CHAPTER IV:

DEGRADABILITY OF BIOCOMPOSITES PREPARED FROM CELLULOSE AND PE, PP, EP COPOLYMERS
4.1. Introduction
The need of biodegradable plastics has been increased during the past decades not only due to the increasing environmental concerns but also for its biomedical applications. The terms ‘biodegradation’ and ‘compostability’ are very common but are frequently misused. In biodegradation, the enzymes of the biosphere essentially take part at least in one step during cleavage of the chemical bonds of the material. Notably, biodegradation does not ensure that a biodegradable material will always degrade. In fact, degradation will only occur in a favorable environment and the biodegradable material will not necessarily degrade within a short time. It is, therefore, important to couple the term biodegradable with the specification of the particular environment where the biodegradation is expected to happen, and of the time-scale of the process. Some commodity plastics can be degraded at every stage of production in both the stabilized [1] and unstabilized form [2] and also undergo very slow biodegradation. [3,4]. It is now well evident that polymer / plastics waste management through biodegradation or bio-conversion is the most suitable solution for ‘Plastic Waste Management’ among the other traditional methods like incineration, pyrolysis, land filling etc. Several means [5-13], have been used to achieve the biodegradability / biodeteriobility / photo-biodegradability in polymers. Scott et.al [5-8] developed a wonderful photo-biodegradable film which can be successfully used to reduce the polymer waste. Polysaccharides have been used more frequently as natural fillers for this purpose and 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 polymer matrix where the complex mechanism of coupling through coupling agents, morphology of interfaces, surface energy and wetting phenomenon considerations are also necessary [14,15]. Thermoplastic composite made from cellulosic materials either by change in surface tension [16], where hydrophilicity is closely related to surface energy [17], impregnation or by coupling through graft copolymerization [18-21], 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 studies have been reported in the literature on the physical strength and thermal properties of fiber reinforced polymer composites where it has been established that these properties improved after reinforcement [16-21]. Few attempts have been made regarding the photo-/bio-degradation of polymer fiber composite, for example in aqueous
media [22], in terrestrial environment [23], biodegradation after exposing in oxidizing, reducing, hydrogen producing bacteria in bath culture [24] and fungal degradation [25]. There has been no real discussion / report in the literature about the effect of preparation manner as well as UV irradiation on biodegradability of polymer-agro waste composites in composting and culture environments, those 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 FT-IR, were used for the study of the performance against microbial attack in compost and culture of A. niger before and after UV irradiation by measuring the weight loss and fungal growth, respectively, with surface morphology changes through SEM and variation in molecular structure by infra red spectroscopy in comparison of controlled PP samples.

4.2. Experimental part

4.2.1. Material

Polymer material was the same as given in Chapter 1. Maleic anhydride (MAH) was obtained from E. Merck India, and was used after recrystallization. Benzophenone and dicumyl peroxide (DCP) were obtained from Aldrich and were used as received. All the solvents of A.R. grade were taken from S.D.Fine Chem.Pvt. Ltd., India, Coir (Cocos nucifera) fibers were collected from raw material by retting process and activated by immersion in water for 15 days. After sun drying of 10 days and cutting into pieces ~2.5-3.0 mm in length, fiber were washed with distilled water and further dried in vacuum at 55 ± 5°C till constant weight is achieved.

4.2.2. Preparation of composites

Grafting of MAH (2.0 M) onto polymers was done in a UV reactor (λ ≥ 290 nm) for 2h in dry acetone (30 ml) taking benzophenone (0.29M) as a photosensitizer at 65± 5°C. This obtained copolymer was dried under vacuum to a 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 composite (GFC). Second type of composites were prepared by direct reactive mixing of polymers, MAH (2% wt.), DCP, 0.2 % wt. and fiber (50: 50 as polymer) at 145± 5°C followed by thoroughly washing in toluene. These composites were named as direct fiber composite (DFC). Polymers 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 films were used as received. Both the composite samples and neat polymers were molded as films (~100 μm) by carver press.

4.2.3. Characterization and performance evaluation

FT-IR, SEM and photo-/bio-degradation was carried out as were performed in Chapter 3 [29-30]. The biodegradability was measured as % weight loss in samples after composting. The constitution of 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. The temperature of the compost increased rapidly during the last days of incubation after an extra addition of the same quantity of cow dung as had initially been added. The samples were kept inside the compost at a depth of 3.5 feet. The surface of test specimen (2.5 X 2.5 cm) was inoculated by spraying the spore suspension for fungal (A.niger) growth. To avoid the contamination, petri dishes were wax sealed after incubation at 27-30°C and 85-90 % humidity.

4.3. Results and discussion

4.3.1. Compatibility of fiber and polymer matrix

To characterize the DFC, GFC samples and to measure the esterification extent, FT-IR spectroscopy was performed. The spectra of samples of PP are shown in Figure 4.1-4.5, as all the spectra in this region were same for all the samples. Esters have two characteristic strong 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 4.1 The absence of any observable peaks at 1360 and 1580 cm⁻¹ indicates the absence of anionic form of anhydride with one carboxylic acid i.e., the maleic anhydride is present either as dicarboxylic acid dimer or cyclic form in both forms of PP-MAH samples. This was confirmed by the appearance of peaks at 1780,1863 cm⁻¹ for cyclic anhydride and 1718 cm⁻¹ for carboxylic acid dimmer; this peak was again confirmed by O-H stretching peak (3200-3300 cm⁻¹) because cyclic dimer has a center of symmetry. Figure 4.2 shows the spectra of both MAH bound PP after fiber treatment where a significantly detectable additional peak from 1740-1750 cm⁻¹ is due to the C=O stretching of ester bond, formed between the coupling agent and fiber in the case of GFC whereas in DFC, it was hardly detected which could not be used for conformation of esterification. Thus,
more esterification takes place in GFC compared to that of DFC. This fact was again supported by the presence of high area under the peak at 1160 cm⁻¹ in DFC for secondary free –OH group, indicating the presence of unreacted cellulose fiber as shown in Figure 4.3. The good extent of esterification in GFC was again confirmed by the lower water absorption (11-13%) than DFC (26%) after 35h at room temperature, and it was due to the lesser number of OH groups in GFC. The appearance of less detectable peak at 1050 cm⁻¹ suggesting that primary alcoholic groups of cellulose are also participate in esterification and are likely due to the steric hindrance effect of bulky groups that prohibits the reaction. The broad spectrum near 3330 cm⁻¹ (Figure 4.4) arises from -OH groups in polymeric structure and since this is present at comparatively lower frequency (bathochromic effect) than the free hydroxyl group (3200-3600 cm⁻¹), this is due to intermolecular hydrogen bonding by the interaction between -COOH of anhydride and the –OH of fiber. In all the samples grafting efficiency of GFCs were higher than DFCs and the effect of monomer concentration on the grafting efficiency in copolymers was not observed.

Figure 4.1. FT-IR spectra of PP after treatment with MAH
Figure 4.2. FT-IR spectra of esterification in MAH treated PP by cellulose fiber

Figure 4.3. FT-IR spectra for free OH groups in the composites
4.3.2. Photodegradation

During UV irradiation, cellulosic material undergoes depolymerization or chain scission, leading to the formation of carbonyl groups and fragmentation into non-volatile or volatile products [31]. Bleek et.al. [32] found glucose (6 carbon atom) and arabinose (5 carbon atom) reducing units during the irradiation of oligosaccharides. The photoproducts generated on UV degradation of PP, PE, E-P copolymers have 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 FT-IR is a conventional technique for measuring the photodegradation in polyolefins as the area of these regions increases 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 host polymer of composite during degradation but also for cellulose materials because of high overlapping of peaks to each other. The changes in hydroxyl and carbonyl region for both composites of PP are presented in Figure 4.5 (a),(b) & 4.6 (a),(b) where it is clear that carbonyl and hydroxyl regions increase in both the composites, also showed more increase for DFC in this region during irradiation which can be used as an
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 in these regions of composites were not as sharp as in neat polymers. The E-P copolymer containing more ethylene was less degradable than copolymer with less ethylene content. No significant difference was observed among DFC samples which were attributed to the higher and almost equal degradation under UV light due to the peroxide generated degradation during preparation.

The bands around 3400 cm$^{-1}$ in polymers during photo-oxidation indicated the generation of intramolecular hydrogen bonded hydroperoxides and alcohols. The increase in the unsaturation, as the two peaks generated at 974 & 1009 cm$^{-1}$ for alkene and vinylene groups, respectively, in the case of both composites of PP (Figure 4.7), was attributed to the abstraction of H atom corresponding to carbonyl group. This effect is more in DFCs than neat polymers suggesting the sensitization effect of CO groups of the compatibilizing agent.

Figure 4.5. (a), Changes in the FT-IR spectra (carbonyl region) of DFC of PP upon irradiation.
Figure 4.5. (b), Changes in the FT-IR spectra (hydroxyl region) of DEC of PP upon irradiation.

Figure 4.6. (a), Changes in the FT-IR spectra (carbonyl region) of GFC of PP upon irradiation.
4.3.3. Biodegradation

4.3.3.1. Composting

Biodegradability was measured periodically up to 6 months in compost. It was estimated in the term of % weight loss of samples (~100μm thickness, 5 replicates) after washing with distilled water and drying in oven for 24h at 50°C. 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 and irradiated samples of composites are shown in Figure 4.8-4.14. where the decrease in weight of neat polymers was less than both composites, indicating fiber degrade 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 free radical generator peroxide. Figure 4.9, illustrates the degradation for 20h UV treated samples of PP. The significant degradation was not observed in 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 matrix of polymer after consuming the nutrients present on the surface and this fact has been eliminated for longer hour irradiation. Weight loss markedly increased for 50 and 100h UV treated samples (Figures 4.10 & 4.11).

**Figure 4.8. Weight loss of unirradiated samples**

**Figure 4.9. Weight loss of 20 h irradiated samples**
Figure 4.10. Weight loss of 50 h irradiated samples

Figure 4.11. Weight loss in 100 h irradiated samples

All the 100h treated samples were unrecoverable after 5 months and DFCs samples could not be recovered after 4 month, here it should be noted that these samples had already became brittle during UV treatment. Figure 4.12-4.14 shows the biodegradation in 100 h UV irradiated and composted samples of PE and E-P copolymers. Higher weight loss of DFCs, that could not be recovered after 4 months, than GFCs can be explained as discussed earlier i.e. the higher degradation of DFCs during preparation. The samples prepared from PE showed degradation lesser than EPQ and EPF .EPF was more degradable in both the environment which indicates that the concentration of monomer can significantly alter the durability. Decreasing carbonyl / ester bond region in FT-IR spectra again strongly suggested the use of polymer as nutrients by microbes through the
well established Albertsson et. al [38-40] mechanism (Figure 4.15). Some facts are appearing necessary to take into consideration for the discussion at this stage. GFC weight loss increased around 68% after 5 months (in case of PP) and samples could be recovered very carefully whereas DFC weight loss ~ 55%, (in case of PP) could not be recovered in the present system. The protection against brittleness in GFC must be due to the more extent of esterification i.e. more compatibilization, but since ester bond facilitate biological attack by providing a active site for coenzyme A (Co-ASH) during hydrolysis, these samples underwent high weight loss and retained in the compost for 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 the samples were not recoverable due to the brittleness which was caused mainly through extreme chain scission in polymer matrix suggesting chain scission is also an important unit during biodegradation. In all the cases photo degradation enhanced degradability in biotic environment [41, 42].

Figure 4.12. Weight loss of 100 hr UV irradiated DFC and GFC of LDPE after composting (DFC after 4 months and GFC after 5 months)
Figure 4.13. Weight loss of 100 hr UV irradiated DFC and GFC of EPQ after composting (DFC after 4 months and GFC after 5 months)

Figure 4.14. Weight loss of 100 hr UV irradiated DFC and GFC of EPF after composting (DFC after 4 months and GFC after 5 months)
4.15. FT-IR Spectra of GFC of PP (100h, irradiated sample) after compost incubation

4.3.3.2. 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 longer time is necessary for degradation by fungus, spores were sprayed in more quantities on the surface of specimens including unirradiated samples and at a slightly increased temperature. During the incubation period, the composites were degraded gradually from the surface and characteristic morphology appeared according to SEM. Visual growth rate of irradiated and unirradiated samples are tabulated in the Table 4.1-4.4, 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 to unirradiated samples. Fungal coverage was markedly affected by the manner of preparation of composites and copolymer composition.
Table 4.1. Visual growth rating of A. niger on PP composites

<table>
<thead>
<tr>
<th>Days</th>
<th>PP</th>
<th>DFC</th>
<th>GFC</th>
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<tbody>
<tr>
<td></td>
<td>0</td>
<td>20</td>
<td>50</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0</td>
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</tr>
<tr>
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<td>0</td>
<td>0</td>
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</tr>
<tr>
<td>30</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 4.2. Visual growth rating of A. niger on polymer composites of EPF

<table>
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<tr>
<th>Days</th>
<th>EPF</th>
<th>DFC</th>
<th>GFC</th>
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<td>40</td>
<td>1</td>
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Among the 50 & 100h irradiated composites, DFCs were highly colonized on surface than GFCs within 10-15 days, which is quite obvious due the more use of DFCs as energy source by fungus i.e, easy fungal consumable products were present in more amount on the surface of specimens. In the case of GFCs samples, colonization increased gradually from 20-40 days in comparison to DFCs, where a marked increase was not observed which must be due to the large availability of easily fungal consumable products initially and as soon as it becomes limited, fungal growth slowed down whereas in GFCs, slow ester link cleavage was in progress, consequently biodegradation rate increased as a function of time. The greater degradation (visual colonization) of DFCs in the case of unirradiated samples than in GFCs as it was same during composting, indicates that the
functional groups generated during photooxidation, are initially responsible for the consumption of films by A.niger.

Table 4.3. Visual growth rating of A. niger on polymer composites of EPQ

<table>
<thead>
<tr>
<th>Days</th>
<th>EPQ</th>
<th>DFC</th>
<th>GFC</th>
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<tr>
<td></td>
<td>Irradiation time in hrs.</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td>1</td>
<td>1</td>
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<tr>
<td>40</td>
<td>1</td>
<td>1</td>
<td>2</td>
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</table>

Table 4.4. Visual growth rating of A. niger on polymer composites of PE

<table>
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<th>Days</th>
<th>PE</th>
<th>DFC</th>
<th>GFC</th>
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<tbody>
<tr>
<td></td>
<td>Irradiation time in hrs.</td>
<td>0</td>
<td>20</td>
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<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
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4.3.4. Morphological aspects

SEM is a significant and reliable tool to measure the morphological changes of degraded polymer and crucial photographs of some interesting observations of photo-, bio- and photo-biodegraded samples are highlighted in Figure 4.16-4.18. The morphological changes of UV irradiated and compost / culture incubated samples have been studied in the earlier report [30] where highly cracked network and deep eroded surface was found during the degradation of samples. The fiber coupling which may be responsible for binding of the polymer matrix during degradation supported from the Figure 4.16 (a) and
4.16 (b) of 100h irradiated and 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 and two type of area, one partially intact and other degraded, showed that fungus is attacking in different mode of intensity according to the substrate i.e degradation process occurring in a selective manner. From the Figure 4.16 (a), it seems that two parts of the polymer were joined together by fiber and as soon as fungus consumed this fiber, these parts start to separate and probably due to the absence of such type coupling in DFC, fragmentation takes place more rapidly and specimens could not be recovered. Cracked structures were observed in SEM micrograph of one part of GFC after last limit of compost incubation, where PP portion was cut down carefully (Figure 4.16 d). SEM micrograph of only polymer part of 100h irradiated and 4 months compost incubated DFC is shown in Figure 4.16(c) where a perfect separation of polymer surfaces is clearly visible. SEM of same sample (Figure 4.17 (e)), showed the presence of large cavity and fine fragmentation of GFC of polymer. Small vacant tracks in 100h irradiated and 40 days culture incubated sample (Figure 4.17 (f)) clearly indicated that mycelia of fungus had grown but was washed out during the washing. Figure 4.17 (g), and (h) shows the micrographs of 100h irradiated GFC and DFC of PP respectively. The formation of cavities on DFC surface is due to the removal of volatile oxidation products. Figure 4.18 (i) and (k) showed the morphological changes of degraded samples of EPF (GFC and DFC respectively) where, crack formation was lesser in GFC than DFC. In this case, highly cracked surface of DFC were observed which strongly suggest higher biodisintegration in DFC. From Figure 4.18 (j) and (l) of 50h irradiated and culture incubated GFC of EPQ, it is evident that the mycelium of fungus were grown clearly which may penetrate the film surface with time of culture incubation.
Figure 4.16. SEM micrographs of different degraded samples of a-d.

Figure 4.17. SEM micrographs of different degraded samples of e-h.
Thus, over all study of degradability of cellulose fiber and thermoplastic composites indicated that compatibilization played a dominant and key role during actual biodegradability in agro waste polymer composites. The mechanism of photodegradation in composites followed similar pattern as in neat polymers [37]. This conclusion was evidenced from the FT-IR spectral pattern upon irradiation where the absorption at 1712, 1722, 1740 and 1785 cm\(^{-1}\) for carboxylic acid, ketone, ester and lactones, respectively, were observed [35,36,38]. These functionalized chains must be biodegraded by enzymatic action of microbes as was indicated from the FT-IR spectra of GFC of PP (100h, irradiated sample) after compost incubation where a clear decrease in ester region was observed and similar findings has been reported by Albertsson et.al. [3,4]. The tentative mechanism was further supported by surface morphology where two type of areas were observed, one partially intact and other degraded, showed that fungus is attacking in different mode of intensity according to the substrate i.e degradation process occurring in a selective manner. This type surface must be due to the easy consumption of degraded product.
4.4. Conclusions

Photodegradation study shows that composites prepared from direct mixing method were more photodegradable than commercial polymers and composite prepared by grafting method. Biodegradability was increased with the increasing time of UV treatment. There was a significant effect of method of preparation of samples on the durability. In compost incubation, weight loss of unirradiated samples for directly prepared composites was more than composite prepared by grafting method. It must be because of additional degradation which has already been 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, irradiated graft composites were showing uniform coverage of surface by fungus. Composition of E-P copolymer significantly influence the degradation behavior of composites and degradation decrease with increase in ethylene content. From the overall observation of the study, in general it was concluded that thermoplastic-agro waste composites may play a key role as an ecofriendly material.
4.5. References:


