4.4 Biodegradability studies

4.4.1 Soil Burial Test Method

Biodegradability of polymer blends is a critical functionality for their application in the commercial market. The biodegradability of organic substances such as starch and cellulose that were incorporated in the polymer blends is the assessment of the degree of changes in physical and chemical characteristics and molecular structure of the substances under degradation by microorganisms (Mohee & Unmar, 2007). The assessment is very important if these composites are going to be biologically treated in the future. Several different methods can be used to determine the biodegradability of a polymer blend. The enzyme method (Tomasi, Scandola, Briese, & Jendrossek, 1996), the microbiological method (Benedict, Cook, Jarrett, Cameron, Huang, & Bell, 1983) and the soil burial method (Mergaert, Webb, Anderson, Wouters, & Swings, 1993) (Xu & Hanna, 2005) have been used extensively by other researchers. In this study, the degradation of PVA/starch and PVA/starch/fibers composites were evaluated by an outdoor and indoor soil burial experiment for 70 days. Soil burial is probably the most appropriate test method to determine the biodegradability of the blended composites because under suitable conditions, microorganisms in the soil can remove starch and cellulose particles by enzymatic action. For the outdoor soil burial experiment, the specimens were buried in compost soil in an uncovered area outside the laboratory whilst the indoor experiment was carried out in a series of plastic boxes (60 cm × 30 cm × 30 cm) containing compost soil in the laboratory. The evaluations of biodegradability of both experiments are based on the weight loss of the blended composite films and on

the SEM micrographs of the composite film's surface. The weight loss of the samples buried refers to the erosion of different molecules from the solid phase of the composites into the aqueous phase. This value does not always indicate complete degradation of the molecules. However, the molecules released from the blended composite films might be starch, cellulose or PVA metabolites such as low molecular organic acids and ketonic compounds. The molecules released are not recalcitrant and would be easily degraded by microorganisms in the compost soil. Therefore, the evaluation of the composites degradation based on weight loss seems practical. It is also important to note that weight loss measurement is not the best alternative for evaluating degradation in the compost soil, mainly because many potential errors can exists in measuring degradation rate by weight loss. Soil occluded on the surface and inside the samples is difficult to extract without damaging the specimens and also bacteria and dirt not removed during washing may account in errors in determining the residual mass (Goheen & Wool, 1991) (di Franco, Cyras, Busalmen, Ruseckaite, & Vazquez, 2004). However, in spite of the drawbacks mentioned, the analysis of the weight loss data allowed us to evaluate quantitatively the influence of the presence of starch and fibers during degradation in the compost soil.

PVA/different starches composites

Figure 4.190 and 4.191 show the weight loss of the PVA/starch blended samples buried for 70 days for the indoor and outdoor soil burial experiment.

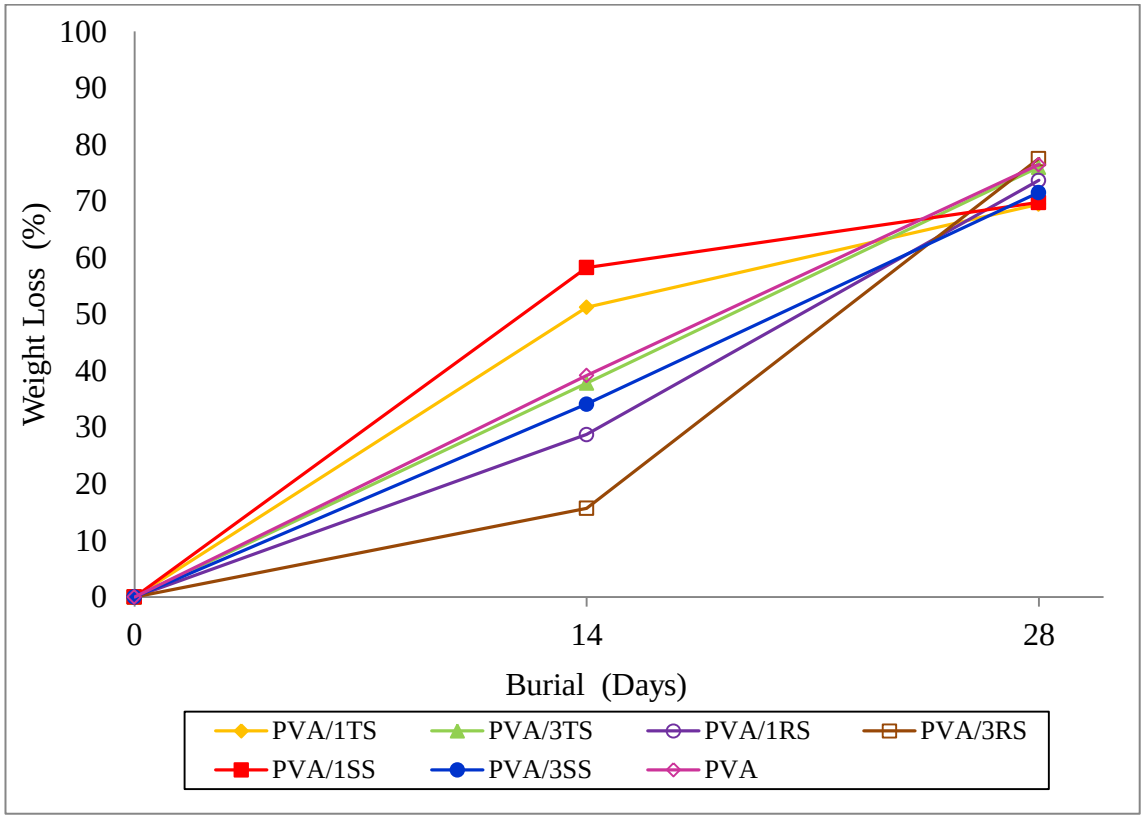

Fig. 4.190 Weight loss of PVA /starch blends for the outdoor soil burial experiment

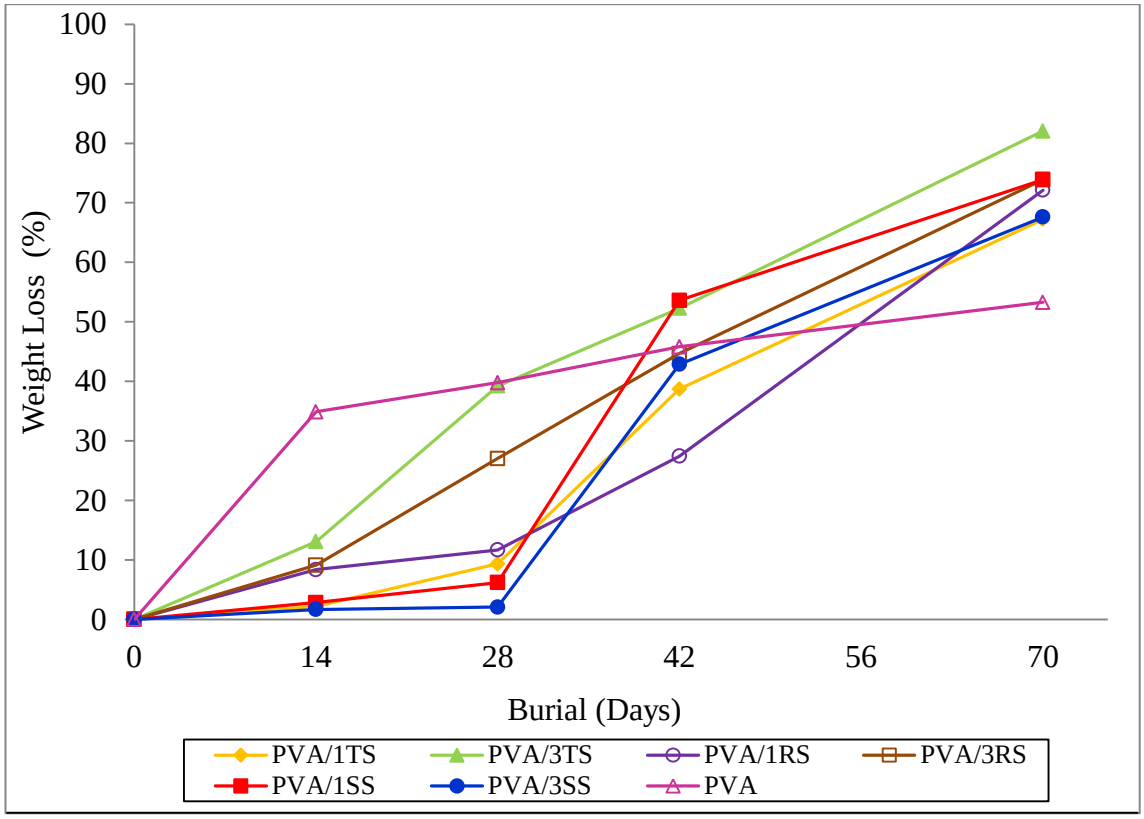

Fig. 4.191 Weight loss of PVA/starch blends for the indoor soil burial experiment

From the weight loss data shown in the graphs, it can be observed that for the outdoor soil burial experiment, the data for weight loss can be taken only up to 28 days because the samples could not be tested any more due to their advanced macroscopic deterioration. It can also be observed for both the experiments, the weight loss of all the samples increased almost literally with elapsing burial time with the outdoor experiment showing a higher rate of degradation. The extent and rate of weight loss for both simulations were not the same. For the outdoor soil burial experiment, the degradation of pure PVA film is as advanced as the PVA/starch composite films but for the indoor experiment, pure PVA film degraded rather slowly with 60% of its total weight remaining after 28 days. According to literature, pure PVA films exhibits a higher resistance against soil burial biodegradation (Guohua, Ya, Cuilan, Min, Caiqiong, & Zongdao, 2006) (Yang & Huang, 2008). The rapid weight loss of pure PVA in the outdoor experiment may be contributed by the presence of excess water. Even though the compost soil was kept moist by sprinkling water at a regular time interval, under rainy conditions, excess water permeated through the soil and into the specimens causing the films to swell and becomes soft. As for PVA, the excess water will increase the rate of its deterioration to at par with the PVA/starch composites. From the outdoor soil burial experiment results, as a whole, the buried biocomposites degraded rapidly leaving only about 20% of its total weight remaining after only 3 weeks of burial and this show that the outdoor or nature provides a much more realistic environment where soil humidity temperature and amount of microorganisms are in less control and change with different weather. To gain more information regarding the biodegradation of the PVA/starch blended composites, the change of morphology of the film surface during biodegradation was carried out by SEM microscopy and visual observation.

Figure 4.192 to 4.205 show the SEM micrographs of PVA/starch composite film's surface after being buried for 2 weeks in the indoor and outdoor soil burial experiment

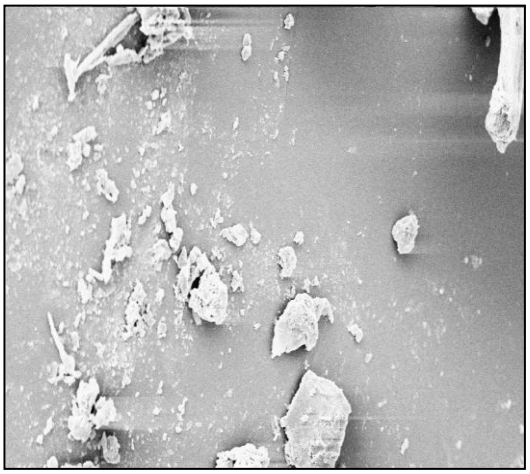

Fig. 4.192 SEM micrograph of pure PVA film surface after 2 weeks of indoor burial

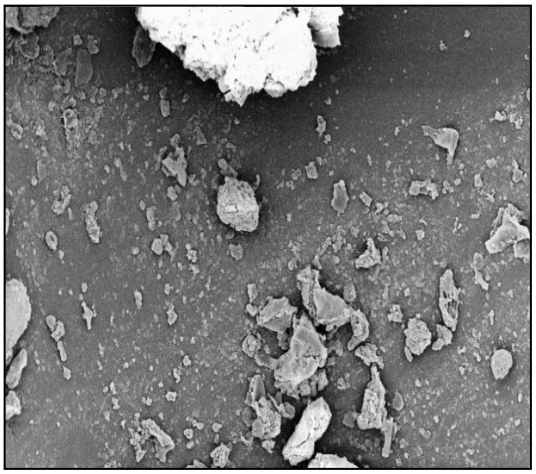

Fig. 4.193 SEM micrograph of pure PVA film surface after 2 weeks of outdoor burial

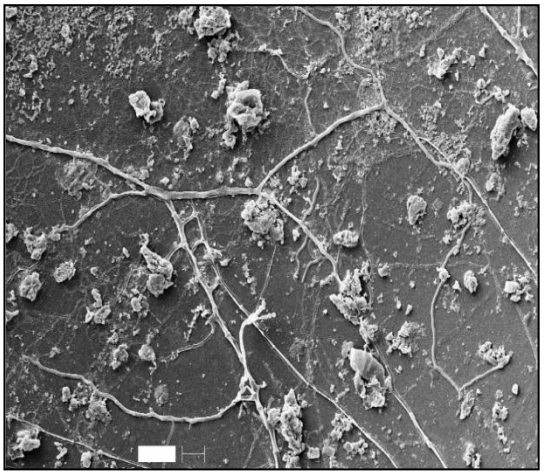

Fig. 4.194 SEM micrograph of PVA/1TS film surface after 2 weeks of indoor burial

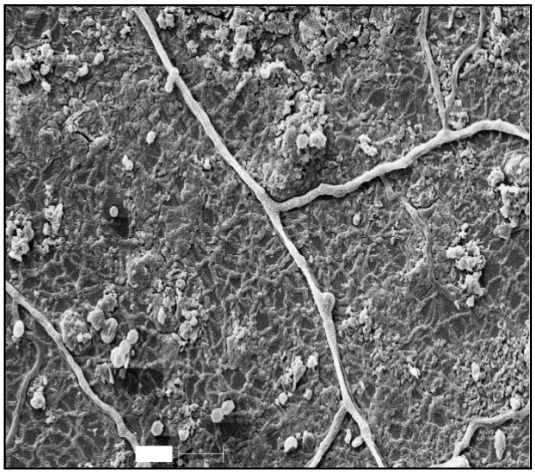

Fig. 4.195 SEM micrograph of PVA/1TS film surface after 2 weeks of outdoor burial

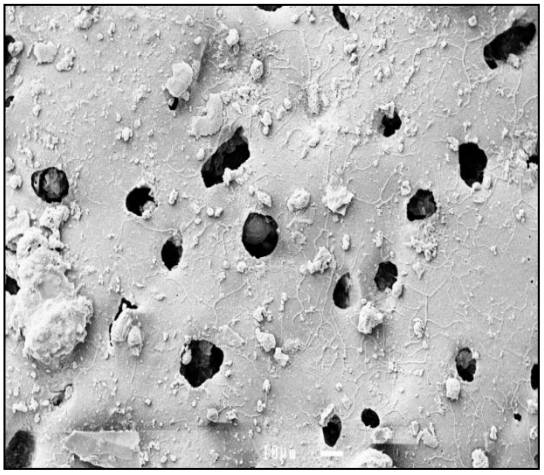

Fig. 4.196 SEM micrograph of PVA/3TS film surface after 2 weeks of indoor burial

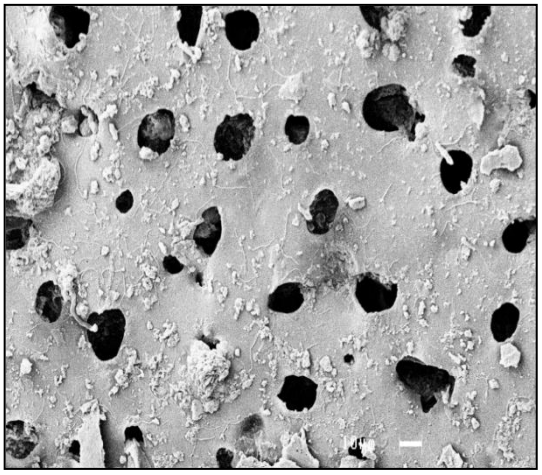

Fig. 4.197 SEM micrograph of PVA/3TS film surface after 2 weeks of outdoor burial

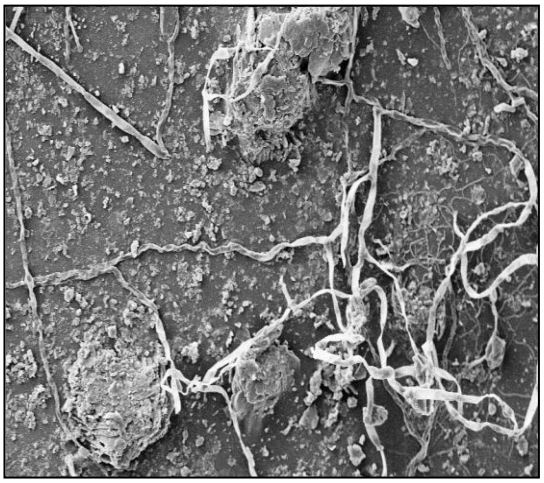

Fig. 4.198 SEM micrograph of PVA/1RS film surface after 2 weeks of indoor burial

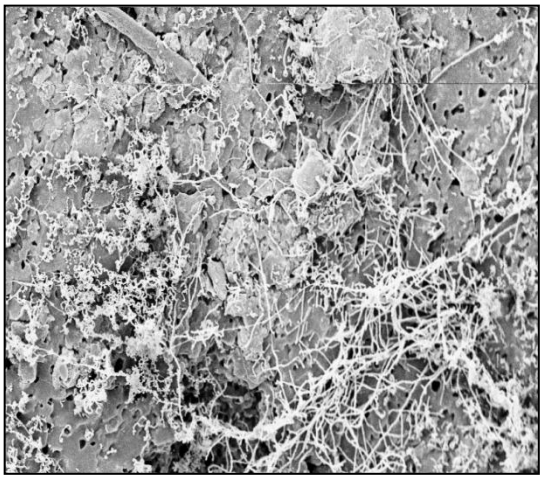

Fig. 4.199 SEM micrograph of PVA/1RS film surface after 2 weeks of outdoor burial

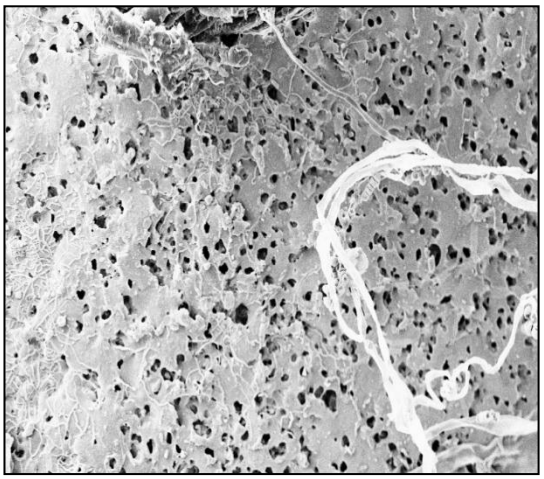

Fig. 4.200 SEM micrograph of PVA/3RS film surface after 2 weeks of indoor burial

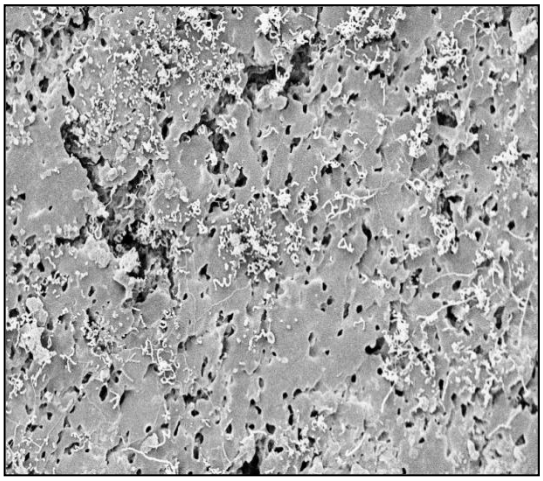

Fig. 4.201 SEM micrograph of PVA/3RS film surface after 2 weeks of outdoor burial

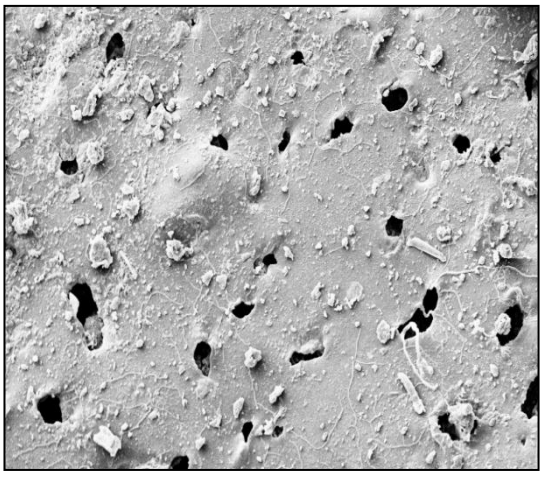

Fig. 4.202 SEM micrograph of PVA/1SS film surface after 2 weeks of indoor burial

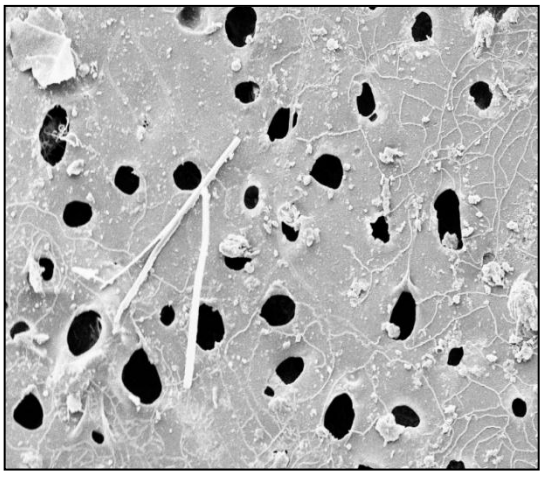

Fig. 4.203 SEM micrograph of PVA/1SS film surface after 2 weeks of outdoor burial

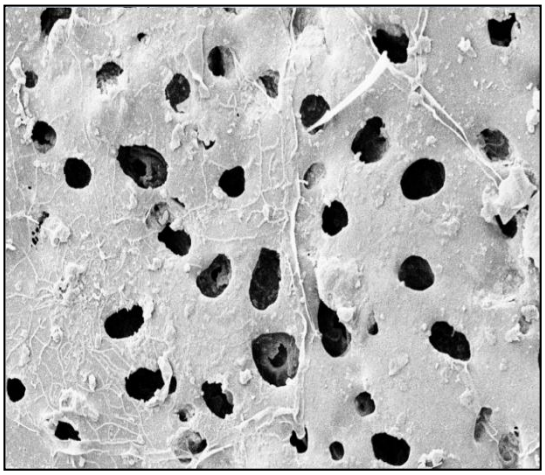

Fig. 4.204 SEM micrograph of PVA/3SS film surface after 2 weeks of indoor burial

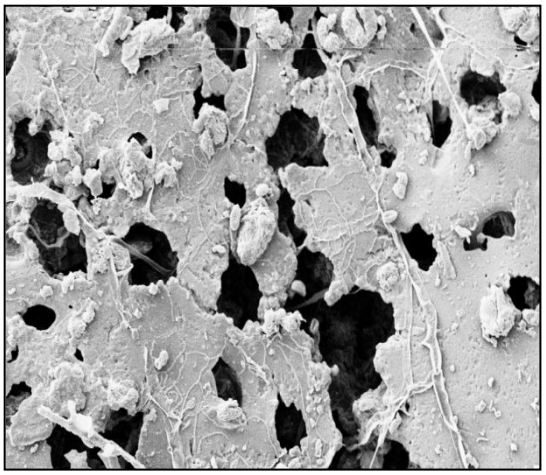

Fig. 4.205 SEM micrograph of PVA/3SS film surface after 2 weeks of outdoor burial

From the SEM images of pure PVA film, no deterioration can be seen on the surface of the film. The impurities seen on the images may be specks of dirt from the compost soil that has not been entirely removed during washing. Generally, observation on the SEM images of the PVA/starch composites revealed that the degradability of the blend was enhanced with the addition of the different starches. The growth rate of the microorganisms on the surface of the blends was also found to be increasing with increasing content of starch in the PVA/starch blends. As can be seen from the outdoor and indoor soil burial experiment, at the end of the 2 weeks, the entire composite films were covered with holes and voids. A gradual increase in the surface roughness, including deformation, wrinkles and cracks can also be seen in the porous films. From the visual observation of the composite films it can also be noted that extensive growth of bacteria and fungi was quite apparent of the film's surface. Perforations seen on the surface of the composite films may be due to the removal of starch granules by soil microbes and/or leaching that will eventually lead to surface agglomerates and cracks. This rapid degradation of the starch phase in the PVA/starch matrix leaves an open

surface within the residual PVA matrix and this will further allow microbial adhesion and subsequently aiding the biodegradation of the composites. For blends of PVA with 3 g of sago starch, the specimen shows continuous holes and voids and this proves that agglomeration of starches has occurred inside the blended composite. It was interesting to note that the colonization of the bacteria and fungi does not only occur on the surface of the films but the microbes were able to penetrate into the interior of the composites. This migration of microorganisms into the holes and voids created by the leaching of starch granules may help stimulate the composite degradation upon disposal.

PVA/different starches/different fibers composites

To evaluate the weight loss of the PVA/starch/fibers blended samples buried for 70 days for the indoor and outdoor soil burial experiment, Figure 4.206 to 4.211 shows the weight loss versus burial time data.

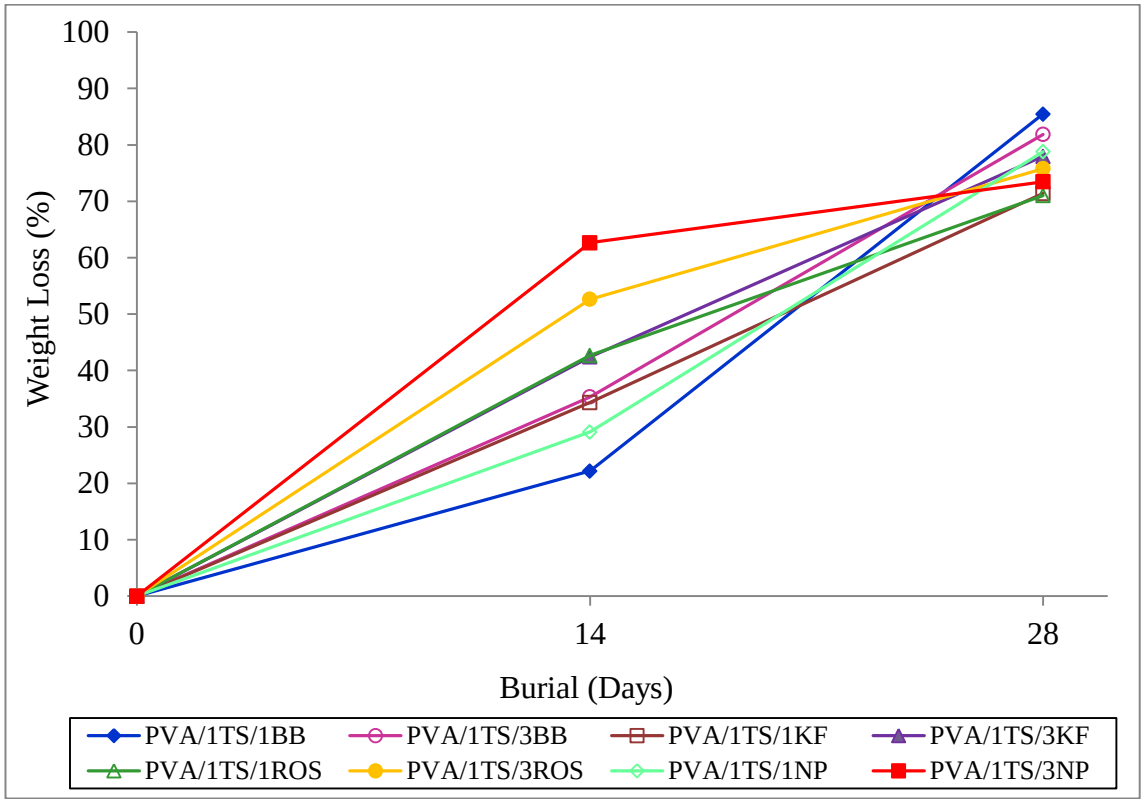

Fig. 4.206 Weight loss for the composites of PVA blended with tapioca starch and different concentrations of different fibers for the outdoor soil burial experiment.

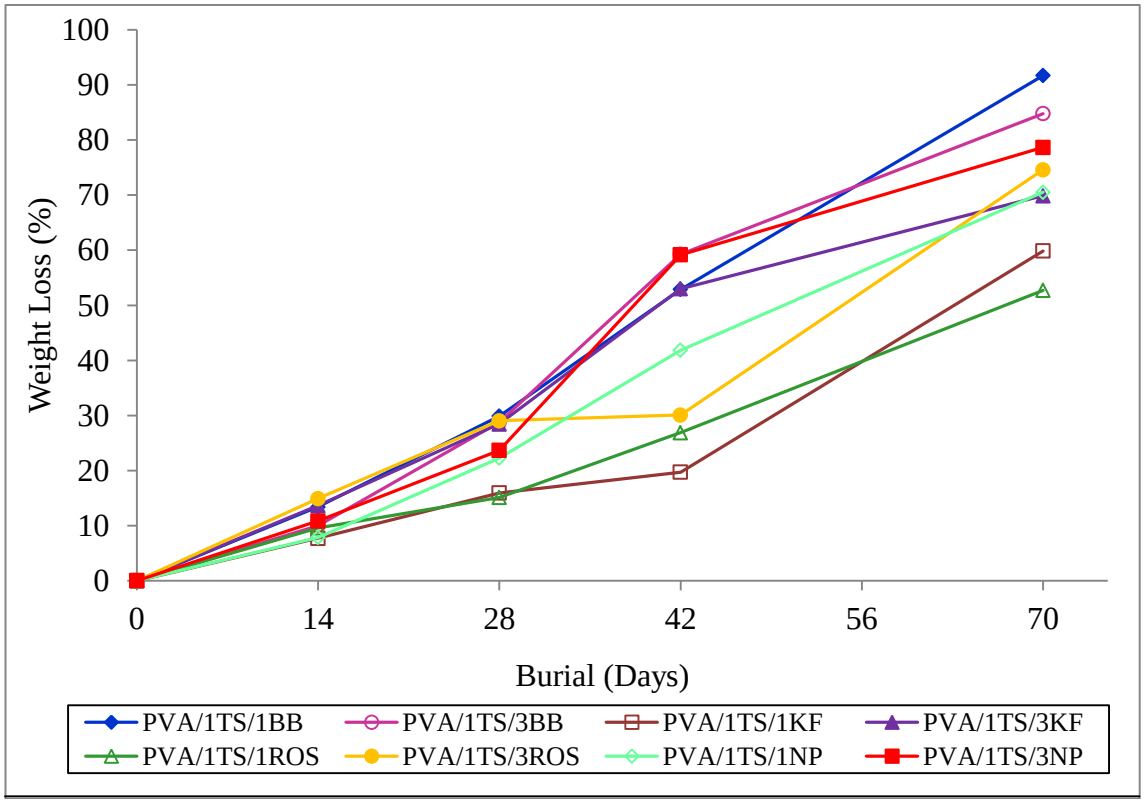

Fig. 4.207 Weight loss for the composites of PVA blended with tapioca starch and different concentrations of different fibers for the indoor soil burial experiment

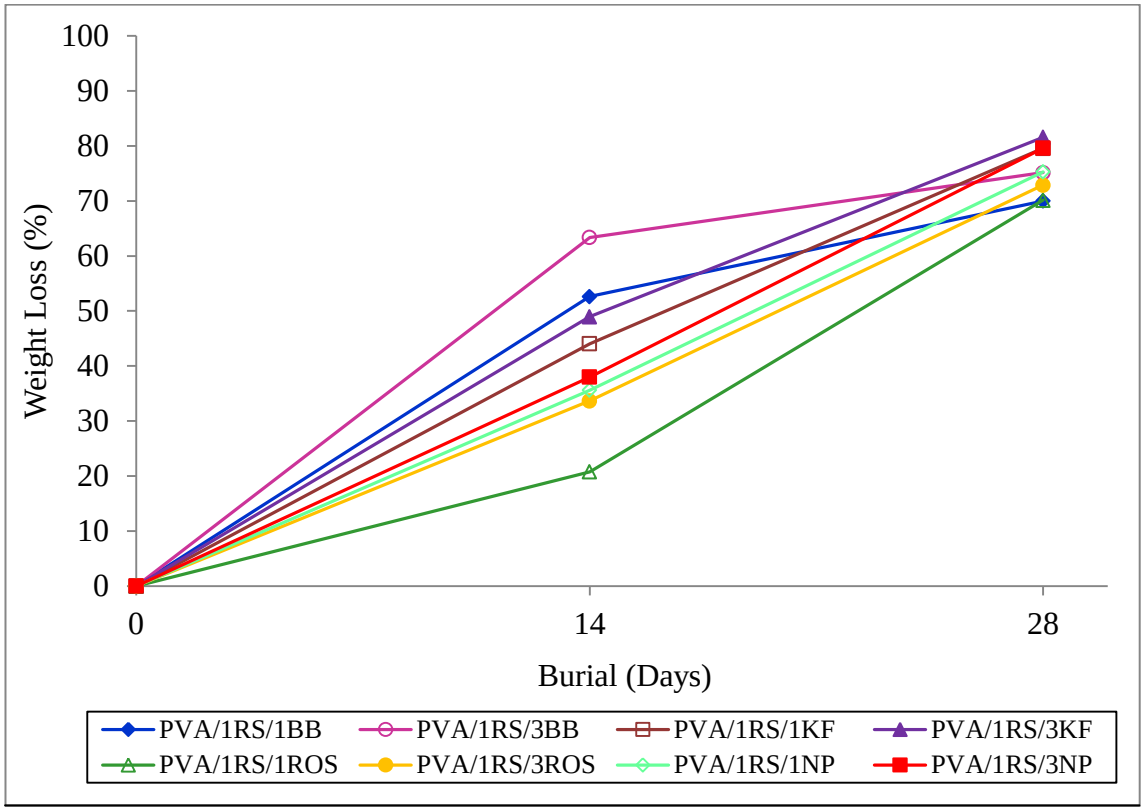

Fig. 4.208 Weight loss for the composites of PVA blended with rice starch and different concentrations of different fibers for the outdoor soil burial experiment.

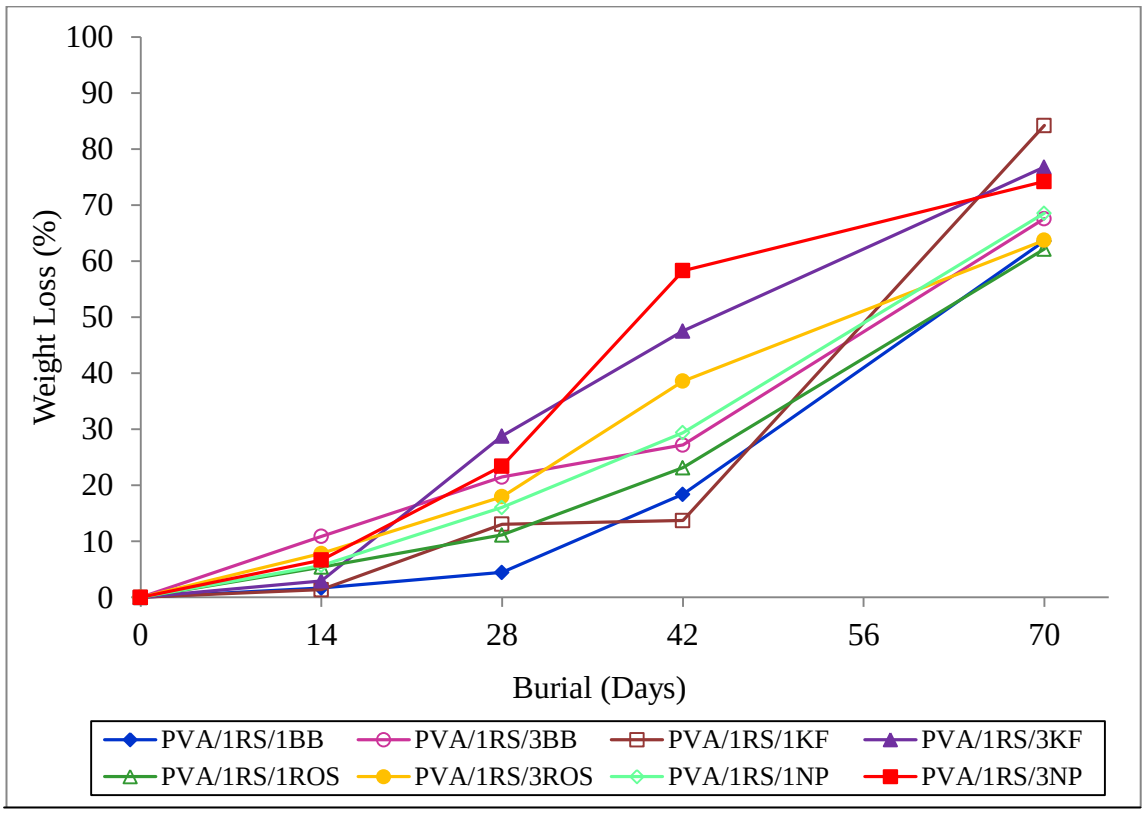

Fig. 4.209 Weight loss for the composites of PVA blended with rice starch and different concentrations of different fibers for the indoor soil burial experiment.

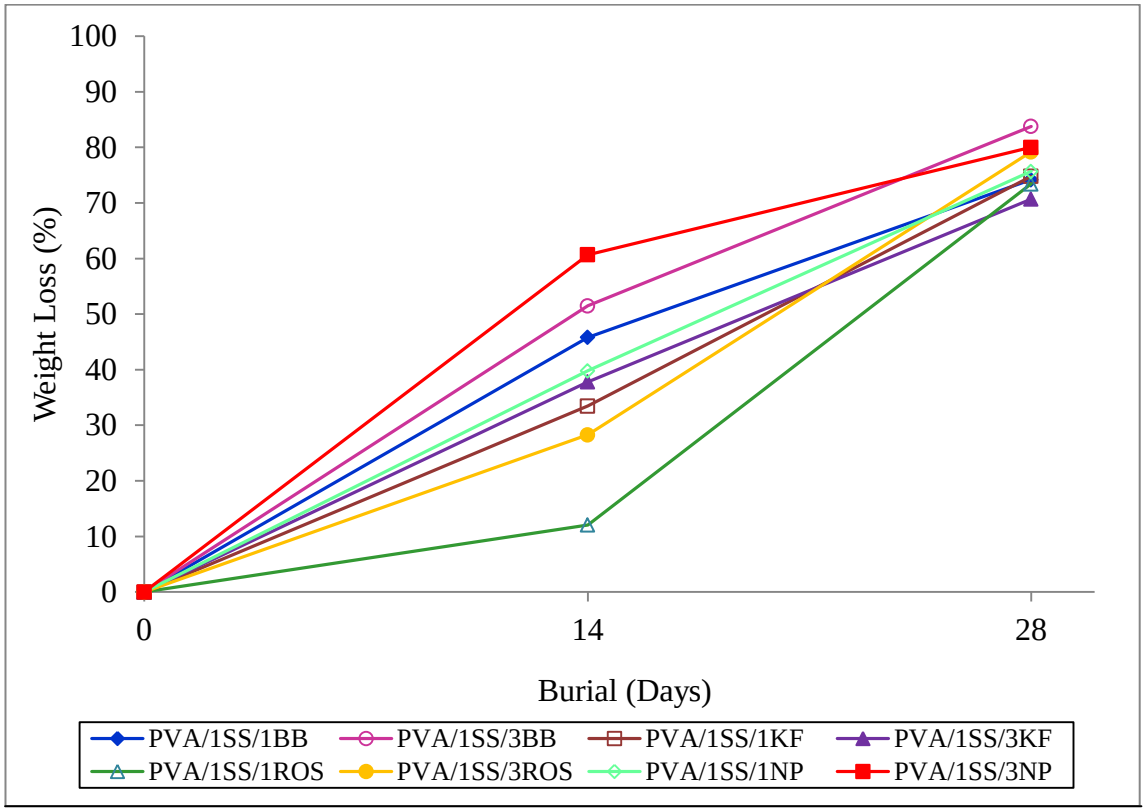

Fig. 4.210 Weight loss for the composites of PVA blended with sago starch and different concentrations of different fibers for the outdoor soil burial experiment.

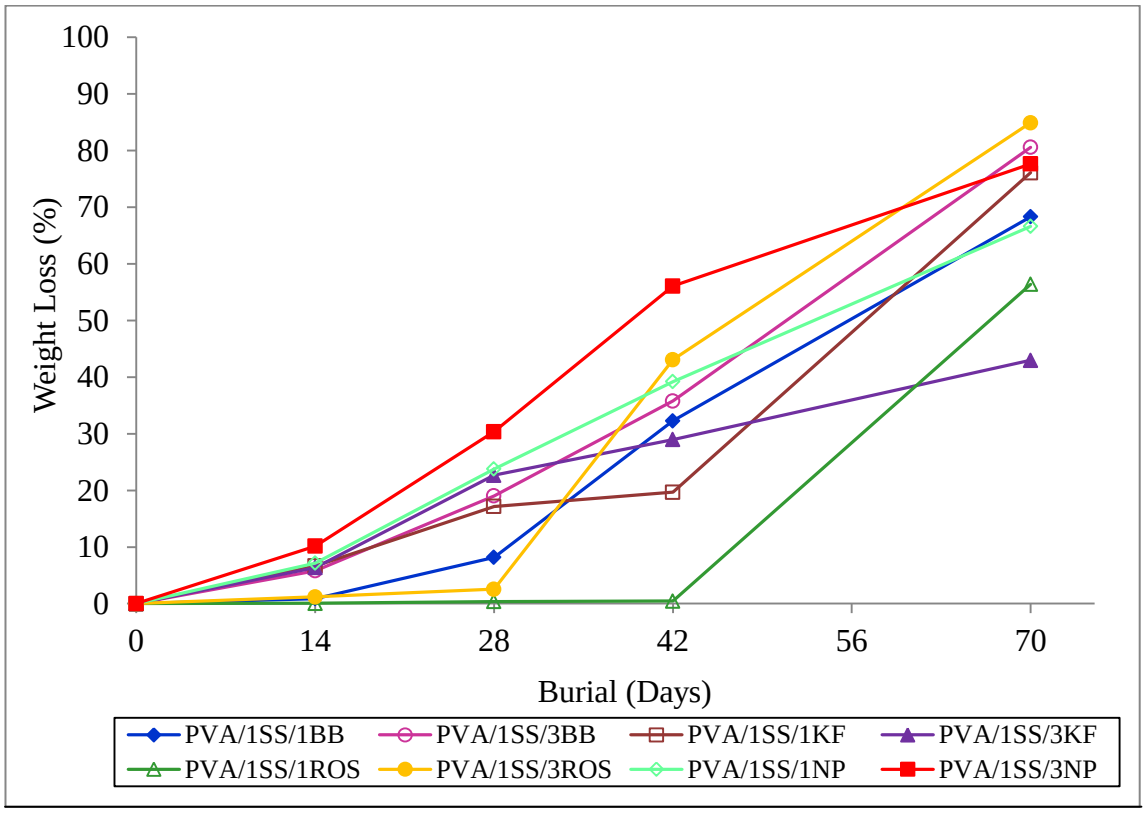

Fig. 4.211 Weight loss for the composites of PVA blended with sago starch and different concentrations of different fibers for the indoor soil burial experiment.

From the weight loss data shown in the graphs, a similar situation was observed for the outdoor soil burial experiment where the data for weight loss can be taken only up to 28 days because the samples could not be tested any more due to their advanced macroscopic deterioration. Both the PVA/starch and PVA/starch/fibers composites show similar trends of biodegradation where the weight loss of all the samples increased almost literally with elapsing burial time with the outdoor experiment showing a higher rate of degradation. Addition of fibers into the PVA/starch matrix slightly decreases the biodegradation rate and this can be clearly seen in the SEM micrographs of PVA blended with different starches and fibers films surfaces. As evident for the weight loss data shown in the graphs, Figure 4.212 to 4.259 shows the SEM micrographs of PVA/starch/fibers composites film surface after soil burial for 2 weeks.

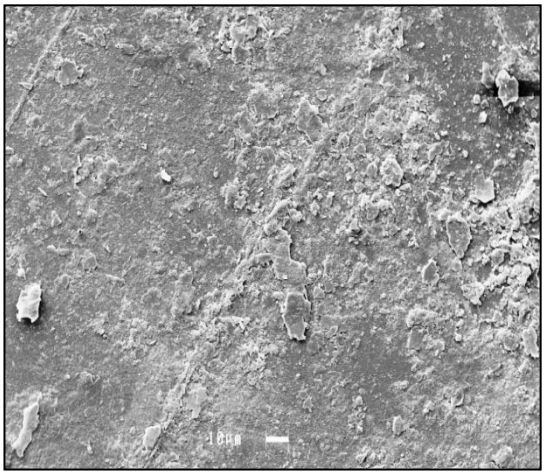

Fig. 4.212 SEM micrograph of PVA/1TS/1BB film surface after 2 weeks of indoor burial

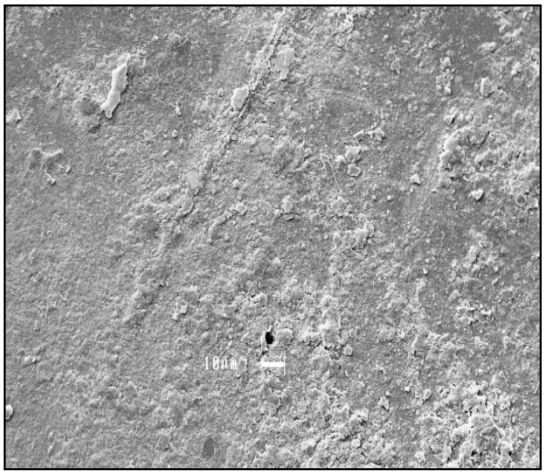

Fig. 4.213 SEM micrograph of PVA/1TS/1BB film surface after 2 weeks of outdoor burial

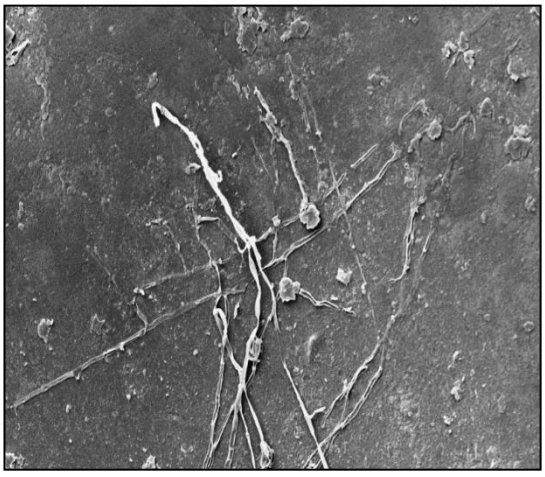

Fig. 4.214 SEM micrograph of PVA/1TS/3BB film surface after 2 weeks of indoor burial

Fig. 4.215 SEM micrograph of PVA/1TS/3BB film surface after 2 weeks of outdoor burial

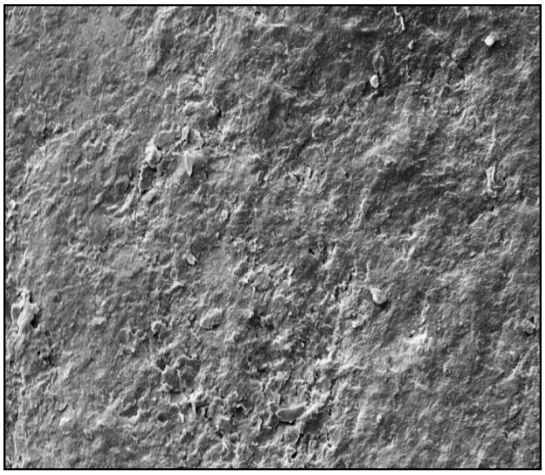

Fig. 4.216 SEM micrograph of PVA/1TS/1KF film surface after 2 weeks of indoor burial

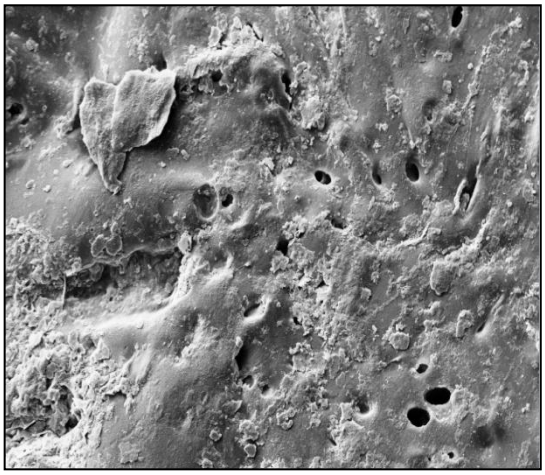

Fig. 4.217 SEM micrograph of PVA/1TS/1KF film surface after 2 weeks of outdoor burial

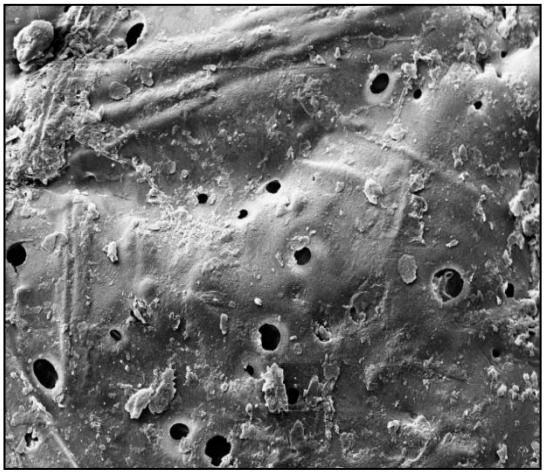

Fig. 4.218 SEM micrograph of PVA/1TS/3KF film surface after 2 weeks of indoor burial

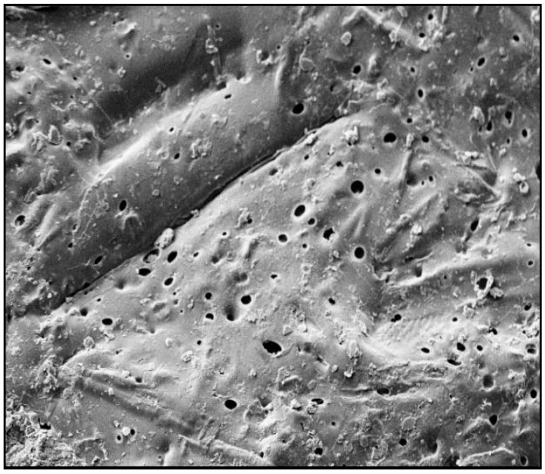

Fig. 4.219 SEM micrograph of PVA/1TS/3KF film surface after 2 weeks of outdoor burial

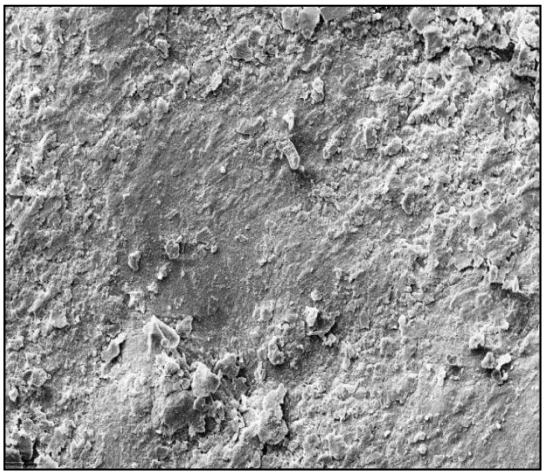

Fig. 4.220 SEM micrograph of PVA/1TS/1ROS film surface after 2 weeks of indoor burial

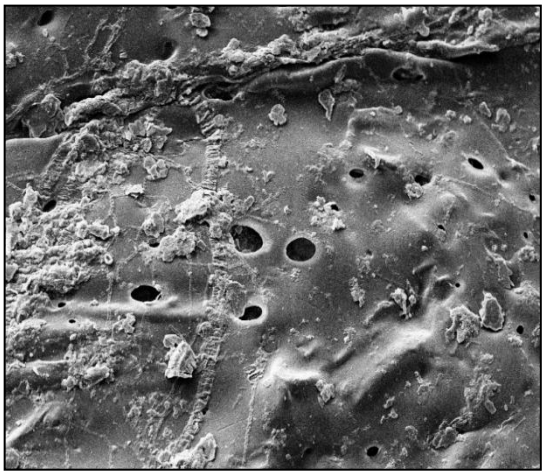

Fig. 4.221 SEM micrograph of PVA/1TS/1ROS film surface after 2 weeks of outdoor burial

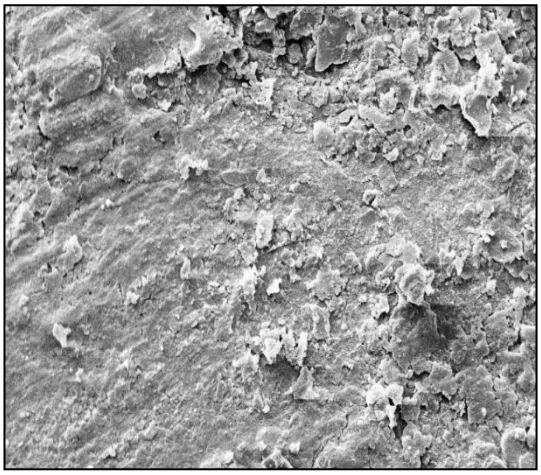

Fig. 4.222 SEM micrograph of PVA/1TS/3ROS film surface after 2 weeks of indoor burial

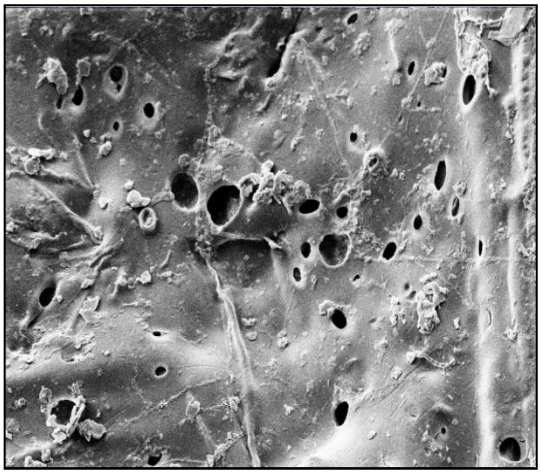

Fig. 4.223 SEM micrograph of PVA/1TS/3ROS film surface after 2 weeks of outdoor burial

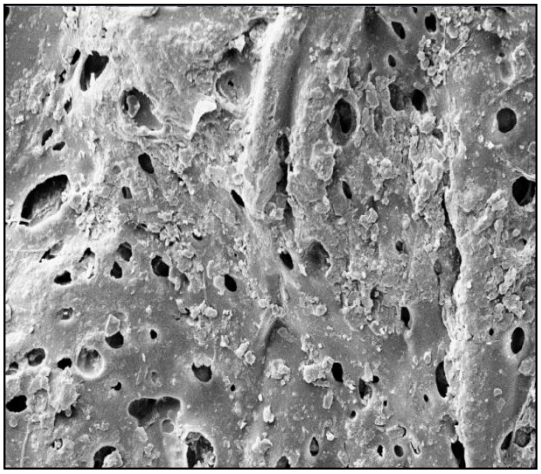

Fig. 4.224 SEM micrograph of PVA/1TS/1NP film surface after 2 weeks of indoor burial

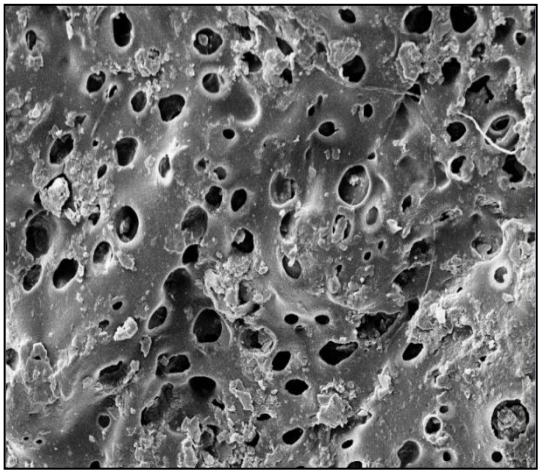

Fig. 4.225 SEM micrograph of PVA/1TS/1NP film surface after 2 weeks of outdoor burial

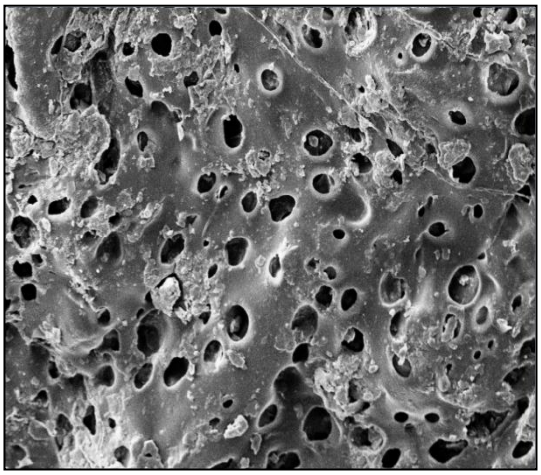

Fig. 4.226 SEM micrograph of PVA/1TS/3NP film surface after 2 weeks of indoor burial

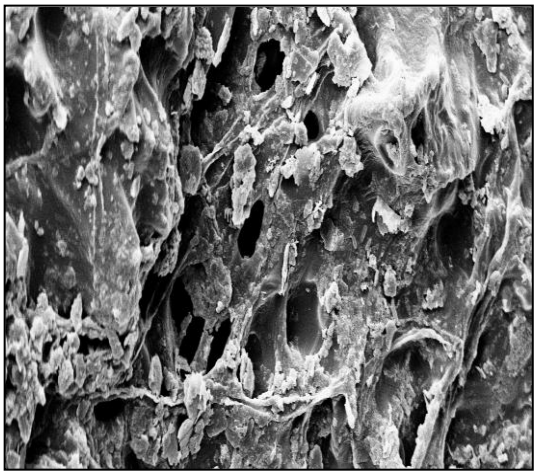

Fig. 4.227 SEM micrograph of PVA/1TS/3NP film surface after 2 weeks of outdoor burial

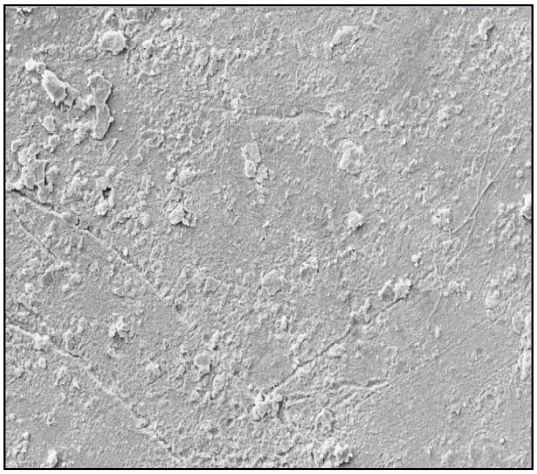

Fig. 4.228 SEM micrograph of PVA/1RS/1BB film surface after 2 weeks of indoor burial

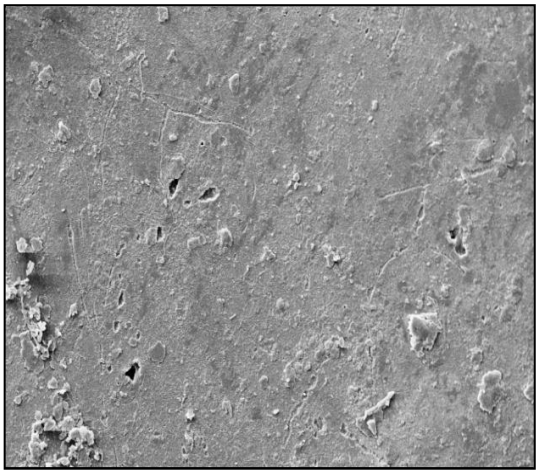

Fig. 4.229 SEM micrograph of PVA/1RS/1BB film surface after 2 weeks of outdoor burial

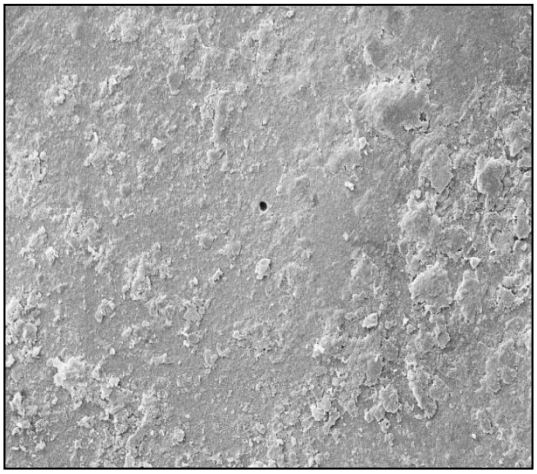

Fig. 4.230 SEM micrograph of PVA/1RS/3BB film surface after 2 weeks of indoor burial

Fig. 4.231 SEM micrograph of PVA/1RS/3BB film surface after 2 weeks of outdoor burial

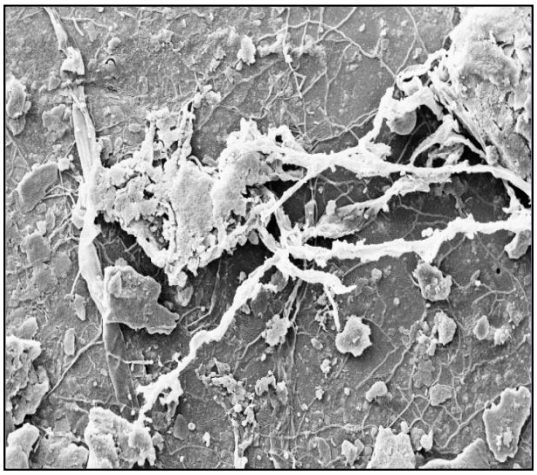

Fig. 4.232 SEM micrograph of PVA/1RS/1KF film surface after 2 weeks of indoor burial

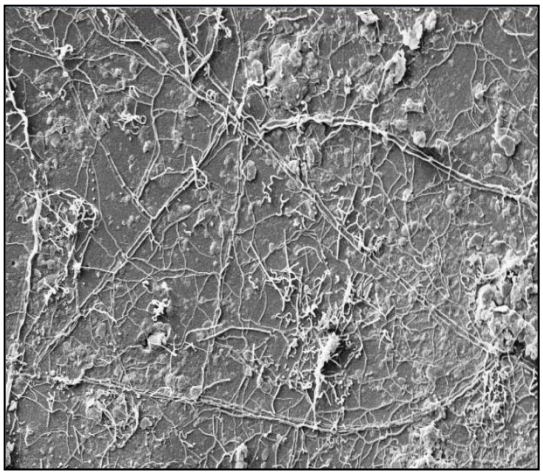

Fig. 4.233 SEM micrograph of PVA/1RS/1KF film surface after 2 weeks of outdoor burial

Fig. 4.234 SEM micrograph of PVA/1RS/3KF film surface after 2 weeks of indoor burial

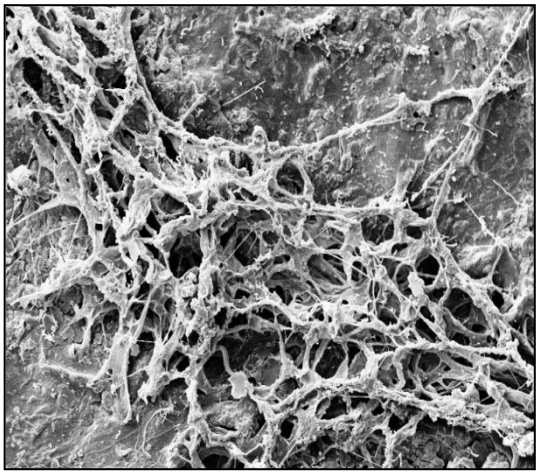

Fig. 4.235 SEM micrograph of PVA/1RS/3KF film surface after 2 weeks of outdoor burial

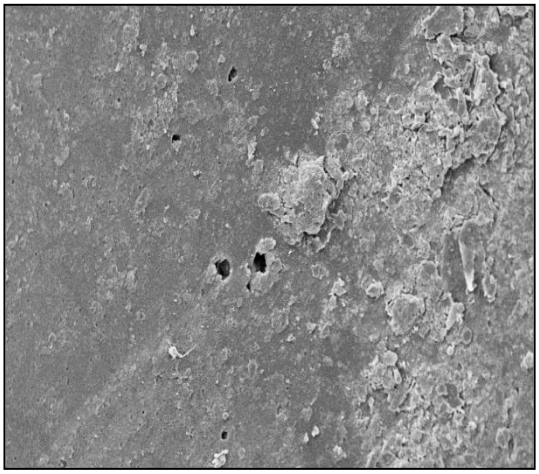

Fig. 4.236 SEM micrograph of PVA/1RS/1ROS film surface after 2 weeks of indoor burial

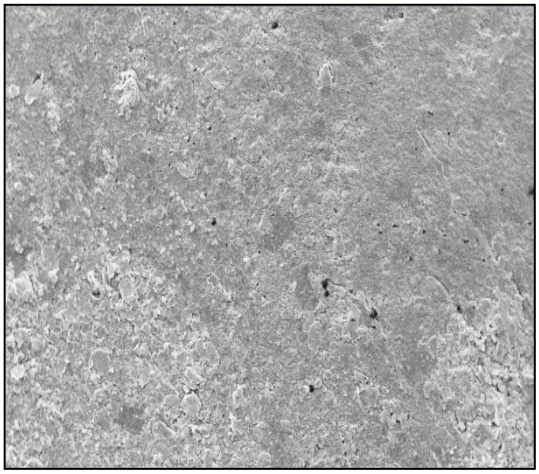

Fig. 4.237 SEM micrograph of PVA/1RS/1ROS film surface after 2 weeks of outdoor burial

Fig. 4.238 SEM micrograph of PVA/1RS/3ROS film surface after 2 weeks of indoor burial

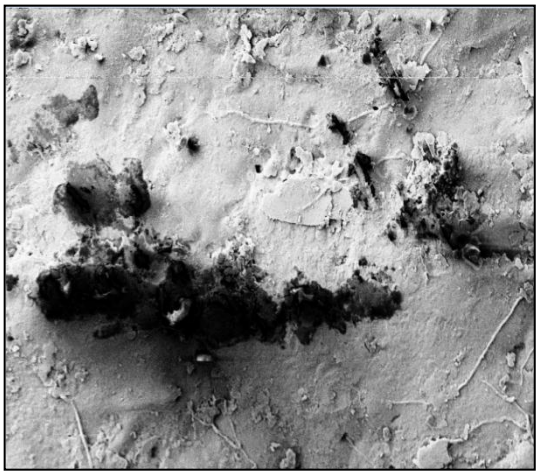

Fig. 4.239 SEM micrograph of PVA/1RS/3ROS film surface after 2 weeks of outdoor burial

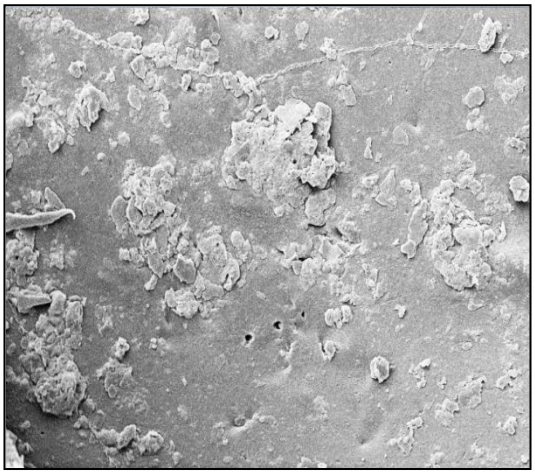

Fig. 4.240 SEM micrograph of PVA/1RS/1NP film surface after 2 weeks of indoor burial

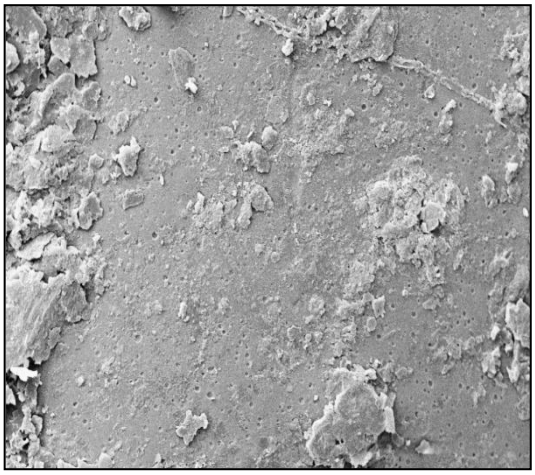

Fig. 4.241 SEM micrograph of PVA/1RS/1NP film surface after 2 weeks of outdoor burial

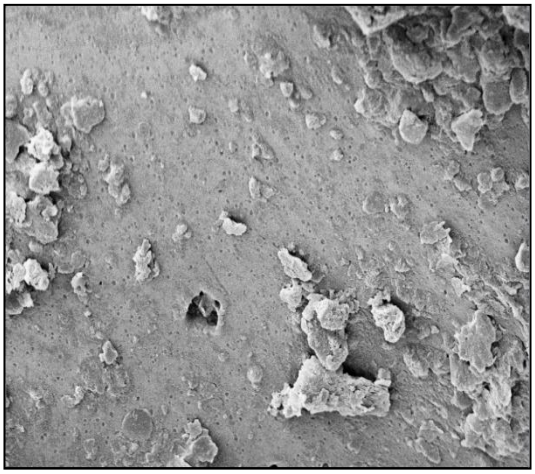

Fig. 4.242 SEM micrograph of PVA/1RS/3NP film surface after 2 weeks of indoor burial

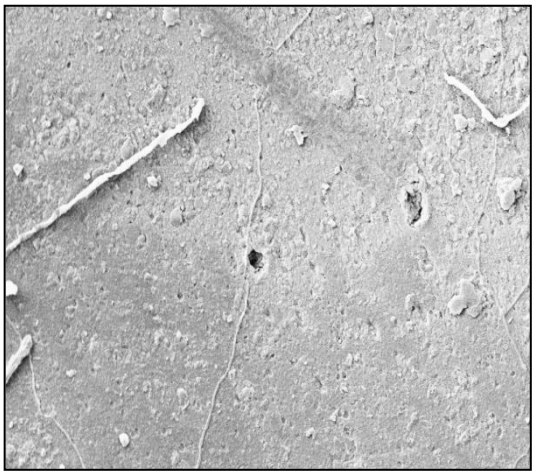

Fig. 4.243 SEM micrograph of PVA/1RS/3NP film surface after 2 weeks of outdoor burial

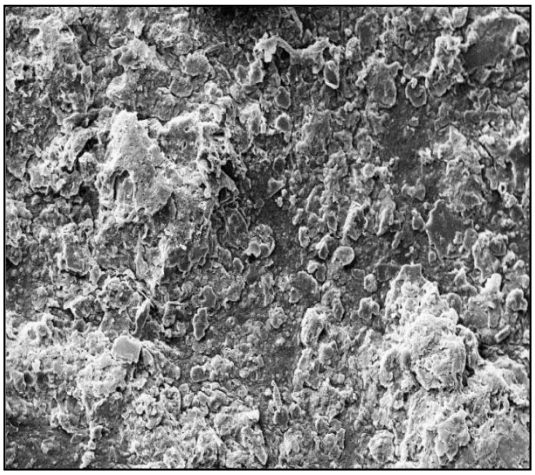

Fig. 4.244 SEM micrograph of PVA/1SS/1BB film surface after 2 weeks of indoor burial

Fig. 4.245 SEM micrograph of PVA/1SS/1BB film surface after 2 weeks of outdoor burial

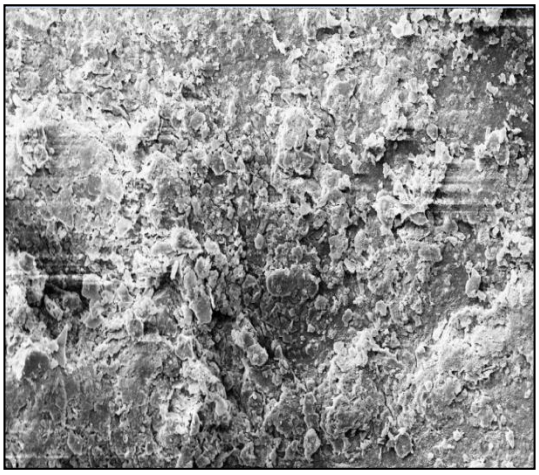

Fig. 4.246 SEM micrograph of PVA/1SS/3BB film surface after 2 weeks of indoor burial

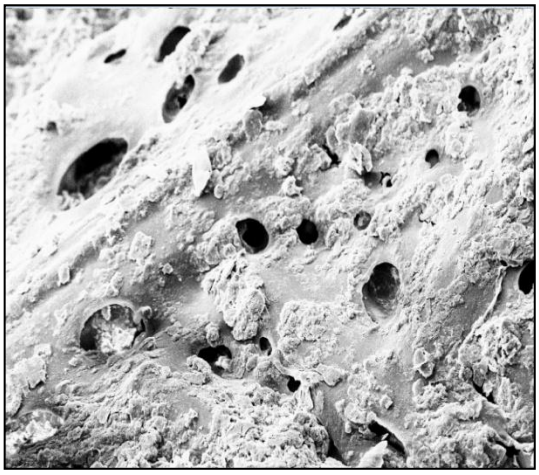

Fig. 4.247 SEM micrograph of PVA/1SS/3BB film surface after 2 weeks of outdoor burial

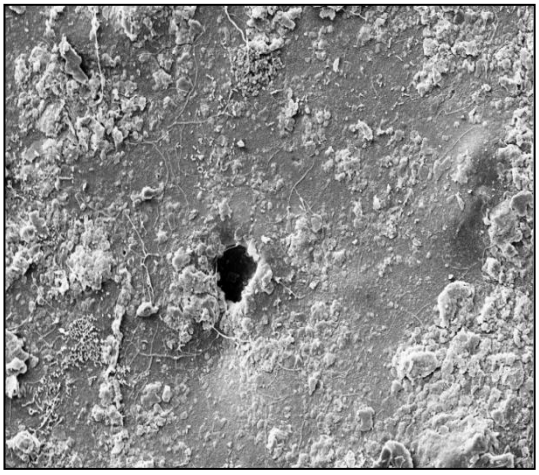

Fig. 4.248 SEM micrograph of PVA/1SS/1KF film surface after 2 weeks of indoor burial

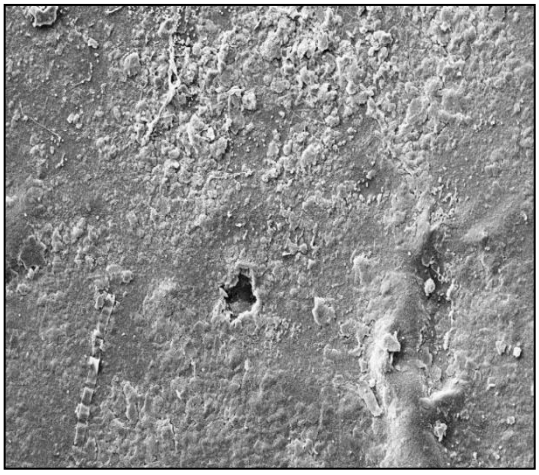

Fig. 4.249 SEM micrograph of PVA/1SS/1KF film surface after 2 weeks of outdoor burial

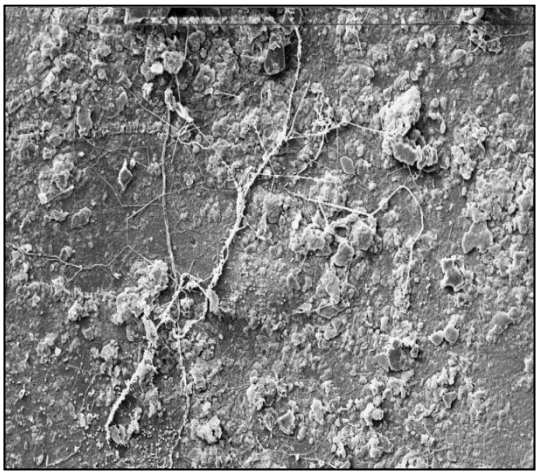

Fig. 4.250 SEM micrograph of PVA/1SS/3KF film surface after 2 weeks of indoor burial

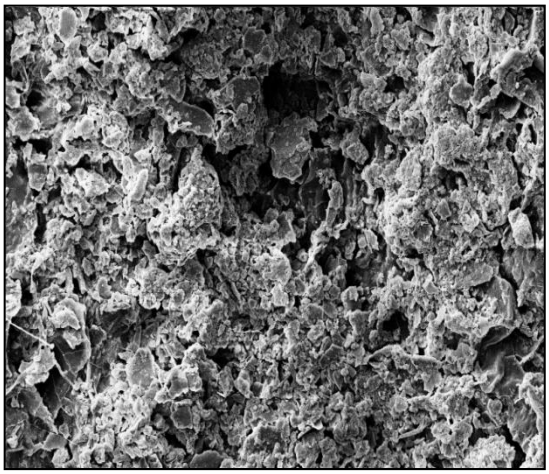

Fig. 4.251 SEM micrograph of PVA/1SS/3KF film surface after 2 weeks of outdoor burial

Fig. 4.252 SEM micrograph of PVA/1SS/1ROS film surface after 2 weeks of indoor burial

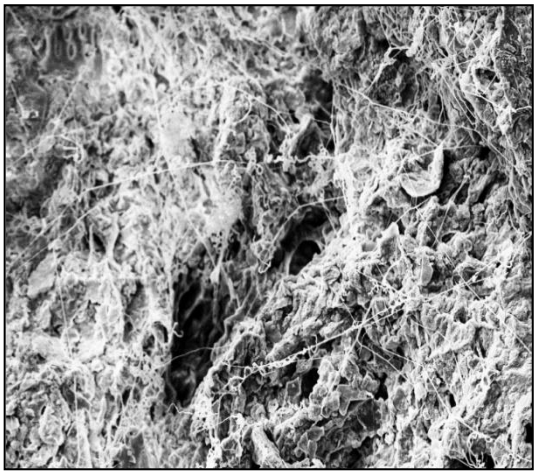

Fig. 4.253 SEM micrograph of PVA/1SS/1ROS film surface after 2 weeks of outdoor burial

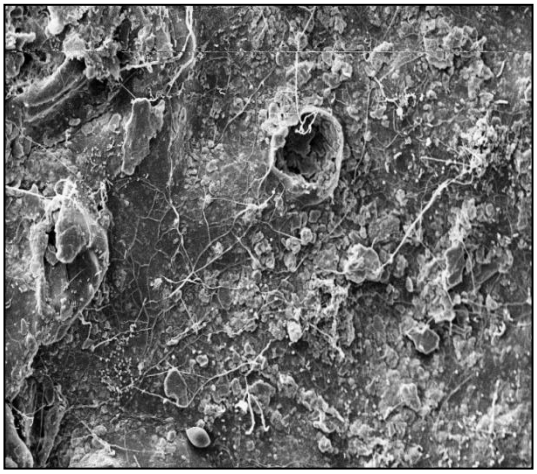

Fig. 4.254 SEM micrograph of PVA/1SS/3ROS film surface after 2 weeks of indoor burial

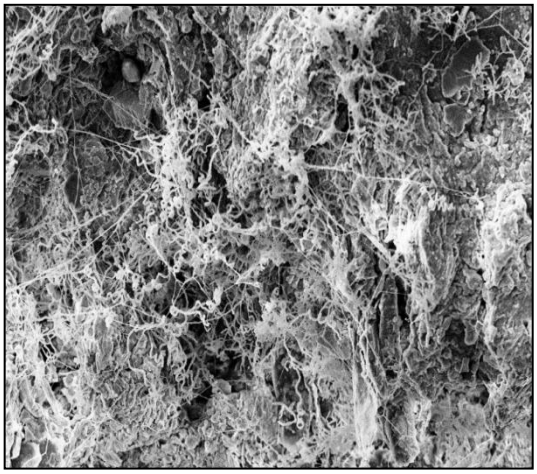

Fig. 4.255 SEM micrograph of PVA/1SS/3ROS film surface after 2 weeks of outdoor burial

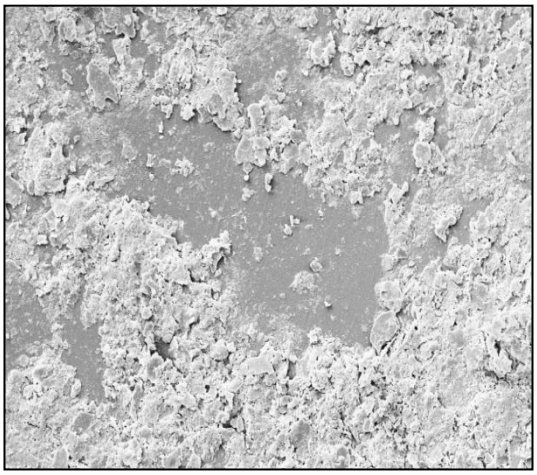

Fig. 4.256 SEM micrograph of PVA/1SS/1NP film surface after 2 weeks of indoor burial

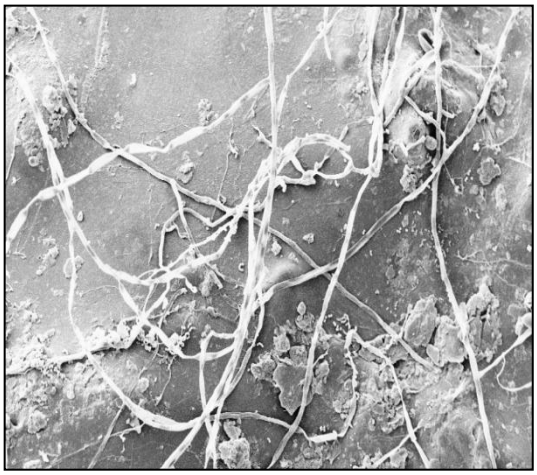

Fig. 4.257 SEM micrograph of PVA/1SS/1NP film surface after 2 weeks of outdoor burial

Fig. 4.258 SEM micrograph of PVA/1SS/3NP film surface after 2 weeks of indoor burial

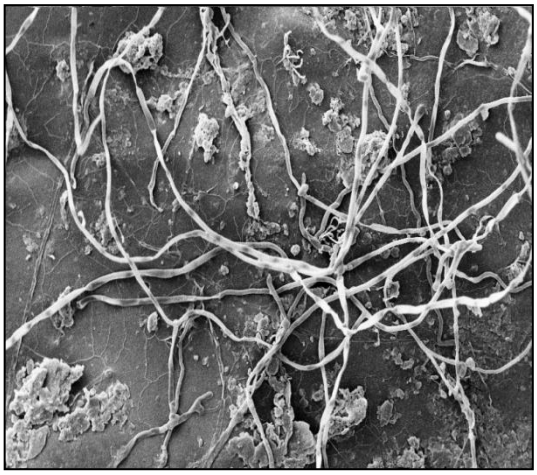

Fig. 4.259 SEM micrograph of PVA/1SS/3NP film surface after 2 weeks of outdoor burial

In general, from the SEM images shown, compared with the PVA/starch blended films, the PVA/starch fibers films have fewer holes and less disfigurement, indicative of a slower rate of degradation. This phenomenon may be caused by the addition of the different fibers into the blends. The presence of cellulosic fibers in the blended composite is directly correlated with the slowdown in the deterioration of the composite films and this indicates that the fibers were either resistant to microbial attack or it restricts the availability of hydrolytic enzymes to the PVA/starch matrix. The addition

of these cellulosic fibers also increases the compatibility between the different components in the blend and this subsequently forms a dense structure between the PVA/starch matrix and cellulose fibers, which in turn reduced the infiltration velocity of the microorganisms. On the other hand, as seen from the SEM analysis, some of the composites (Figure 4.218, 4.219, 4.221, 4.223, 4.234 and 4.247) shows that the cellulosic fibers incorporated into the blends are still intact and visible. This observation indicates that the surface of the cellulosic fibers promoted water entrance and the swelling of the starch component and also served as a support for the attack of the microorganisms. The images also revealed the presence of bacterial cluster growing on the composite film's surface, particularly at location near where there are holes and voids. This event is most likely to be associated with the preferential removal of starch particles and the infiltration of microorganisms into the interior of the matrix. The entrapment of these bacteria and fungi in the bulk of the samples helps stimulate the composite degradation upon disposal. In the later stages of the biodegradation, the cellulose fibers chain breakdown may contribute to the higher weight loss suffered by the composites.

From the visual observation of the PVA/starch and PVA/starch/fibers composites, after 70 days of exposure in compost soil, the specimens appeared brittle, fragile and diminished in size indicating the natural biodegradation of these composite films in the soil environment. Even though complete degradation was not seen after 70 days of burial, with the addition of the different starches and fibers, it truly lowers the environmental impact with the application of these environmentally friendly materials.