Ecofriendly Behavior of Host Matrix in Composites Prepared from Agro-Waste and Polypropylene

Jitendra K. Pandey,[1] A. Ahmad,[2] R. P. Singh[1]

[1]*Polymer Chemistry Division, National Chemical Laboratory, Pune-411008, India*
[2]*Division of Biochemical Sciences, National Chemical Laboratory, Pune-411008, India*

ABSTRACT: Composites were prepared by two methods: (1) graft copolymerization (GFC) of isotactic polypropylene (PP) with coupling agent maleic anhydride (MAH), followed by esterification with coir fiber; (2) by direct reactive mixing (DFC) of PP, MAH, and peroxide with coir fiber in a minimax molder. These composites, after molding in films (5 × 5 cm, ~100 μm thickness) were examined for susceptibility to biological attack by measuring the percentage weight loss in compost up to 6 months, periodically, and fungal colonization on surface of the samples, when kept as sole carbon source for the growth of *Aspergillus niger* in culture medium up to 40 days. Photodegradation was evaluated by monitoring the variations in a Fourier transform infrared spectrum and crack formation after successive treatment with ultraviolet (UV) light ($\geq$290 nm) for 0, 20, 50, and 100 h at 60°C in the presence of air. Specimens of virgin PP were taken as a reference during all periods of photo- and biodegradations. Significant consequences of the manner of composite preparation on photo/biodegradation were observed during the whole study. DFC samples degraded faster than GFC during the composting whereas, in culture, GFC was covered by fungi in a highly well-uniform way. It is shown that photo-oxidative aging directly enhanced the biodegradability of composites, as an increase in fungal growth rate and decrease in weight during composting was found. It was concluded that extent of compatibilization has a profound effect on photo/biodegradation of composite material; consequently, ester bonds were the main units during fungal consumption. Surface erosion was maximum in the case of 100 h UV-treated GFC and minimum for unirradiated PP after culture exposure, as shown by scanning electron microscopy, which is due to the use of composite films as energy source by microbes. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1009–1017, 2003

Key words: compatibilization; composites; biodegradation; photodegradation

INTRODUCTION

The need for biodegradable plastics has increased in past decades not only due to increasing environmental concerns but also due to they biomedical applications, even though extremely useful polyolefins can be degraded at every stage of production in both stabilized[1] and unstabilized samples[2] and some traditional plastics also undergo very slow biodegradation.[3,4] It is now well evident that polymer/plastics waste management through biodegradation or bioconversion is the most suitable solution for plastic waste management among the other traditional methods like incineration, pyrolysis, and land filling. Several means[5–13] have been used to achieve biodegradability/biodeteriobility/photobiodegradability in polymers. Scott et al. developed a wonderful photobiodegradable film that can be successfully used to reduce polymer waste.[5–8] Polysaccharides have been used more frequently as natural fillers for this purpose and have been well investigated by Griffin[9,10] and Bastioli,[11] particularly in polyolefins at fairly low concentrations.[12,13]

The major problem in this area seems to be incompatibility between hydrophilic polysaccharides and generally the hydrophobic nature of the polymer matrix, where the complex mechanism of coupling through coupling agents, morphology of interfaces, surface energy, and wetting phenomenon are also necessary.[14,15] Cellulose occurs naturally in the crystalline state in the plant cell wall and is isolated as microfibrils by convenient extraction methods, made up of βD-(+)glucose residues, and shows biodegradability, the rate of which is dependent upon the extent and nature of modification, chemical structure, and type of substituents with degree of substitution. Thermoplastic composite made from cellulosic materials either by change in surface tension,[16] where hydrophilicity is closely related to surface energy,[17] impregnation,[18] or coupling through graft copolymerization,[19–21] may be advantageously utilized for the development of biodegradable material with good physical properties and can be helpful to reduce the polymer waste and must also contribute their utility to reduce the vegetal biomass.

Several kinds of study have been reported in literature on the physical strength and thermal properties of fiber-reinforced polymer composites, where it has been established that these properties improved after

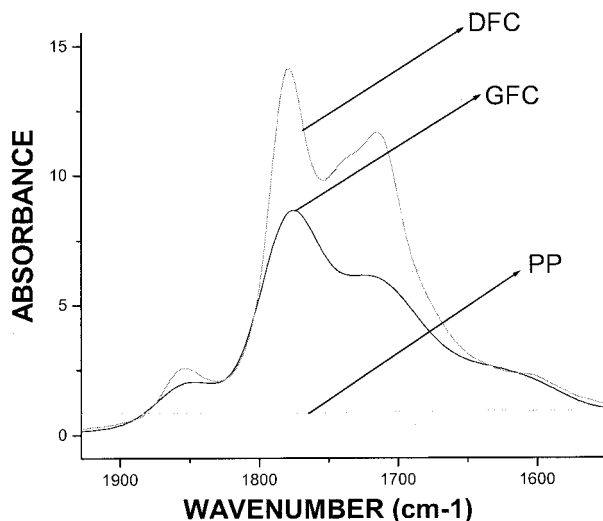**Figure 1** Polymer after treatment with MAH.

Figure 2 MAH-treated polymer with cellulose fiber.

reinforcement. Few attempts have been made, however, regarding the biodegradation of polymer fiber composite—for example, in aqueous media,[22] in terrestrial environments, [23] in biodegradation after exposing in oxidizing, in reducing, in hydrogen-producing bacteria in bath culture,[24] and in fungal degradation.[25] There has been no real discussion or report in the literature about the effect of the preparation manner as well as ultraviolet (UV) irradiation on biodegradability of additive-free polypropylene (PP) agrowaste composites in composting and culture environments, which could be applicable in our daily life as naturally degradable materials.

In the present investigation, two composites, prepared as in earlier studies[26–28] and characterized by Fourier transform infrared (FTIR), were used for the performance against microbial attack in compost and in a culture of *Aspergillus niger* before and after UV irradiation by measuring the weight loss and fungal growth, respectively, with surface morphology changes through scanning electron microscopy (SEM) and variation in molecular structure by IR spectroscopy in comparison to controlled PP samples.

EXPERIMENTAL

Material

Commercial samples of isotactic polypropylene (i-PP, Koylene S30330), supplied by the M/s Indian Petrochemicals Corp. Baroda, India, served as a matrix material during preparation of composites. Maleic anhydride was obtained from E. Merck (Mumbai, India), and was used after recrystallization. Benzophenone and dicumyl peroxide were obtained from Aldrich (USA) and were used as received. All the solvents of A.R. grade were taken from S. D. Fine Chemicals Ltd., Baroda, India. Coir (*Cocos nucifera*) fibers were collected from raw material by retting process, and acti-
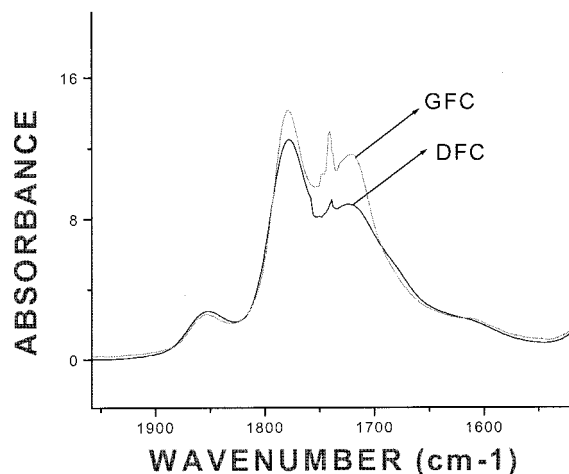
vated by immersion in water for 15 days. After sun drying for 10 days and cutting into pieces ~2.5–3.0 mm in length, fibers were washed with distilled water and further dried in vacuum at 55 ± 5°C until a constant weight was achieved.

Preparation of composites

Grafting of maleic anhydride (MAH, 2.0M) onto PP was done in a UV reactor ($\lambda \geq 290$ nm) for 2 h in dry acetone (30 mL) taking benzophenone (0.29M) as a photosensitizer at 65 ± 5°C. These obtained copolymers was dried under vacuum up to constant weight after soxhlet extraction in acetone for the removal of unbounded moieties. Coir fiber were immersed in the solution of graft copolymer in toluene at 80 ± 5°C for 5 min. Keeping the concentration 5 wt % of copolymer and soxhlet extracted, dried in the same way as mentioned above. These samples were designated as graft fiber composites (GFC). A second type of composite was prepared by direct reactive mixing of PP, MAH (2% wt) dicumyl peroxide (DCP, 0.2% wt), and fiber (50:50 as PP) in a minimax molder (CEAST) at 145±
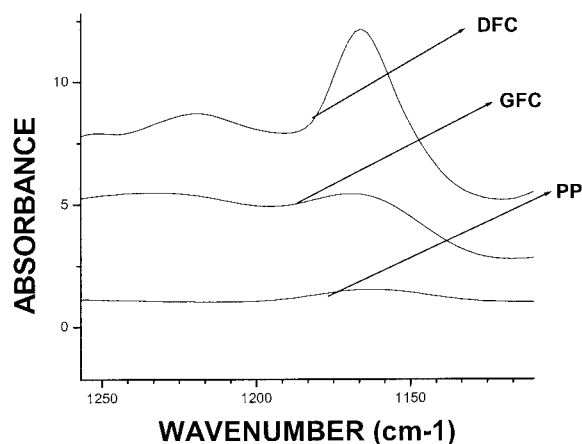

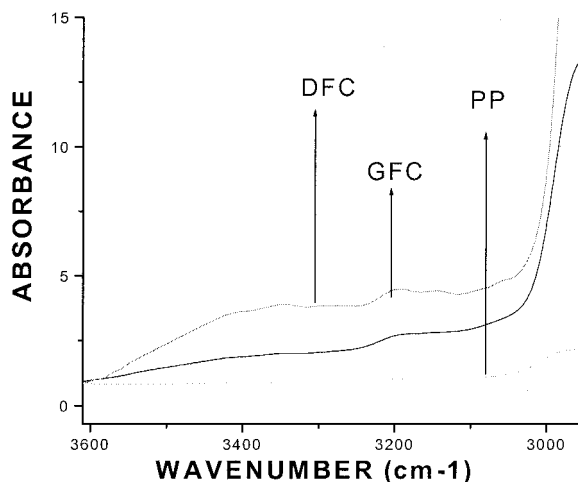**Figure 3** Peaks for free OH groups in composites.

Figure 4 Hydroxyl bonding in the composites, PP spectrum used as baseline.

5°C followed by thoroughly washing in toluene. This composite was labeled as direct fiber composite (DFC). PP used in this preparation was purified by dissolving in xylene under nitrogen atmosphere followed by solvent extraction in methanol for removal of the additives, and it was presumed that now these samples were additive free. Reference PP films were used as received. Both the composite samples and PP were molded between two Teflon sheets into thin films (~100 μm) at 140 $\pm$ 5°C by applying 150 kg/cm^2 pressure for 30 s using a preheated hydraulic press. These films were quenched cooled in tap water for 2 min.

FTIR spectroscopy

FTIR (Fourier Transform Infrared 16PC Spectrometer) was used for the characterization and monitoring of changes in samples during irradiation.

Photodegradation

Photoirradiation of the films were carried out in an accelerated weathering chamber (SEPAP 12/24) at 60°C. The chamber consisted of (4 × 400 W) medium-pressure mercury vapor lamps supplying radiation ($\lambda \geq 290$ nm). The details of the equipment are described elsewhere.[29]

Biodegradation

Samples were incubated in compost and culture. The constitution of solid compost and preparation method of carbon-free culture medium of test fungi *A. niger*, used for the biodegradability testing of sample has already been described in our earlier studies.[30] The was determined by measuring the gravitational weight loss in percentage after composting on a digital

balance. The surface of the test specimen (2.5 × 2.5 cm) was inoculated by spraying the spore suspension. To avoid contamination, petri dishes were wax sealed after incubation at 82–86°F and 85–90% humidity for ~6 weeks. Growth rating procedure was according to ASTM G21 70.

Scanning electron microscopy

Surface changes of composted, culture-incubated, and irradiated samples were examined. The stained samples dried under vacuum for 24 h at 50°C and these gold-coated samples were examined under an electron microscope (Leica Cambridge Stereoscan 440 model).
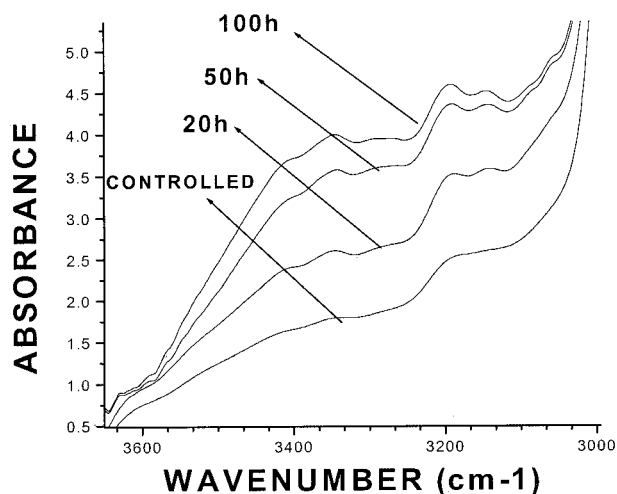
RESULTS AND DISCUSSION

Compatibility of fiber and polymer matrix

To characterize the DFC and GFC samples and to measure the esterification extent, FTIR spectroscopy was performed. Esters have two characteristic strong
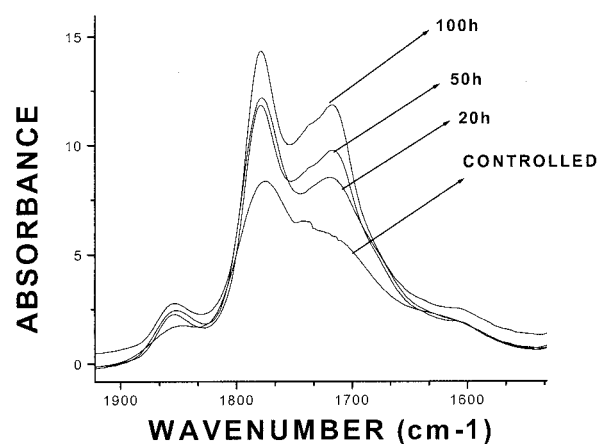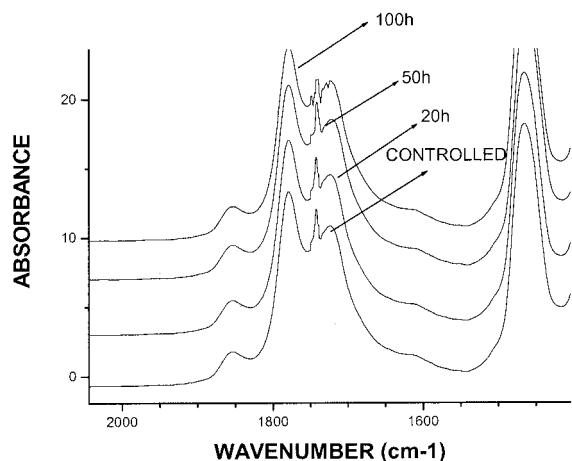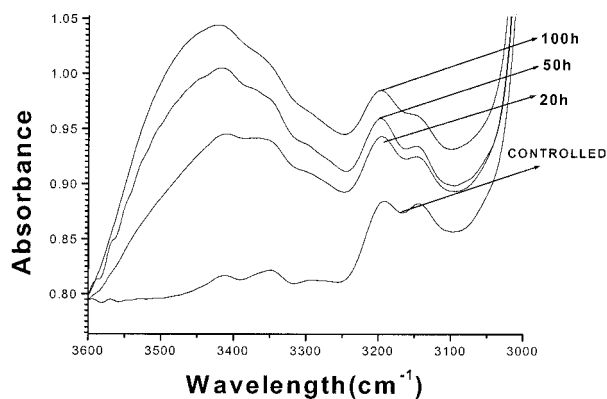

(a)

(b)

Figure 5 (a) Changes in carbonyl group region of DFC during irradiation. (b) Changes in hydroxyl group region of DFC during irradiation.
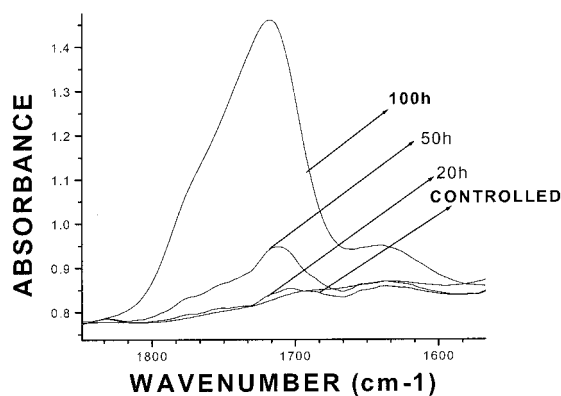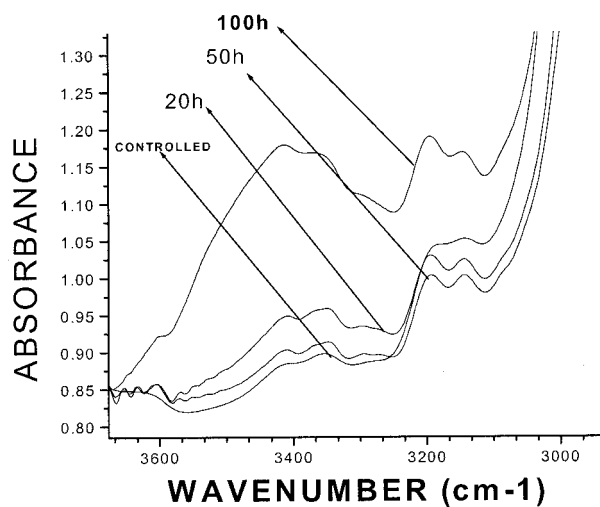
Figure 6 (a) Changes in carbonyl group region of GFC during irradiation. (b) Changes in hydroxyl group region of GFC during irradiation.

Figure 7 (a) Changes in carbonyl region of PP during irradiation. (b) Changes in hydroxyl region of PP during irradiation.

absorption bands arising from C=O and C—O stretching vibrations at shorter wavelengths due to the negative inductive effect of adjacent oxygen atoms that increase the force constant. The spectra of PP-g-MAH and PP-blended MAH are shown in Figure 1. The absence of any observable peaks at 1360 and 1580 cm^{-1} indicates the absence of the anionic form of anhydride with one carboxylic acid, i.e.., the maleic anhydride is present either in dicarboxylic acid dimer or cyclic form in both forms of PP–MAH samples. This was confirmed by the appearance of peaks at 1780 and 1863 cm^{-1} for cyclic anhydride and 1718 cm^{-1} for carboxylic acid dimer; this peak was again confirmed by the O—H stretching peak (3200–3300 cm^{-1}) because the cyclic dimer has a center of symmetry. Figure 2 shows the spectra of both MAH-bound PP after fiber treatment where a significantly detectable additional peak from 1740 to 1750 cm^{-1} is due to the C=O stretching of ester bond, formed between the coupling agent and cellulosic fiber in the case of GFC, whereas in DFC it was hardly detected, which could not be used for conformation of esterification. Thus for the

esterification, chemically joined cellulose moieties were present in a greater amount in GFC compared to DFC; this fact was again supported by the high area under the peak at 1160 cm^{-1} in DFC for secondary free
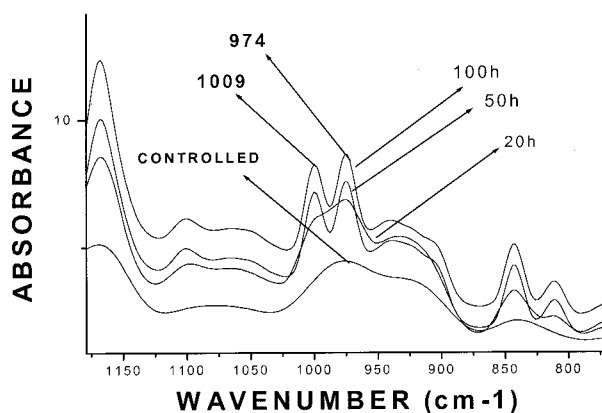

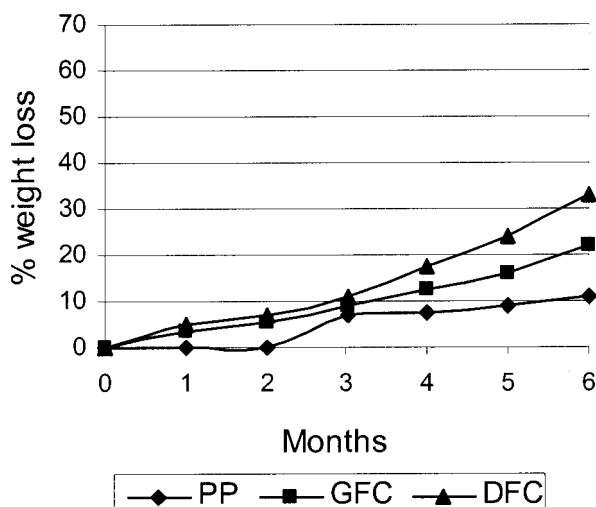Figure 8 Unsaturation variations in DFC composite upon irradiation.

Figure 9 Weight loss of unirradiated samples.

—OH, group, supporting the presence of a high amount of unreacted cellulose fiber than of GFC as shown in Figure 3. The good extent of esterification in GFC was again confirmed by the lower water absorption (11–13%) than in DFC (26%) after 35 h at room temperature, and this was due to the lesser number of OH groups in GFC. The appearance of less detectable peaks at 1050 cm^{-1} suggested that primary alcoholic groups of cellulose also participate in esterification and are likely due to the hindrance effect of bulky groups that prohibit the reaction. The broad spectrum near 3330 cm^{-1} (Fig. 4) arises from the —OH group in polymeric structure and since this is present at comparatively lower frequency (bathochromic effect) than for the free hydroxyl group, this is due to intermolecular hydrogen bonding by the interaction between the —COOH of anhydride and the —OH of fiber.

Photodegradation

During UV irradiation, cellulosic material undergoes depolymerization or chain scission, formation of carbonyl and carboxyl groups, and fragmentation into nonvolatile or volatile products, but chain scission remains unchanged during storage after removal of samples from the irradiation chamber.[31] Bleek et al. [32] found glucose (6 carbon atom) and arabinose (5 carbon atom) reducing units in the irradiation- generated oligosaccharides. The photoproduct generation on UV degradation of PP has been extensively explained.[33,34] The absorption at 1712, 1722, 1740, and 1785 cm^{-1} for carboxylic acid, ketone, ester, and lactones, respectively, are also well studied.[35,36] Monitoring of variations in hydroxyl and carbonyl regions in FTIR is a conventional technique for measuring the photodegradation in polyolefins as these regions increase during irradiation, but in the composites both groups are already present, and therefore their appearance creates practical difficulties for the assignment of all

peaks in our present system, not only for those forming in the host polymer of the composite during degradation but also for cellulose materials because of high overlapping of peaks to each other. The changes in hydroxyl and carbonyl regions for both composites are presented in Figures 5(a,b) and 6(a,b), where it is clear that the carbonyl and hydroxyl regions increase in both composites; also detectable is more of an increase for DFC in this region during irradiation, which can be used as a indication for more photodegradability. Further, it is supported by earlier crack formations in DFC and this is because of peroxide-initiated photodegradation and consequently generation of keto/carbonyl species. The overall increase of these regions of composites were not as sharp as in PP. Figure 7(a,b) shows the carboxyl and hydroxyl regions of PP. Hydroxyl (3600–3200 cm^{-1}) and carbonyl (1800–1600 cm^{-1}) groups were increasing gradually from 0 to 100 h UV irradiation. The bands around 3400 cm^{-1} in PP during photo-oxidation indicate the generation of intramolecular hydrogen-bonded hydroperoxides and alcohols. The increase in the unsaturation, as the two peaks generated at 974 and 1009 cm^{-1} for alkene and vinylene groups, respectively, in the case of both composites (Fig. 8), and it may attributed to the abstraction of H atom corresponding to carbonyl group. This effect is more in DFC than PP, suggesting the sensitization effect of CO groups of the compatibilizing agent.

Biodegradation

Composting

Biodegradability was measured periodically up to 6 months in compost.[30] It was estimated in the term of % weight loss of samples (5×5 cm, ~100 μm thickness, 5 replicates) after washing with distilled water and drying in the oven for 24 h at 50°C, until constant weight. The effect of UV irradiation on biodegradation rate (gravitational weight loss) was also studied for this period. Results of degradation in compost among the unirradiated samples of composites are shown in Figure 9, where the decrease in weight of PP was less than both composites, indicating fiber degrades initially by providing hydrophilic surface for microbial adhesion. The higher weight loss of DFC than GFC after 6 months of composting must be due to the presence of an additional "facility" for microbial action in the form of degradation products, which have already been generating during its preparation in the presence of the free radical generator peroxide. Figure 10 illustrates the degradation for 20 h UV-treated samples. The significant degradation was not observed initially exposed films, which may be attributed to the formation of initial crosslinking via combination of free radicals[37] as at this stage microbes may try to penetrate into the matrix of the polymer after consuming the nutrients present on the surface, and this fact has been
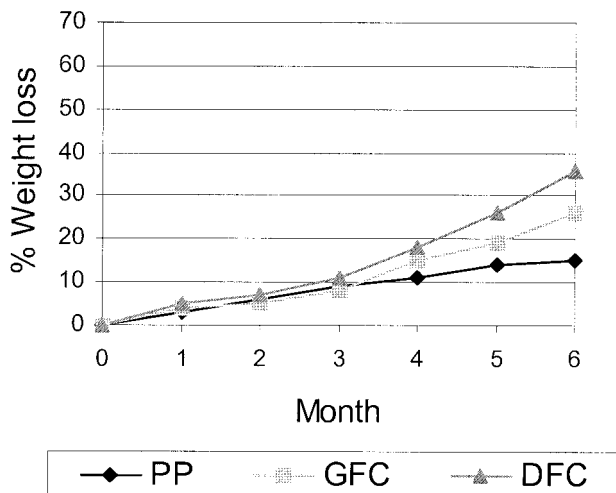
Figure 10 Weight loss of 20 h irradiated samples.

eliminated for longer hour irradiation. Weight loss markedly increased for 50 and 100 h UV-treated samples (Figs. 11 and 12) and was observed much more for 100 h irradiated samples after the last limit of compost incubation. All the 100 h treated samples were unrecoverable after 5 months and the DFC sample was not recovered after 4 month; here it should be noted that these samples were already becoming brittle during subjection to UV treatment. The decreasing carbonyl/ester bond region in FTIR spectra again strongly suggested the use of polymer in samples as nutrients by microbes through the well-established Albertsson et al.[38-40] mechanism (Fig. 13). Some facts are appearing necessary to take into consideration for discussion at this stage. GFC weight loss increased around 68% after 5 months and the sample could be recovered very carefully whereas DFC weight loss ~55%, could not recovered in the present system. The protection against brittleness in GFC must be due to the greater extent of esterification, i.e., more compatibilization, but since the ester bonds facilitate biological attack by providing a active site for coenzyme A (Co-ASH) during hydrolysis, these samples underwent
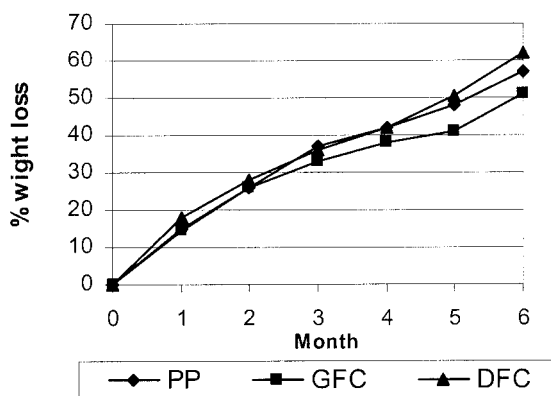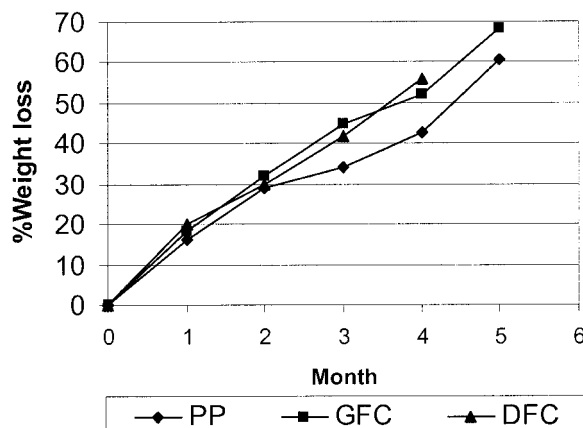
high weight loss and stayed in the compost for a longer time, indicating that ester groups play a significant role in the biodegradation. On the other hand, weight loss of DFC (very less esterified or no esterification) was less but not recoverable due to the brittleness, which was caused mainly through extreme chain scission in polymer matrix, suggesting chain scission is the more important unit during biodisintegration. Some more research seems to be essential for a potential and final conclusion. In all cases photodegradation enhanced degradability in the biotic environment as this fact is broadly investigated by Scott et al.[41,42]

Culture testing

The samples were kept in the culture medium of *A. niger* as a sole carbon source for 40 days and biodegradation characteristics were compared with those in composting. Since a longer time is necessary for degradation by fungus, spores were sprayed in more quantities on the surface of specimens including unirradiated PP and at a slightly increased temperature. During the incubation period, the composites were
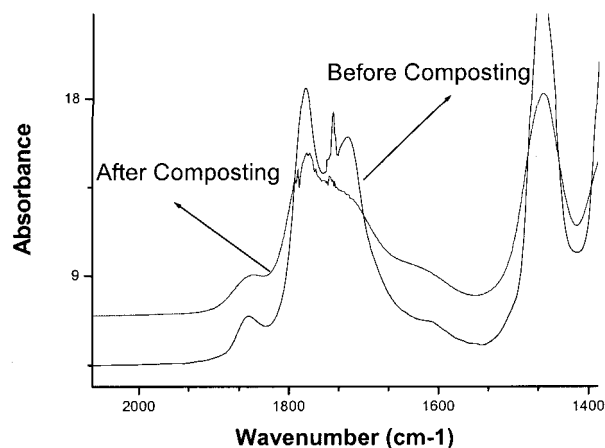

Figure 12 Weight loss of 100 h irradiated samples.

Figure 11 Weight loss 50 h irradiated samples.

Figure 13 IR spectra of GFC (100 h, irradiated sample) after compost incubation.

TABLE I
Visual Growth Rating of *A. niger* on Polymer Composites

Days	i-PP				DFC				GFC			
	0	20	50	100	0	20	50	100	0	20	50	100
10	0	0	0	1	1	1	2	2	0	0	1	2
20	0	0	1	1	1	1	3	2	1	1	2	2
30	1	1	1	2	2	2	3	3	2	2	3	3
40	1	2	2	4	2	3	3	4	3	3	4	4

degraded gradually from the surface and characteristic morphology appeared according to SEM. The visual growth rating of irradiated and unirradiated samples is tabulated in the Table I, and the growth could be seen microscopically after one week. Further, the degradability rate was dependent on the irradiation time and irradiated samples were highly colonized by fungus in comparison of unirradiated samples. Fungal coverage was markedly affected by the manner of preparation of composites. Among the 50 and 100 h irradiated composites, DFC was highly colonized on the surface than was GFC with in 10 days, which is quit obvious due the greater use of DFC as an energy source by fungus, i.e., easy fungal-consumable products were present in more amounts on the surface of specimens. In the case of GFC samples, colonization increased gradually from 15 to 40 days in comparison to DFC, where such a marked increase was not observed and this must be due to the initial large availability of easy fungal-consumable products. As soon as it becomes limited, fungal growth slowed down whereas in GFC, slow ester link cleavage was in progress—consequently, biodegradation rate increased as a function of time. The greater degradation (visual colonization) of DFC in the case of unirradiated samples than in GFC—as it was same during composting—indicates that the functional groups have been generated during photo-oxidation, and therefore are initially responsible for the consumption of films by *A. niger* than cellulosic moieties by providing the hydrophilic surface for adhesion of fungus.

Morphological aspects

SEM is a significant and reliable tool to measure the morphological changes of degraded polymer. These morphological changes of DFC and GFC were mainly focused on the fiber-intact polymer part, and crucial photographs of some interesting observations of photo-, bio-, and photobiodegraded samples are highlighted in Figures 14, 15, and 16. The morphological changes of UV-irradiated and compost/culture- incubated PP have been studied in our earlier report,[30] where a highly cracked network and deep eroded surface were found during the degradation of samples. Figure 14(a) and (b) shows the micrographs of 100 h irradiated GFC and DFC. The formation of cav-

ities on the DFC surface is due to the removal of volatile oxidation products. The fiber coupling that may be responsible for binding the polymer matrix during irradiation is supported by Figure 15(a) and (b), showing 100 h irradiated and 40 days culture incubated GFC on high and low magnification respectively, where it can be seen that fibers degraded much more than the other portion of composite; two types of area, one partially intact and other degraded, show that fungus is attacking in different modes of intensity according to the substrate, i.e., the degradation process occurring in a selective manner. From Figure 15(a), it seems that two parts of the polymer were joined together by fiber, and as soon as fungus consumed this fiber, these parts started to separate; prob-
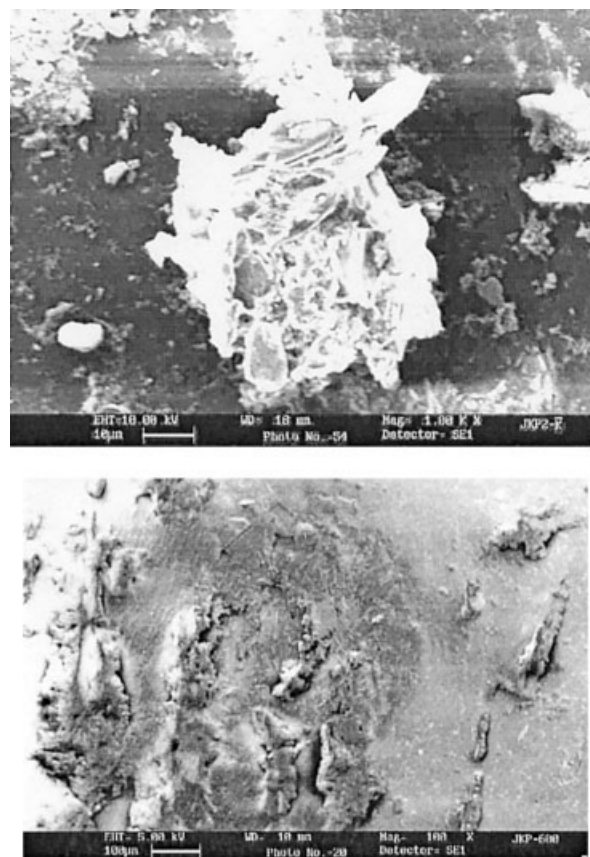

Figure 14 (a) SEM micrograph of 100 h UV-irradiated GFC. (b) SEM micrograph of less fiber crowded portion 100 h UV-irradiated DFC.
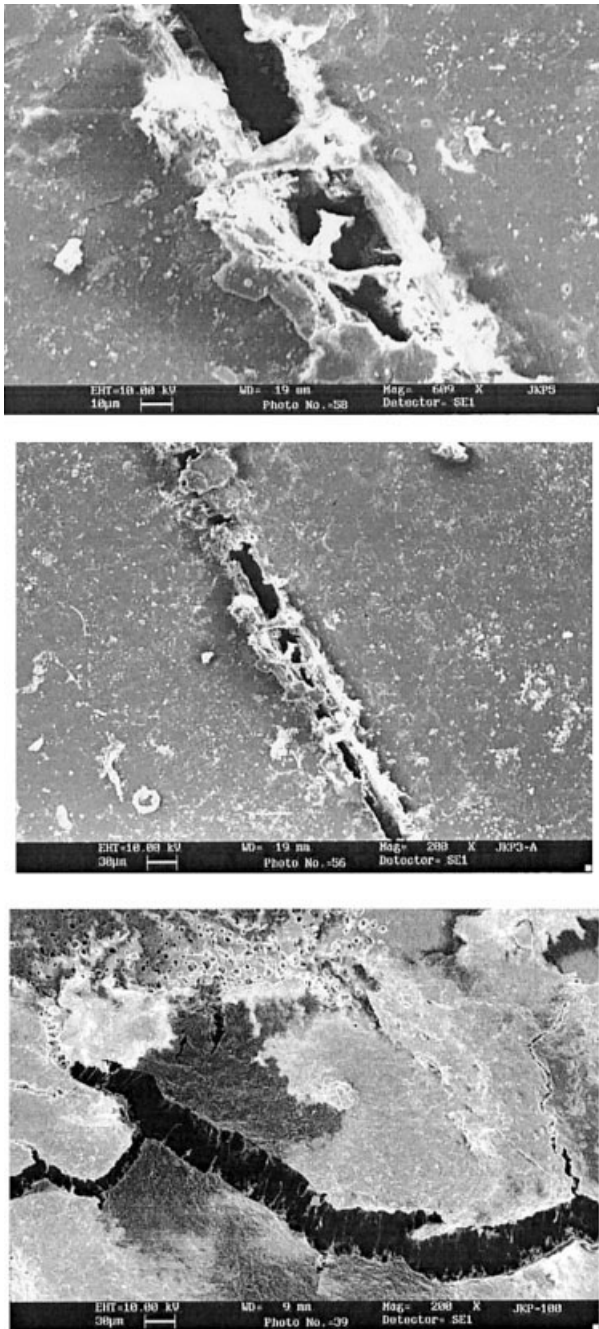
Figure 15 (a) SEM micrograph of 100h UV-irradiated and culture-incubated GFC. (b) SEM micrograph of 100 h UV-irradiated and culture-incubated GFC at low magnification. (c) SEM micrograph of a very less fiber-crowded portion of 100 h UV- irradiated and compost-incubated GFC.

ably due to the absence of such type of coupling in DFC, fragmentation takes place more rapidly and specimens could not be recovered. Cracked structures were observed in the SEM micrograph of one portion of GFC after the last limit of compost incubation, where the PP portion was cut down carefully [Fig. 15(c)]. The SEM micrograph of 100 h irradiated and 4 months' compost-incubated DFC [Fig. 16(a)] shows the presence of a large cavity and fine fragmentation

of polymer; a micrograph of only the polymer part of the same DFC is shown in Figure 16(b), where a perfect separation of polymer surfaces is clearly visible. Small vacant tracks in 100 h irradiated and 40 days cultured sample [Fig. 16(c)] clearly indicates that mycelia of fungus had grown but washed out during the washing.
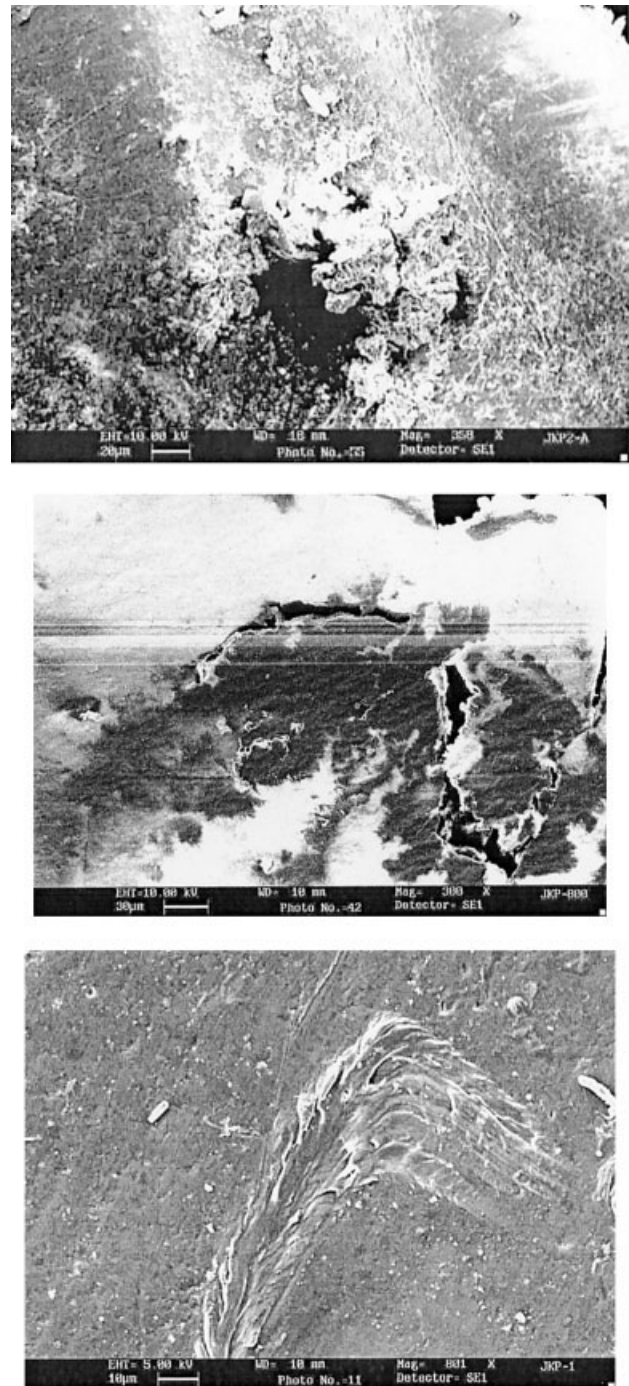

Figure 16 (a) SEM micrograph of 100 h UV-irradiated and compost-incubated DFC. (b) SEM micrograph of a very less fiber-crowded portion of 100 h UV-irradiated and compost-incubated DFC. (c) SEM micrograph of DFC after culture incubation.

CONCLUSIONS

Photodegradation study shows that composites prepared from the direct mixing method were more photodegradable than commercial polypropylene and composite prepared by the grafting method. Biodegradability was increased with the increasing time of UV treatment. There was a significant effect of method of preparation of samples. In compost incubation, weight loss of unirradiated samples for directly prepared composites was more than for the composite prepared by the grafting method. This must be because of additional degradation, which had already taken place during preparation through peroxide-initiated photo-oxidation—consequently, there was generation of more active sites for microbial attack by providing functional groups. In culture incubation, the irradiated graft composite showed very uniform coverage of surface by fungus than the directly grafted composites, suggesting that compatibilization played a dominant and key role during actual biodegradability in agro-waste PP composites. From the overall observation of the study, in general we can conclude that DFC underwent biodisintegration or bioerosion simultaneously. GFC samples may be biodegraded through ester bond cleavage, and thermoplastic agro-waste composites can play a key role as nature-friendly material. Further research is in progress for evaluation of the effect of polymer composition by taking heterophasic ethylene-propylene (E-P) copolymers of different monomer concentrations on photo/biodegradability of composites with agro-waste that may be applicable for the development of ecofriendly commodity plastics of enhanced physical properties as well as advantageous for reduction of vegetal/plastic solid waste generated pollution in the environment.

References

1. Scott, G. Atmospheric Oxidation and Antioxidants; Scott, G., Ed.; Elsevier: New York, 1965, p 276.
2. Grassie, N.; Scott, G. Degradation and Stabilization of Polymers; Cambridge University Press: New York, 1985; p 91.
3. Albertsson, A. C.; Karlsson, S. J Appl Polym Sci 1988, 35, 1289.
4. Albertsson, A. C. J Appl Polym Sci 1978, 22, 3419.
5. Scott, G. In Degradable Polymers Principles and Applications; Scott, G., Gilead, D., Eds.; Chapman & Hall, London; 1995; Chap 9.
6. Gilead, D.; Scott, G. Br. Pat. 1 586 344, 1978.
7. Gilead, D.; Scott, G. In Developments in Polymer Stabilization, Vol. 5; Scott, G., Ed.; Applied Science: London, 1995, 182:71.
8. Gilead, D. In Degradable Polymers Principles and Applications; Scott, G., Gilead, D., Eds.; Chapman & Hall: London, 1995; Chap 10.
9. Griffin, G. J. L. U.S. Pat. 40,16,117, 1997.
10. Griffin, G. J. L. Pure Appl Chem 1980, 52, 399.
11. Bastioli, C. In Degradable Polymers Principles and Applications; Scott, G., Gilead, D., Eds.; Chapman & Hall, London, 1995; Chap 6.
12. Evans, J. D.; Sikdar, S. K. Chemtech 1990, 20, 38–42.
13. Johnson, R. In Proceedings of Symposium on Degradable Plastics Society of Plastics Industry, Washington, DC, June 10, 1987, 6–13.
14. Schick, M. J. Surface Characteristic of Fiber and Textiles, Part II; Marcel Dekker: New York, 1977.
15. Raj, R. G.; Kokta, B. V.; Daneault, C. Int J Polym Mater 1992, 2, 86.
16. Raj, K. G.; Kokta, B. V.; Dembelef, S. B. J Appl Polym Sci 1989, 38, 1987–1996.
17. Westerlind, B. S.; Berg, J. C. J Appl Polym Sci 1988, 36, 523.
18. Gebner, W. Chemiefasern/Textilind (Ind-Text) 1989, 39, 185.
19. Kroschwitz, J. I. Polymers: Fibers and Textiles; Wiley: New York, 1990.
20. Maldas, D.; Kokta, B. V.; Daneault, C. J Appl Polym Sci 1989, 37, 751–775.
21. Felix, J. M.; Gatenhalm, P. J Appl Polym Sci 1991, 42, 609–620.
22. Prian, L.; Barkatt, A. J Mater Sci 1999, 34, 3977–3989.
23. Wool, R. P. In Degradable Polymers Principles and Applications; Scott, G., Gilead, D., Eds.; Chapman & Hall: London, UK, 1995; p 138–152.
24. Wagner, P. A.; Little, B. J.; Hart, K. R.; Richard, I. Int Biodeterior Biodegrad 1996, 38, 125.
25. Gu, J.-D.; Lu, C.; Mitchell, R.; Thorp, K.; Crasto, A. Mater Perform 1997, 3, 37.
26. Sathe, S.; Rao, G .S. S.; Devi, S. J Appl Polym Sci 1994, 53, 239.
27. Felix, J. M.; Gatenholm, P. J Appl Polym Sci 1991, 42, 609.
28. Desai, S. M.; Pandey, J. K.; Singh, R. P. Macromolecular Symposia 2001, 163, 121.
29. Tang, L.; Sallet, D.; Lemaire, J. Macromolecules 1981, 15, 1437.
30. Pandey, J. K.; Singh, R. P. Biomacromolecules 2001, 2, 880.
31. Stilling, R.; Van Nostrand, R. J. J Am Chem Soc 1944, 66, 753.
32. Beelik, A.; Hamilton, J. K. Das Paier 1959, 13, 77.
33. Adams, J. Polym Sci A1 1970, 8, 1279.
34. Adams, J. Polym Sci A1 1972, 8, 1279.
35. Mani, R. Ph.D thesis, India, 1994.
36. Allen, N. S.; Edge, M. In Fundamentals of Polymer Degradation and Stabilization; Elsevier Science Publishers Ltd.: England, 1992.
37. Ranby, B.; Rabek, J. F. Photodegradation, Photo-oxidation and Photostabilization of Polymers; Wiley: New York, 1975.
38. Albertsson, A. C.; Andersson, S. O.; Karlsson, S. Polym Degrad Stab 1987, 18, 73.
39. Albertsson, A. C.; Karlsson, S. Acta Polym 1995, 46, 114.
40. Albertsson, A. C.; Barenstedt, C.; Karlsson, S.; Lindberg, T. Polymer 1995, 36, 3075.
41. Scott, G. In Degradable Polymers Principles and Applications; Scott, G., Gilead, D., Eds.; Chapman & Hall, London, 1995; Chap 1.
42. Arnaud, R.; Davin, P.; Lemaire, J.; Al-Malaika, S.; Chohan, S.; Coker, M.; Scott, G.; Fauve, M. A. Polym Degrad Stab 1994, 46, 211.