Chapter 6

Thermogravimetric and Dynamic Mechanical Properties of PALF/LDPE Composites

Part of the results presented in this chapter has been published in
(i) Materials Letters, 18, 163 (1993); and

6.1 Introduction

Thermal analysis is a widely used method in materials characterisation. It is essential to monitor not only the properties of the composite but also the basic raw materials through the processing cycle to the end product. Optimisation of the processing temperature and time with an understanding of matrix, reinforcing element and interface between matrix and reinforcing agent can lead to the best balance of composite properties such as modulus, thermal stability and energy damping.

Thermal properties, in particular the thermal or oxidative degradation of cellulose fibre reinforced polymer composites, have received little attention. However, this is an important design factor which sets the limits of processing temperature and thereby the type of matrices that can be reinforced by these fibres.
Thermogravimetric analytical (TGA) technique offers a more precise control of heating condition, such as variable temperature range and accurate heating rate, using only a small quantity of sample for analysis. In addition, it is possible to quantify the amount of moisture and volatiles present in the composites which have a deteriorating effect. In the case of cellulose fibres, degradation of lignin sets in at around 200°C, and other polysaccharides mainly cellulose are oxidised and degraded at higher temperatures.1 Most natural fibres lose their strength at about 160°C. Thermal analysis studies of cellulose fibres have been carried out and the effects of crystallinity, orientation and crosslinking on the pyrolytic behaviour of cellulose have been reported.2,5 Major6 reported that the oxidative degradation of cellulose takes place in the amorphous region. Less crystalline materials are degraded more rapidly by heat. Ramiah7 speculated that crystallinity, crystalline size, order, degree of polymerisation and crystal structure might influence the pyrolysis rates. The effect of grafting of various polyacrylates onto cellulose and its influence on temperature and heat of degradation have been investigated by Kokta and Valde8 using DSC and TGA. Kessira and Richard9 studied the thermal behaviour of ungrafted and methyl methacrylate and acrylate grafted bagasse and wood pulp loaded with CaCO₃.

Dynamic mechanical thermal analysis is a widely used tool for understanding structure-property relations in polymeric materials. The dynamic properties are generally expressed in terms of storage modulus, loss modulus and damping factor which are dependent on time and temperature. Much work has been done on the dynamic mechanical properties of particulate or fibrous composite materials with two objectives: (1) to understand the chemical or physical modifications induced by the introduction or and surface treatment of fibre/matrix and (2) to study the behaviour as a function of the properties of each phase. When the interfacial link is lacking, the value of the energy loss is higher than that of the polymer matrix due to the fibre ends that act as stress raisers, thus contributing to mechanical energy loss.10 Generally, the introduction of a filler in a polymeric matrix leads to reduction of the mobility of the macromolecular chains in
the vicinity of filler. This is manifested as the increase in the temperature of the main relaxation, associated with the glass transition.

The present chapter deals with the thermal properties of PALF/LDPE composites with special reference to the effect of fibre-matrix interface bonding. The dynamic properties of these composites are also examined with special reference to the effects of fibre loading, fibre orientation, fibre treatment, frequency and temperature.

6.2 Results and discussion

6.2.1 Thermogravimetric analysis

(a) Effect of fibre loading

Figure 6.1 shows the TGA curves of LDPE, PALF and PALF/LDPE composite containing 20% fibre. Thermal decomposition of each sample takes place in a programmed temperature range of 30 to 400°C. For PALF in the temperature range 75 to 175°C dehydration as well as degradation of lignin occurs and most of the cellulose is decomposed at a temperature of 350°C. The decomposition of LDPE occurs at a temperature of 400°C, which is higher than that of the fibre. Fibre filled system degrades after the polyethylene matrix as shown by thermogravimetric scan. It shows that thermal stability of composites is increased. This is also evident from derivative thermogravimetric curves (DTG) (Figure 6.2). Step analysis of neat polyethylene thermogravimetric scan (Figure 6.1) from 30-100°C shows a percentage mass drop of 0% whereas scan of PALF fibre shows a mass drop of about 6%. At 200°C the mass loss of fibre is 7.6%. This is associated with the lignin degradation. The major source of stability in cellulose is due to hydrogen bonding which allows thermal energy to be distributed over many bonds. As the less ordered region increases, the decreasing mobility of cellulose chains will strain and weaken the existing hydrogen bond, thus decreasing stability. In the case of PALF about 16% weight loss occurs at 300°C while in the case of LDPE thermal decomposition starts only at 250°C. In
PALF/LDPE composites a slight degradation occurs at 150°C due to the dehydration and the main decomposition is shifted to higher temperature region. Thus on comparing the weight losses at 300°C, it can be seen that the values are 16%, 2% and 3.2% for PALF, LDPE and PALF/LDPE composite, respectively. Weight losses at different temperatures are shown in Table 6.1. At 550°C LDPE is completely decomposed. But in PALF and fibre composites a residue of 94% and 84.8%, respectively is observed. This may be carbonaceous products. Kilzer and Broido\textsuperscript{15} reported that thermal pyrolysis of whole cellulosic material occurs through two simultaneous and competitive mechanisms, dehydration at about 200 to 270°C involving mainly loss of water to yield a dehydrocellulose and stepwise depolymerisation to yield a leavo glucose above 270°C. Formation of the latter is characteristic of crystalline region.

Figure 6.1. TGA curves of (a) LDPE, (b) PALF and (c) PALF/LDPE composite containing 20% fibre.
Table 6.1. Weight losses at different temperatures.

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100°C</td>
</tr>
<tr>
<td>PALF</td>
<td>6.0</td>
</tr>
<tr>
<td>LDPE</td>
<td>0.0</td>
</tr>
<tr>
<td>PL(^a)</td>
<td>1.0</td>
</tr>
<tr>
<td>PL(^b)</td>
<td>1.0</td>
</tr>
</tbody>
</table>

PL - PALF/LDPE composite (Fibre loading 20%)

a - Untreated fibre composite

b - PMPPIC treated.

In DTG curve, a peak is observed at 75°C in PALF which corresponds to the dehydration (Figure 6.2). The major peak at 350°C corresponds to the thermal degradation of dehydrocellulose. The DTG curve of LDPE shows a peak at 400°C which indicates the degradation of saturated and unsaturated carbon atoms in polyethylene. In PALF/LDPE composite two peaks are obtained. The minor peak at 410°C corresponds to the degradation peak of LDPE and the major peak at 510°C corresponds to the degradation of dehydrocellulose. It is interesting to note that in the composite the major peak is shifted to higher temperature region compared to PALF and LDPE peak, i.e. thermal stability is increased in composite compared to pure PALF due to improved fibre-matrix interaction. This can be further understood from the weight losses at definite temperatures, for example, the weight losses at 400°C for LDPE, PALF and PALF/LDPE composites are 40%, 58.8% and 18.8%, respectively (Table 6.1).
Figure 6.2. DTG curves of (a) LDPE, (b) PALF and (c) PALF/LDPE composite containing 20% fibre.

(b) *Effect of chemical treatment*

The extent of degradation of PALF/LDPE composite treated with PMPPIC is less than that of the untreated fibre composite up to 500°C. This is evident from Figures 6.3 and 6.4. At 450°C, the weight losses are 30% and 24% for the untreated and PMPPIC treated composite respectively, at a fibre loading of 20%. The slightly higher thermal stability of treated fibre composite can be attributed to the additional intermolecular bonding between fibre and matrix induced due to isocyanate treatment. The PMPPIC treatment of the fibre makes the composites thermally more stable than the untreated one. This is associated with the better interaction between fibre and matrix, due to the formation of covalent bond between the -N=C=O group of PMPPIC and -OH group of cellulose as explained earlier in Chapter 4.
Figure 6.3. TGA curves of PALF/LDPE composites: Effect of fibre treatment: (a) Untreated fibre, (b) PMPPIC treated (Fibre content 20%).

Figure 6.4. DTG curves of PALF/LDPE composites: Effect of fibre treatment: (a) Untreated fibre, (b) PMPPIC treated (Fibre content 20%).
6.2.2 Dynamic mechanical thermal analysis

(a) Effect of fibre loading

The temperature dependence of storage modulus $E'$ and loss tangent ($\tan \delta$) for LDPE and LDPE filled with 10% PALF fibre is depicted in Figure 6.5. At low temperature, $E'$ values of LDPE and composite are very close, i.e. at low temperature fibres do not contribute much to imparting stiffness to the material. In the case of pure LDPE, $E'$ drops steeply as temperature is increased above $-30^\circ$C due to the increased segmental mobility. However, in the case of composite, the reduction in modulus of matrix is compensated by the fibre stiffness. As a result, the change in modulus of composite is gradual up to $100^\circ$C. In the case of $\tan \delta$ as seen in Figure 6.5, two peaks are obtained one at low temperature ($-65^\circ$C) and other at higher temperature ($75^\circ$C). The relaxation spectra of composites in the transition regions depend mainly on the mechanical relaxation of matrix and loaded fibre and are affected to different extent by the interface between fibre and matrix. Normally, $\tan \delta$ values of polymer composites show two dispersion peaks, one at low temperature corresponding to the main relaxation of the matrix and another at high temperature due to the relaxation of the loaded fibres. In the case of neat PE, the peak at a temperature of $-65^\circ$C is due to the glass transition of PE. The high temperature peak at $75^\circ$C is associated with the onset of melting of the PE crystallites. In the case of 10% fibre filled system, it is interesting to note that the $T_g$ and $T_m$ are shifted to higher temperature, i.e. $-65^\circ$C to $-55^\circ$C and $75^\circ$C to $120^\circ$C, respectively. This is associated with the decreased mobility of the chains by the addition of fibres. The damping peak of the composites is lower and broader than that of polyethylene. This is due to the fact that, when strain is applied to the fibres, the greater stiffness of the fibres causes the strain to be controlled by the fibres in such a way that the interface which is assumed to be the more dissipative component of the composite is strained to a lesser degree.$^{16,17}$
Figure 6.5. Temperature dependence of storage modulus ($E'$) and mechanical loss factor ($\tan \delta$) of PALF/LDPE composites having different fibre loading (Fibre length 6 mm).

Figure 6.6 shows the effect of fibre loading on storage modulus and $\tan \delta$ of PALF/LDPE composites. It can be seen that $E'$ depends largely on fibre loading and it increases with fibre loading. At any particular temperature the storage modulus increases with fibre loading and decreases with increasing temperature which is clearly evident from Figure 6.7. The increase in modulus with fibre loading indicates that LDPE matrix gets stiffened by the addition of fibres. All the filled systems display similar dependence of $E'$ with temperature (Figure 6.7). The decrease of $E'$ with temperature is gradual up to $90^\circ$C. At $90^\circ$ all the filled systems exhibit nearly the same modulus and the influence of fibre in stiffening the matrix is marginal due to the melting of polyethylene crystallites. Compared to LDPE, $E'$ of composites become flatter and extends to the higher temperature side with fibre loading indicating the increased thermal stability of the composites. From Figure 6.6 it is clear that, $\tan \delta$ values increase with temperature.
Figure 6.6. Effect of fibre loading on $E'$ and $\tan \delta$ of PALF/LDPE composites (Oscillation frequency 35 Hz).

Figure 6.7. Effect of fibre loading on $E'$ of PALF/LDPE composites at different temperatures.
Figure 6.8 shows the variation of the loss modulus \( (E'') \) as a function of temperature at different fibre loading. As in the case of storage modulus \( (E') \), the loss modulus increases with fibre loading and decreases with increasing temperature.

![Figure 6.8](image)

Figure 6.8. Temperature dependence of loss modulus \( (E'') \) of PALF/LDPE composites having different fibre loading (Fibre length 6 mm).

(b) **Effect of orientation**

The dependence of storage modulus on temperature for PALF/LDPE composites at different fibre orientations is depicted in Figure 6.9. It is seen that at any temperature, longitudinally oriented fibre composites show the maximum value of storage modulus, whereas the transversely oriented fibre composites show the minimum. The storage modulus of the random composites shows intermediate
minimum. The storage modulus of the random composites shows intermediate values. This is due to the fact that the maximum properties are obtained when fibres are aligned in the direction of the applied force. When the fibres are oriented in the direction of application of load, the load will be taken by the fibres and hence a high modulus is obtained. In all cases the storage modulus decreases with the increase of temperature and the decrease is sharper at higher temperatures (>90°C) where the LDPE-phase undergoes melting. The effect is more prominent in the case of filled systems due to the deterioration of the fibre-matrix interface at higher temperature.

Figure 6.9. Temperature dependence of storage modulus (E') of PALF/LDPE composites having different fibre orientations (Fibre length 6 mm, fibre content 30%).
(c) *Effect of chemical treatments*

Fibre surface treatment has great influence on the dynamic mechanical properties of composites. The effects of chemical treatments on the $E'$ of PALF/LDPE composites at 20% fibre loading at a frequency of 35 Hz is shown in Figure 6.10. It is clear from the figure that a significant improvement in modulus is observed for treated fibre composite, which is attributed to the increase in interfacial stiffness achieved through more intense fibre-matrix interaction. This improvement increases with the fibre loading which is evident from Figure 6.11. Introduction of functional groups by the coupling agents enhances the fibre-matrix adhesion resulting in lesser molecular mobility in the interfacial region. The maximum improvement is observed in the case of PMPPIC treated composite.

![Figure 6.10. Effect of different chemical treatments on $E'$ of PALF/LDPE composites.](image-url)
Figure 6.11. Effect of chemical treatments on $E'$ and $E''$ of PALF/LDPE composites at different fibre loading (Temperature 27°C).

The effect of surface treatment on tan $\delta$ of PALF/LDPE composites is shown in Figure 6.12. In the case of PMPPIC treated composite a peak is observed at 52°C which corresponds to the interface effect. The melting peak is shifted to the higher temperature region in all treated composites. The damping of the composite increases proportionately to the increase of the modulus.
Figure 6.12. Effect of chemical treatments on tan $\delta$ of PALF/LDPE composites at different temperatures (Fibre loading 20%)
Figure 6.13. Effect of oscillation frequency on $E'$ and $E''$ of untreated PALF/LDPE composites (Fibre loading 20%).

Figure 6.14. Effect of oscillation frequency on $E'$ and $E''$ of PMPPIC treated PALF/LDPE composites (Fibre loading 20%).
The viscoelastic properties at a given frequency $f$ is quantitatively equivalent to those of an experiment carried out over a time $t = \frac{1}{2\pi f}$. Viscoelastic data collected at one given temperature can be superimposed upon data collected at different temperatures by shifting the curves, i.e. by using the time-temperature superposition principle.\textsuperscript{18-20} Figure 6.15 shows the $E'$ versus log frequency graph for temperatures from 30 to 110°C. Here experimental curves of the modulus for different temperatures are plotted against log $t$. The modulus curve at a particular temperature is then shifted along the frequency axis until it overlaps with the next curve. The distance between curves gives the value of the shift factor $\log a_T$. The shift factor $a_T$ characterises the rate of the relaxation mechanism at some temperature $T_i$ in comparison with the rate at a higher temperature $T_{i+1}$. In this way the $\log a_T$ values for all temperatures are determined.

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{figure6_15.png}
\caption{E' versus log $f$ curves of PALF/LDPE composites for temperatures from 30 to 110°C.}
\end{figure}
The temperature of 110°C was taken as the reference temperature in constructing the log \( a_T \) versus \( T \) graph illustrated in Figure 6.16. On this curve the value for a given temperature \( T \) shows how many times slower the relaxation mechanism at that particular temperature takes place than at the reference temperature, \( T_m = 110°C \) of the range under study. Using the time temperature superposition principle it is possible to predict the viscoelastic behaviour of a material well outside of the frequency or time range of mechanical equipment.

![Figure 6.16. Plot of log \( a_T \) versus \( T \).](image)

Figure 6.17 shows the Cole-Cole plot, where the loss modulus (\( E'' \)) data are plotted as a function of the storage modulus (\( E' \)). It is reported that homogeneous polymeric systems show a semicircle diagram whilst two-phase systems show two modified semicircles.\(^{17,21}\) In the present case the composites show a behaviour different from homogeneous system, possibly because of the presence of dispersed fibres and due to the different interphase effects.
Figure 6.17. Cole-Cole plots of PALF/LDPE composites.

6.3 References