

# Assessing Biodegradability of PVA/Starch Based Composite Films Reinforced With Long Chain Fatty Acid Grafted Barley Husk

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## Research Article

**Keywords:** composite film, biodegradability, soil burial degradation, activated sludge, aerobic environment

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1 **Assessing biodegradability of PVA/starch based composite films reinforced with long**  
2 **chain fatty acid grafted barley husk**

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7 **Abstract**

8 The main objective of this study is the preparation of poly (vinyl alcohol) PVA/starch based composite films  
9 reinforced with barley husk and grafted barley husk (prepared using lauric acid, palmitic acid and arachidic  
10 acid) for packaging applications and assessment of their biodegradability. The biodegradability test of the films  
11 was performed by measuring weight loss of the films after degradation in soil under natural environmental  
12 conditions and by measuring evolved carbon dioxide (CO<sub>2</sub>) during degradation under aqueous aerobic  
13 environment containing activated sludge. Physico-chemical variation in the films after degradation were  
14 observed using scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). The  
15 composite films containing barley husk showed highest degradation in soil (70 % after 180 days) as well as in  
16 aqueous aerobic medium (58.83 % after 30 days). The results of scanning electron microscopy showed the  
17 formation of cracks and holes over the surface of the composite films after degradation. The degradation of the  
18 films occurred inside the composite films, not only on their surface. The incorporation of starch and barley husk  
19 in PVA matrix enhanced the degradation rate of films.

20 **Keywords** composite film, biodegradability, soil burial degradation, activated sludge, aerobic environment

21 **1. Introduction**

22 There has been introduction of new regulations considering the processing and manufacturing of the plastic  
23 products using modified natural polymers or synthetic raw materials in the European Union (Directive EU  
24 2019/904) (Borowski et al. 2020). The marketing of single use plastic products will be prohibited from 2021  
25 onwards. There is also possibility that the composites made from non-degradable and synthetic polymers may  
26 be replaced with biocomposites containing natural fillers in the near future (Ibrahim et al. 2020). Therefore, the  
27 research is more focused towards replacement of non-degradable synthetic plastic with environment friendly  
28 and biodegradable materials (Liu et al. 2019). The interest towards utilization of environmentally degradable  
29 biopolymers such as starch, cellulosic materials, chitosan, poly vinyl alcohol for packaging applications have  
30 been increasing because of their complete and faster biodegradation compared to synthetic polymers (More et  
31 al. 2017; Garg et al. 2019; Priya et al. 2013, Popescu et al. 2010; Jain et al. 2018; Dolez et al. 2017). Poly vinyl  
32 alcohol (PVA) is one of the most widely used synthetic polymer in packaging industries as it is degradable  
33 under natural environmental conditions (Kaur et al. 2018). Incorporation of various cellulosic fillers with  
34 polymer matrix has been preferred to improve the biodegradability of the composite films (Elhussieny et al.  
35 2020; Priya et al. 2013).

36 The biodegradation of complex biomaterials results into small and environmentally acceptable products such as  
37 CO<sub>2</sub>, water and biomass by naturally available microorganisms (bacteria and fungi) and other biological activity  
38 under natural environmental conditions. However, now-a-days there have been an increased demand for  
39 biodegradability and more reliable biodegradation data of the packaging films due to raised concerns about the  
40 environment quality. Therefore, many researchers have made efforts towards establishment of different methods  
41 for biodegradation of packaging films by observing change in physical and chemical properties of films (Garg  
42 and Jana, 2011; Mittal et al. 2020b; Hoffman et al. 2003; Tripathy et al. 2018; Kaith et al. 2009; Negim et al.  
43 2014; Abdullah et al. 2017; Castro-Aguirre et al. 2018, Borowski et al. 2020). Soil burial degradation method is  
44 the most common method based on the direct measurement of weight loss of the film after biodegradation under  
45 natural environmental condition (Mittal et al. 2016, Garg and Jana, 2011). Another indirect method for  
46 evaluation of biodegradability is based on the measurement of evolved CO<sub>2</sub> during the biodegradation of film in  
47 aqueous aerobic medium (Strotmann et al. 2004; Hoffmann et al. 2003). The biodegradability of the PVA/corn  
48 starch based composite films reinforced with orange fiber was measured using soil burial degradation method  
49 and by measuring evolved CO<sub>2</sub> during degradation (Imam et al. 2005). The addition of orange fiber and starch  
50 in the blend also stimulated the degradation of PVA as starch and lignocellulosic fiber are easily degraded by  
51 microbes. In literature, neither PVA/starch based composite films reinforced with BH and grafted BH (prepared  
52 using lauric acid, palmitic acid and arachidic acid) were synthesized nor the effect of their reinforcement on the  
53 biodegradability of composite film by measuring evolved CO<sub>2</sub> during degradation of films was studied.

54 Therefore, present work deals with the biodegradation study of the PVA/starch based composite films  
55 containing BH and grafted BH (prepared using lauric acid, palmitic acid and arachidic acid) by soil burial  
56 degradation test in natural environmental conditions and by CO<sub>2</sub> evolution method in aqueous medium. The  
57 composite films were characterized by using scanning electron microscopy (SEM) and Fourier transform  
58 infrared spectroscopy (FT-IR) before and after biodegradation test.

## 59 **2. Materials and Methods**

### 60 **2.1 Materials**

61 Barley was obtained from the local market of Jalandhar, India. Lauric acid (purity, 99.0%) was procured from  
62 Himedia Laboratories Pvt. Ltd. (Mumbai, India). Palmitic acid (purity, 99.5%) was received from Sisco  
63 Research Laboratories Pvt. Ltd. (Bombay, India). Arachidic acid (purity, > 99%) was obtained from Sigma-  
64 Aldrich (Mumbai, India). Dimethyl sulphoxide (DMSO), potassium per sulphate (KPS) and ferrous ammonium  
65 sulphate (FAS) were provided by Loba Chemie Pvt. Ltd. (Mumbai, India). Polyvinyl alcohol with average  
66 molecular wt. 14,000, glycerol, formic acid, urea and formaldehyde (37-40% formalin solution) were purchased  
67 from s. d. fine Chemicals Ltd. (Mumbai, India). Corn starch was received by Sukhjit Starch and Chemicals Ltd.  
68 (Phagwara, India). All the chemicals were of analytical grade and used without any further purification.

### 69 **2.2 Methods**

#### 70 **2.2.1 Preparation of films**

71 PVA/St blend films were prepared by casting method as reported in our earlier studies (Mittal et al. 2016; Mittal  
72 et al. 2020a, b). Starch (5g) was gelatinized in hot water and mixed with PVA solution. The mixture of PVA and  
73 starch was continuously stirred for 45 min at 50°C using mechanical stirrer (400 rpm) to form a homogeneous  
74 gel solution. Plasticizing agent (glycerol) was added to the above mixture. The PVA/St suspension was poured  
75 onto the glass petri dish (dia. 14 cm), dried in hot air oven (24h at 45°C) and the dried film was peeled off from  
76 the dish. Cross linked films were prepared using urea formaldehyde as crosslinking agent in PVA/St matrix  
77 (Mittal et al. 2016). Urea formaldehyde prepolymer was prepared by refluxing of formalin solution with urea  
78 (molar ratio 1:1.5) for 15 min. The crosslinker was added slowly in PVA/St suspension in acidic condition (pH  
79 3.0) and the mixture was continuously stirred. The crosslinked films were prepared by solvent casting method  
80 with urea/starch ratio 0.5(w/w).

81 The composite films were prepared by reinforcing BH and fatty acid grafted BH within crosslinked PVA/St  
82 matrix. The preparation of grafted BH (LBH 45, PBH 41.5 and ABH 48.2) using lauric acid, palmitic acid and  
83 arachidic acid has been reported in our previous studies (Mittal et al. 2019a and Mittal et al. 2019b). BH and  
84 grafted BH (0.2- 2% (w/w)) were mixed with cross linked PVA/St suspension using a mechanical stirrer. The  
85 composite mixture was poured onto petri dishes and dried at 45°C. The dried composite films were peeled off  
86 after 24h. Composition of various films has been shown in Table 1.

## 87 2.2.2 Characterization

88 IR spectra of the films before and after degradation was recorded in order to study the chemical changes  
89 occurred in the films after degradation. The film samples were equilibrated at 50°C and analyzed by FT-IR  
90 instrument (Perkin Elmer, Model RX – 1) at a resolution of 4 cm<sup>-1</sup> within range 4000-400 cm<sup>-1</sup> using KBr pellets  
91 obtained from Sigma Aldrich. The surface morphology of the films before and after degradation was studied  
92 using a scanning electron microscope (JEOL JSM-6100, JEOL, Tokyo, Japan) at a magnification up to 2000X.  
93 To avoid the charging under electron beam, the film samples were coated with gold in argon.

## 94 2.2.3 Biodegradation study

### 95 2.2.3.1 Soil burial degradation test

96 The soil burial degradation test of the films (3cm×10 cm) was performed by burying all the samples in soil at  
97 10cm depth under natural environmental conditions. The moisture and microbial concentration was maintained  
98 by sprinkling sewage water over the soil. The samples were taken out after every 15 days and washed with  
99 distilled water. The samples were dried in hot air oven and the weight loss (%) was calculated as (Mittal et al.  
100 2016).

$$\text{Weight loss (\%)} = \frac{W_d - W_i}{W_i} \times 100$$

101 Where  $W_i$  is initial weight of the sample and  $W_d$  is final weight of the sample after degradation.

### 102 2.2.3.2 Evaluation of biodegradability of films using CO<sub>2</sub> evolution test

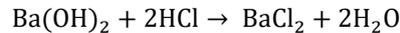
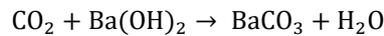
103 The test was done by determining the evolved carbon dioxide during degradation of films by ISO 9439:2000  
 104 procedure. The produced CO<sub>2</sub> during the degradation of sample was dissolved in the solution of hydroxide and  
 105 the subsequent amount of produced CO<sub>2</sub> was determined by titration. The percentage of degradation of the  
 106 sample was further calculated by knowing the amount of produced CO<sub>2</sub> during the degradation test.

107 The experimental setup used is shown in Fig 1. The set up consists of three parts: common cleaning part, two  
 108 reactors and absorbers. The cleaning part consists of two gas washing vessels containing 500 mL of NaOH  
 109 solution (10 mol/L) and 100 mL of Ba(OH)<sub>2</sub> solution (0.0125 mol/L), respectively. CO<sub>2</sub> free air from cleaning  
 110 part was then supplied to two reactors (Erlenmeyer flask) which were continuously stirred. First reactor contains  
 111 inorganic medium, inoculum and test sample while second reactor contained inorganic medium and inoculum.  
 112 The sample was the nominal sole source of organic carbon and energy in the cultivating aqueous medium. CO<sub>2</sub>  
 113 evolved during degradation of sample was passed through third part (absorbers). Third part consists of three  
 114 absorbers: one safety absorber and two absorbers containing 30 mL of Ba(OH)<sub>2</sub> solution (0.0125 mol/L). The  
 115 flow rate of air was maintained to 50-100 mL/min in the whole apparatus. The degradation test was performed  
 116 in dark and the total volume of test mixture in individual reactor was maintained to 2500 mL. Inorganic test  
 117 medium was prepared in accordance to ISO 9439:2000 procedure. Inoculation was done using activated adapted  
 118 sludge in a dose of approx. 0.5 g/L. The concentration of test sample in the medium was maintained to 40 mg/L.  
 119 The abiotic test was also performed with mercuric chloride (10 g/L) by similar method. Aniline was used a  
 120 reference compound for the degradation test with same concentration as test sample.

### 121 Investigating CO<sub>2</sub> production

122 Absorbers containing Ba(OH)<sub>2</sub> were exchanged daily with freshly prepared Ba(OH)<sub>2</sub> solution. Amount of  
 123 produced CO<sub>2</sub> was determined by titrating the replaced Ba(OH)<sub>2</sub> solution with HCl solution (0.05 mol/L) using  
 124 phenolphthalein as an indicator to determine the end point.

125 Produced CO<sub>2</sub> reacted with Ba(OH)<sub>2</sub> to form precipitation of BaCO<sub>3</sub> as shown in the following reactions.



126 The mass of CO<sub>2</sub> dissolved in the absorber vessel was calculated using Eq. 1.

$$m_T = \left\{ \frac{2c_{\text{Ba}} \cdot V_{\text{B0}}}{c_{\text{HCl}}} - V_A \frac{V_{\text{BT}}}{V_{\text{BZ}}} \right\} \cdot c_{\text{HCl}} \times 22 \quad (1)$$

127 Where  $m_T$  is the mass of CO<sub>2</sub> trapped in the absorber of vessel (mg),  $c_{\text{HCl}}$  is the concentration of the HCl  
 128 solution (mol/L),  $c_{\text{Ba}}$  is the concentration of the Ba(OH)<sub>2</sub> solution (mol/L),  $V_{\text{B0}}$  is the volume of the Ba(OH)<sub>2</sub>  
 129 solution (mL) at the beginning of the test,  $V_{\text{BT}}$  is the volume of the Ba(OH)<sub>2</sub> solution (mL) at time t;  $V_{\text{BZ}}$  is the  
 130 volume of the aliquots of the Ba(OH)<sub>2</sub> solution (mL) used for titration;  $V_A$  is the volume of the HCl solution  
 131 (mL) used for titration of the Ba(OH)<sub>2</sub> solution.

132 When volume of the Ba(OH)<sub>2</sub> solution before and after absorption is exactly 100 ml and the complete solution is  
 133 used

$$134 (V_{\text{BT}} = V_{\text{B0}} = V_{\text{BZ}})$$

135 The theoretical amount of CO<sub>2</sub> produced in the test vessel is given by

$$\text{ThCO}_2 = \rho_c \times V_L \times 44/12 \quad (2)$$

136 Where  $\rho_c$  is the concentration of organic carbon of the test compound in the test vessel (mg/L),  $V_L$  is the volume  
137 of test solution in the reactor (L)

138 The percentage of biodegradation D (%) can be calculated as

$$D = \frac{\sum m_{Tt} - \sum m_{Bt}}{\text{ThCO}_2} \times 100 \quad (3)$$

139 Where  $\sum m_{Tt}$  is the mass of CO<sub>2</sub> released (mg) between the start of the test and time t and  $\sum m_{Bt}$  is the amount  
140 of CO<sub>2</sub> released (mg) in blank control between the start of the test and time t.

### 141 3. Results and discussion

#### 142 3.1 Soil burial degradation

143 Biodegradability of the films is one of the major properties which potentially control their applications. The  
144 degradation test of the blend films (PVA, PVA/St and PVA-0.5C St) and composite films containing BH, LBH  
145 45, PBH 41.5 and ABH 48.2 was performed after burying the films for 180 days in soil under natural  
146 environmental conditions. Weight loss (%) of films was measured with time and results are shown in Fig. 2. It  
147 was observed that after burying the films in the soil, the size of the films reduced and the surface of films  
148 became hard and fragile. Results indicated that the weight loss (%) of the films was rapid upto 120 days of  
149 burial in soil and thereafter it was constant. PVA film showed 1.86% weight loss after 45 days and it increased  
150 to 16.4% after 180 days. The degradation rate of film (PVA/St) increased after blending 50% starch in PVA  
151 matrix and showed 59% weight loss after 180 days. However, weight loss of the film (PVA-0.5C St) decreased  
152 to 44.6% after 180 days of incubation in soil.

153 It was observed that biodegradability of composite films improved after incorporation of BH (0.2-2%) in  
154 crosslinked PVA/St matrix (Fig. 2a). After reinforcement of 0.2% BH in the matrix, weight loss of the film  
155 (PVA-0.5C St-0.2BH) was 26.6% after 45 days of soil burial and increased to 54.3% after 180 days. Composite  
156 film (PVA-0.5CSt-1BH) containing 1% BH showed approximately 42.2% weight loss after 45 days of  
157 degradation test which increased to 70% after 180 days. % Weight loss of the film (PVA-0.5C St-2BH)  
158 increased to 73.4% after 180 days with increase in BH content to 2% in the matrix. The degradation rate of BH  
159 composite film was higher due to their ability to absorb higher amount of moisture (Imam et al. 2005). The  
160 water absorbed by the films caused the swelling of the films and allowed the growth of microbes on their  
161 surface by utilizing the nutrients present in the films leading to their disruption and weight loss (Ooi et al. 2012).  
162 Ibrahim et al. (2020) also observed increase in biodegradability of starch based films after reinforcement of corn  
163 husk fiber. The starch based film showed 47.13% weight loss after 18 days whereas, the starch based composite  
164 film containing 8% corn husk fiber resulted in 73.22% weight loss after 18 days due to increase in number of  
165 hydroxyl groups with incorporation of fiber in starch matrix.

166 The results of soil burial degradation test of grafted BH composite films are shown in Fig. 2. It was observed  
167 that incorporation of grafted BH (LBH 45, PBH 41.5 and ABH 48.2) into crosslinked PVA/St matrix resulted in  
168 increase in % weight loss of the films. Composite films (PVA-0.5C St -1LBH 45, PVA-0.5C St-1PBH 41.5 and  
169 PVA-0.5C St-1ABH 48.2) showed 68.1%, 65.1% and 64.2% weight losses, respectively after 180 days of soil  
170 burial degradation test. Results indicated that reinforcement of grafted BH into cross-linked PVA/St matrix  
171 resulted in lower degradation of the films as compared to BH composite films due to improved water resistant  
172 properties of composite films containing grafted BH and lower affinity towards microbial attack.

### 173 3.2 CO<sub>2</sub> evolution test

174 Biodegradation test of the films (PVA, PVA-0.5C St-1BH, PVA-0.5C St-1LBH 45, PVA-0.5C St-1PBH 41.5,  
175 PVA-0.5C St-1ABH 48.2) was also performed in an aqueous medium containing activated sludge from the  
176 waste water treatment plant and biodegradability was measured by measuring the evolved CO<sub>2</sub> during the  
177 degradation process. Biodegradability of the samples was evaluated on the basis of evolved CO<sub>2</sub> using ISO  
178 9439:2000 procedure. The results of CO<sub>2</sub> production during biodegradation of the films and reference compound  
179 (aniline) as a function of time (days) are shown in Fig. 3. The abiotic test was performed under the same  
180 conditions to check the abiotic degradation of the test sample (film). The results showed that abiotic test resulted  
181 in very low CO<sub>2</sub> production (approx. 5% of total production). The blank tests containing inoculum and inorganic  
182 medium were run in parallel with all the test samples. The CO<sub>2</sub> production in all the blank tests was low and  
183 contributed to approximately 33% of total CO<sub>2</sub> produced in the degradation test. Aniline was taken as reference  
184 compound and showed highest CO<sub>2</sub> production (331.7 mg) as it is highly degradable in the given test conditions.  
185 The CO<sub>2</sub> production during degradation of PVA film was 161.37 mg after 30 days of test. However, composite  
186 film (PVA-0.5C St-1BH) containing 1% BH showed 315 mg of CO<sub>2</sub> production after 30 days and was much  
187 higher than blank test.

188 There was not much significant variation in the amount of CO<sub>2</sub> produced during degradation of composite films  
189 containing BH and grafted BH. Composite film (PVA-0.5C St-1LBH 45, PVA-0.5C St-1PBH 41.5 and PVA-  
190 0.5C St-1ABH 48.2) showed 300.85 mg, 293.48 mg and 290.73 mg of CO<sub>2</sub> production after 30 days,  
191 respectively. The incorporation of starch and BH into the PVA matrix stimulated the degradation of PVA. Imam  
192 et al. (2005) also reported that in the PVA-starch matrix first starch degraded quickly. When the starch  
193 concentration is below than percolation threshold, the microbes switched to another easily available, accessible  
194 and abundant carbon source such as PVA.

195 The degradation rate of various films and reference compound (aniline) was calculated (Eq. 3) based on the CO<sub>2</sub>  
196 production and the results are shown in Fig. 4. The biodegradation curves of all the films showed four phases:  
197 lag phase of 3 days; a short exponential phase of 3-4 days, linear phase and plateau phase (reached  
198 approximately after 20 days of biodegradation of the films) (Lefaux et al. 2004). Results emphasized that  
199 degradation of aniline (reference compound) was 65.2% after 30 days. PVA film showed degradation of 9.36%  
200 after 20 days of the degradation test and increased to 12.7% after 30 days.

201 The degradation of BH composite film (PVA-0.5C St-1BH) was 58.83% after 30 days and was higher than PVA  
202 film due to addition of biodegradable starch and BH within PVA matrix. Composite films (PVA-0.5C St-1LBH  
203 45, PVA-0.5C St-1PBH 41.5 and PVA-0.5C St-1ABH 48.2) containing LBH 45, PBH 41.5 and ABH 48.2

204 showed degradation of 54.66%, 52.33% and 51.43%, respectively after 30 days of the degradation test.  
205 Composite films containing grafted BH showed higher degradation rate as compared to PVA film.

206

207

### 208 **3.3 Scanning electron microscopy**

209 The change in the surface morphology of PVA, PVA/St and crosslinked film (PVA-0.5C St) was studied after  
210 180 days of soil burial degradation test and the results are shown in Fig. 5. It was observed that the surface of  
211 the films was deteriorated and showed surface irregularities after degradation. The large longitudinal cracks, holes  
212 and cavities were formed on the surface of the films indicated that microorganisms have attacked the surface of  
213 the films when buried in soil under natural environmental conditions. The surface micrograph of PVA/St film  
214 was rough and eroded compared to PVA film due to degradation of starch within PVA/St matrix Jayasekara et  
215 al. (2003) also studied the biodegradation behavior of PVA/starch films by composting method and reported the  
216 increased roughness on the surface of PVA/starch blend film after 45 days of degradation test due to rapid  
217 degradation of starch.

218 Results showed that incorporation of BH and grafted BH into the crosslinked PVA/St matrix increased the  
219 degradation of the films. The surface morphology of composite films containing BH and grafted BH (LBH 45,  
220 PBH 41.5 and ABH 48.2) before and after degradation test is shown in Fig. 6. SEM images of BH composite  
221 film (PVA-0.5C St-1BH) showed the formation of big holes and pits on the surface of the films after 180 days  
222 of degradation. After burying of BH composite film into the soil, the microorganisms evidently attacked the  
223 starch and cellulosic material (BH) present in the film leading to degradation of other components also (Stelescu  
224 et al. 2017; Jayasekara et al. 2003). Before degradation, the surface of the composite films containing grafted  
225 BH was homogenous and smooth as compared to BH composite film due to improved adhesion between grafted  
226 BH and PVA/starch matrix leading to improved mechanical properties and barrier properties of the films (Mittal  
227 et al. 2016). After degradation, the surface of the composite films (PVA-0.5C St-1LBH 45, PVA-0.5C St-1PBH  
228 41.5 and PVA-0.5C St-1ABH 48.2) became heterogeneous and rough, while holes and cavities also appeared on  
229 the surface of the films (Kaith et al. 2009).

### 230 **3.4 FT-IR analysis**

231 After 180 days of degradation of the films in soil, fragments of the degraded samples were analyzed by FT-IR  
232 spectroscopy. Fig 7 showed the IR spectra of PVA film, PVA/St film, crosslinked film (PVA-0.5C St) and  
233 composite films (PVA-0.5C St-1BH, PVA-0.5C St-1LBH 45, PVA-0.5C St-1PBH 41.5 and PVA-0.5C St-  
234 1ABH 48.2) before and after 180 days of degradation.

235 IR spectra of all degraded film samples showed the decrease in peak intensity corresponding to hydroxyl (3100-  
236 3500  $\text{cm}^{-1}$ ) and methylene (2700-2900  $\text{cm}^{-1}$ ) groups due to breakage of bonds during degradation. In addition,  
237 the reduction in peak intensity in the range 1100-1400  $\text{cm}^{-1}$  (C-O stretching), 910-920  $\text{cm}^{-1}$  ( $-\text{CH}_2$  rocking) and  
238 820-830  $\text{cm}^{-1}$  (C-C stretching) was observed in the spectra of degraded film samples (Kibédi-Szabó et al. 2012).  
239 However, the sharp peaks were observed in the range 1600-1670  $\text{cm}^{-1}$  and 1500-1580  $\text{cm}^{-1}$  in the spectra of all

240 the degraded film samples corresponding to amides I and amides II groups due to the presence of protein  
241 produced during microbial growth on the film surface (Klemenčič et al. 2010).

## 242 **Conclusions**

243 Various composite films using PVA/starch as polymer matrix and barley husk or grafted barley husk as  
244 reinforcing agent were synthesized. Biodegradability studies were performed using soil burial degradation  
245 method and carbon dioxide evolution method. The biodegradation rate of the films was measured by measuring  
246 weight loss after soil burial of the films and by evaluating evolved CO<sub>2</sub> during degradation in aqueous aerobic  
247 medium. PVA film showed 16.4% degradation after 180 days under soil however, it increased to 54% after  
248 addition of 50% starch into the PVA matrix. Further, crosslinking of PVA/starch matrix with urea formaldehyde  
249 resulted in decrease in degradation of the films by 5.6%. After incorporation of BH (1%) in crosslinked  
250 PVA/starch matrix, 70% degradation of the composite films was achieved after 180 days of soil burial. Under  
251 aqueous aerobic environment, BH composite film (PVA-0.5C St-1BH) showed 314.93 mg of CO<sub>2</sub> production  
252 and 58.83% degradation after 30 days of test. However, composite films containing grafted BH showed slight  
253 decrease in the evolved CO<sub>2</sub> and % degradation than of BH composite film. The addition of starch and BH  
254 improved the degradation rate as they are completely biodegradable materials. The results of scanning electron  
255 microscopy showed the formation of cracks, holes and cavities over the surface of the composite films  
256 incorporated with BH after degradation. In conclusion, the addition of biomaterials such as starch and barley  
257 husk enhanced the degradation rate of the films. PVA/starch based composite film reinforced with barley husk  
258 and grafted barley husk may provide a potential and ecofriendly alternative to the conventional packaging films.

## 259 **Declarations**

260 **Ethics approval and consent to participate:** Not applicable

261 **Consent for publication:** Not applicable

262 **Availability of data and material:** All data generated or analyzed during this study are included in this  
263 published article.

264 **Competing interests:** The authors declare that they have no competing interests.

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266 **Author Contributions:** Aanchal Mittal has conducted all the research work, data organization, writing of  
267 original draft and editing. Dr. Sangeeta Garg is responsible for supervision, reviewing and editing. Dr.  
268 Shailendra Bajpai is responsible for supervision and editing. All authors read and approved the final manuscript.

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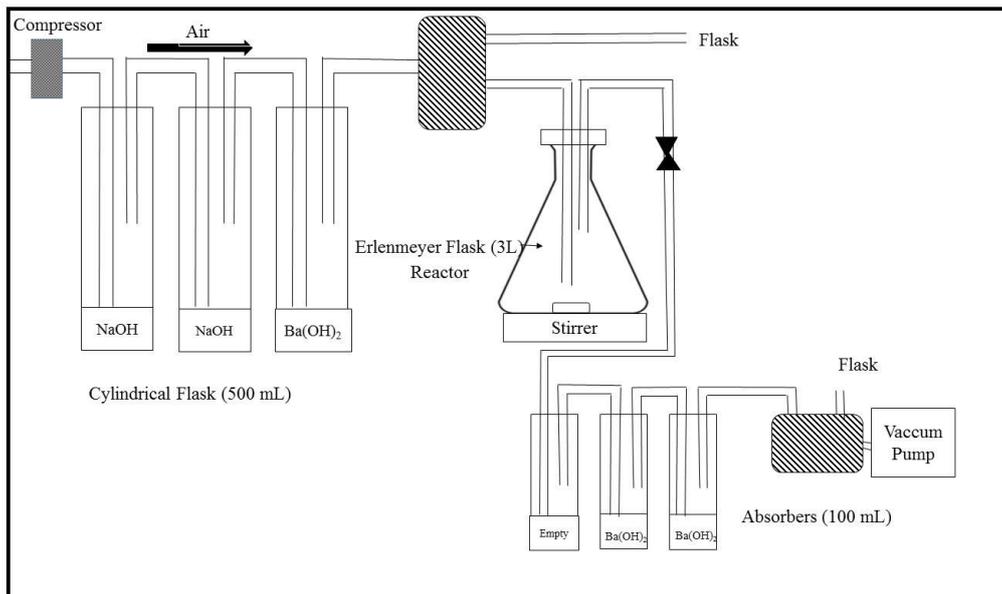
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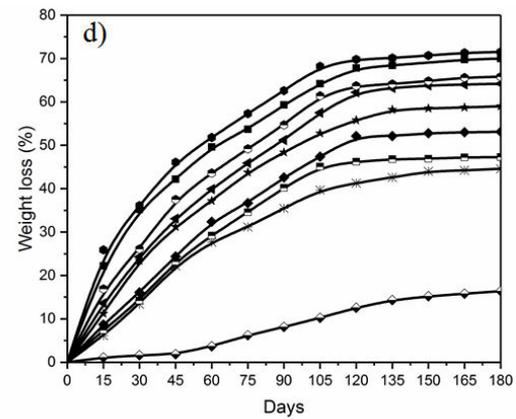
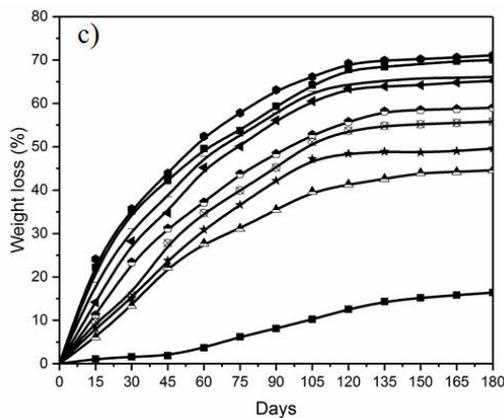
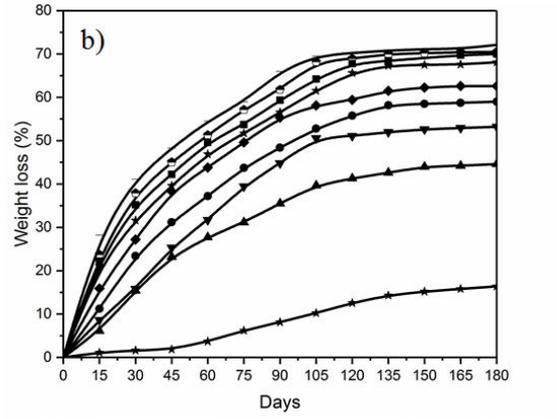
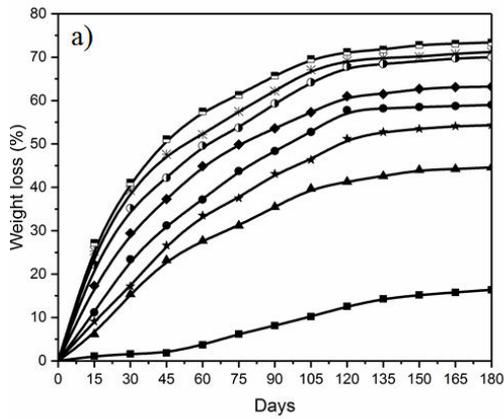
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375 **Fig. 1** Experimental setup for measuring evolved CO<sub>2</sub> during degradation of composite films in aqueous aerobic  
 376 medium (1 of 2 reactors is shown).

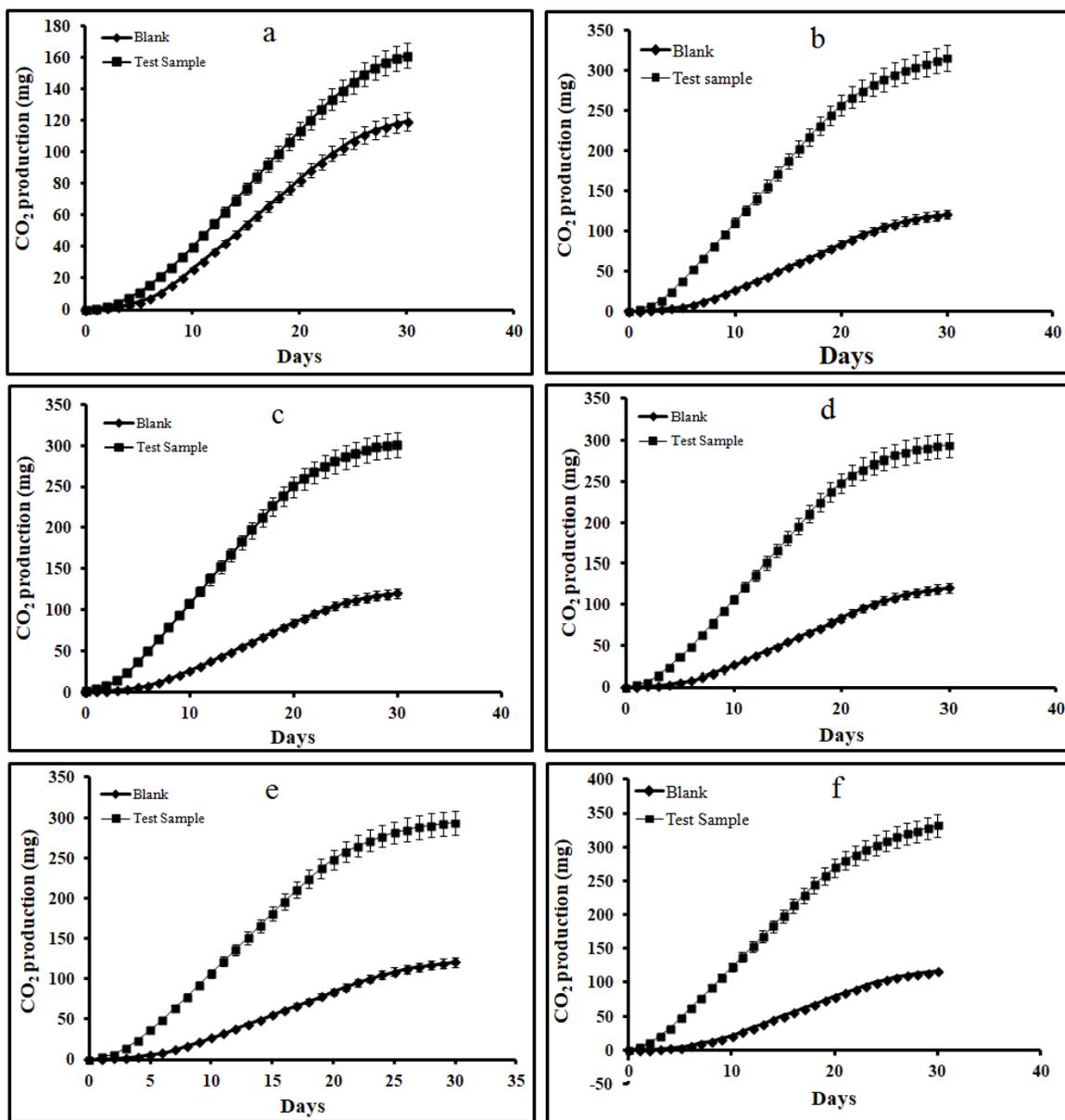


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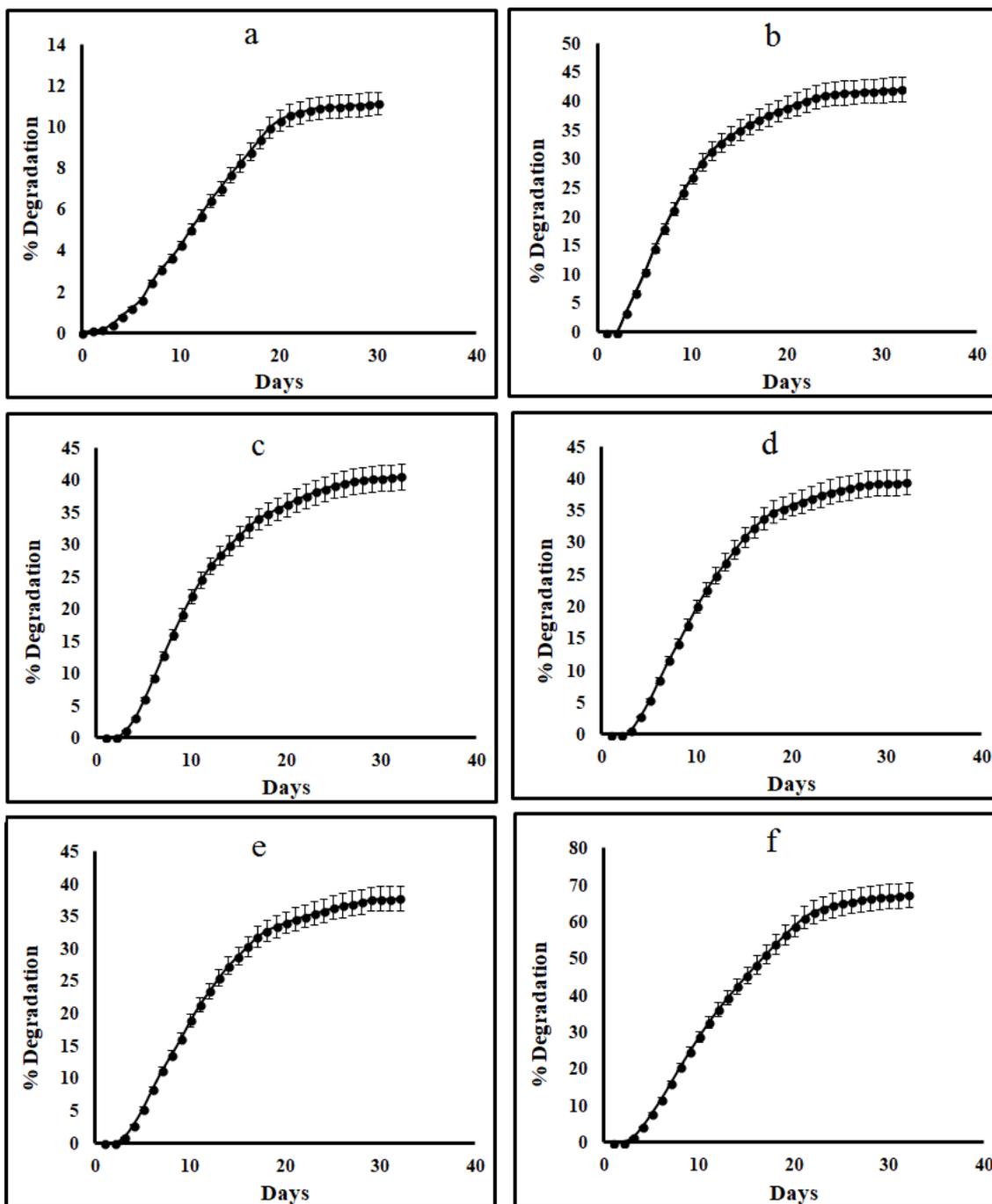
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**Fig. 2** Biodegradability of PVA/St based composite films reinforced with a) BH b) LBH 45, c) PBH 41.5, and d) ABH 48.2 in soil.



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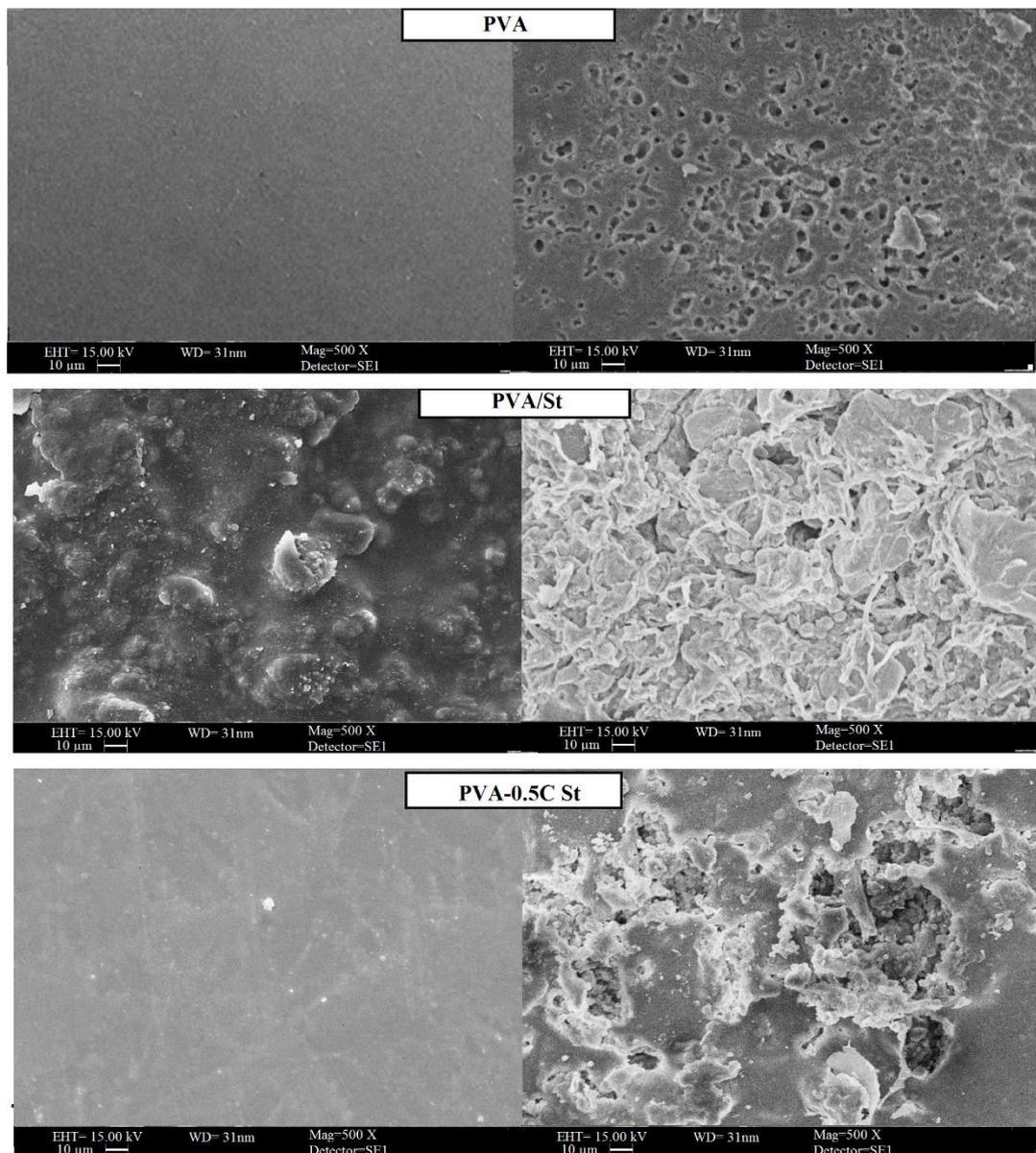
381 **Fig. 3** CO<sub>2</sub> production during degradation of a) PVA b) PVA-0.5CSt-1BH c) PVA-0.5CSt-1LBH 45 d) PVA-  
 382 0.5CSt-1PBH 41.5 e) PVA-0.5CSt-1ABH 48.2 and f) aniline in aqueous aerobic medium.



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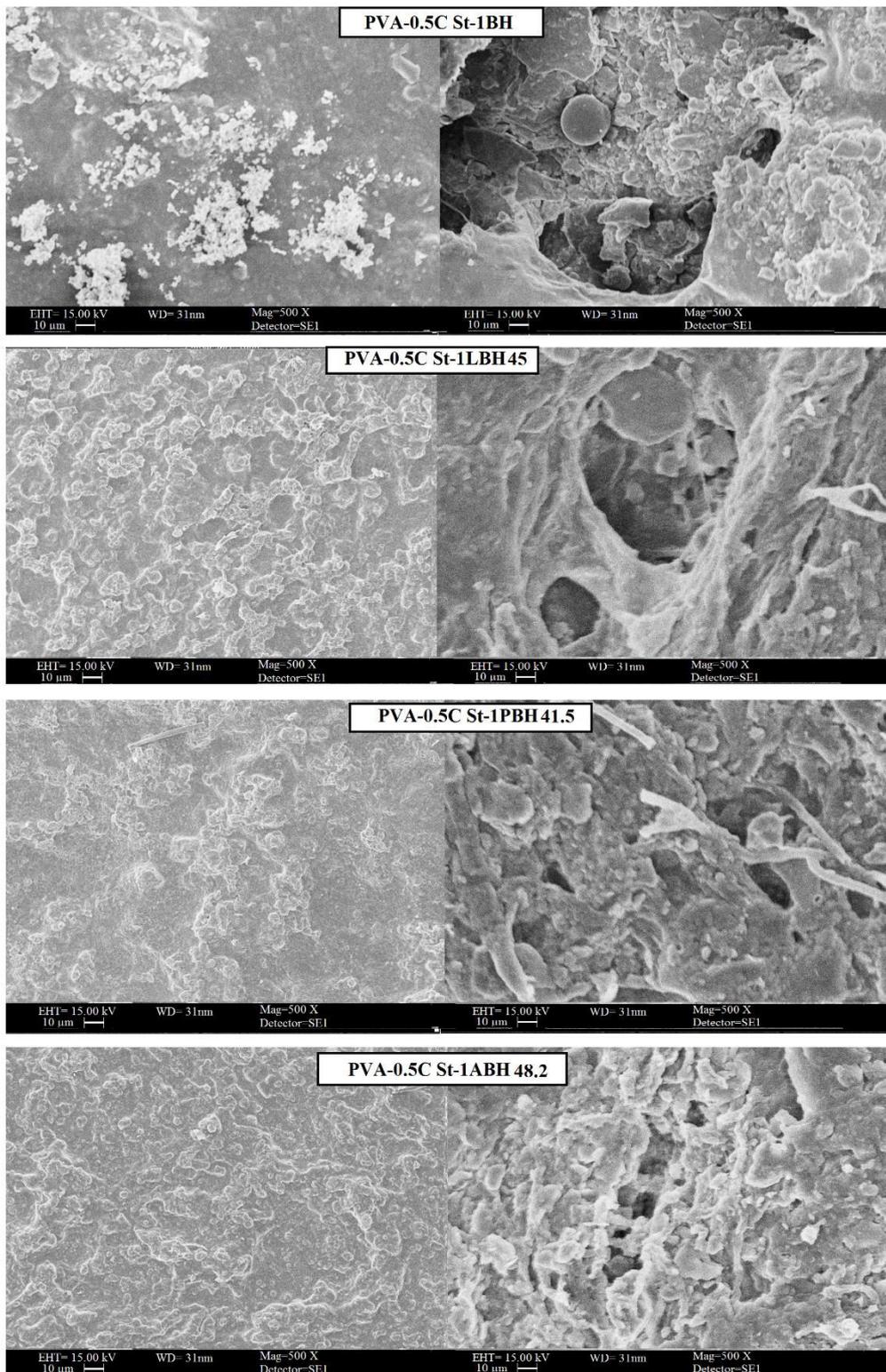
384 **Fig. 4** % Degradation of a) PVA b) PVA-0.5CSt-1BH c) PVA-0.5CSt-1LBH 45 d) PVA-0.5CSt-1PBH 41.5 e)

385 PVA-0.5CSt-1ABH 48.2 and f) aniline in aqueous aerobic medium.



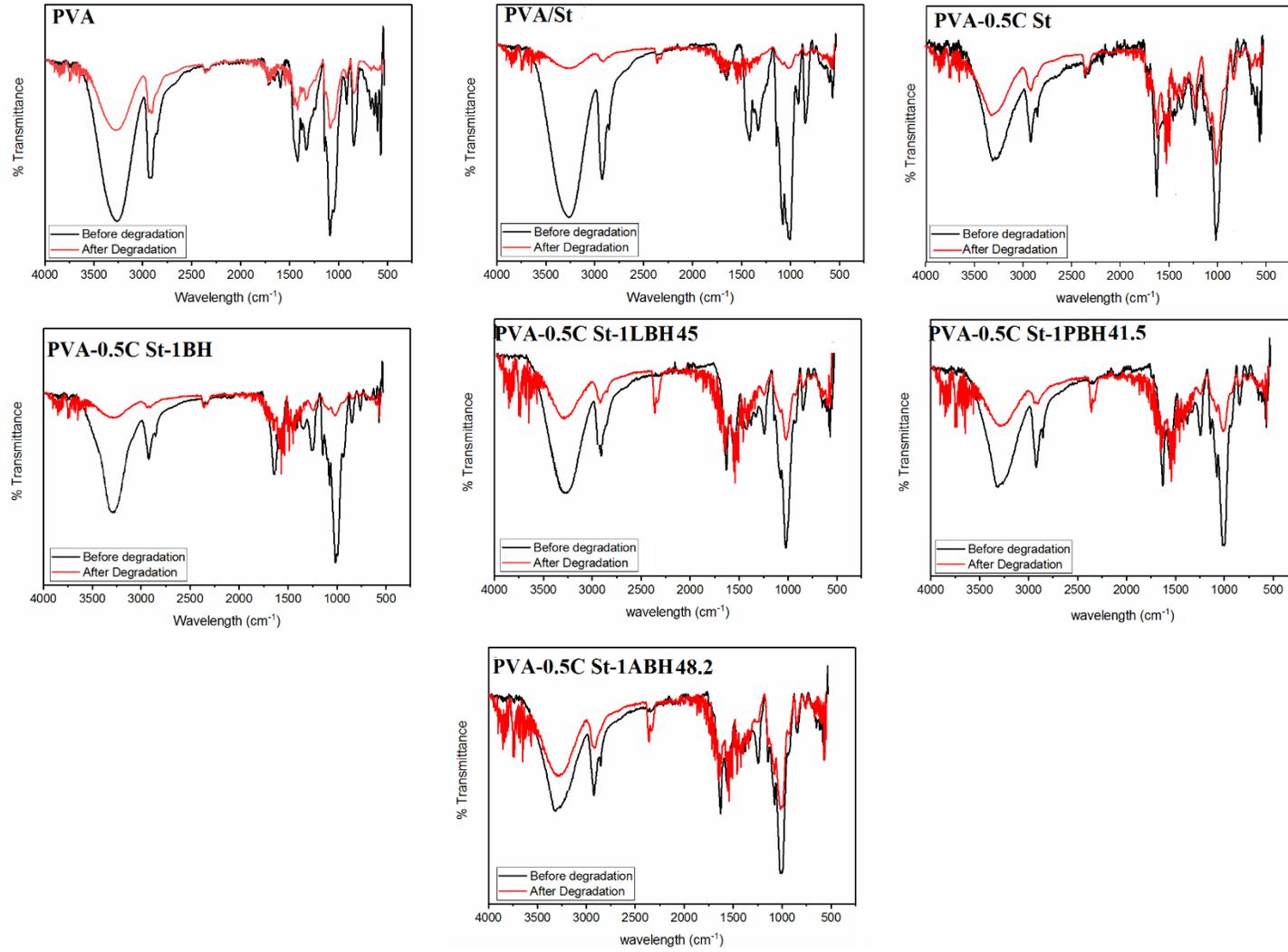
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387 **Fig. 5** SEM images of the PVA, PVA/St and crosslinked film (PVA-0.5C St) before and after 180 days of soil  
388 burial degradation test.



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**Fig. 6** SEM images of the composite films before and after 180 days of soil burial degradation test.



**Fig. 7** FT-IR spectra of the films before and after 180 days of biodegradation



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**Table 1** Composition of various blend and composite films.

Films	PVA/starch (w/w)	Urea/ starch (w/w)	BH (% wt)	Grafted BH (% wt)
PVA	1/0	-	-	-
PVA/St	1/1	-	-	-
PVA/St-0.5C St	1/1	0.5	-	-
PVA/St-0.5C St-0.2BH	1/1	0.5	0.2	-
PVA/St-0.5C St-0.5BH	1/1	0.5	0.5	-
PVA/St-0.5C St-1BH	1/1	0.5	1	-
PVA/St-0.5C St-1.5BH	1/1	0.5	1.5	-
PVA/St-0.5C St-2BH	1/1	0.5	2	-
PVA/St-0.5C St-0.2LBH 45	1/1	0.5	-	0.2
PVA/St-0.5C St-0.5LBH 45	1/1	0.5	-	0.5
PVA/St-0.5C St-1LBH 45	1/1	0.5	-	1
PVA/St-0.5C St-1.5LBH 45	1/1	0.5	-	1.5
PVA/St-0.5C St-2LBH 45	1/1	0.5	-	2
PVA/St-0.5C St-0.2PBH 41.5	1/1	0.5	-	0.2
PVA/St-0.5C St-0.5PBH 41.5	1/1	0.5	-	0.5
PVA/St-0.5C St-1PBH 41.5	1/1	0.5	-	1
PVA/St-0.5C St-1.5PBH 41.5	1/1	0.5	-	1.5
PVA/St-0.5C St-2PBH 41.5	1/1	0.5	-	2
PVA/St-0.5C St-0.2ABH 48.2	1/1	0.5	-	0.2
PVA/St-0.5C St-0.5ABH 48.2	1/1	0.5	-	0.5
PVA/St-0.5C St-1ABH 48.2	1/1	0.5	-	1
PVA/St-0.5C St-1.5ABH 48.2	1/1	0.5	-	1.5
PVA/St-0.5C St-2ABH 48.2	1/1	0.5	-	2

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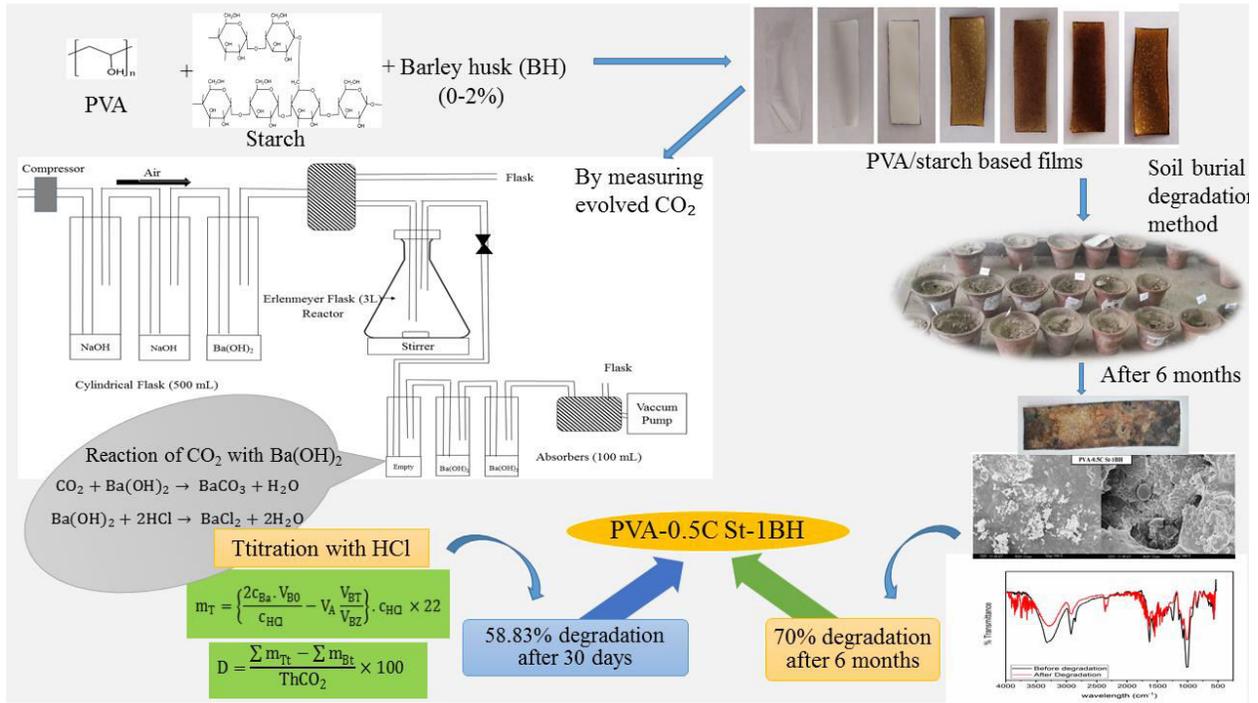
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### Graphical Abstract



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