Chapter 7

UV ageing and biodegradation studies

Abstract

The effects of environmental degradation on the physical and mechanical properties of oil palm fiber reinforced NR and NBR composites have been discussed in this chapter. The composites were subjected to UV ageing and soil immersion. Effect of oil palm fiber loading and chemical treatment on the degradability of the composites in different environments has been evaluated. The tensile properties of oil palm fiber reinforced NR composites exposed to UV radiation were studied. The tensile properties were found to decrease with increase in time of exposure to UV radiation. The reduction in tensile properties is due to chain scission and degradation occurring to NR molecules as a result of photo oxidation promoted by ultraviolet radiation. The retention of tensile properties increases with increase of fiber loading and chemical modification. Bio-degradation tests were carried out in soil burial conditions. It was seen that the durability of the composites was greatly depend on chemical treatment and fiber content. NR and NBR composites containing chemically treated oil palm fibers were found to be less resistant to soil erosion.

Results in this chapter have been communicated to Radiation Chemistry and Physics
7.1 Introduction

Natural fiber composites combine good mechanical properties with a low specific mass. New applications and end uses of natural fiber composites for automobile applications, packaging, and outdoor facilities and their exposure to atmosphere or contact with aqueous media have made it necessary to evaluate the environmental effects of natural fiber reinforced rubber composites (1). The high level of moisture absorption by natural fibers, its poor wettability and the insufficient adhesion between untreated fibers and the polymeric matrix lead to debonding with age (2). The biodegradability of natural fibers can contribute to a healthy ecosystem while their low costs and high performance are able to fulfill the economic interests of industries.

Synthetic and natural polymers are normally not biodegradable until they are biodegraded into low molecular mass species that can be assimilated by microorganisms (3). The principal types of damage that occur to composites are interlaminar cracking, interlayer delamination, fiber breakage, fiber/matrix interface failure, and fiber pullout. They propagate and interact as a consequence of environmental aging, which leads to the progressive degradation of the properties of the material (4, 5).

The durability of biocomposites utilized for building components has been a subject of recent concern and questioning. The long-term effects of weathering on biocomposites used as building components were evaluated using an accelerated weatherometer by Mehta et al. (6). Degradation behaviour of natural rubber–aluminium powder composites: effect of heat, ozone and high energy radiation was investigated by Vinod et al. (7). The cracks generated due to ozone exposure are small and discontinuous in aluminium powder filled vulcanizates, whereas the cracks are deeper, wider and continuous for other filler incorporated samples.
Environmental durability of banana-fiber-reinforced phenol formaldehyde composites was investigated by Seena et al. (8). The composites were subjected to water aging, thermal ageing, soil burial, and outdoor weathering. Selden et al. (9) studied the effect of accelerated UV-ageing on properties of PP/wood-fiber composites. Joseph et al. (10) studied the environmental effects on the degradation behavior of sisal fiber reinforced polyethylene composites with special reference to the influence of ageing conditions like treatment with water and UV radiation. The influence of the tensile properties of sisal/PP composites exposed to UV radiation was studied. The tensile properties were found to decrease with increase in the time of exposure to UV radiation. The reduction in properties was due to chain scission and degradation occurring to PP molecules as a result of photo oxidation promoted by UV radiation.

Natural rubber (NR) unlike many other polymers is highly susceptible to degradation, due to the presence of double bonds in the main chain. Degradation of NR is accelerated mainly by heat, light, humidity, ozone and UV radiation (11). In technological evaluation, rubber vulcanizates are subjected to accelerated ageing tests to get information about the service life. Baker (12) examined the effect of temperature on the ageing behavior of natural rubber compounds. Effects of high energy radiation, thermal and ozone exposure in natural rubber composites containing sisal fiber were reported by Varghese et al. (13). Many of the chemically unsaturated rubbers are prone to attack by even the minute quantities of ozone present in the atmosphere. Such attack not only detracts from the surface appearance of rubber products but also causes loss of physical properties, especially in thin walled articles. Natural rubber when properly compounded with suitable waxes or antioxidants will have ozone resistance as good as or even better than many synthetic rubbers (14). Natural fibers seem to have little resistance towards environmental
influences. This can be recognized in the composite and can be advantageously utilized for the development of biological degradable composites with good physical properties (15).

In this chapter, the performance of oil palm fiber reinforced NR and NBR composites under various environmental conditions has been discussed. Natural rubber and nitrile rubber composites are subjected to UV ageing and soil burial test. The environmental tests helps to evaluate the outdoor application of these composites in various applications. The changes in the physical and mechanical properties of composites as a result of UV ageing and soil immersion have been analyzed. SEM studies helps to assess the environmental effects on various composites.

7.2 Results and Discussion

7.2.1 Ageing by UV radiations of NR composites

7.2.1.1 Effect of fiber loading

Natural rubber (NR), unlike many other polymers, is highly susceptible to degradation, due to the presence of double bonds in the main chain. The degradation behavior of oil palm/NR composites by UV radiation is of considerable importance. Figure 7.1 shows the variation of tensile strength of fiber reinforced rubber composites as a function of fiber loading, when exposed to UV radiation for different periods of time. As the time of exposure to UV radiation increases the tensile strength decreases (16). This is true for all fiber loadings. The reduction in properties is due to the chain scission and degradation occurring to natural rubber molecules during irradiation for a longer duration. Oxidative reactions initiated by ultraviolet radiation is represented in Fig. 7.2. The degradation of NR is due to photooxidation promoted by ultraviolet (UV) radiation. For the reaction, oxygen is used up before it can diffuse to the interior so that degradation is
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concentrated near the surface, even in polymers in which high UV levels are present in the interior. Schematic representation of NR molecules after extensive photo degradation is shown in Fig. 7.3.

**Figure 7.1** Variation of tensile strength of oil palm/NR composites when exposed to UV radiation for different periods of time

Initiation RH(polymer) \[ \text{hv} \rightarrow \text{R.} \]
Propagation \[ \text{R.} + \text{O}_2 \rightarrow \text{ROO.} \]
\[ \text{ROO.} + \text{RH} \rightarrow \text{ROOH} + \text{R.} \]
Branching \[ \text{ROOH} \text{hv} \rightarrow \text{RO.} + \cdot \text{OH} \]
\[ 2\text{ROOH} \rightarrow \text{ROO.} + \text{RO.} + \text{H}_2\text{O} \]

**Figure 7.2** Schematic representations of oxidation reactions initiated by UV radiation
The formation of surface cracks in the case of NR after exposure to UV radiation for 3 months can be understood from the SEM photographs given in Fig. 7.4 a and b. Figure 7.4 a represents SEM photograph of unaged NR and Fig. 7.4 b that of NR after exposure to 3 months. It is observed that the NR sample developed surface degradation after 3 months of exposure to UV radiation. This can also be evidenced from Fig. 7.1 i.e., the tensile strength of NR sample after 3 months of exposure to UV radiation is decreased by 90%. Surface cracks can also be caused by thermal stresses during outdoor exposures due to the day night variations in temperature or due to the assistance of tensile residual stresses that develop at the surface of some polymers during weathering (17). Crack propagation can be controlled to some extent by the addition of fibers to NR. Figure 7.5 and 7.6 show the SEM photographs of oil palm microfiber / NR composite containing 10% and 30% fiber after exposure to UV radiation for 3 months. Surface cracks can be observed here also. By the incorporation of oil palm fiber in to NR matrix, the extent of NR degradation during UV irradiation can be reduced. This can be evidenced from Fig. 7.1. From the
figure it is clear that the extent of degradation for NR after 3 months is 85% where as that for 10% fiber loading is 60% and 20% fiber loading is 38% and for 30% fiber loading is 33%. It is interesting to note that with increase in fiber loading the extent of retention in tensile properties increases (Table 7.1).This is true for all irradiation times from 2 to 12 weeks. This can be evidenced from Table 7.1. It is observed from Fig. 7.1 that after 8 weeks of irradiation, the tensile strength almost remains a constant.

Figure 7.4  SEM photographs of (a) unaged NR and (b) NR after UV exposure to 3 months

Figure 7.5  SEM photographs of oil palm / NR composite containing 10% fiber (NRM10) after exposure to UV radiation for 3 months
Figure 7.6 SEM photographs of oil palm / NR composite containing 30% fiber (NRM30) after exposure to UV radiation for 3 month

Table 7.1 Retention in tensile strength of untreated oil palm/NR composites with fiber loading after irradiation for varying time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Retention in tensile strength (MPa) after</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 weeks</td>
</tr>
<tr>
<td>NR</td>
<td>70.2+ 2.86</td>
</tr>
<tr>
<td>NRM10</td>
<td>90.2+4.2</td>
</tr>
<tr>
<td>NRM20</td>
<td>92.5+4.64</td>
</tr>
<tr>
<td>NRM30</td>
<td>93.3+4.45</td>
</tr>
</tbody>
</table>

Figure 7.7 depict the loss in elongation at break of NR composites as a function of fiber loading. It can be seen that as fiber loading increases the loss in elongation at break increases. As the time of exposure to UV radiation increases, loss in elongation at break increases.
Figure 7.7  Variation of loss in elongation at break (%) as a function of fiber loading

7.2.1.2 Effect of chemical treatment

The effect of chemical treatments on the tensile strength of composites after exposure to UV radiation for different periods of time is given in Fig. 7.8. Chemically treated composites show a decrease in tensile strength with increase of exposure time. Although the treated fiber composites show higher strength the relative extent of the decrease is greater in treated composites. In the case of chemically treated oil palm /NR composites the surface appearance is badly damaged and fibers lying near to the surface become exposed up on UV irradiation. This can be evidenced from the SEM photographs given in Fig. 7.9 and 7.10 which show benzoylated, silane treated oil palm /NR composites respectively after exposure to UV radiation for 3 months. In the case of silane treated composite, the extent of surface degradation is more compared to benzoylated treatment. This can be evidenced by comparing the Fig. 7.9 and 7.10. The extent of degradation after 3 months in the case of
benzoylated composite is 38%, silane treated composite is 39%, resorcinol (bonding agent) treated composite is 41% and untreated composite is 33% respectively. It can be understood from Table 7.2 that the extent of retention in tensile strength of treated composites is less compared to untreated composites i.e., the treated composites undergo severe degradation compared to untreated composites. Table 7.3 shows the effect of chemical treatments on the modulus of oil palm/NR composites at 30% fiber loading after exposure to UV radiation for different periods of time. It is very clear that the tensile modulus decreases with increase of irradiation time. The reduction in the modulus values may be due to degradation as a result of chain scission.

![Graph showing the effect of chemical treatments on tensile strength of composites after exposure to UV radiation for different periods of time.](image)

**Figure 7.8** Effect of chemical treatments on the tensile strength of composites after exposure to UV radiation for different periods of time.
**Figure 7.9** SEM photographs of benzoylated oil palm / NR composite (NRMB30) after exposure to UV radiation for 3 month

**Figure 7.10** SEM photographs of silane treated oil palm / NR composite (NRMS30) after exposure to UV radiation for 3 month
Table 7.2  Retention in tensile strength of chemically treated oil palm/NR composites after UV irradiation for varying time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Retention in tensile strength (MPa) after</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 weeks</td>
</tr>
<tr>
<td>NRM30</td>
<td>93.3+4.45</td>
</tr>
<tr>
<td>NRMB30</td>
<td>89.8+3.97</td>
</tr>
<tr>
<td>NRMS30</td>
<td>90.9+4.67</td>
</tr>
<tr>
<td>NRMH30</td>
<td>88.5+4.13</td>
</tr>
</tbody>
</table>

Table 7.3  Modulus of chemically treated oil palm/NR composites after UV irradiation for varying time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 100% elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>uninirradiated</td>
</tr>
<tr>
<td>NRM30</td>
<td>3.02+0.14</td>
</tr>
<tr>
<td>NRMB30</td>
<td>4.37+0.16</td>
</tr>
<tr>
<td>NRMS30</td>
<td>4.86+0.18</td>
</tr>
<tr>
<td>NRMH30</td>
<td>3.56+0.14</td>
</tr>
</tbody>
</table>

7.2.2  Biodegradation of oil palm microfiber reinforced natural rubber composites

Among all the microorganisms involved in the degradation of cellulose, the most active are found in the fungal genera Chaetomium, Myrothecium, Memnoniella, Stachybotrys, Verticillium, Alternaria, Trichoderma, Penicillium and Aspergillus. The two last genera are very important, since they include species that can grow at relatively much lower conditions of moisture
availability than other cellulolytic fungi (18). It is known that brown rot fungi are rather effective in decomposing cellulose and hemicellulose, while white rot fungi are able to degrade lignin. The species that degrade cellulose belong mainly to the genera Cytophaga, Cellulomonas, Cellvibrio, Bacillus, Clostridium and Sporocytophaga.

The degradation of the (1, 4)-\(\beta\)-D-glucan cellulose results from the action of cellulolytic enzymes produced by a range of bacteria and especially fungi. In native cellulose, the antiparallel long-chain molecules cellulose molecules are composed of up to \(10^4\) D-anhydroglucose units and form micelles that are aligned in microfibrils. Lateral linking of the molecules by hydrogen bonding gives highly ordered crystalline regions within the microfibrils, but there are also the presence of ordered paracrystalline and non-crystalline (amorphous) regions (19). During microbiological attack, three types of hydrolytic enzymes appear to act synergistically on the glucose that is present in cellulose, which can be used by the microorganisms as a source of carbon for growth and development.

The hydrolytic breakdown of the cellulose in plant fibers is dependent on destruction of waxy protective layer, the cuticle, on the surface of the fibers by other enzymes. It is only after degradation of this layer, the destruction of cellulose in the fibers proceeds. Obviously, a principle effect of cellulolytic enzymes is to decrease the degree of polymerization of the long-chain cellulose molecules, so that fiber structure is impaired and fiber strength decreased (20). The actual rate of deterioration is largely dependent on the degree of crystallinity of the cellulose since amorphous cellulose is more easily attacked than crystalline cellulose, but other characteristics such as the degree of polymerization are also important.
Biodegradation, according to Albertsson and Karlsson (21) is defined as an event, which takes place through action of enzymes or chemical decomposition associated with living organisms such as bacteria, fungi, etc. and their secretion products. Biodegradation of the high molecular weight cellulose weakens the lignocellulosic cell wall because crystalline cellulose is primarily responsible for the strength of the lignocellulosics and due to degradation of cellulose, the strength is lost. Bio fibers change their dimensions with varying moisture content because the cell wall of polymers contain hydroxyl and other oxygen containing groups which attract moisture through hydrogen bonding. The hemicelluloses are mainly responsible moisture sorption, but the noncrystalline cellulose, lignin and surface of crystalline cellulose also plays major roles. In an interesting study, Lu et al. (22) used the enzyme cellulase to investigate the biodegradability of the self-reinforced sisal composites. The degradation behavior of the materials was evaluated with reference to the effects of ageing in water, enzyme solution and soil. The authors were of the opinion that unlike cellulase induced biodegradation of the composites, in which cellulose degrades preferentially; microbiological deterioration takes place in all the components, leading to a more substantial decay of the mechanical performance of the composites.

7.2.2.1 Effect of fiber loading

In the present study, tensile specimens were buried in soil for a period of 6 and 12 months and the tensile strengths were compared before and after burial. Figure 7.11 presents the losses in tensile strength of the rubber composites as a function of fiber loading. It can be seen that as fiber loading increases the loss in tensile strength increases reaching a maximum of about 31%. This can be attributed to the fact that the presence of lignocellulosic fibers paves the way for biodegradation.
Vulcanized natural rubber is not biodegradable and it is the presence of the biofibers that accounts for this loss. It can be further seen that as the time of exposure increases the loss in tensile strength also increases. Figure 7.12 depicts the loss in modulus at 100% elongation of various composites. It can be seen that as fiber loading increases the loss in these parameter increases. For the samples exposed to the soil for 12 months, a 10% increase in loss of modulus was seen. Figure 7.13 depict the weight loss of the tensile samples on exposure to soil. It can be seen that as fiber content increases the weight loss also increases indicating that fibers play a prominent role in degradation. Figure 7.14(a) shows the SEM of pure NR and 7.14 (b) that of NR after soil burial for 6 months. The NR surface is eroded and crack formation is on the surface. Figure 7.15 SEM of 10% fiber composite (NRM10) and 7.16 that of 30% fiber (NRM30) composites. In the case of composites, fiber pull out and peeling can be seen in the figure. SEM picture clearly indicates the deterioration of properties of soil immersed fiber composites.

![Graph](image)

**Figure 7.11** Variation of loss in tensile strength with fiber loading
Figure 7.12 Variation of loss in modulus at 100% with fiber loading

Figure 7.13 Variation of weight loss as a function of fiber loading
Figure 7.14 SEM photographs of NR (a) before soil burial (b) after soil burial for 6 months

Figure 7.15 SEM photographs of NRM10 (10% fiber) after soil burial for 6 months
7.2.2.2 Effect of treatment

The use of chemically treated fibers to reinforce matrix has a profound influence on the properties of the composites. Chemical modifications of fibers have resulted in enhanced tensile properties and durability characteristics. Acetylation is known to improve the dimensional stability, strength and biological properties of wood and wood composites. Coupling agents like silanes have been used commonly for improvement of properties in man-made fibers and particulate-filled composites. Basically, the function of coupling agents in the polymer composites industry is to provide stable bonds between two otherwise, hydrophilic fibers and hydrophobic matrix. Mercerization is yet another economic but effective method of increasing the adhesion between fibers and matrix.

Figure 7.17 exhibits the losses in tensile strength of the chemically treated samples. It can be seen that chemical modification of the composites has resulted in a decrease of loss of tensile strength by 15%. Among the composites containing treated fibers, the minimum loss in tensile strength is found in composites containing fibers treated with silane coupling agent. This can be attributed to the high level of adhesion in these composites. For the
composites containing silane treated fibers the loss in tensile strength ranges around 10 to 12%. Composites exposed to soil burial for 12 months exhibited greater losses in mechanical properties.

![Figure 7.17 Variation of loss in tensile strength with chemical modification](image)

Figure 7.17 Variation of loss in tensile strength with chemical modification

Figure 7.18 represents the variation of loss in modulus at 100% elongation with chemical modification. It can be seen that upon silane treatment the loss in modulus decreases by 8% while upon resorcinol treatment the loss in modulus decreases by 10%. Figure 7.19 shows the variation of weight loss as a function of chemical modification. It can be understood that chemically modified fibers are more resistant to biodegradation compared to untreated ones, as weight loss decreases with treatment. Also the composites exposed to soil burial for 12 months show higher degradation. It is clearly evident that chemical modification of composites has resulted in a lowering of loss of mechanical properties. Chemical modification of the lignocellulosic fibers results in decreased hydrophilicity of the fibers leading to proper wetting between matrix and fibers,
consequently a stronger interface which is resistant to decay by microbes. Another reason is that the presence of alkali and silane coupling agents act as a protective covering on the fibers making it resistant to the action of microorganisms present in the soil.

Figure 7.18 Variation of loss in modulus with chemical modification

Figure 7.19 Variation of weight loss as a function of chemical modification (30phr)
7.2.3 Soil burial studies of NBR composites

7.2.3.1 Effect of fiber loading

The lignocellulosic natural fibers are degraded biologically because organisms recognize the carbohydrate polymers, mainly hemicellulose in the cell wall and have very specific enzyme systems capable of hydrolyzing these polymers into digestible units. In the present study, tensile specimens of oil palm/NBR composites were immersed in soil for a period of 6 and 12 months and the tensile strengths were compared before and after burial. Figure 7.20 and 7.21 present the losses in tensile strength, modulus at 100% elongation respectively of NBR composites as a function of fiber loading. It can be seen that as fiber loading increases the loss in tensile strength increases reaching a maximum of about 22%. This can be attributed to the fact that the presence of lignocellulosic fibers paves the way for biodegradation (23). Vulcanized nitrile rubber is not biodegradable and it is the presence of the biofibers that accounts for this loss (24). It can be further seen that as the time of exposure increases the loss in tensile strength also increases. It can be seen that as fiber loading increases the loss in modulus also increases. Figure 7.22 (a) shows the SEM of pure NBR and 7.22 (b) that of NBR after soil burial for 6 months. Surface degradation can be seen in the picture (b). Figure 7.23 shows the SEM of 30% microfiber added composite (NBRM30) after soil burial for 6 months. In the case of composites, fiber pull out and void formation can be seen in the figure. SEM picture clearly indicates the degradation of properties of soil buried fiber composites.
Figure 7.20 Variation of loss in tensile strength with fiber loading

Figure 7.21 Variation of loss in modulus at 100% with fiber loading
7.2.3.2 Effect of chemical treatment

Figure 7.24 shows the losses in tensile strength of the chemically treated samples. It can be seen that chemical modification of the composites has resulted in a decrease of loss of tensile strength by 13% in the case of
NBR composites. Among the composites containing treated fibers, the minimum loss in tensile strength is found in composites containing fibers treated with resorcinol bonding agent. This can be attributed to the high level of adhesion in these composites. Composites exposed to soil burial for 12 months exhibited greater losses in mechanical properties. Also the composites exposed to soil burial for 12 months show higher degradation. It is clearly evident that chemical modification of composites has resulted in a lowering of loss of mechanical properties. Figure 7.25 shows the SEM of silane treated fiber composite (NBRMS30) and Fig. 7.26 that of resorcinol treated composite (NBRMH30) after soil burial for 6 months. In the case of composites, fiber peeling from the matrix and void formation can be seen in the photograph. SEM picture clearly indicates the degradation of properties of soil buried modified fiber composites.

![Figure 7.24 Variation of loss in tensile strength with chemical modification](image-url)
Figure 7.25 SEM photographs of NBRMS30 (30% fiber) after soil burial for 6 months

Figure 7.26 SEM photographs of NBRMH30 (30% fiber) after soil burial for 6 months
7.2.4 Comparison between NR and NBR composites

Environmental studies were conducted on NR and NBR composites by soil burial of the tensile samples for a period of 12 months.

Figure 7.27  Variation of loss in tensile strength for NR and NBR composites for 12 months soil burial

Figure 7.28  Variation of loss in modulus% for NR and NBR composites for 12 months soil burial
From Fig.7.27 it can be inferred that the loss in tensile strength% is higher for NR composites than NBR composites. Thus NBR composites are more resistant to environmental effects. From Fig.7.28 the loss in modulus% is higher for NR composites for a period of 12 months soil burial.

7.3 Conclusions

The physical and mechanical properties of the composites under different environmental conditions were studied. The influence of the tensile properties of oil palm/NR composites exposed to UV radiation was studied. It is observed that at all fiber loadings, the tensile strength decreases with increase in exposure time to UV radiation due to chain scission of NR molecules as a result of photo oxidation promoted by UV radiation. It is interesting to note that at higher fiber loadings (30% by weight); the tensile strength remains a constant at higher irradiation time. The tensile properties were found to decrease with increase in the time of exposure to UV radiation. Tensile properties of NR and NBR composites decrease with soil immersion. The decrease of properties increases with increase in oil palm fiber loading. The maximum deterioration in properties is observed for 30% composites. Chemical treatments reduced the degradation of the composites due to strong fiber/ matrix adhesion.

References

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