

Biodegradability Studies on Natural Fibers Reinforced Polypropylene Composites

Sanjay K. Chattopadhyay,¹ Sanjay Singh,¹ Nilay Pramanik,¹ U. K. Niyogi,¹
R. K. Khandal,¹ Ramagopal Uppaluri,² Alope K. Ghoshal²

¹*Shriram Institute for Industrial Research, New Delhi, Delhi 110 007, India*

²*Indian Institute of Technology, Guwahati, Assam 781 039, India*

Received 17 August 2010; accepted 23 November 2010

DOI 10.1002/app.33828

Published online 16 March 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Various composites of polypropylene (PP) produced using natural fibers such as pineapple leaf fiber, banana fiber, and bamboo fiber were studied for their degree and rate of aerobic biodegradation. Composites used contained 10, 15, and 50% volume fractions of pineapple leaf fiber, banana fiber, and bamboo fiber, respectively, which are the optimum fiber percentages of the respective composites as reported by these authors in their previous works. Cellulose has been used as positive reference material. All the composites exhibited partial biodegradation in the range of 5–15% depending on the fiber content. Degradation had not taken place in the covalent

ester linkages between the natural fiber and the MA-g-PP compatibilizer but in those areas of the fibers which have remained only physically embedded in the resin matrix. Thus, although natural fibers reinforced PP composites are not excellent biodegradable material, they can address to the management of waste plastics by reducing the amount of polymer content used that in turn will reduce the generation of nonbiodegradable polymeric wastes. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2226–2232, 2011

Key words: biodegradable; composites; fibers; polypropylene; waste

INTRODUCTION

Plastics, the wonder materials of present times have become indispensable in many ways because of their versatility, durability, strength, and cost-effectiveness. The commodity polymers such as polypropylene (PP) and polyethylene (PE) with which we are most familiar were developed to provide durability and resistance to various forms of degradation including photodegradation, as well as attack from fungi and microbial agents. However, the disposal of plastic products that are nonbiodegradable has become the major cause of concern for the environmentalists. Developments of biodegradable plastics or modifying the existing ones to make them biodegradable have become the focus of research world over. The characteristics of the biodegradable plastics should be such that they cannot only be processed alike conventional polymers in the standard processing equipment or machinery and retain their end use property requirements, but could also be readily degradable in a biologically rich environment. Rising per capita consumption of plastics at the existing rate would need landfill sites all round. Thus, the landfill material should be made to

degrade, to relinquish the space it once occupied.¹ The goal should be to improve the ecological balance while appreciably decreasing the land filling.

It has been the experience so far that for developing biodegradable plastics the monomers will have to be derived from the renewable resources rather than from the petroleum resources. Otherwise, the degradability can be initiated in the nonbiodegradable plastics by incorporation of special additives which become responsible for degradation of plastics. In any case it will add to the cost if plastics are made degradable. Since biodegradable polymers are relatively costly, their use would be restricted to specific high-value added applications only. The high prices of the synthetic biodegradable/compostable plastics available in the market have brought about renewed interest in their research and development. Biodegradable plastics from the time of their first inroad into the market have graduated steadily into a matured industry today. Newer polymers with more susceptibility to microbial attack are available in the market. International Standards have been developed, which assess the propensity of the material to degrade biologically. Researchers have developed composites in which different plant fibers serve both as reinforcement and matrices, the concept originating from chemical modification of wood to thermoplastic by etherification or esterification.^{2–5} Development of biodegradable composites based on

Correspondence to: A. K. Ghoshal (aloke@iitg.ernet.in).

natural fiber with biopolymers such as polylactic acid, starch-plastics, soyabean-plastics, cellulosic-plastics, and polyhydroxy alkanooates (PHA's) have also been reported extensively.^{6–10}

Natural fiber reinforced composites as alternative to artificial fiber composites have advantages like renewable, environmental friendly, low cost, light-weight, and high specific performance ascribed to the natural fiber. The biodegradability of plastics is dependent on the chemical structure and constitution of the composites. Biodegradation is brought about by biological activity predominantly by enzymatic action of microorganisms and can be measured by standard tests in a specified period of time.

Over the past few years, considerable number of studies has been performed on biodegradable composites containing biodegradable plastics with reinforcement of biodegradable natural fibers¹¹; but to the best of our knowledge, no such studies have been carried out or reported on biodegradability of composites made of synthetic polymers such as PP or PE with reinforcement of renewable natural fibers such as pineapple leaf fiber, banana, or bamboo fiber. The advantages of reinforcing the PP for improved physico-mechanical properties have already been demonstrated in our recent publications.^{12–15} Today, biodegradability is tested by measuring the end products of microbial metabolism instead of measuring the resistance of the plastic material to microbial growth as was done earlier. This study is to assess the degree and rate of aerobic biodegradation of high strength composites reinforced with biofibers such as pineapple leaf fiber, banana, and bamboo fiber in PP matrix, in contact with soil under laboratory conditions. The PP–natural fiber composites were exposed to soil as a matrix and a source of inoculum and then aerobic biodegradability was determined by measuring the CO₂ evolved by the microorganisms as a function of time, and assessing the degree of biodegradability. The biodegradation study was performed according to the ASTM D 5988-96.

An attempt has been made here to make an estimation of the time period over which the PP–natural fiber composite will remain intact in an aerobic soil environment and assess their extent of biodegradation in relation to composting conditions. The time taken to reach the plateau level of CO₂ evolution and the extent of degradation will suggest the rate and degree of biodegradability of the natural fiber-reinforced PP composites.

EXPERIMENTAL

Apparatus

Soil contact incubation apparatus fabricated from glassware procured locally as per ASTM D 5988-96

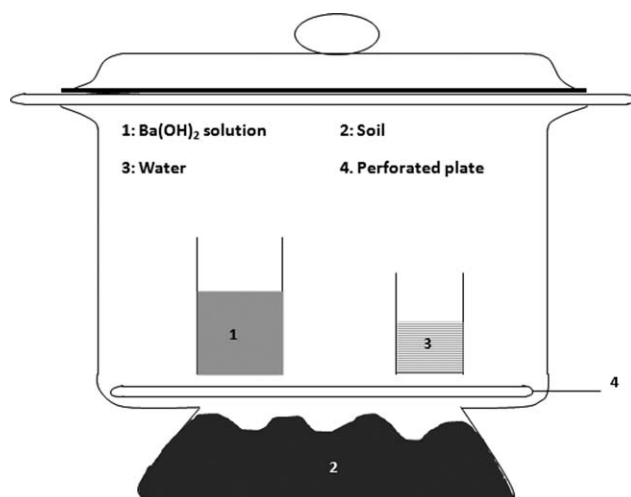


Figure 1 Soil-contact incubation apparatus.

(Standard Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials after Composting) consisted of (Fig. 1) the following:

1. a set of sealed air-tight 150 mm diameter soil incubation vessels (similar to desiccators) of 3 L internal volume. Three such vessels (Fig. 1) were taken for soil only control, three for positive control material, i.e., cellulose, and three for each composite test specimens of pineapple leaf fiber, banana, and bamboo fiber reinforced PP.
2. sets of 150 and 100 mL beakers equal in number to soil incubation vessels (for placing barium hydroxide solution and distilled water, respectively),
3. perforated plates to hold the beakers above the soil inside each incubation vessels, and a
4. darkened chamber or cabinet in which temperature was maintained at 21°C ± 2°C.

CO₂ evolved due to degradation reacted with barium hydroxide and precipitated as barium carbonate. The amount of CO₂ produced is determined by titrating the remaining barium hydroxide with 0.05N hydrochloric acid to a phenolphthalein end-point.

Chemicals

1. Ammonium phosphate, ((NH₄)₂ HPO₄), 4.72 g/L,
2. Barium hydroxide solution, [(Ba(OH)₂, 0.025N], prepared by dissolving 4.0 g of anhydrous Ba(OH)₂ per liter of distilled water. 15 L of this solution was prepared by filtering it free of solid material, normality confirmed by titration with standard acid, and then sealed stored as a clear solution to prevent absorption of CO₂ from the air.

TABLE I
Details of Biodegradability Test as per ASTM D 5988

Description of material	Weight of material (g)	Fiber volume (%)	Organic carbon content (%)	Cellulose (%)	Biodegradation (%)	Test duration (days)	pH of soil medium (before)	pH of soil medium (after)
Positive control (cellulose)	2.5	100	42.36	100	85	90	7.2	7.2
Bamboo-PP composite	2.5	50	66.57	60	15	90	7.2	7.2
PALF-PP composite	2.5	10	81.14	81	10	90	7.2	7.3
Banana-PP composite	2.5	15	81.74	64	5	90	7.2	7.1

The total dry solids and volatile solids contents (based on total dry solids) of the soil are 42.6% and 26.4%, respectively.

3. Hydrochloric acid, 0.05N HCl
4. Phenolphthalein indicator

All the reagents and chemicals were of analytical grade and procured from S. D. Fine Chemicals (Mumbai, India) through their authorized agents in New Delhi, India.

Soil

The soil taken was a mixture of equal parts (by weight) of sand and composted manure from livestock excrement. The soil was sieved through 2 mm sieve. Plant materials, stones, and other inert materials were removed. The soil was then stored in a sealed container at $4^{\circ}\text{C} \pm 1^{\circ}\text{C}$. The pH of the soil was kept about 7. The solid content analysis was determined using the APHA-AWWA-WPCP 2540 D.¹⁶ The total dry solid content was determined from the weight loss after drying in an oven for 24 h at a temperature of 105°C , and allowing the sample to cool in a desiccator. The volatile solid content was obtained after incinerating the dried solid in a furnace at 550°C for 2 h, and subtracting the amount of residues obtained from the total dry solid content. Upon analysis, the soil used for testing had 42.6% total dry solids content and 26.4% volatile solids content based on total dry solids.

Test specimens

Rectangular test specimens of dimension 1 in. \times 2 in. weighing approximately 2.5 g were cut from the pineapple leaf fiber, banana fiber, and bamboo fiber-PP composite samples prepared as per the method described elsewhere by the same authors^{12–15} with maleic anhydride grafted PP (MA-g-PP) compatibilizer and added directly to the soil matrix. Details of parameters such as weights, fiber volume percentage, cellulose percentage, percentage organic carbon content of test specimens and positive control samples,

soil medium conditions such as pH, total dry solids (%), and volatile solids (%) were monitored for the test duration and are shown in Table I. The percentage organic carbon content of the test specimens was determined using CHNS analyzer (of Elementar, Germany, Vario EL 111). Thin-layer chromatography (TLC) grade cellulosic fibers with particle size $18\ \mu\text{m}$ were taken as positive-control reference material.

Procedure

Accurately weighed soil (500.2 g) consisting of equal parts of sand and composted manure from livestock excrement were taken at the bottom of each vessel. The soil in each vessel was amended with ammonium phosphate solution, to maintain the C:N ratio between 10 : 1 and 20 : 1, where C is the added carbon content in the test specimen and N is the total nitrogen content in the soil. The total nitrogen content in the soil was measured by using Elementar CHNS-O analyzer (model Vario EL III, Germany). It is based on the principle of high temperature combustion and dynamic separation of the resultant gases in the CHNS-O analysis by the Dumas method. 100 mL of 0.025N $\text{Ba}(\text{OH})_2$ and 50 mL distilled water were taken in 150 and 100 mL beakers, respectively. The beakers were placed on the perforated plates above the soil inside the vessel. Each of the vessels containing soil only control, positive control material, and the test specimens were then sealed, weighed, and placed in the dark cabinet at $21^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

The 150 mL beaker containing barium hydroxide traps the evolved CO_2 and barium carbonate is precipitated. Because of the static incubation, the barium carbonate builds up on the surface of the liquid and has to be broken up periodically by shaking the vessel gently to ensure continued absorption of the evolved CO_2 . For the first 2–3 weeks, after every 3–4 days, the barium hydroxide traps were removed and titrated with 0.05N hydrochloric acid to a phenolphthalein end-point. Thereafter, once in every 5 days the traps

were removed and titration carried out. Each time during the removal of the traps, the vessel was weighed to monitor moisture loss from the soil and allowed to sit open for around 30 min so that the air is refreshed before replacing 100 mL of fresh barium hydroxide and resealing the vessel. Distilled water was added back periodically to maintain the initial weight of the soil. The test was terminated when the CO₂ evolution rate reached a plateau i.e., when all of the accessible carbon had been oxidized. At the end, the pH, moisture, and ash content of the soil were measured and recorded.

Calculation

The theoretical quantity of CO₂ evolved was calculated (according to the ASTM D 5988-96) as shown below from the total organic carbon content of the test specimens obtained from their elemental analysis:

Let the material contain “w %” carbon, then, “w/100 × amount of material charged in mg” is equal to total or “Y” mg of carbon charged to the vessel.

From the basic equation [Eq. (1)], it is possible to calculate the total CO₂ generated as below:



Therefore, Y mg C would yield $\frac{44 \times Y}{12}$ mg CO₂.

The total CO₂ generated during the experimental period is obtained using the value of $Z_n = Z_b - Z_t$.

Where, Z_n , Z_b , and Z_t are themL of HCl (0.05N) needed to titrate the CO₂ generated solely from the test substance, to titrate the blank, and to titrate the test substance respectively.

The quantity of CO₂ evolved is based on the equations [Eqs. (2) and (3)] as given below:

Barium hydroxide reacts with CO₂ and HCl as per the following reactions:



From the above reactions, it can be seen that

2 mol of HCl is equivalent to 1 mol of CO₂, i.e., consumption of m moles of HCl is equivalent to $m/2$ moles of CO₂ generated

So, amount of CO₂ generated that consumed Z_n mL HCl is $(0.05 \times Z_n/2000)$ moles. Thus, CO₂ evolved in terms of mg of CO₂ is $(0.05 \times 44 \times Z_n/2) = 1.1 Z_n$.

Thus, the percentage of biodegradation is evaluated using the expression:

$$\frac{\text{mg of CO}_2 \text{ produced}}{\text{mg of CO}_2 \text{ theoretical}} \times 100 = \frac{1.1 \times Z_n \times 12}{44 \times Y} \times 100$$

From the data obtained above, the degree (%) of biodegradation versus time (days) curves were plotted.

The degradation process has been understood through three basic phases i.e., lag phase, degradation phase and plateau phase as defined below:

- The lag phase*: The time, measured in days from the start of the test until the degree of biodegradation has increased to about 10%, of the maximum level of biodegradation
- The degradation phase*: The time, measured in days from the end of the lag phase of the test until about 90% of the maximum level of biodegradation has been reached, and
- The plateau phase*: the time measured in days, from the end of the biodegradation phase until the end of the test.

SEM analysis

The surface topography of both the interface and fractured surfaces of the natural fibers–PP composites after completion of biodegradability studies were scanned with the Variable Pressure Scanning Electron Microscope (model: LEO 435 VP) at the Scanning Electron Microscope Center of All India Institute of Medical Sciences (AIIMS), New Delhi. The samples were mounted on special stubs, given a coating of gold, which renders them conductive to be studied under the scanning electron microscope (SEM). Coatings were applied at a thickness of about 20 nm, which is too thin to interfere with dimensions of surface features.

Thermal analysis

Thermal analysis of all the composites studied here before exposure in composting conditions has already been reported by the same authors.^{12–15} In this study, the thermal analysis of selected samples were so chosen depending on our recommended compositions of fiber volume % in the pineapple leaf fiber, banana, and bamboo–PP composites. Therefore, TGA–DTG studies were carried out with simultaneous DTA–TGA instrument model SDT 2960, TA Instruments, USA, for the banana–PP composites with 15% fiber volume,¹⁴ bamboo fiber–PP composites with 50% fiber volume,¹⁵ and pineapple leaf fiber–PP composites with 10% fiber volume,^{12,13} before and after exposure in composting conditions to compare their thermal stabilities.

RESULTS AND DISCUSSION

Thermal degradation studies of the partially biodegraded pineapple leaf fiber, banana, and bamboo fiber–PP composites

The results of TGA and DTG (derivatives of thermogram) of the partially biodegraded banana, bamboo

fiber, and pineapple leaf fiber composites with PP are presented in Figure 2. The partially biodegraded bamboo fiber–PP composites containing 50% fiber volume show a two-stage degradation process. The first weight loss at 347°C is due to the degradation of bamboo fiber, and the second weight loss at 466°C is due to degradation of PP. In case of pineapple leaf fiber and banana fiber–PP composites containing 10 and 15% fiber volume, respectively, there is only one stage degradation at around 450°C. When the results of TGA along with the DTG after biodegradation as obtained earlier are compared with those obtained before by Hujuri et al.¹² and Chattopadhyay et al.,^{13–15} no perceptible changes in the results of thermal degradation are seen. This suggests only partial biodegradation that might have occurred in the composite test specimens due to which there is possibly not much impact on their degree of thermal degradation.

Biodegradation studies

Figure 3 illustrates the biodegradation curves. Figure 3 indicates that the time taken for the lag phase, and the degradation phase, before reaching the plateau phase in case of the positive reference (i.e., cellulose) material are 10 and 50 days, respectively. The maximum level of biodegradation achieved in the positive reference cellulose material is 85%. As per international standard ISO 14855-1 : 2005, and other related specifications one of the condition for the test to be considered as valid is that the degree of biodegradation of the reference material should be more than 70% after 45 days is fulfilled here. In contrast to the behavior of the control, the lag phases, and the degradation phase, before reaching the plateau phase in case of test materials i.e., pineapple leaf fiber, banana, and bamboo–PP composites are 30 and 75 days respectively.

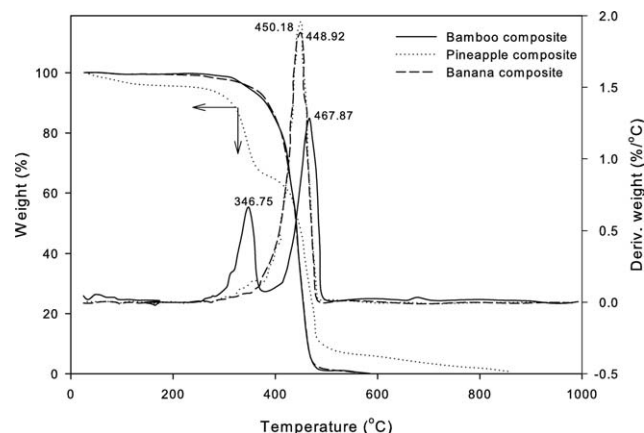


Figure 2 TGA–DTG of partially biodegraded PALF, banana, and bamboo fiber–PP composites.

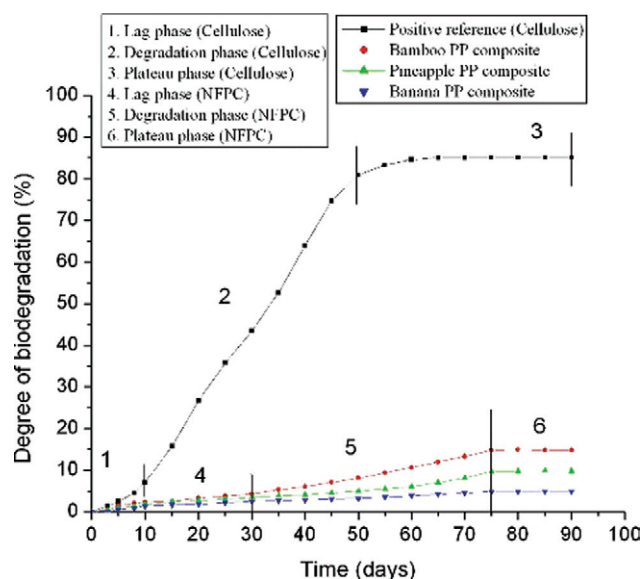
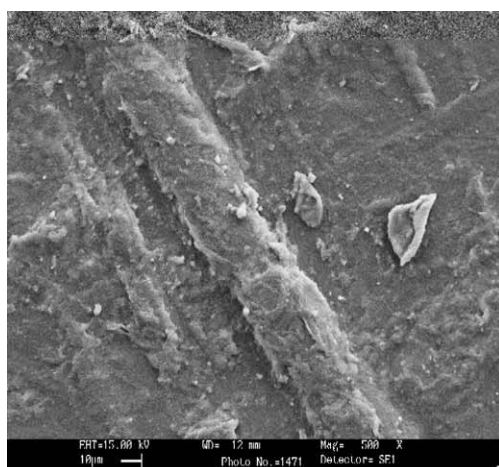


Figure 3 Biodegradation curves for various natural fiber PP composites (NFPC). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

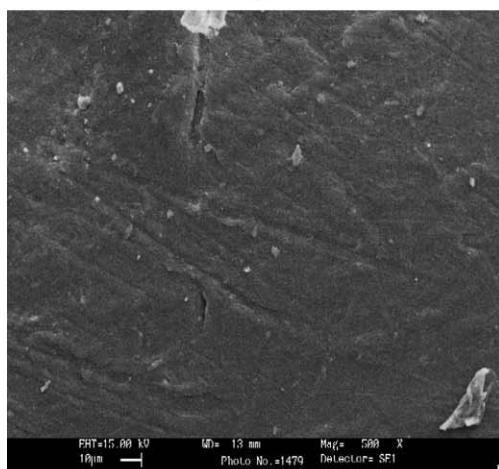
The maximum level of biodegradation achieved in the test materials banana, bamboo, and pineapple leaf fiber–PP composites are 5, 15, and 10% respectively. From the data of the extent of biodegradation obtained in case of the test specimens, it can be concluded that degradation has not taken place in those portion where the hydroxyl groups of the natural fibers have formed covalent ester linkages through the maleic anhydride groups of MA-g-PP compatibilizer. Degradation has taken place only in those areas of the fibers that have remained only physically embedded in the resin matrix and contributed to the reinforcement.

Morphology of the interface

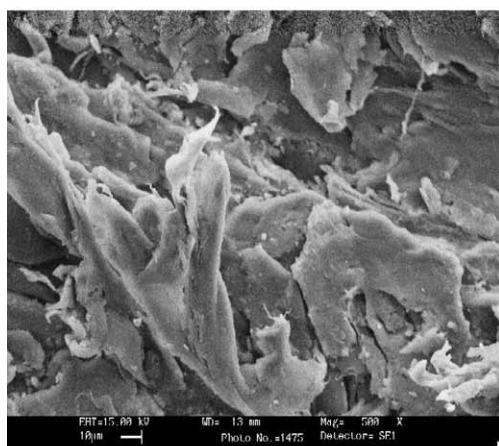
SEM studies of the partially biodegraded natural fibers (pineapple leaf fiber, banana fiber, and bamboo fiber)–PP composite interfaces are shown in Figure 4(a–c). From Figure 4(a), the SEM micrograph of partially biodegraded pineapple leaf fiber–PP interface, it is seen that areas where the fibers are exposed have been partially damaged whereas those deeply embedded in the matrix are more or less unaffected. Almost similar phenomenon is seen in Figure 4(b), in the SEM micrograph of partially biodegraded banana fiber–PP interface. In Figure 4(c), from the SEM micrograph of partially biodegraded bamboo fiber–PP interface, it is seen that the extent of partial biodegradation is much higher that is obvious considering the fact that the bamboo fiber volume % in the composites is much higher (50%) compared to pineapple leaf fiber (10%) and banana fiber (15%) composites.



(a)



(b)

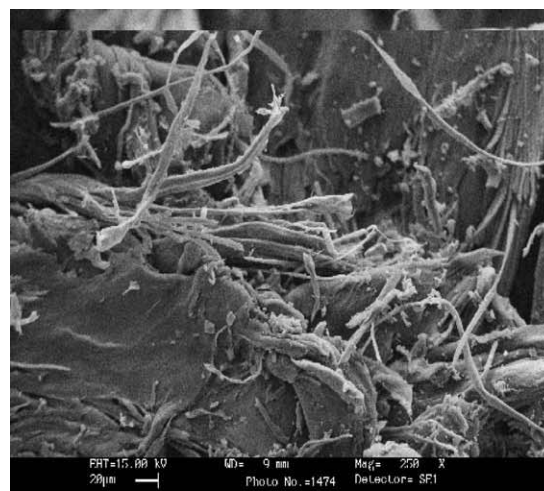


(c)

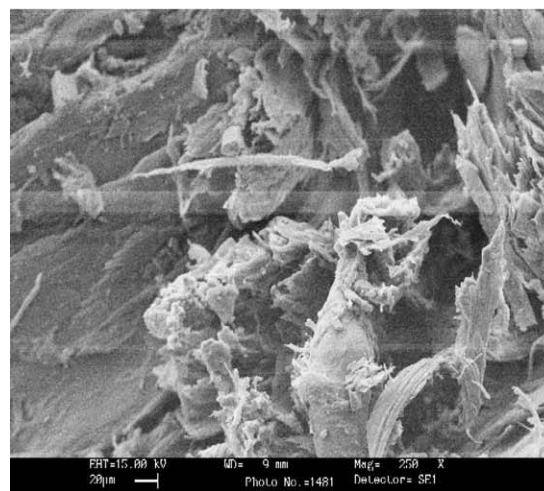
Figure 4 SEM micrographs of (a) partially biodegraded PALF fiber-PP interface, (b) partially biodegraded banana fiber-PP interface, and (c) partially biodegraded bamboo fiber-PP interface.

Morphology of the fractured surface

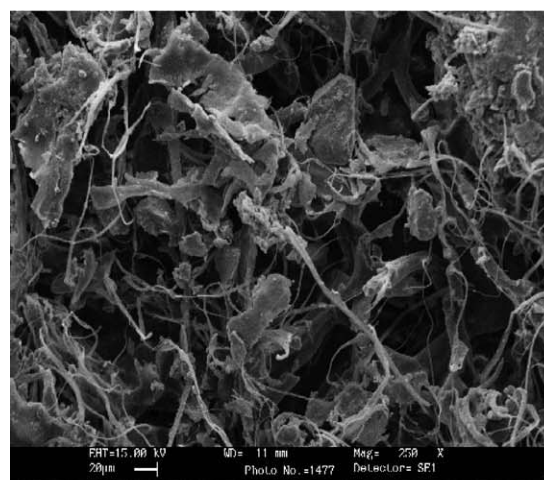
The morphology of the partially biodegraded surfaces of natural fibers (pineapple leaf fiber, banana fiber, and bamboo fiber)-PP composites observed



(a)



(b)



(c)

Figure 5 SEM micrographs of (a) partially biodegraded PALF fiber-PP fractured surface, (b) partially biodegraded banana fiber-PP fractured surface, (c) partially biodegraded bamboo fiber-PP fractured surface.

under the SEM are shown in Figure 5(a–c). It is seen in Figure 5(a), SEM micrograph of partially biodegraded pineapple leaf fiber–PP fractured surface and in Figure 5(b), SEM micrograph of partially biodegraded banana fiber–PP fractured surface, the gap areas from fiber pullout regions have widened due to aerobic partial biodegradation of the composite in soil. In Figure 5(c), the SEM micrograph of partially biodegraded bamboo fiber–PP fractured surface shows multiple gap areas which is evident due to higher extent of degradation on account of high fiber volume concentration.

CONCLUSIONS

The natural fibers from renewable resources, such as banana, bamboo, and pineapple leaf fiber reinforced PP composites studied in this study, showed that all these reinforced composites are partially biodegradable. The time taken to reach the plateau level of CO₂ evolution in the test specimens were around 75–90 days. The extent of biodegradation in the natural fiber–PP composites prepared showed 5–15% degradation which might be because of the fact that degradation could not possibly taken place in those portions where the hydroxyl groups of the natural fibers have formed covalent ester linkages through the maleic anhydride groups of MA-g-PP compatibilizer. Degradation has taken place only in those areas of the fibers that have remained only physically embedded in the resin matrix and contributed to the reinforcement. Thus, it can be concluded from the above that the natural fibers from renewable resources which act as a reinforcing agent in various synthetic polymers and commodity plastics can address to the management of waste plastics, by reducing the amount of polymer content used which

in turn, will reduce the generation of waste of the nonbiodegradable polymers.

We thank Shri Raman Dhyani, Shri Nandalal Rajak, Miss Indu Upadhyaya, and Shri Bhubaneswar Rai of Shriram Institute for Industrial Research, Delhi for their help and assistance in conducting various instrumentation analysis.

References

1. Biodegradable Polymers: A Review; Environment and Plastics Industry Council (EPIC), Canadian Plastic Industry Association, Ontario, Canada; November 24, 2000.
2. Zhang, M. Q.; Rong, M. Z.; Lu, X. *Compos Sci Technol* 2005, 65, 2514.
3. Hon, D. N. S. *Polym News* 1992, 17, 102.
4. Morita, M.; Sakata, J. *J Appl Polym Sci* 1986, 31, 832.
5. Lorand, E. J.; Georgi, B. A. *J Am Chem Soc* 1937, 59, 1166.
6. Avella, M.; Martuscelli, E.; Pascucci, B.; Raimo, M.; Focher, B.; Marzetti, A. *J Appl Polym Sci* 1993, 49, 2091.
7. Cyrus, V. P.; Martucci, J. F.; Iannace, S.; Vazquez, A. *J Thermplas Compos Mater* 2002, 15, 253.
8. Liu, Z. S.; Erhan, S. Z.; Xu, J.; Calvert, P. D. *J Appl Polym Sci* 2002, 85, 2100.
9. Lundquist, L.; Marque, B.; Hagstrand, P. O.; Leterrier, Y.; Manson, J. A. E. *Compos Sci Technol* 2003, 63, 137.
10. Yang, X.; Zhao, K.; Chen, G. Q. *Biomaterials* 2002, 23, 1391.
11. Ochi, S. *Compos: Part A* 2006, 37, 1879.
12. Hujuri, U.; Chattopadhyay, S. K.; Uppaluri, R.; Ghoshal, A. K. *J Appl Polym Sci* 2008, 107, 1507.
13. Chattopadhyay, S. K.; Khandal, R. K.; Uppaluri, R.; Ghoshal, A. K. *J Appl Polym Sci* 2009, 113, 3750.
14. Chattopadhyay, S. K.; Khandal, R. K.; Uppaluri, R.; Ghoshal, A. K. *J Appl Polym Sci* 2010, 117, 1731.
15. Chattopadhyay, S. K.; Khandal, R. K.; Uppaluri, R.; Ghoshal, A. K. *J Appl Polym Sci* 2011, 119, 1619.
16. American Public Health Association (APHA), APHA-AWWA-WPCP 2540 D "Standard method for the examination of water and wastewater", 17th Edition, 1015, Fifteenth street NW, Washington, D.C., (1989).