Chapter 7

Dynamic Rheology and Thermal Degradation Properties of Microfibrillar Composites from PP and PET

The chapter deals with the dynamic rheology analysis and thermal degradation properties of PP/PET microfibrillar blends and composites. Dynamic rheology studies indicated that the storage and loss modulus of MFCs enhanced as draw ratio increased up to an optimized level beyond which they decreased. When the draw ratio was increased up to the optimized level the MFCs tended to be more viscous, especially at low frequency, whereas further increase in the draw ratio resulted in a decrease in the complex viscosity. The microfibrils of PET in the MFC were found to perturb the relaxation of molten PP matrix. The thermal decomposition studies revealed the capability of microfibrillar blends to delay the degradation better than the microfibrillar composites.

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7.1. Introduction

The fibre reinforced composites have the benefit of remarkably high modulus and strength for the weight of material used. It is an effective approach for producing a high-modulus, high-strength composite material to embed existing fibres, such as glass, carbon, and Kevlar fibres, in a surrounding polymer matrix. The incorporation of fibres, however, inevitably deteriorates the processing properties of the composites, especially in the short fibre reinforced thermoplastics. Up to now, the rheological behaviours of polymer composites have attracted much attention since they were closely related to their morphology and microstructure [1–3]. The overall understanding of the rheological behaviours of short fibre reinforced thermoplastics can also guide the choice of suitable processing conditions for the composites [4, 5].

The rheological behaviours of a short fibre filled polymer depend on many factors, such as fibre features (aspect ratio, length distribution), fibre orientation, polymer matrix, composition as well as interaction between fibres and polymer matrix [6–10]. In glass fibre filled polyethylene (PE) composites, there was a significant increase in viscosity with increasing fibre loading at low shear rates while there was little change at higher rates due to orientation of fibres [11]. The deformation and interaction of fibres often happen in shear field, which greatly influence the rheological behaviours of the materials [5, 12-13]. There are number of reports to prove the great impact of the thermal stability of polymers on blending [14–23]. The thermal stability of the blends depends strongly on the compatibility of the polymers [24]. Different polymers decompose over different ranges of temperatures
yielding different proportions of volatiles and residues. One of the most accepted methods for studying the thermal properties of polymeric materials is the thermogravimetry. Thermogravimetric curve represents the drop in the weight (W) of the sample with temperature (T). The normal (TGA) and derivative (DTG) thermogravimetric curves provide information about the nature, number of stages of thermal break down, weight loss of the materials in each stage, threshold temperature, stability and extent of degradation of the polymeric materials [25]. Normally, polymers and blends must encounter elevated temperatures at almost every stage in manufacturing, compounding, and processing stages, in service and during the repairing step. Therefore, an understanding of thermal stability and thermal decomposition behaviour of polymers and their blends is essential information for the development and extension of their applications.

The rheological behaviour of in-situ microfibrillar PET/HDPE and PC/HDPE polymer blends was investigated in a recent study [26-27]. For both PET/HDPE and PC/HDPE microfibrillar blends, the viscosity increased with PET and PC microfibril concentration. In another study, Xu et al [28] reported that the flexible microfibrils of PET and a thermoplastic polyester elastomer (HT) reduced the melt elasticity and viscosity of HDPE/PET/thermoplastic elastomer microfibrillar blends. The flexibility of the PET/HT microfibrils has influences on the rheological behaviour of the PET/HT/HDPE microfibrillar blends. With the increase of microfibrils flexibility, less energy was dissipated during geometry transformation or movement, and they became straighter, when
arriving in equilibrium state, which led to the reduction of melt viscoelasticity.

Saikrasun et al [29] studied the thermal and thermo oxidative stability of PP and a liquid crystalline polymer containing microfibrillar blend using nonisothermal TGA. A single step of weight loss was observed for the neat PP, whereas two and three weight loss steps were observed for microfibrillar blends in nitrogen and in air, respectively. In another study by Saikrasun et al [30], they found that the incorporation of LCP or rPET into PP matrix in the form of microfibrils retard the thermal degradation significantly in air but not in nitrogen.

An understanding of the rheology of newer materials like MFCs is extremely important in order to choose suitable processing conditions. The flow behaviour of MFCs is quite different from the corresponding polymer blends on account of the low processing temperatures involved and the fibrillar morphology of the dispersed phase. The in-situ composites are expected to behave like short fibre filled composites due to the reduction in the processing temperature. The elevated service temperature in most of the applications of the in-situ composites makes it necessary to have an understanding of their thermal degradation characteristics. Also they are expected to behave differently with respect to the normal blends at elevated temperatures.

In this chapter, dynamic rheological characteristics of PP, neat blend and all the MFCs are analyzed. In the second section of the chapter, the thermal decomposition behaviour of the neat blend, microfibrillar blends and MFCs are compared.
7.2. Results and discussion
7.2.1. Dynamic rheology

The frequency sweep experiments for rheological measurements were carried out at a temperature of 205°C. At this temperature, the PET phase is in a semi crystalline state, whereas the PP matrix is molten. Hence, the PET inclusions can be considered rigid in comparison with the viscoelastic nature of PP. Moreover, the fibrillar morphology of the PET phase is preserved in the isotropic PP matrix to create an environment similar to that of fibre reinforced thermoplastic composites.

7.2.1.1. Storage modulus

The storage modulus (G’) values of all the samples are found to increase with angular frequency (ω) as evident from Figure 7.1. The storage modulus values are highest for MC5 in the entire test frequency range. The obvious reason for the high G’ values for MC5 is the presence of PET microfibrils with a high aspect ratio. NB exhibits higher storage modulus values than MC2 and MC10 at low frequencies. However, at higher frequencies the G’ values of NB drops in comparison with MC2 and MC10. This phenomenon can be attributed to the contribution of PET microfibrils towards the elastic properties of the MFC.
Figure 7.1. Variation of storage modulus with frequency for PP, injection moulded neat blend and microfibrillar composites prepared at draw ratios 2, 5, 8, 10 carried out at 205°C.

NBI contains only spherical domains of PET, which are not capable of contributing to the storage modulus like the microfibrils especially at higher frequencies. PP exhibits the lowest storage modulus values in the test frequency range. It should be mentioned that the storage modulus obtained from the dynamic mechanical analysis in our earlier study [31, 32] also exhibited highest value for MC5 even at elevated temperatures at 1Hz.

7.2.1.2. Loss Modulus

The loss modulus ($G''$) values at 205°C are also found to increase with frequency ($\omega$) as shown in Figure 7.2. However, at frequency nearing 100 rad/sec the difference in loss modulus for the various MFCs is
negligible. This indicates the viscous behaviour at higher frequencies is identical for the MFCs irrespective of the stretch ratio. The loss modulus of NB is greater than MC2 and MC10 at low frequencies whereas it is lesser at higher frequencies. The difference in $G''$ values of MC5 with MC2 and MC10 at low frequencies is lower than the corresponding difference in the $G'$ values. This indicates that the PET microfibrils have a more significant effect on the elastic behaviour than the viscous behaviour of the composite.

![Figure 7.2](image)

**Figure 7.2.** Variation of loss modulus with frequency for PP, injection moulded neat blend and microfibrillar composites prepared at draw ratios 2, 5, 8, 10 carried out at 205°C.
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The values of $G'$ and $G''$ at low frequency generally provide information about long range (beyond entanglement distance) relaxation, while the values at high frequency provide information about short-range (motion with entanglement) relaxation [33]. As seen from Figures 7.1 and 7.2, $G'$ and $G''$ of all samples increase with increasing $\omega$, indicating a dependence of viscoelastic properties on the time scale of molecular motion. The value of $G'$ is higher than the corresponding $G''$ over the whole frequency range, meaning that the elastic characteristics for these samples are the dominant factor. In addition, the dependence of shear frequency on the elastic and viscous characteristics of PP is more pronounced than that of NB and MFCs, as seen from the rapid change in $G'$ and $G''$ of PP over the entire range of $\omega$ being studied. It can be noted that the variation of storage modulus and loss modulus for MC5 and MC8 in the analyzed frequency range is the least amongst all the samples. It should also be mentioned that for MC2 and MC10 this variation is much appreciable than even NB. The inadequacy of the PET microfibrils they possess in reinforcing the PP matrix could be further explained with this observation.

7.2.1.3. Complex viscosity

Figure 7.3 gives the complex viscosity ($\eta^*$) versus angular frequency ($\omega$) curves at 205°C. $\eta^*$ is calculated using the following equation:

$$\eta^* = \left[\left(\frac{G'}{\omega}\right)^2 + \left(\frac{G''}{\omega}\right)^2\right]^{1/2} \quad (7.1)$$
The complex viscosity of all the samples decreases with increase in frequency. The complex viscosity of MC5 is the maximum at low frequencies. At higher frequencies, MC5 and MC8 possess almost identical viscosity. NB has a higher $\eta^*$ than MC2 and MC10 at low frequency. However, at higher frequencies the viscosity of MC2 and MC10 are identical with that of NB. This is indicative of the reinforcing effect of PET microfibrils on the PP matrix at higher frequencies. PP has the lowest viscosity in the test frequency range. The change in $\eta^*$ is quite small for PP in the frequency range and it exhibits Newtonian behaviour at low frequencies. A linear reduction in the viscosity with frequency is exhibited by MC5 and MC8.

![Figure 7.3](image_url)

**Figure 7.3.** Variation of complex viscosity with frequency for PP, injection moulded neat blend and microfibrillar composites prepared at draw ratios 2,5,8 10 carried out at 205°C.
7.2.1.4. Tan delta

The tan δ curves delineated in Figure 7.4 indicate sharp decrease with frequency for all the samples except MC5 and MC8. The plateau region in the tan δ curve for MC8 is an indication of the formation of a physical network between the solid PET fibrils and the molten PP matrix, which hinder the relaxation of the PP phase. The microfibrils with low aspect ratio in MC2 and MC10 are not capable of affecting the relaxation mechanism of the matrix. This behaviour is similar to the observations of Monticciolo et al [34] where poly (butylene terephthalate) (PBT) microfibrils having higher aspect ratios restricted the relaxation of polyethylene (PE) matrix and reduced the solvent permeability of PE/PBT microfibrillar blends.

![Figure 7.4](image.png)

**Figure 7.4.** Variation of tan δ with frequency for PP, injection moulded neat blend and microfibrillar composites prepared at draw ratios 2,5,8,10 carried out at 205°C.
7.2.2. Thermogravimetric analysis

TGA studies were carried out to assess the effect of the dispersed phase and its morphology on the thermal decomposition of PP/PET blends, MFBs and MFCs. To clearly compare them in a more quantitative way, the thermal decomposition parameters are summarized in Table 7.1. \( T_{onset} \) represents the onset degradation temperature. \( T_{max} \) represents the temperature at the maximum weight loss rate \( (\frac{d\alpha}{dt})_{max} \). The char yield at 700°C is also reported.

George et al [14] and Peterson et al [35] have studied the thermal decomposition of PP and reported that the degradation mechanism of PP has been found to occur through a random scission followed by radical transfer process. However, PP degradation does not involve chain branching or crosslinking. The formation of the most abundant degradation products for the thermal decomposition of PP was suggested by Peterson et al [35] as illustrated in Figure 7.5. Several studies have been conducted on the thermal degradation products of PET which suggest that the thermal degradation of PET is initiated by chain scission of ester linkage, yielding carboxyl and vinyl ester groups [36-37] as illustrated in Figure 7.6.

7.2.2.1. Thermal degradation of microfibrillar blends and composites

The non-isothermal TG profiles of PP, NB and MFBs are given in Figure 7.7. The presence of PET significantly affected the degradation characteristics of the blend. For PET, the maximum weight loss of 60% occurs at 440 °C due to thermal degradation of the PET backbone. For NB also it was a single weight loss step but in the range of 330 to 450°C
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without any char yield. MFBs show a different trend in the thermal degradation in comparison with PP and normal blends.

![Thermal degradation scheme for PP](image)

**Figure 7.5.** Thermal degradation scheme for PP [35]

![Thermal degradation scheme for PET](image)

**Figure 7.6.** Thermal degradation scheme for PET [36]

The fibrillar morphology of the dispersed phase delays the onset of degradation of the MFBs. The $T_{onset}$ temperature of the MS8 samples is the highest in the MFBs followed by MS5. The high aspect ratio and the abundance of the PET microfibrils contribute to the delayed degradation
in MS5 and MS8. The lowest onset degradation temperature in the stretched blends is recorded by MS10 which can be attributed to the breakage of PET microfibrils as evidenced from the SEM images. The highest $T_{\text{max}}$, the temperature at the maximum weight loss rate is exhibited by MS8.

**Table 7.1.** Non-isothermal decomposition characteristics of PP, PET, NB, microfibrillar blends and microfibrillar composites in nitrogen

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>$(\text{da/dt})_{\text{max}}$ (%/min)</th>
<th>Char yield at 700°C (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>360.3</td>
<td>431.1</td>
<td>24.3</td>
<td>0</td>
</tr>
<tr>
<td>PET</td>
<td>396.7</td>
<td>437.9</td>
<td>18.9</td>
<td>12.2</td>
</tr>
<tr>
<td>NB</td>
<td>395.0</td>
<td>447.5</td>
<td>25.9</td>
<td>0</td>
</tr>
<tr>
<td>MS2</td>
<td>416.6</td>
<td>455.2</td>
<td>24.1</td>
<td>1.4</td>
</tr>
<tr>
<td>MS5</td>
<td>421.4</td>
<td>456.8</td>
<td>23.9</td>
<td>3.5</td>
</tr>
<tr>
<td>MS8</td>
<td>422.4</td>
<td>457.2</td>
<td>22.8</td>
<td>7.5</td>
</tr>
<tr>
<td>MS10</td>
<td>412.5</td>
<td>456.6</td>
<td>25.2</td>
<td>2.1</td>
</tr>
<tr>
<td>MC2</td>
<td>414.8</td>
<td>453.3</td>
<td>26.0</td>
<td>0.7</td>
</tr>
<tr>
<td>MC5</td>
<td>415.6</td>
<td>457.2</td>
<td>24.2</td>
<td>1.2</td>
</tr>
<tr>
<td>MC8</td>
<td>414.1</td>
<td>456.7</td>
<td>23.5</td>
<td>2.2</td>
</tr>
<tr>
<td>MC10</td>
<td>410.9</td>
<td>456.3</td>
<td>26.3</td>
<td>0.6</td>
</tr>
</tbody>
</table>
The conversion of MFBs into MFCs affects the orientation and aspect ratio of the PET microfibrils negatively as revealed by the morphology studies. This is reflected in the thermal degradation characteristics (Figure 7.8) of the isotropized samples. A reduction in the $T_{\text{onset}}$ temperature, increase in the weight loss rate and reduction in char yield % are observed. The weight loss rate of MC8 is however marginally lower than MS8.

![Dynamic TG curves of PP, PET, neat and microfibrillar blends](image)

**Figure 7.7.** Dynamic TG curves of PP, PET, neat and microfibrillar blends

The possible reason could be the maintenance of microfibrils with high aspect ratio in MC8 which entangled with the isotropized PP matrix
during injection moulding as seen from the SEM images. It should be mentioned that MC8 samples had the highest impact strength [31], which further substantiates the “entanglement phenomenon” of the microfibrils. The weight loss rate of PET, 18.9% is the lowest amongst all the samples.

**Figure 7.8.** Dynamic TG curves of PP, PET, neat blend and microfibrillar composites

The weight loss rate is the lowest for MS8 followed by MS5 in the case of MFBs. The same trend is followed in the case of MFCs also. For PP and NB, at 700°C no char residues are left. Pure PET leaves a char residue of over 12%, obviously indicating its superior thermal stability. MS8 samples which possessed the microfibrils with the smallest diameter...
gave a char yield of 7.5%. MS5 samples gave a char yield of 3.5% whereas MS2 and MS10 yielded only 1.4 and 2.1% respectively. In the case of MFCs, the char yield is lower than MFBs, indicating that randomly oriented short PET microfibrils are prone to degradation more easily than the oriented ones.

7.2.2.2. Derivative thermograms

The degradation characteristics of the MFBs and MFCs can further be compared using the derivative thermograms.

![Derivative thermograms for PP, PET, neat and microfibrillar blends](image)

**Figure 7.9.** Derivative thermograms for PP, PET, neat and microfibrillar blends
From Figure 7.9, the initial decomposition temperature of the microfibrillar blends is found to be higher than that of PP and PET. The initial decomposition temperature of the neat blend takes an intermediate position between those of the neat polymers. The initial decomposition temperature of MS5 is found to be the highest amongst all the samples. The fibrillar morphology of PET offsets the degradation temperatures to higher levels.

![Derivative thermogram for PP, PET, neat blend (NB), MS5(MFB) and MC5(MFC)](image)

**Figure 7.10.** Derivative thermogram for PP, PET, neat blend (NB), MS5(MFB) and MC5(MFC)
An effort was made to compare the degradation characteristics of MFB and MFC using DTG curves (Figure 7.10). For this, MS5 and MC5 were selected since MS5 gave the best results for thermal stability amongst the MFBs. From the plot it is clear that the initial decomposition temperature of MFC i.e MC5 is lower than that of MS5. The delay in the initialization of degradation for MS5 can be attributed to the PET microfibrils they possess. On comparing the decomposition tendencies with the neat blend it can be commented that NB degradation starts at a temperature which is lower than that of PET. The dispersed phase in the form of spherical domains (as available in the case of NB) are not capable to delay the degradation. It could be generally commented that the microfibrillar blends are much more resistive to degradation since both the phases (PP and PET in this case) have fibrillar morphology. On the other hand, once the MFB is converted into MFC the aspect ratio of the PET microfibrils are reduced and also the PP phase morphology changes from fibrillar to isotropized type resulting in a relatively low thermal stability.

7.2.2.3. Kinetics of thermal degradation

The thermal degradation kinetics of the MFBs and MFCs are analyzed using the Horowitz and Metzger [38] method to estimate the activation energy required.
Figure 7.11. Arrhenius plots for calculating the activation energy of degradation for PP, PET, neat and microfibrillar blends.

In this method the activation energy is calculated using the equation

\[
\ln \left( \frac{1}{(1 - \alpha)^{-1}} \right) = Ea \left( \frac{Ea \theta}{RT_{max}^2} \right) \tag{7.2}
\]

where, \( \alpha \) is the decomposed fraction of the sample

\[
\alpha = \frac{(C_i - C)}{(C_i - C_f)} \tag{7.3}
\]

where \( C \) is the weight at the temperature chosen, \( C_i \) is the weight at the initial temperature and \( C_f \) is the weight at the final temperature. \( T_{max} \) is the temperature at which the rate of weight loss is maximum. \( R \) is the universal gas constant 8.314 J/mol°K, and \( \theta \) is given by \( T - T_{max} \). Kinetic plots are made with \( \theta \) as the X axis and \( \ln \left( \frac{1}{(1 - \alpha)^{-1}} \right) \) as the Y axis to get the slope of the straight line plots as shown in Figures 7.11 and 7.12. The slope of the kinetic plots is determined and the activation energy for
all the samples are computed using equation 7.2. The activation energies are reported in Table 7.2.

![Arrhenius plots for calculating the activation energy of degradation for PP,PET, neat blend and microfibrillar composites.](image)

**Figure 7.12.** Arrhenius plots for calculating the activation energy of degradation for PP,PET, neat blend and microfibrillar composites.

The activation energy for PP is the lowest and the highest was recorded by PET. The incorporation of PET into the PP matrix has improved the thermal stability of the blend. The neat blend also possesses higher activation energy than PP. Amongst the microfibrillar blends MS5 followed by MS8 displayed the highest activation energy. Once the microfibrillar blends are converted into MFCs the activation energy for degradation reduces. The activation energies for MC2 and MC10 were almost identical with that of the neat blend. The activation energy obtained for the samples indicate the influence of the morphology of the phases in a blend system on its degradation.
### Table 7.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation Energy (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>138</td>
</tr>
<tr>
<td>PET</td>
<td>245</td>
</tr>
<tr>
<td>NB</td>
<td>154</td>
</tr>
<tr>
<td>MS2</td>
<td>167</td>
</tr>
<tr>
<td>MS5</td>
<td>201</td>
</tr>
<tr>
<td>MS8</td>
<td>192</td>
</tr>
<tr>
<td>MS10</td>
<td>165</td>
</tr>
<tr>
<td>MC2</td>
<td>140</td>
</tr>
<tr>
<td>MC5</td>
<td>163</td>
</tr>
<tr>
<td>MC8</td>
<td>165</td>
</tr>
<tr>
<td>MC10</td>
<td>149</td>
</tr>
</tbody>
</table>

A combination of fibrillar - fibrillar morphology for the phases involved has the highest resistance to degradation. The aspect ratio and abundance of the fibrils also have telling influence on the degradation characteristics. Activation energy for the samples with high percentage crystallinity (MS5 and MS8) is found to be on the higher side.

#### 7.3. Conclusion

From the dynamic rheological studies, the storage and loss modulus values are the highest for MFC prepared at stretch ratios 5 and 8 (MC5 and MC8). The dynamic viscosity values are found to be higher for MC5 and MC8. The randomly distributed PET microfibrils can form a physical network with the PP matrix which has a significant effect on the
elastic behaviour than the viscous behaviour of the composite. The high aspect ratio and the abundance of the PET microfibrils contribute to the delayed thermal degradation in MS5 and MS8. The char yield of the MFBs during thermal decomposition is found to be higher than the corresponding MFCs. The activation energies for thermal degradation of the MFBs are found to be higher than PP and neat blends but lower than that of PET. The microfibrillar composites exhibit lower activation energy for degradation than the microfibrillar blends.

Reference


