

Structural Changes of Starch/Polyvinyl Alcohol Biocomposite Films Reinforced with Microcrystalline Cellulose Due to Biodegradation in Simulated Aerobic Compost Environment

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ABSTRACT: Starch/Polyvinyl alcohol (PVA) based biocomposite films reinforced with micro crystalline cellulose (MCC) (10 wt %) particles were prepared by solution casting method, incorporating glycerol as plasticizer. These biocomposite films were subjected to biodegradation at ambient temperature in a simulated aerobic compost pit. The extent of biodegradation of these films was studied in terms of weight loss. The corresponding changes in the structure of the films were observed using scanning electron microscopy, X-Ray diffraction study, and differential scanning calorimetry. The melting point of PVA compo-

nent of the biocomposite film shifted from 204 to 223°C with increase in biodegradation time and a remarkable difference was observed in their melt crystallization behavior. The unreinforced films also showed a similar trend, but the increase in the crystallinity of PVA was more pronounced in MCC reinforced films than that observed in the unreinforced ones. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2503–2511, 2011

Key words: biodegradation; composites; differential scanning calorimetry; morphology; electron microscopy

INTRODUCTION

The development of biodegradable polymers has gained increasing attention over the years due to the environmental pollution and ecological limitation induced by synthetic polymers.¹ Widespread studies on the biodegradation of polymers have been carried out to overcome the environmental problems associated with synthetic plastic waste.^{1,2} The use of biopolymers in packaging is considered to render a partial solution towards solid waste management.¹ The biodegradable polymers are often made into biocomposites with suitable fillers to get enhanced properties.³ Hence, studies on the biodegradation behavior of such biocomposites are necessary to estimate their environmental impact.⁴

Starch is an inexpensive, abundantly available biopolymer, which is often used by the researchers to develop biodegradable materials for diversified applications.³ Starch, to overcome its inherent drawbacks like poor mechanical properties, is often blended with other polymers like PVA etc. to prepare green, biodegradable films.³ Starch/PVA honeycomb like biocomposite sponges were prepared and their structural properties were investigated by Wang et al.⁵ Several studies were reported on the properties of such films^{6,7} and on their biodegradation behavior.^{8–10} Jayasekara et al.¹¹ reported that the starch component of starch-PVA films degraded first and more rapidly than PVA in the compost and surface modification with chitosan did not interfere with starch degradation. They prepared starch/PVA/glycerol films and examined the biodegradation by composting for 45 days. Within this time, the starch and glycerol components were fully degraded, leaving the PVA component intact. However, it was reported that addition of PVA slowed down the biodegradation procedure in starch-glycerol-PVA films.¹² The degradability of thermoplastic starch and thermoplastic dialdehyde starch exhibited

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three phases under controlled composting conditions. The biodegradation in the first phase was slow, accelerated in the second phase and leveled off in the third phase. Thermoplastic starch degraded faster than thermoplastic dialdehyde starch under controlled conditions.¹³ A methodological comparison of eco-friendly materials like starch/PVA blends was done by Chai et al.¹⁴ They studied the aqueous degradation by enzyme, water absorption, and biodegradation behavior of starch/PVA blends. The biodegradability of those materials was followed by bio-reactivity kinetics model. This kinetic model also estimated the probable time for complete degradation. Some researchers have reported that the rate of biodegradation depends on the shape of the specimens, since that may affect aeration behavior in the compost initially.¹⁵ Yun et al.¹⁶ investigated the degradation of chemically modified starch/PVA blend films and reported that the degradation by enzyme was more in glycerol added films than that in citric acid added films. However, the result was opposite for microbiological and soil burial analysis of the same films.

Although, the biodegradation behavior of starch/PVA films has been widely investigated by several researchers,^{8–12} the biodegradation reports on starch/PVA film reinforced with MCC particles are sparse. Cellulosic fillers form strong hydrogen bonds with chemically similar starch and PVA and strongly influence the biodegradation behavior.³ In this work, an attempt has been made to study the biodegradability of starch/PVA biocomposite films reinforced with MCC. The detailed preparation method and properties of these films were reported in our previous work.¹⁷ The structural changes in the biocomposite films in composting environment were examined from their X-Ray diffraction patterns, differential scanning calorimetry (DSC) analysis, and Scanning Electron Microscopy (SEM) investigations. These results were analyzed to understand the changes occurring in the molecular structures of the polymers.

EXPERIMENTAL

Materials

Starch from Merck (101253-Starch soluble extra pure) and PVA (Product of Central Drug House, New Delhi, India) with molecular weight 14,000 were used as the matrix material. Glycerol used was a SRL (Sisco Research Laboratories, Mumbai, India) product. Cotton was collected from Hada Textile Mill (Kolkata, India), for preparing the MCC particles. Concentrated sulfuric acid (Merck) of 64 volume % was used for acid hydrolysis of cotton.

Materials for compost

The composition of the compost was (dry weight): 40.8% cow dung, 11.4% sawdust, 15.8% newspaper and computer paper, 2% white bread, 7.8% shredded leaves, 19.2% food waste (dry milk, potato, carrot, banana, and other vegetables), and 3.0% urea.¹⁸

Film preparation

MCC particles were prepared from cotton by acid hydrolysis using 64% sulfuric acid at 45°C for 1 h under stirring. The suspension was sonicated and neutralized with 0.5 mol L⁻¹ NaOH, centrifuged and washed with distilled water to maintain a neutral pH. The MCC particles were freeze dried in SCAN-VAC Coolsafe TM. Starch/PVA/MCC biocomposite films were prepared by taking starch : PVA in the weight ratio 1 : 1 and glycerol 30 wt % based on total dry weight of starch and PVA. The films were reinforced by adding 10 wt % MCC particles based on the total dry weight of starch and PVA. Only 10 wt % filler loading was done because most uniform dispersion and enhancement in properties were observed at 10 wt % filler loading, which has already been reported in our previous communication.¹⁷ The control samples were prepared with starch : PVA in the weight ratio 1 : 1 and with 30 wt % of glycerol, based on total dry weight of starch and PVA, without any MCC filler.

Compost and biodegradation

The composting bin was filled with aerobic compost having a standard composition.¹⁸ The moisture content was maintained by spraying water at regular time intervals (150 mL/day). The duration of the test was 30 days and the ambient temperature range was from 30 to 34°C. The experiment was done once. The composting temperature varied with the temperature of the surrounding atmosphere. The films were cut into 20 × 20 mm² size and the samples were subjected to degradation at about 4 cm beneath the surface. Starch/PVA film with glycerol as plasticizer was used as the control sample here. The biodegradability was determined by measuring the weight loss of composted samples after thorough washing with distilled water and drying under vacuum until constant weight was reached. The samples (three samples for each composition) were picked up from the compost at regular time intervals and were investigated for their change in properties. The compost and biodegradation experiment was performed only one time and our aim was to make a comparative study in the same environment, which we did in our set of experiment. Depending on climate and temperature, the nature

of degradation may vary. The biodegraded samples with MCC were designated as BDX and control samples as CBDX, where X denoted the number of days of degradation.

Characterization

Weight loss study

The weight loss of the samples on biodegradation was measured following the equation,

$$\text{Weight loss (\%)} = \{(W_o - W_t)/W_o\} \times 100$$

where, W_o is the weight of the sample before biodegradation and W_t is the weight of the sample after biodegradation at time t .

The change in weight was measured for three samples of each set for each time interval. The mean weight has been reported and the error bar corresponds to the standard deviation value.

X-ray diffraction study

The X-Ray diffraction (XRD) study was done using XPert PRO with a scanning rate $2^\circ/\text{min}$ and scanning range $2\theta = 2-60^\circ$ using $\text{CuK}\alpha$ radiation (wavelength 0.1542 nm) at 45 KV and 40 ma.

Scanning electron microscopy

SEM images were taken by using HITACHI S-3400 Scanning Electron Microscope. All samples were coated with a thin layer of gold prior to observation. All samples were observed with 15 kv voltage under $1000\times$ magnification.

Differential scanning calorimetry (DSC)

DSC measurements were performed in nitrogen atmosphere by using Perkin-Elmer Pyris Diamond calorimeter. Samples were heated from 0 to 250°C at a heating rate of $10^\circ\text{C}/\text{min}$ (first heating), cooled to 0°C from 250°C at the same rate (cooling), and then heated again to 250°C at $10^\circ\text{C}/\text{min}$ (second heating).

Fungi isolation

Isolation of two fungi for degradation of starch and PVA respectively, was done from compost by serial dilution method. Compost sample (0.1 g) was taken and dispersed in 10 mL sterile physiological saline. The compost suspension was serially diluted up to 10^{-6} . Then 50 μL of the supernatant was plated on minimal media where sole source for carbon was starch. The same experimental method was followed on minimal media where sole source for carbon was PVA. The minimal media was supplemented with

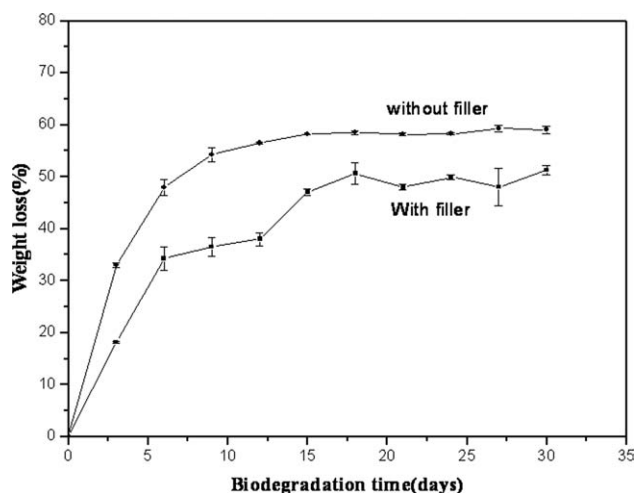


Figure 1 The % weight loss of the starch/PVA films and starch/PVA/MCC biocomposite films as a function of composting time.

100 μL of 12 mg/mL tetracycline solution to inhibit the growth of bacterial colonies. The incubation temperature was 30°C . To maintain the isolated fungi culture LB medium was used.

RESULTS AND DISCUSSION

The biodegradation behavior of starch/PVA films with and without MCC was investigated in the same composting environment and the loss in weight with time is shown in Figure 1. The control starch/PVA films had a sharp loss in weight up to 9 days and then reached almost a constant value (60% weight loss) after 15 days. But starch/PVA/MCC biocomposite films exhibited two phase degradation between 1 and 12 days and 12–30 days, having a weight loss of nearly 50% after 30 days, which was 10% less than that of the control films. Similar two phase degradation was reported by Ramaraj⁷ and Singh et al.¹⁸

To visualize the morphological changes due to biodegradation, the specimens were collected from the compost at different intervals of degradation and SEM micrographs were taken. The surface morphology of the control starch/PVA film (without MCC) before and after biodegradation is shown in Figure 2. Many small but uniform holes were formed throughout the surface after 15 days of degradation (CBD15) and the smooth surface had a porous look. After 27 days, some of these pores turned bigger. Figure 2 also shows the surface morphology of the starch/PVA/MCC biocomposite films before and after biodegradation. BD0 (before biodegradation) exhibited a smooth surface morphology, but the irregularity of the surface increased with the time of biodegradation. Many holes and cracks were created on the surface and a jagged surface was formed. The extent of holes increased significantly with time. It

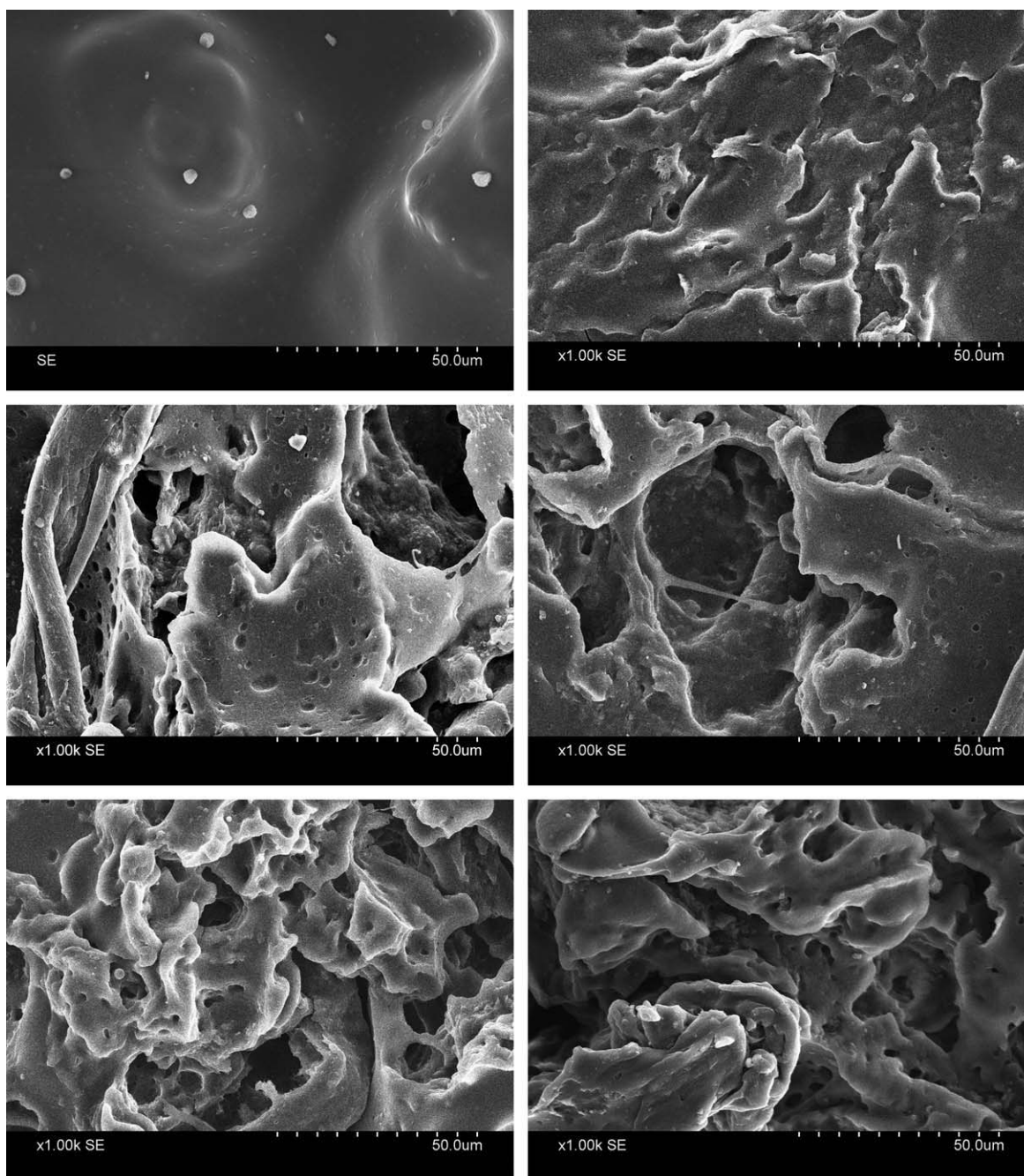


Figure 2 SEM micrographs of starch/PVA (1 : 1 by weight with 30 wt % of glycerol) control films (CBD0, CBD15, and CBD27) and starch/PVA/MCC biocomposite films before and after 15 and 27 days of degradation. Biocomposite samples denoted as BDX, where X denotes the number of days of biodegradation.

was therefore evident from the micrographs that degradation occurred more uniformly throughout the matrix in the control samples, but in the biocomposite films, more uneven surface revealed the complex biodegradation process.

XRD analysis of the individual components was done to investigate the structural changes occurring in the samples. The XRD diffractograms of the gelatinized starch, glycerol plasticized PVA film and the prepared MCC particles are shown in Figure 3(a,b) respectively. A sharp peak appeared at

$2\theta = 17^\circ$ and small peaks appeared at 15° , 19° , and 22° in the gelatinized starch sample. In PVA film, sharp peaks were observed at 19.6° and 40.5° . MCC exhibited a hump at 14.8° and sharp peaks at 22° , 23° , 31° , 34° , and 37° .

The XRD pattern of the starch/PVA control films before and after biodegradation are shown in Figure 4. As MCC was absent in the control, the peaks at 22° and 17° were due to contribution of gelatinized starch. The peak at 19.6° appeared due to PVA. After 15 and 27 days of biodegradation, the

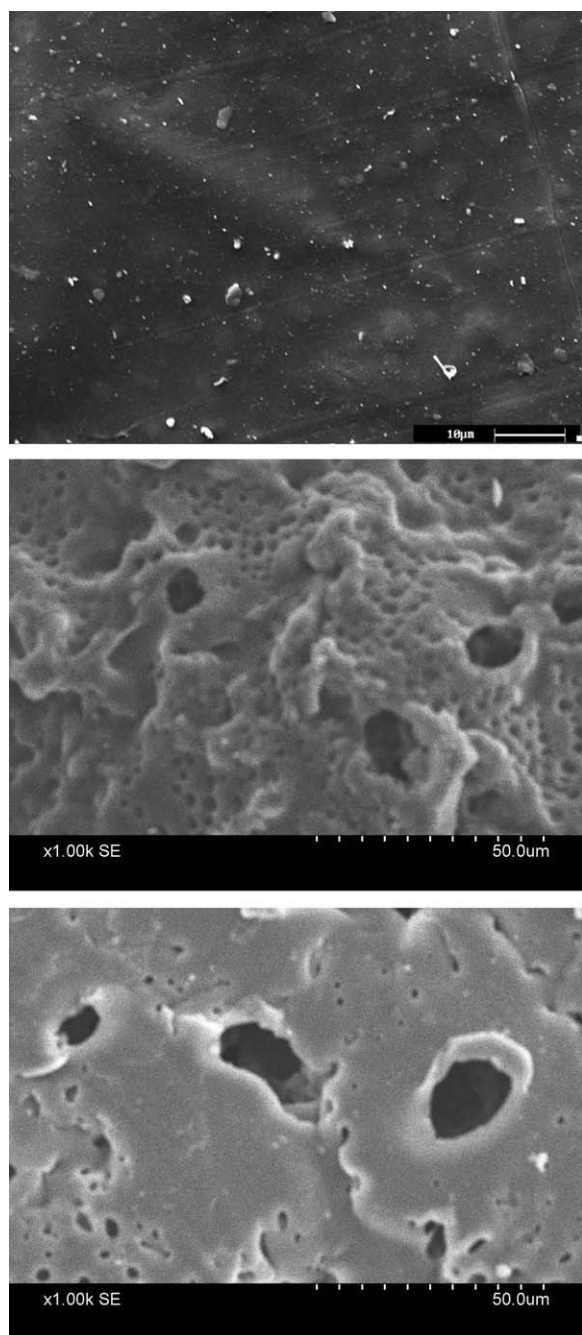


Figure 2 Continued

17° peak decreased significantly and the intensity of 19.6° peak increased considerably. The small hump at 40.5° also changed to a sharper peak after 27 days of biodegradation (CBD27). These observations clearly indicate that there was a rise in the crystallinity of the PVA component in the blend. The rise in crystallinity of PVA was because of the biodegradation initiated in amorphous zones. Then, the crystallinity of PVA increased because amorphous zones were selectively degraded at a higher rate.

The 22° peak appeared sharper after 15 days of biodegradation, but decreased appreciably after

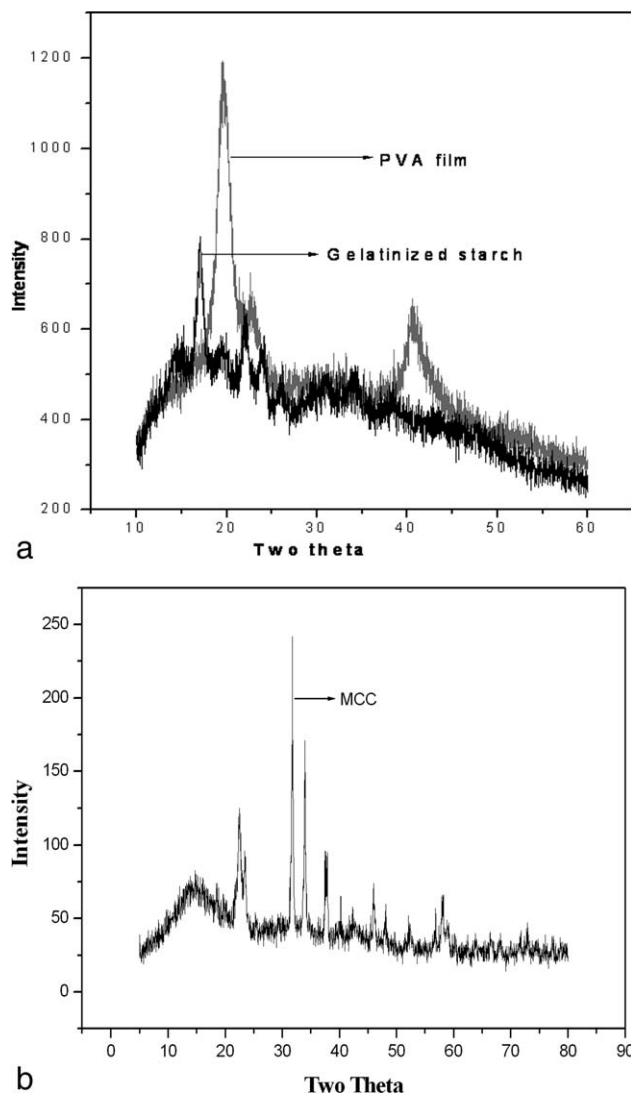


Figure 3 The XRD patterns of (a) starch with 30 wt % glycerol and PVA with 30 wt % glycerol and (b) MCC.

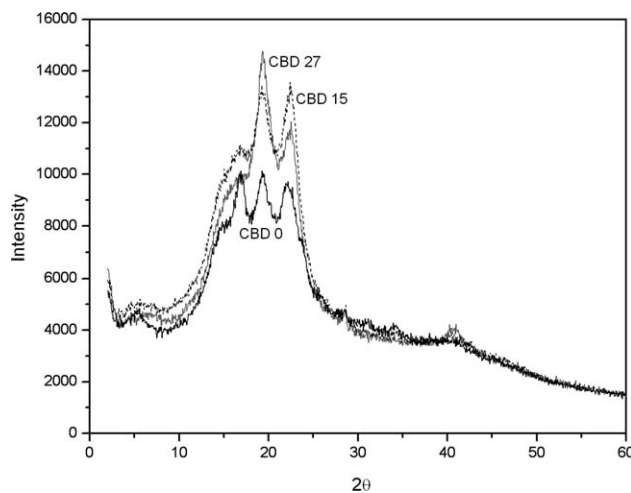


Figure 4 The XRD pattern of the unreinforced starch/PVA control sample before and after 15 and 27 days of biodegradation designated as CBD0, CBD15, and CBD27, respectively.

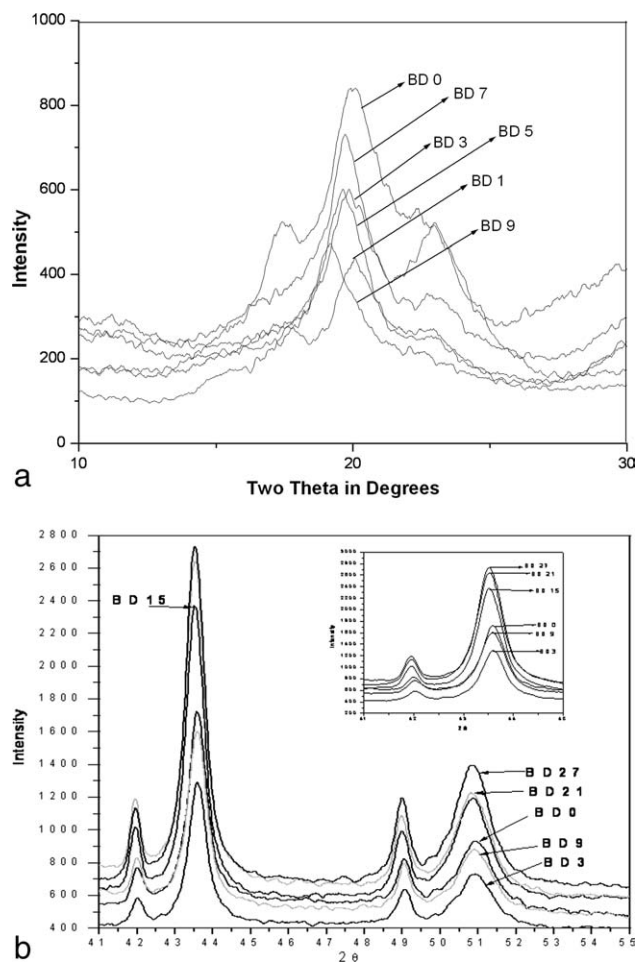


Figure 5 The XRD patterns of the starch/PVA/MCC (starch : PVA, 1 : 1 by weight, with 30 wt % glycerol and 10 wt % MCC based on the total dry weight of starch and PVA) biocomposite films before and after biodegradation (a) in the range $2\theta = 10^\circ - 30^\circ$ and (b) $41^\circ - 55^\circ$.

27 days. This indicates that initially a part of the starch fraction was consumed by the microorganisms, which lowered the 17° peak, while another part of starch was reorganized, which increased the 22° peak intensity. But with further degradation, the remaining fraction of starch also began to degrade and the intensity of 22° peak decreased.

Figure 5(a,b) show the XRD peaks of the starch/PVA/MCC biocomposite films before and after biodegradation. In Figure 5(a), BD0 showed a sharp peak at 19.9° , which was due to the contribution of PVA. A second prominent peak appeared at 17.4° due to starch molecules. A broad peak with a small hump appeared at 22° , which might be attributed to both starch and MCC. In BD3, the intensity of all the peaks was lowered. In BD9, 19.9° peak became sharper and the 17.6° peak disappeared completely. This might be due to higher consumption of starch by the microorganisms and increasing prevalence of PVA. With the increase of biodegradation time, the 19.8° peak became sharper indicating the rise in

crystallinity of PVA. The intensity of the PVA peaks at 42° , 43° , 49° , and 51° also increased significantly in the biocomposites with the biodegradation time [Fig. 5(b)].

The XRD observations indicated that the MCC reinforced films had a higher increase in their crystallinity due to biodegradation than the control samples and hence, they were more resistant to degradation which was reflected in the weight loss graph (Fig. 1). The increase was not so pronounced in the control samples where MCC was absent. Similar change in crystallinity of PVA due to degradation of starch was reported by Jayasekara et al.¹¹

The DSC curves of the control sample before and after biodegradation are shown in Figure 6(a-c). The control sample before biodegradation (CBD0) showed a glass transition at 172°C and a melting peak at 220°C during the first heating cycle [Fig. 6(a)]. After 15 days of biodegradation (CBD15), the glass transition shifted to 178°C and melting point was seen at 190°C . While in CBD27, the glass transition was more prominent and was observed at 201°C . The melting peak shifted to 226°C . During cooling, melt crystallization was evident in CBD27, but not in CBD0 and CBD15 [Fig. 6(b)]. During the second heating, only CBD27 showed a melting endotherm [Fig. 6(c)]. This clearly shows that the crystallinity of PVA increased significantly after 27 days degradation.

Figure 7(a) shows the DSC thermograms of the biocomposite samples corresponding to first heating before and after degradation in compost. Any structural change, which influences the molecular mobility of the polymers, is reflected in its thermal transitions. BD0 exhibited a glass transition at 45°C and showed a small endothermic hump at 204°C , which could be attributed to the melting of PVA. PVA, in spite of being a crystalline polymer, exhibited a small melting endotherm. This could be due to the presence of extensive physical crosslinks between PVA, starch molecules and MCC, which hindered their mobility. In BD3, a sharp but small peak appeared at 223°C , which could be attributed to melting of PVA molecules. This melting peak became sharper with the increase in biodegradation time. This shift of melting peak from 204 to 223°C , the increase in melting peak intensity and increase in melting enthalpy from 8.3 J/g for BD0 to 33.2 J/g for BD3, 30.68 J/g for BD9, 68.3 J/g for BD15, 63 J/g for BD21, and 70 J/g for BD27 clearly revealed the increase in crystalline packing of PVA molecules on biodegradation. Thus, it was apparent that degradation of the starch and MCC resulted in a crystallinity change of the PVA. Similar observation was reported by other researchers also.¹⁹ In all samples after biodegradation, a broad melting endothermic peak was evident around 76°C which could be ascribed to the

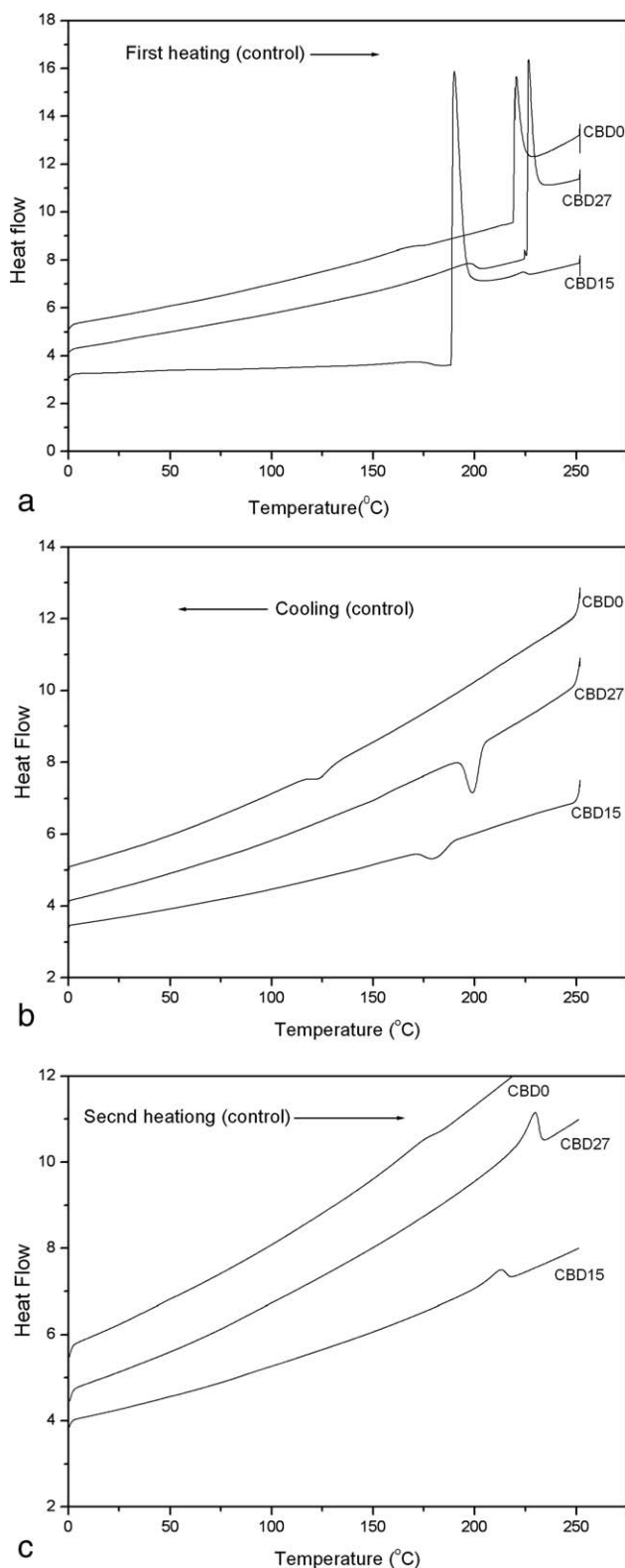


Figure 6 DSC curves of the unreinforced starch/PVA (starch : PVA, 1 : 1 by weight, with 30 wt % glycerol) control sample before and after 15 and 27 days of biodegradation (a) first heating, (b) cooling, and (c) second heating. CBDX indicates the control samples, where X is the number of days of biodegradation.

regeneration of starch. It could be proved by disappearance of these peaks during the second round of heating, because the crystals regions were melted at high temperature.

The cooling curves are shown in Figure 7(b). On cooling, BD0 showed a small exothermic melt crystallization peak at 177°C and in BD3, the melt

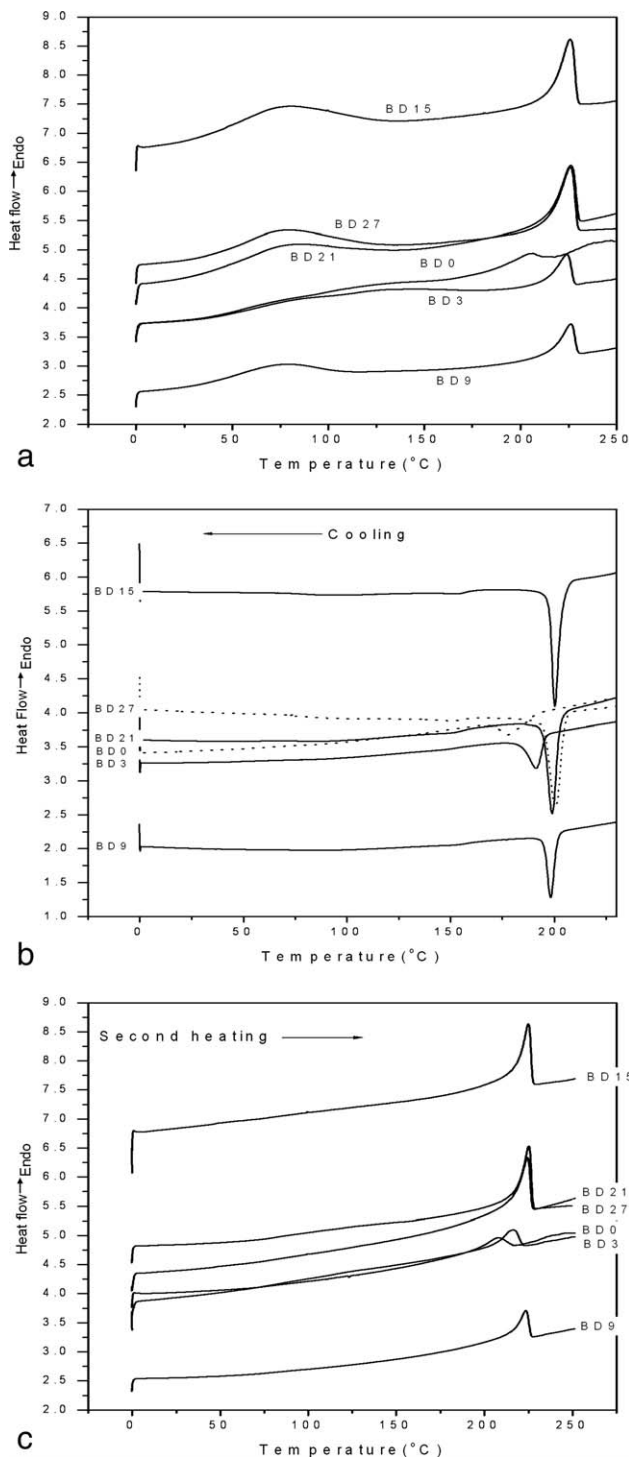


Figure 7 The DSC thermograms of starch/PVA/MCC biocomposite films before and after degradation (a) first heating, (b) cooling, and (c) second heating.

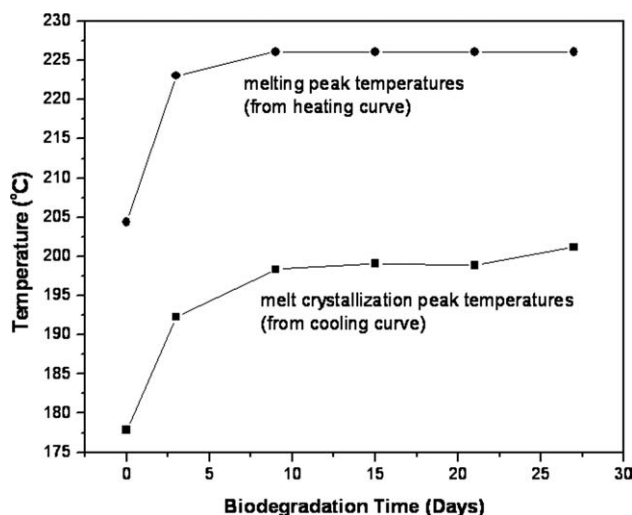


Figure 8 The variation of melting peak temperature and cold crystallization temperature of starch/PVA/MCC biocomposite films as a function of biodegradation time.

crystallization began at 191°C. In BD9, it was further shifted to 198°C, while in BD21 and BD27, the melt crystallization began at 200°C [Fig. 7(b)]. The rearrangement of the PVA molecules from molten state to a close packed ordered structure was much more facilitated after biodegradation and melt crystallization began at a faster rate. This indicated the lowering of the physical crosslinks, which increased the mobility of the PVA molecules. During second heating also [Fig. 7(c)], the PVA melting peaks became sharper with increase in biodegradation time. The change of melting peak temperatures and the melt crystallization temperatures as a function of biodegradation time, shown in Figure 8, clearly indicated the increased crystallinity of PVA component of the films.

Thus, DSC results also revealed that the increase in crystallinity of the starch/PVA/MCC films on biodegradation in aerobic compost environment was much higher than that in the control samples. These results were in agreement with the XRD observations. Therefore, it can be concluded that the increased crystallinity was responsible for lower weight loss in the biocomposite samples and lead to a two-phase degradation behavior.

Isolation of two fungi for degradation of starch and PVA respectively, was done from compost by serial dilution method. Then replica plating was done separately on minimal media where the sole source for carbon was starch and PVA, respectively. The two fungi showing most growth for starch and PVA were isolated from the plate of minimal media. The optical microscopic images of these two fungal strains isolated for starch and PVA are shown in Figure 9(a,b) respectively. As the sizes of the fungi colonies were larger than the bacteria in minimal media, hence it could be said that degradation by

fungi was predominant than that by bacteria. After 5 days of degradation of the composite films by each fungus, the degraded films were observed under optical microscope, which confirmed the susceptibility to degradation by fungi.

CONCLUSIONS

Incorporation of MCC (10 wt %) in starch/PVA matrix decreased the rate of biodegradation in comparison to the unreinforced starch/PVA film. SEM investigations showed that the films lost their structural integrity and the films became highly porous with increase in composting time. The melting peak of PVA component shifted from 204 to 223°C with a significant increase in melting enthalpy, while a melting hump appeared at 76°C for the remaining starch fraction in the degraded biocomposite samples. This reflected a loosening in the packing of remaining starch molecules and increase in compactness of PVA molecules. The increase in crystallinity of PVA due to biodegradation was much higher in the biocomposite films than that observed in the

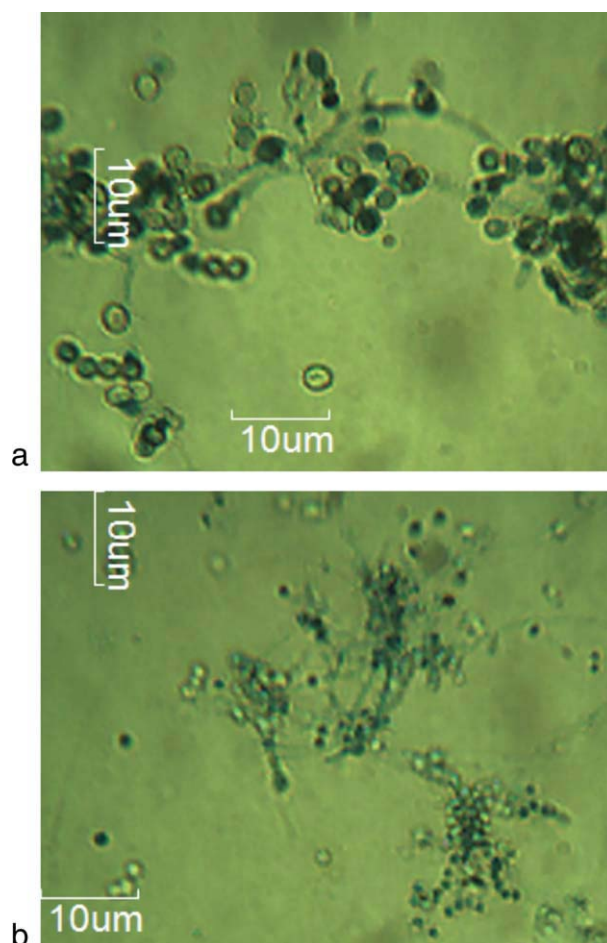


Figure 9 Fungal strains for (a) for degrading starch and (b) for degrading PVA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

control samples. This was responsible for the decreased weight loss of the biocomposites. These results gave an indication that by incorporating MCC in different amounts, the rate of degradation of starch/PVA film could be modified, which can open their new areas of application.

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