Study of Compostable Behavior of Jute Nano Fiber Reinforced Biocopolyester Composites in Aerobic Compost Environment

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ABSTRACT: Jute nano fiber (JNF) reinforced biocopolyester-based composite sheets were prepared with 2% and 10 wt % filler loading and compostability tests were performed in simulated aerobic compost environment at ambient temperature for a period of 50 days. Weight loss study revealed that the incorporation of JNF enhanced the rate of degradation significantly. The unreinforced sample exhibited a steady loss in weight, whereas, the JNF reinforced samples showed three phase degradation. They had a steady weight loss up to 30 days followed by a plateau zone between 30 and 40 days and after that, there was again an increase in weight loss up to 50 days. The biodegraded samples were investigated for their change in molecular weight by Gel Permeation Chromatography (GPC). The change in structure was examined by Differential Scanning Calorimetry (DSC) and morphological change was observed by Scanning Electron Microscopy (SEM). Molecular weight study revealed the fact that Biocopolyester molecules had a significant breakdown in chain length during melt mixing with 10 wt % JNF, which was much less predominant in 2 wt % JNF loaded composites. Such a decrease in chain length and presence of 10 wt % JNF might have facilitated the biodegradation process resulting in highest weight loss. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2952–2958, 2012

Key words: biopolymers; composites; differential scanning calorimetry; gel permeation chromatography (GPC)

INTRODUCTION

Use of renewable resources as reinforcement in composites is one of the probable solutions towards sustainable development.[1,2] The growing of global environmental concern, high rate of petroleum depletion, and new environmental regulations have forced the material scientists to search for new natural fiber reinforced composite materials that are compatible with the environment. Biodegradable composites have thus emerged from biodegradable polymers and natural fibers.[3–5]

In recent years, researchers are investigating the nature of biodegradation of different types of natural fiber reinforced polymer matrix composites to study their impact on environment and to judge their suitability in context of waste disposal. Barreto et al.[6] reported the biodegradability of phenolic resin (matrix) based on cashew nut shell liquid, reinforced by natural jute fibers. Biodegradability of PBS/jute fiber composites was investigated by Liu et al.[7] by compost soil burial test. Regarding the effect of fiber content on the biodegradability of composites, the order of higher weight loss was found to be PBS/10% jute composite > PBS/20% jute composite > PBS/30% jute composite > pure PBS film > bulk jute fiber. In another study, biodegradabilty of the composites of aliphatic polyesters (PCL, PHBV, PBS, and PLA) with untreated abaca and acetic anhydride-treated (AA)-abaca fibers was investigated by soil burial test by Teramoto et al.[8] Kim et al.[9] prepared rice husk flour (RHF) and wood flour (WF) filled polybutylene succinate (PBS) biocomposites and reported that the addition of agro-flour to PBS produced a more rapid decrease in the tensile strength, notched Izod impact strength, and percentage weight loss of the biocomposites during the natural soil burial test.

Apart from these biocomposites, biopolymers are also being examined by the researchers for their biodegradation behavior. Rizzarelli et al.[10] investigated

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controlled soil burial and enzymatic degradation of different aliphatic copolyesters. Some researchers reported that in comparison to poly(propylene), its blend with poly (hydroxybutyrate-*co*-valerate) in the ratio of 4 : 1, had a higher microbial attack with major changes in soil.[11] Tserki et al.[12] showed that poly (butylene succinate-*co*-butylene adipate) (80/20) was the polyester possessing good mechanical properties and quite high biodegradability. Cosgrove et al. studied biostimulation and bioaugmentation with polyurethane and used some fungi for this purpose.[13]

Researchers are now focusing their work on developing cellulosic nanofiller reinforced biocomposites.[14] In our previous work, we reported various properties of jute nanofiber reinforced biocopolyester composites.[15] However, for real life application of these materials, their biodegradation study is required. In this work, the biodegradation behavior of jute nano fiber reinforced biocopolyester composites was investigated in simulated aerobic compost environment and isolation of one fungus, which was expected to degrade the biocopolyester, was done from the compost. The degraded polymers were characterized for their weight loss, molecular weight determination, the morphological study, and the change in molecular structure was examined with differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

The biocopolyester used in this study was [poly (tetramethylene adipate-*co*-terephthalate)], whose tradename was Eastar Bio GP copolyester, Eastman Company USA. Jute felts were obtained from the local market. NaOH, Dimethyl sulphoxide (DMSO) and concentrated H_2SO_4 (laboratory-grade, Merck) were used for the preparation of jute nano fibers (JNF).

Preparation of JNF

Shredded jute felt was soaked in 5*M* NaOH solution and heated at 80°C for about 2 h. After neutralization with 10% H_2SO_4 solution, the mass was dried at 70–80°C for 24 h. The dried mass was then dipped in DMSO (liquor ratio 1 : 20) followed by heating at 70°C on a water bath. Again after washing several times with distilled water, it was oven-dried at 70–80°C for 3 h. Finally, it was acid hydrolyzed with 47% H_2SO_4 solution to obtain JNFs following the standard procedure of Dong et al.[16] The JNFs were then freeze-dried at −110°C for two days.

Preparation of biocomposites

Composites were prepared by incorporating JNF as filler into the poly(tetramethylene adipate-*co*-terephthalate) (BCP) matrix by melt mixing (Brabender 30/50 E apparatus) in 2 wt %, 2 and 10%. The resultant mass was then compression molded to form sheets. Another set was also prepared by melt mixing of poly(tetramethylene adipate-*co*-terephthalate) followed by compression molding without any filler loading in it. The sample code used here is BCPX, where X is the amount of filler present in the material and BCP stands for bicopolyester. Only 2 wt % (2 and 10%) were chosen in this study because they represented two distinctly apart filler loadings, one low and the other high. The effect of filler content on the extent of biodegradation was our main focus and hence, selecting 2 and 10% reflected the extreme effects.

Compost

The aerobic compost was prepared by using a composition stated in literature.[17] The composition of the compost in dry weight is shredded leaves, 40.8%; cowdung, 11.4%; white bread, 2%; newspaper, 15.8%; saw dust, 7.8%; food waste, 19.2%; urea, 3%. The biodegradation was carried out in a perforated glass pot.

Biodegradation

The biodegradation study was performed in compost with specimen size 20 × 20 × 1.6 mm^3 for 50 days.[17] The samples were placed 4 cm beneath the surface of the compost. The temperature was ambient ranging from 20 to 25°C. The moisture content was maintained by spraying water at regular time intervals. The sample code used here is as BCPXBDY where Y is the biodegradation days.

CHARACTERIZATION

Weight loss study

Three samples for each composition were taken out from the compost after specific time interval. After washing with distilled water thoroughly, samples were dried in vacuum at 30°C until a constant weight was reached. The average % weight loss was studied by using this formula:

$$\%\text{weight loss} : \frac{\{W_0 - W_t\} \times 100}{W_0}$$

Determination of weight average molecular weight (M_w)

Weight average molecular weight (M_w) and polydispersity index (M_w/M_n) of the biocomposite samples before and after biodegradation were determined by Gel Permeation Chromatography (GPC) experiments

conducted in THF solution at 30°C at a constant flow rate of 1 mL min^{-1}. The instrument used was Perkin Elmer, USA Model: series 200 and included a PL gel 300 × 7.5 mm^2, 5 μm mixed column in series.

SEM analysis

Surface morphology of biodegraded samples were studied by HITACHI S-3400 Scanning Electron Microscope. Samples were coated with a thin layer of gold and observed at 15 KV, 500 X magnifications.

Thermal analysis

A differential Scanning Calorimetric (DSC) measurement was carried out in nitrogen atmosphere by using Perkin Elmer Pyris Diamond calorimeter. Samples were heated from −50 to 175°C at a heating rate of 10°C/min and the corresponding heat flow was measured.

Isolation of fungus for degrading biocopolyester

Isolation was done from compost by taking out sample and by immersing it in normal saline solution. This solution was then serial diluted and inoculums were spread over the minimal medium where sole carbon source was the poly(tetramethylene adipate-*co*-terephthalate). Only fungus colonies were taken and streaked onto fresh media. The isolated fungus was taken for morphological observation. Screening was done by using the minimal media with this composition stated by Ishii et al.[18] The composition of the minimal medium was as follows: KH_2PO_4-1.0 g/L; $NaNO_3$-2.0 g/L; $MgSO_4$,$7H_2O$-0.5 g/L; KCl-0.5 g/L; $FeSO_2$,$7H_2O$-0.01 g/L; NH_4Cl-1.0 g/L, pH-6. 2% polymer was emulsified in the medium. For a solid medium 20 g/L agar was added to the medium. Polymer emulsion was prepared by grinding the matrix by a simple grinder and then emulsified in the medium.

RESULTS AND DISCUSSION

Jute fibers are lignocellulosic fibers. As the jute fibers were treated with NaOH solution, followed by DMSO, hence noncellulosic constituents were mostly removed and many gaps were created in-between the cellulose fibrils. As a result, during acid hydrolysis, the acid could easily penetrate within the fibrillar structures and an effective defibrillation and size breakdown took place. Figure 1 shows the defibrillation and structural breakdown of the jute fibers into nano size. The size of the jute nanofibers ranged between 50 and 250 nm. The mechanical properties of such JNF reinforced biocopolyester composites were reported in our previous work.[15]

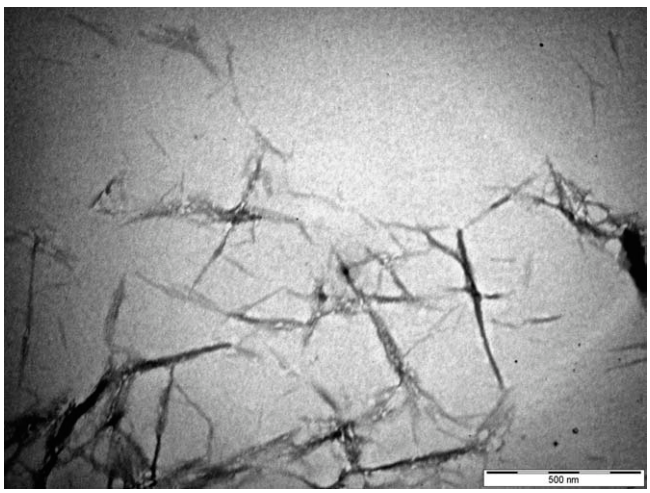

Figure 1 Jute Nano Fiber under TEM.

The biocomposite sheets reinforced with 2 and 10 wt % JNF were subjected to aerobic biodegradation in compost. The rate of biodegradation of the poly(tetramethylene adipate-*co*-terephthalate) laminates in the simulated compost environment was measured in terms of weight loss. In Figure 2, the biodegradation rates of the samples with 0, 2, 10 wt % filler loading are represented. The unreinforced sheet exhibited a steady rate of degradation throughout the entire period of observation. On the other hand, a three stage degradation process was evident with the filler-loaded samples. The filler containing samples, BCP 2 and BCP 10, exhibited an enhanced rate of biodegradation as compared with the unreinforced one during the first stage of biodegradation, up to a period of 30 days. Such accelerated rate of biodegradation might be attributed to the presence of jute nanofibers (JNF) which are easily biodegradable and facilitated the degradation of polymer molecules by the micro organisms causing a significant weight loss.

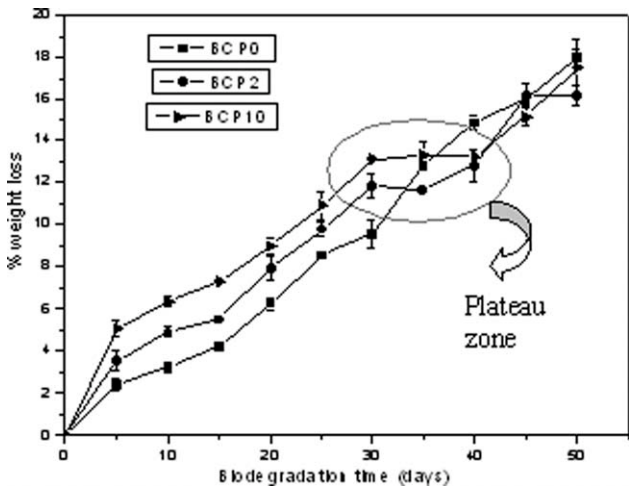

Figure 2 Change in weight loss of the samples with biodegradation time.

As evident from Figure 2, between 30 and 40 days, there was a plateau zone for BCP 2 and BCP 10, when there was no further weight loss of the samples. However, BCP 0 did not show any plateau effect and had a steady loss in weight up to 50 days. After 40 days, both BCP 2 and BCP 10 showed their third phase of degradation when they had a steady loss in weight up to 50 days.

The weight loss curves give an indication that presence of green fillers dispersed within the matrix helped faster weight loss in the initial stage, but after a certain period, the weight loss was delayed. Again gradually, the loss in weight increased. Similar delay in weight loss has been reported by some researchers.[19]

The weight average molecular weights (M_w) of the samples before and after composting were determined by GPC, shown in Figure 3(a). In BCP0, the average molecular weight changed from 21,428 g/mol (BD0) to 12,220 g/mol after 30 days and 12,681 g/mol after 50 days of biodegradation. The significant decrease in average molecular weight after 30 days of composting indicates effective fragmentation of the long chain molecules into smaller ones during this period. This increased the PDI value from 3 (BD 0) to 4.6 (BD 30). This was followed by a little increase in average molecular weight after 50 days of degradation which might be due to the consumption of lower fragments of the molecules by the micro organisms. This is further confirmed by slight decrease in PDI values [4.1 for BD50, shown in Fig. 3(b)].

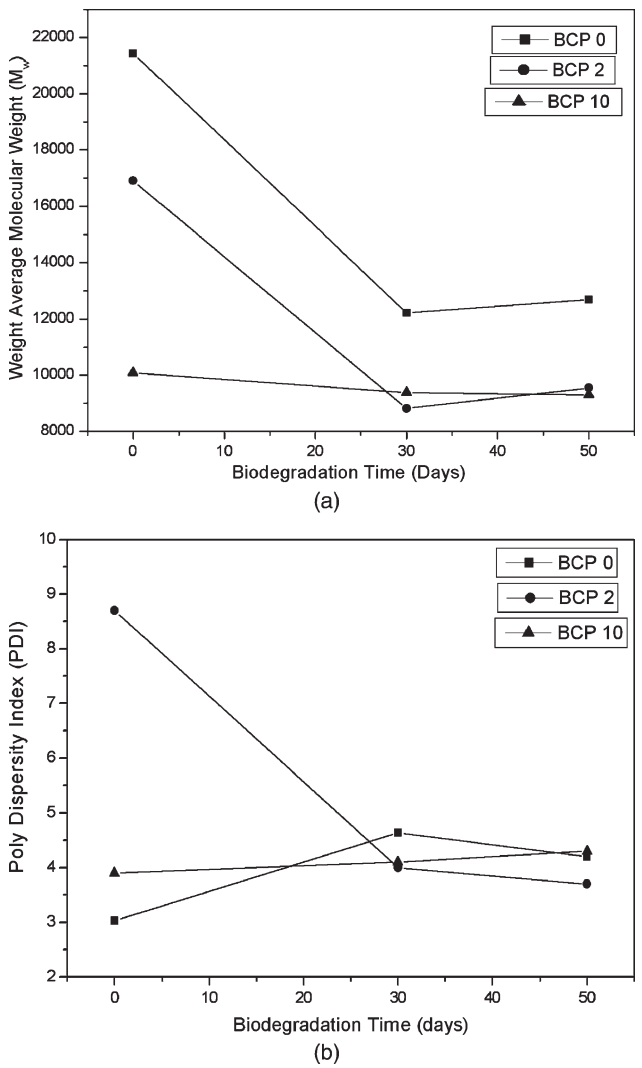

Figure 3 (a) Change in weight average molecular weight (M_w) with biodegradation time. (b) Change in polydispersity index (PDI) with biodegradation time.

In BCP2, the initial molecular weight (BD0) was found to be 16,902 g/mol. This was lower than that observed in BCP0BD0 (21,428 g/mol). It suggests that some chain length breakdown took place during melt mixing with 2 wt % JNF. So the PDI also became high in BCP2 (8.7). The molecular weight and PDI of BCP2 changed to 8818 g/mol and 4 after 30 days of degradation and 9550 g/mol and 3.7 after 50 days of degradation. This indicates further breakdown of the long chain molecules and consumption of lower fragments during the biodegradation period.

The M_w observed for BCP10 BD0 was 10,079 g/mol, which was significantly lower than that of BCP0BD0 samples (M_w, 21,428). The PDI value was found to be 3.89. This indicates that there was a considerable lowering in the chain length of the molecules during melt mixing with 10 wt % JNF and the molecular breakdown was uniform which resulted in a lower PDI (3.9) unlike the high PDI value observed in BCP2 BD0 (8.7). The M_w of BCP10BD30 and BCP10BD50 were observed to be 9375 g/mol and 9292 g/mol, respectively and the PDI was almost same before and after degradation. This suggests that in BCP10, the molecules being of smaller length and remaining in intimate contact with 10 wt % JNF, might have been broken down entirely by the micro organisms, which did not change the average molecular weight and PDI of the samples.

The morphology of the samples during composting was studied by the SEM (Fig. 4). All samples (unreinforced, with 2%, 10% filler) showed comparatively smooth surface before degradation. The activities of the complex microorganisms lead to the erosion of the sample surfaces and the formation of small pits. Further degradation merged the pits, produced large erosion holes and completely cracked the surface. The JNF loaded composites, particularly, BCP10 showed a distinct grainy morphology after 50 days of degradation which was not seen in BCP0.

The samples were subjected to DSC analysis in order to investigate the structural changes that occurred during biodegradation. The DSC curves of the samples before and after biodegradation (30 and 50 days) are shown in Figure 5(a–c). All the samples

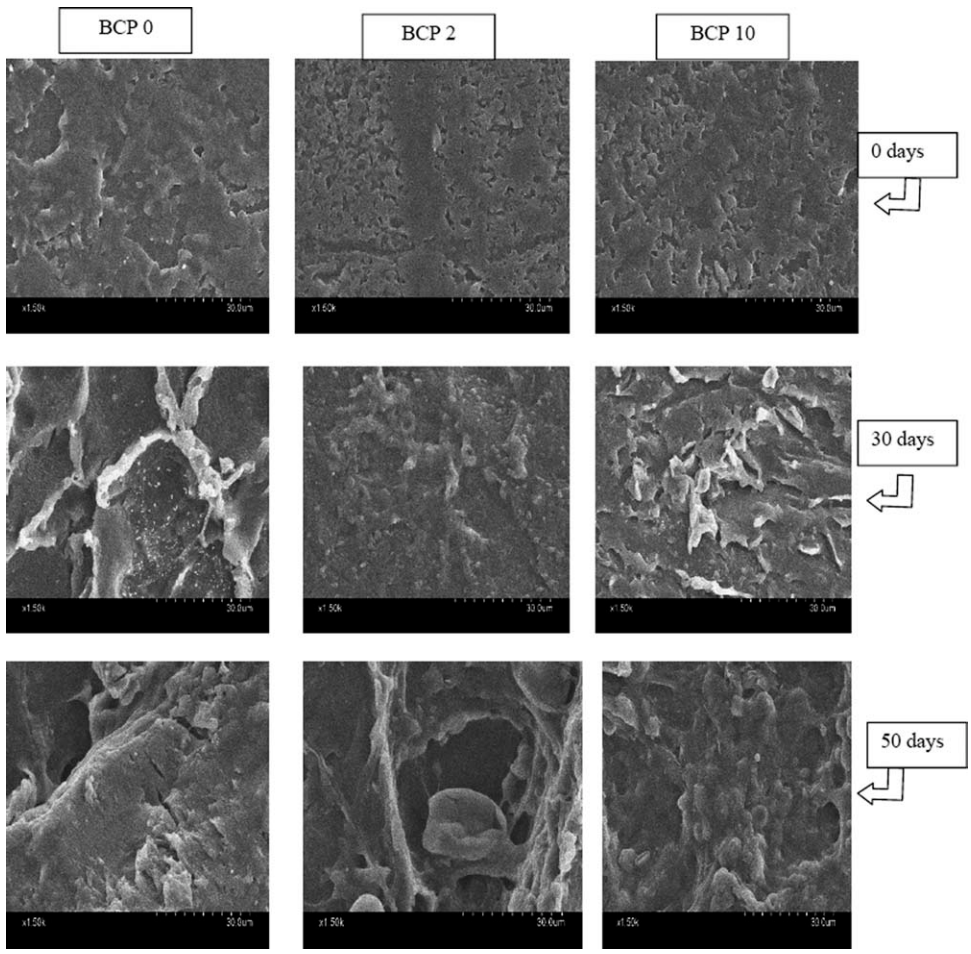

Figure 4 SEM pictures of the biodegraded samples before biodegradation, biodegradation after 30 days and biodegradation after 50 days.

BCP 0, BCP2 and BCP10, exhibited two glass transition temperatures (T_g) before biodegradation [Fig. 5(a)]. A sharp and steep glass transition was observed at 45°C, whereas, a broad and mild T_g was observed at around −6°C. Unlike BCP0 and BCP10, BCP2 only exhibited a small but sharp endothermic peak at 121°C, which could be ascribed to the presence of varied length of molecules as evident from the very high PDI value of BCP2 [Fig. 3(b)].

After 30 days of biodegradation, BCP0 exhibited a small enthalpic relaxation peak at −29°C and a small but sharp melting endotherm at 115°C. These peaks were not observed in BCP2BD30 and BCP10BD30. This was supported by the slightly higher PDI value of BCP0BD30 than that of BCP2BD30 and BCP10BD30. All the three samples showed a broad melting endotherm at 48°C and 71°C.

After 50 days of biodegradation, a glass transition (T_g) was observed at 41°C in all the three samples indicating further degradation and easier segmental mobility of the molecules. A second glass transition was evident at 76°C in all the samples which merged with their enthalpic relaxation peaks. This could be due to the mobility of the higher fragments of molecules. Similar enthalpic relaxation phenomenon at the glass transition temperature was reported by some researchers in case of aliphatic polyesters.[20] A small, sharp melting endothermic peak was observed at 128°C in BCP0BD50, and the endothermic relaxation peak observed at −29°C in BCP0BD30 disappeared after 50 days. This confirmed the fact that the lower fragments of molecules were consumed by the micro organisms during this time period. In BCP10BD50, an exothermic cold crystallization peak was observed at 105°C, which was not evident in BCP0BD50 and BCP2BD50. This was supported by the slightly higher PDI value of BCP10BD50 after 50 days (4.3) compared with that observed after 30 days (4.1).

Thus, it can be concluded that different length of molecular fragments were formed due to biodegradation resulting in a wide PDI value. The extent of shortening of the chain length and complete breakdown of the molecules were dependent on the initial length of the molecules, their molecular weight distribution pattern and the presence of JNF.

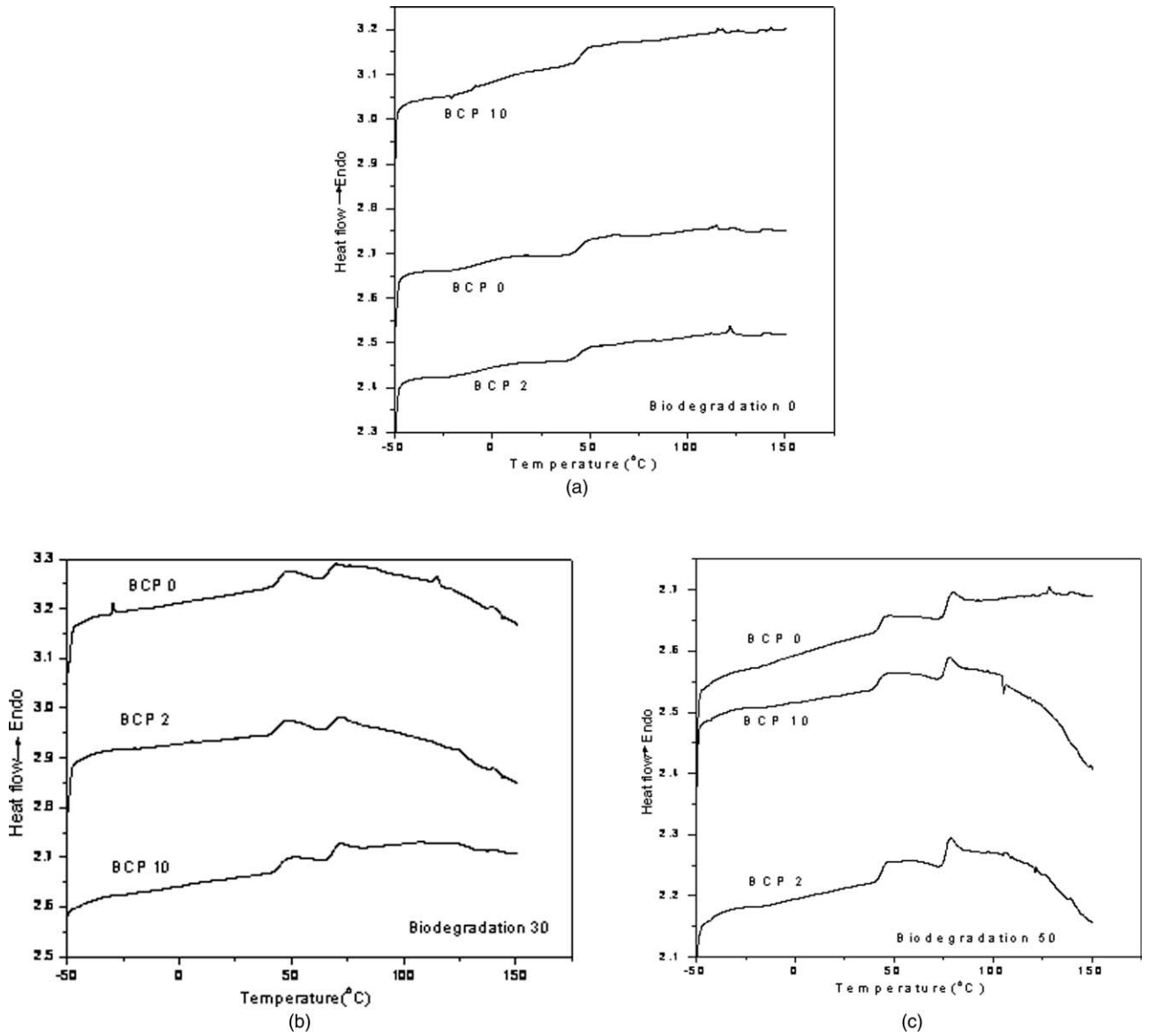

Figure 5 DSC thermograms of the biocomposites. (a) before biodegradation. (b) biodegradation after 30 days. (c) biodegradation after 50 days.

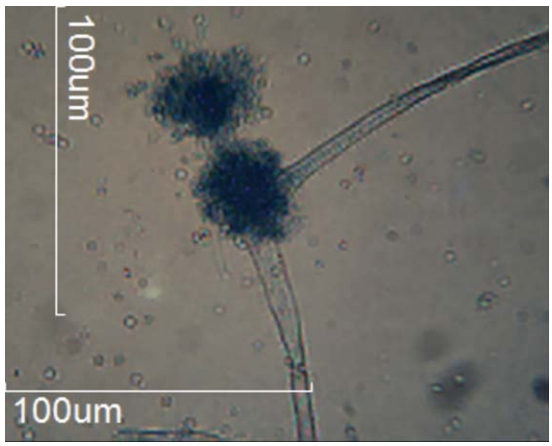

Figure 6 Isolated fungi observed under 40X simple microscope. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As jute is easily biodegradable, hence the isolation of fungus which can degrade the matrix was done. The isolated fungus, shown in Figure 6, showed most growth in minimal media where sole source of carbon was biocopolyester. This means that the efficacy of fungus to degrade the matrix was very high. For that reason it can help in the bioaugementation process during waste disposal.

CONCLUSION

An aerobic biodegradation study was carried out with 2 and 10 wt % JNF loaded biocopolyester matrix-based composites. The structural changes due to biodegradation were investigated. The JNF-loaded composites had a higher rate of degradation compared

with that of the unreinforced one (BCP0). BCP0 showed single phase degradation, while three phase degradation was observed for BCP2 and BCP10. A steady weight loss was evident up to 30 days for BCP2 and BCP10. It was followed by a plateau zone between 30 and 40 days and after 40 days, the weight loss increased steadily. The determination of weight average molecular weight of the samples before and after biodegradation gave an idea about the nature of molecular breakdown in the samples. BCP0 and BCP2 had a significant drop in their molecular weights after 30 days of degradation which could be attributed to the scission of chain length of the polymer molecules by microbes. Between 30 and 50 days, there was slight increase in average molecular weight which indicated the complete breakdown of the lower fragments of molecules by microbial attack. The degradation behavior of BCP10 was different. The molecular weight decreased considerably during melt mixing process during the fabrication of BCP10 composites. Such smaller length of molecules and presence of higher amount of JNF facilitated the weight loss process. The molecules were fully consumed by the micro organisms which did not change the average molecular weight and the PDI of BCP10 after biodegradation. DSC analysis revealed two glass transition temperatures at $-6^{\circ}C$ and $48^{\circ}C$ in the nondegraded samples. Breakdown of long chain molecules into smaller ones and removal of the lower fragments of molecules shifted the glass transition to a higher temperature. Removal of smaller molecules due to biodegradation enhanced the ease of mobility of the remaining larger molecular fragments, which was reflected in their glass transition, enthalpic relaxation, cold crystallization behavior.

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