | 4.8 ± 1 | 1.5 ± 1 |
| (VPLA) ₁₄ Days | 1950 ± 376 | 1720 ± 285 | 28.3 ± 3 | 21.5 ± 3 | 3.7 ± 1 | 1.1 ± 1 |
| (VPLA) ₂₁ Days | 1670 ± 231 | 995 ± 184 | 19.1 ± 3 | 9.8 ± 2 | — | — |
| (VPLA) ₂₈ Days | 955 ± 126 | 385 ± 49 | 8.7 ± 2 | 4.5 ± 1 | — | — |
| (PLA/PBSA) ₀ Days | 3037 ± 485 | 2270 ± 186 | 48.7 ± 5 | 43.3 ± 3 | 7.5 ± 1 | 2.3 ± 1 |
| (PLA/PBSA) ₇ Days | 3023 ± 469 | 2251 ± 173 | 46.2 ± 5 | 42.1 ± 3 | 7.2 ± 1 | 2.1 ± 1 |
| (PLA/PBSA) ₁₄ Days | 2850 ± 435 | 1860 ± 146 | 32.2 ± 4 | 29.8 ± 3 | 5.6 ± 1 | 1.8 ± 1 |
| (PLA/PBSA) ₂₁ Days | 1685 ± 137 | 929 ± 117 | 17.4 ± 2 | 11.3 ± 2 | 3.2 ± 1 | 1.3 ± 1 |
| (PLA/PBSA) ₂₈ Days | 872 ± 126 | 253 ± 71 | 9.8 ± 2 | 3.5 ± 1 | — | — |
| (PLA/TPS) ₀ Days | 1021 ± 76 | 986 ± 54 | 23.5 ± 3 | 20.60 ± 4 | 6.4 ± 1 | 3.25 ± 1 |
| (PLA/TPS) ₇ Days | 1015 ± 68 | 975 ± 54 | 21.7 ± 3 | 19.8 ± 3 | 6.1 ± 1 | 3.1 ± 1 |
| (PLA/TPS) ₁₄ Days | 875 ± 53 | 670 ± 74 | 15.3 ± 3 | 11.8 ± 3 | 4.2 ± 1 | 1.8 ± 1 |
| (PLA/TPS) ₂₁ Days | 252 ± 68 | 185 ± 45 | 9.3 ± 3 | 4.1 ± 2 | — | — |
| (PLA/TPS) ₂₈ Days | — | — | — | — | — | — |

MD machine direction, TD transverse direction

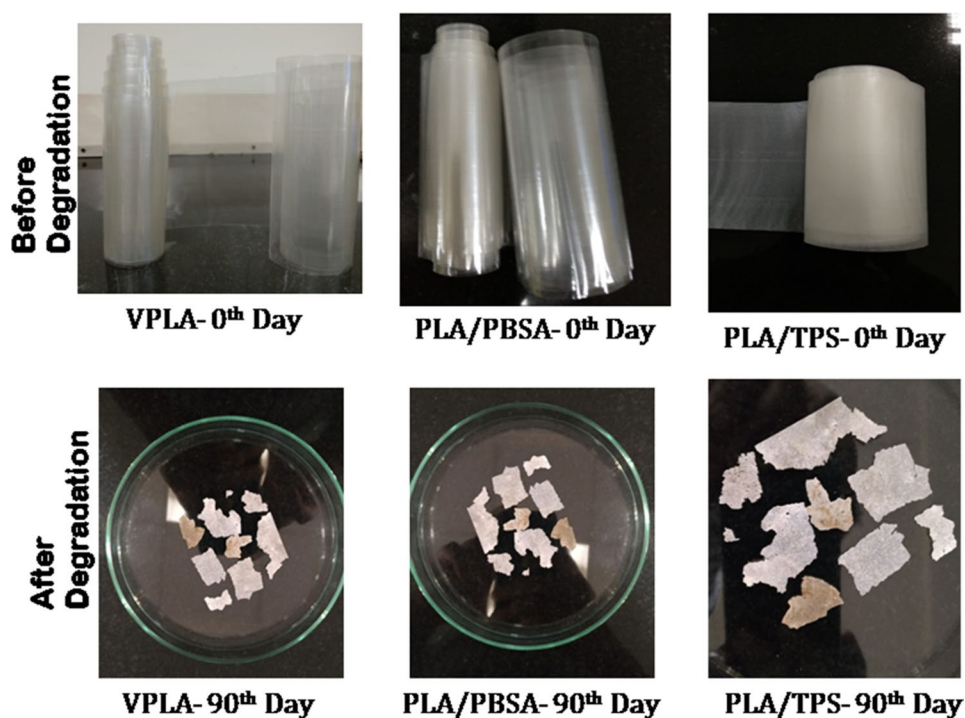
to substantial increment in brittleness of the exposed PLA/TPS film samples. This is the reason behind the absence of elongation at break data on 21st day and complete segment of mechanical data on 28th day of PLA/TPS films.

The biodegradation of PLA in soil or compost is a very complex phenomenon. It proceeds through absorption of water from soil which in turn accelerates the hydrolysis of ester bond due to the formation of cleavage in molecular chain architecture owing to origination of oligomers. Further the fragments of oligomers solubilised and diffused into CO₂ by the action of bacteria, fungus, and other soil microbes responsible for assimilation of PLA [54]. Therefore, both VPLA and PLA/PBSA films undergoes hydrolytic degradation which can be noticed from Fig. 10 where the clear transparent film samples became opaque and brittle within one-month exposure.

After one month the kinetics of degradation proceeded faster and brittleness of the films became prominent such that mechanical tests could not be able to carry out as it became difficult to cut the sample as per prescribed dimension. The brittleness and opacity of the film increased concomitantly till 70 days. After which the disintegration of the film samples occurred and continued till 90 days as represented in Fig. 12. Moreover, the degradation of VPLA and PLA/PBSA films was quite slow as because soil moisture plays a vital role in hydrolytic degradation of PLA and during October to December the soil became dry and arid which resulted in lesser rate of degradation,

which is in well agreement with the findings reports elsewhere [18, 55]. In contrast to VPLA and PLA/PBSA films, PLA/TPS films showed higher rate of degradation kinetics. Although the decaying of PLA/TPS stranded during initial phase of soil burial in par with VPLA and PLA/PBSA films till 14 days, the growth phase from 14 to 70 days depicts an exponential growth until plateau phase. It was also noteworthy that during the growth phase the TPS content phased out which gave rise to generation of small pores on the film surface after the 90 days of recovery. This was due to the readily biodegradable nature of TPS, as the bacterial colony grew on the favourable TPS content of the film, consumed further to penetrate the matrix and biodegradation proceeds, which can be corroborated from SEM, FTIR and GPC analysis of the film. The brittleness of PLA/TPS film was prominently observed at 21st day of soil incubation which resulted in optimum decrement in mechanical properties and on the 28th day the test could not be carried out and left without result. The brittleness was persistent from 14 days, enhanced incessantly till 70 days followed by structural disintegration aided to the superior biodegradation of PLA/TPS films compared to VPLA and PLA/PBSA films. Our findings can also be substantiated from the work of Zuo et al. 2015 [48], in which they observed the deterioration of mechanical properties and structural integrity of soil buried PLA/starch composite specimens within 30 days of exposure, due to faster degradation of starch component resulting loss of interfacial bonding between PLA and starch phases.

Fig. 12 Visual inspection of VPLA, PLA/PBSA, and PLA/TPS soil buried sample



Conclusions

The biodegradation behaviour of VPLA, PLA/TPS and PLA/PBSA blend films was studied via soil burial method for 90 days of time duration. The biodegradation mechanism of VPLA and PLA/PBSA blend films has been found to be predominantly abiotic i.e., autocatalytic hydrolysis of ester bond due to ingress of soil water into the films. On the contrary, the biodegradation mechanism of PLA/TPS film in soil has been influenced via both biotic and abiotic factors. The hydrophilic nature of TPS enhanced the penetration of soil water into the film thereby accelerating the rate of hydrolytic degradation as compared to VPLA and PLA/PBSA films. Moreover, the TPS component phased out from the film coalescence readily assimilated by soil microbes supporting the participation of biotic component in the degradation process. Further, due to the early degradation of TPS, the PLA component of the film system has been more exposed to soil water and microbes thereby sustaining enhanced kinetics of hydrolytic degradation rate. These phenomena have been observed in SEM, FTIR, GPC and elemental analysis. Similarly, variation in T_g , T_m , and T_{cc} determined by DSC and change in crystallinity profile obtained from XRD analysis of film samples pertaining to both prior and later phase of soil exposure enumerated the occurrence of biodegradation in soil environment. The categorization of all three films in descending order of rate of biodegradation is as follows

PLA/TPS > PLA/PBSA > VPLA.

The weight loss study of PLA/TPS film showed optimum rate of degradation at 40.6% with a half-life of 103 days followed by PLA/PBSA film at 8.6% having half-life of 559 days. The VPLA exhibited lowest mass loss rate recorded at 5.8% with the half-life of 835 days. The decaying in mechanical strength, modulus and elasticity has been reported to be drastic between 14 to 28 days of exposure after which the test could not be performed due to severe structural disintegration, establishing the fact that all the films invariably degradable in real soil environment.

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