5: DEGRADATION

STUDIES OF BLENDS
5.1 INTRODUCTION

In general, degradation is the process where deterioration in the properties of polymer takes place due to different factors like, light, heat, mechanical etc. As a consequence of degradation, the resulting smaller fragments do not contribute effectively to the mechanical properties and the article becomes brittle and the life of the material becomes limited. Biodegradation of polymers may be achieved by two major paths (1) design of a polymer from monomers which are vulnerable to micro-organisms and (2) incorporation of biodegradable components/additives in the non-biodegradable polymer [217]. Polymers obtained from biodegradable monomers such as poly-L-lactic acid or poly-b-hydroxybutyrate contains hydrolysable linkages. The biodegradable component in the partial biodegradable polymer blends contains some hydrolysable groups or linkages such as ester, hydroxyl, amide and urea etc. Such hydrolysable groups are hydrolysed under microbial attack as shown below.

In this study the path chosen was to incorporate the biodegradable component (PLLA) in non biodegradable component (LLDPE). The preparation and characterization of blends is given in chapter 3 and 4.

This chapter demonstrates the investigation on degradation studies of blends and their effect on mechanical, thermal, and morphology of PLLA/LLDPE blends in the absence/presence of compatibilizer.
5.2 ABIOTIC DEGRADATION STUDIES

5.2.1 Thermo-Oxidative Degradation

The degradable plastics exposed to heat may be subject to many types of physical and chemical changes. Short exposure times at elevated temperatures generally serve to shorten the induction period of oxidatively degradable plastics. Physical properties, such as tensile strength and elongation may change during this induction period. However, these changes are generally not due to molecular-weight reduction but are merely a temperature dependent response, such as loss of mechanical properties due to embrittlement.

The thermo-oxidative stability of blends was studied by calculating the loss of mechanical properties before and after ageing (K\textsubscript{TO}) of blend films as shown in Table 5.1.

**Table 5.1:** Results of Thermo-oxidation coefficient (K\textsubscript{TO}) of LLDPE 100 and LLDPE blends in presence and absence of M-g-L

<table>
<thead>
<tr>
<th>Blend code</th>
<th>K\textsubscript{TO} according to tensile strength</th>
<th>K\textsubscript{TO} according to elongation at break</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE 100</td>
<td>0.94</td>
<td>0.96</td>
</tr>
<tr>
<td>LLDPE 80</td>
<td>0.81</td>
<td>0.83</td>
</tr>
<tr>
<td>M-g-L 80/4</td>
<td>0.89</td>
<td>0.90</td>
</tr>
<tr>
<td>LLDPE 65</td>
<td>0.72</td>
<td>0.73</td>
</tr>
<tr>
<td>M-g-L 65/4</td>
<td>0.80</td>
<td>0.82</td>
</tr>
</tbody>
</table>

It has been observed that with increasing % of PLLA in blends without compatibilizer the thermo-oxidative stability decreases. K\textsubscript{TO} was much higher for LLDPE 100 as compared to LLDPE 65. This could be due to the presence of PLLA, which is more prone to deterioration in presence of heat and oxygen. However, in presence of
compatibilizer, thermo-oxidative stability of blend increased. This could be due to increase in resistance to oxidative diffusion of LLDPE in compatibilized blends which prevent the diffusion of atmospheric oxygen into molecular chains of polymer blends.

5.2.2 Thermal Degradation Under Inert Medium

Thermogravimetric (TG) traces of PLLA, M-g-L, LLDPE 100 and their blend films are illustrated in Figure 4.9. The thermal stability has been discussed in chapter 4. The thermal decomposition kinetics was studied by using thermogravimetry decomposition data. The determination of kinetic parameters, Arrhenius activation energy and pre exponential factor has been calculated. The calculation of thermal endurance of blends was also performed as per the procedure given in ASTM E1641 and ASTM E1877. The observations from these have been discussed below:

5.2.2.1 Thermal-endurance of blends

The activation energies were calculated from Arrhenius plot of heating rates and temperatures of constant conversions using equation (1)

\[ E_A = -(R/b) \frac{\Delta \log \beta}{\Delta \frac{1}{T}} \]  

(1)

Where,

\[ E_A = \text{Refined Arrhenius activation energy (kJ/mol)} \]

\[ R = \text{Gas constant (8.314 J/mol-K)} \]

\[ b = \text{Approximation derivative (1/K)} \]

\[ \beta = \text{Heating rate (K/min)} \]

\[ T = \text{Temperature at constant conversion (K)} \]

\[ \frac{\Delta \log \beta}{\Delta \frac{1}{T}} = \text{Slope of the Arrhenius plot} \]

Activation energy calculated from these plots was highest for PLLA (230.1 kJ/mol) and
lowest for LLDPE 100. PLLA/LLDPE (80/20) blend and M-g-L 80/4 had activation energy of 172.2 and 192.1 kJ/mol respectively. The calculated activation energies for thermal degradation of pure polymers and their blends are presented in Fig. 5.1.

![Activation energies (E_A) for thermal degradation of PLLA, LLDPE 100, LLDPE 80 and M-g-L 80/4](image)

**Figure 5.1:** Activation energies (E_A) for thermal degradation of PLLA, LLDPE 100, LLDPE 80 and M-g-L 80/4

From the knowledge of activation energy, The Arrhenius activation energies obtained are used to develop a thermal endurance curve using equation (2).

\[
T_F = \frac{E_A}{2.303R[\log t_f - \log(E_A/RT) + a]}
\]  

(2)

*TF = Failure temperature (K) at given value of conversion*

*t_f = Thermal life (hr) at a given value of conversion*

*a = Approximation integral*

The thermal - endurance curves, which estimate the lifetime (duration) of a material
Degradation Studies of Blends

exposed at a certain temperature, are shown in Figure 5.2. A greater value of $E_A$ for PLLA indicates that a larger amount of energy is needed to decompose the matter. Indeed, PLLA showed the greatest thermal endurance of all samples. The effect of its greater activation energy could be noticed on TGA plots also. It has been observed that PLLA took longer to start decomposing than did PLLA/LLDPE blends (with or without compatibilizer). The closeness of $E_A$ values for LLDPE 100, LLDPE 80 and M-g-L 80/4 blends (145.1, 172.2 and 192.1 kJ/mol, respectively) reflects the similarity of their TGA plots. But, this small difference becomes clearly noticeable on their thermal-endurance curves. The M-g-L 80/4 blend showed greater thermal endurance than that LLDPE 80.

Figure 5.2: Thermal endurance curves of PLLA, LLDPE 100, LLDPE 80 and M-g-L 80/4
This difference might be caused by the enhancing effect of compatibilizer i.e., uniform dispersion of PLLA in LLDPE matrix which would require a larger amount of energy to decompose the blend.

5.2.2.2 Relative thermal index (RTI)

Relative thermal index is a measure of the thermal endurance of a material when compared with that of a control with proven thermal endurance characteristics. The RTI is also considered to be the maximum temperature below which the material resists changes in its properties over a defined period of time. In the absence of comparison data for a control material, a time-to-failure of 60000 hr has been arbitrarily selected for measuring RTI.

**Figure 5.3:** Relative thermal index (RTI) of PLLA, LLDPE 100, LLDPE 80 and M-g-L 80/4

RTI is therefore, the failure temperature (RTI\textsubscript{f}), obtained from the thermal endurance curve. The relative thermal indices of LLDPE 100, LLDPE 80 and M-g-L 80/4 are
shown in Figure 5.3. With addition of PLLA to LLDPE, there is a significant increase in RTI due to higher stability of PLLA as compared to LLDPE. Addition of the compatibilizer shows relatively higher RTI (410.4°C) due to improved dispersion of PLLA in LLDPE matrix.

5.2.3 Hydrolytic Degradation

The hydrolytic degradation has also been studied by comparing the mechanical properties loss after and before exposure to acidic and basic media. Figure 5.4a, 5.4b and 5.4c shows the mechanical properties of LLDPE 100, LLDPE 80 and M-g-L 80/4 at different pH levels (7, 9 and 11) respectively. Being a hydrolytically stable material, LLDPE 100 showed insignificant drop in tensile strength at all pH levels. LLDPE 80 showed some drop in tensile properties probably due to degradation of PLLA. Whereas, M-g-L 80/4 showed maximum drop in mechanical properties over the pH range investigated. However, maximum degradation was observed under alkaline condition i.e. pH 11, as indicated by loss of strength (Figure 5.4c). Alkaline pH has been reported to favour the hydrolytic degradation [227]. The loss of mechanical properties can be attributed to surface erosion of amorphous phase and hence the change in the crystalline phase and molecular weight.

5.2.3.1 Morphological characteristics

Figure 5.5a and 5.5b shows the SEM images of the M-g-L 80/4 blend before and after hydrolytic degradation respectively. The before hydrolytic degradation image is shown for reference. There is a uniform dispersion of different phases before the degradation. The change in the uniformity after the degradation can be seen by the white spots, indicating that the surface erosion has taken place due to degradation of PLLA phase.
Figure 5.4: Tensile strength variations during hydrolytic degradation of LLDPE 100, LLDPE 80 and M-g-L 80/4 at different pH levels: (a) pH 7, (b) pH 9, and (c) pH 11.
which would loosen the grip within the matrix resulting in loss of mechanical properties.

5.3 BIOTIC DEGRADATION STUDIES

5.3.1 Degradation Characteristics of Blends in Soil Compost

The degradation of polymeric blends especially under environmental conditions is very important parameter form commercialization point of view. Any inert packaging material if converted into smaller particle size it will resolve the solid waste management problem. If the one component i.e. PLLA degrades from the blend matrix, the films changes into eroded surface having very less mechanical properties. The partial degradation study of blends also gives the idea how the new material perform in soil. Therefore, the degradation was evaluated in alkaline soil compost at pH (7, 9 and11). The degradation at alkaline pH was selected because the polymers are more susceptible to hydrolysis in alkaline medium [228]. The degradation behavior of LLDPE 100, LLDPE 80 and M-g-L 80/4 at pH 7, 9, and 11 are shown, respectively, in Figure 5.6a, 5.6b and 5.6c. It has been observed that PLLA showed some degradation,
whereas LLDPE did not. For the LLDPE 80 blend, the mass loss was maximum after aging in soil compostage for around 210 days, showed 10% degradation compared to LLDPE. The degradation was favored by alkaline soil compostage, as shown by the maximum loss of mass at pH 11. The M-g-L 80/4 blend had the highest degradation, because the presence of M-g-L increases the dispersion of PLLA in LLDPE matrix which leads to faster degradation.

5.3.1.1 Change in morphological properties after degradation

Figure 5.7a and 5.7b shows the SEM images of the M-g-L 80/4 blend before and after degradation of 360 days respectively. The before degradation image is shown for reference. There is a uniform dispersion of different phases before the degradation. The change in the uniformity after the degradation can be seen by spots, indicating that the surface erosion has taken place due to degradation of PLLA phase which would loosen the grip within the matrix resulting in weight loss.

5.3.1.2 XRD analysis

Figure 5.8 shows x-ray diffraction patterns of LLDPE 100, LLDPE 80 and M-g-L 80/4 taken before and after degradation. Table 5.4 summarized the degree of crystallization of LLDPE 100, LLDPE 80 and M-g-L 80/4 calculated before and after degradation. There is an increase in crystallinity in LLDPE 80 and M-g-L 80/4 by 10.13 and 12.81% respectively. This may be due to the assimilation of the amorphous part of the polymer by the bacteria and thus only crystalline region of is left behind leading to increase in the crystallinity. The negligible change in LLDPE 100 indicates there was no effect of soil compost on pure LLDPE films. The results are in support of the SEM.
Figure 5.6: Degradation in soil compost: mass retention of (a) LLDPE 100 (b) LLDPE 80 (c) M-g-L 80/4 at different pH levels: (■) pH 7, (●) pH 9, and (▲) pH 11
Figure 5.7: Scanning electron micrographs of the M-g-L 80/4 blend: (a) before and (b) after soil compost

Figure 5.8: XRD patterns of LLDPE 100, LLDPE 80 and M-g-L 80/4 before and after soil compost
Table 5.2: Crystallinity (%) of LLDPE 100, LLDPE 80 and M-g-L 80/4 before and after soil composting

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity (%) (Before)</th>
<th>Crystallinity (%) (After)</th>
<th>Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE 100</td>
<td>40.61</td>
<td>40.79</td>
<td>0.18</td>
</tr>
<tr>
<td>LLDPE 80</td>
<td>43.06</td>
<td>53.19</td>
<td>10.13</td>
</tr>
<tr>
<td>M-g-L 80/4</td>
<td>43.78</td>
<td>55.59</td>
<td>12.81</td>
</tr>
</tbody>
</table>

5.3.1.3 Thermal behaviour

The change of crystallinity after soil composting was also confirmed by DSC thermograms. The changes of melting enthalpy indicated changes of crystalline degree of blend samples. In Table 5.5, melting enthalpies of crystalline phase is presented.

Table 5.5: Changes of melting enthalpy $\Delta H$ (J/g) of LLDPE 100, LLDPE 80 and M-g-L 80/4 before and after soil composting

<table>
<thead>
<tr>
<th>Samples</th>
<th>Changes of melting enthalpy $\Delta H$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before soil composting</td>
</tr>
<tr>
<td>LLDPE 100</td>
<td>61.63</td>
</tr>
<tr>
<td>LLDPE 80</td>
<td>52.07</td>
</tr>
<tr>
<td>M-g-L 80/4</td>
<td>53.78</td>
</tr>
</tbody>
</table>
The changes of melting enthalpy $\Delta H \ (J/g)$ of films after composting can be seen very clearly. The increase in crystallinity was confirmed by an increase of melting enthalpy of the crystalline phase of polymer blends, because the amorphous phase was degraded first the overall crystallinity has been increased.

5.3.1.4 Thermogravimetric behaviour

The TGA of LLDPE 80, M-g-L 80/4 films before and after the biotic exposure are presented in Figure 5.9. Surprisingly, an increase in the $T_{20}$ from $266.47 \ ^\circ C$ to $328.66 \ ^\circ C$ for LLDPE 80 and $T_{20}$ from $326.07 \ ^\circ C$ to $394.920 \ ^\circ C$ for M-g-L 80/4 was observed. This increase could be attributed to the preferential bioerosion of the amorphous regions and fragments generated during the biotic exposure of the films as they are recognizable by the microbial enzymes [200].

Figure 5.9: Change in the thermal behaviour of LLDPE 80 and M-g-L 80/4 before and after soil composting
5.4 CONCLUSIONS

LLDPE/PLLA blends with and without compatibilizer, using grafted low-density polyethylene maleic anhydride, were prepared at melting condition in an extrusion mixer with post extrusion blown film attachment. Thermal properties show that the PLLA gives higher thermal stability compared to all blends. It has been also observed that the addition of the compatibilizer enhances the thermal stability of blend due to more uniform dispersion of PLLA in the LLDPE matrix. The M-g-L 80/4 blend shows greater thermal endurance and relative thermal index compared to LLDPE 80 blend. Thermo-oxidation stability of LLDPE is higher than that of PLLA. In the presence of compatibilizer, thermo-oxidation resistance increases largely due to filling of the incompatible gaps of LLDPE/PLLA blends with the compatibilizer, which prevents the diffusion of atmospheric oxygen into molecular chains of polymer blends. The M-g-L 80/4 shows maximum tensile strength loss at pH 11.