Chapter 4

Static Mechanical Properties of Microfibrillar Composites from PP and PET

The chapter deals with the static mechanical properties analysis of microfibrillar composites from PP and PET prepared at stretch ratios 1, 2, 5, 8 and 10. The tensile, flexural and impact properties were found increasing with draw (stretch) ratio. The tensile strength and modulus of the MFCs were found to be higher for the samples drawn at stretch ratios 5 and 8 on account of the long PET microfibrils they possessed. However, too high a stretch ratio was not desirable for the reinforcement of PP. The experimental values for tensile strength and tensile modulus were compared with those obtained from the theoretical equations.

Results in this Chapter have been published in
2) European Polymer Journal 45(6), 1738, 2009
4.1. Introduction

The two important factors typical of fibre reinforced composite materials contribute to impressive mechanical property profile: (i) a higher aspect ratio of the filler phase (ii) a good adhesion between the matrix and the microfibrils. There have been several studies on the mechanical properties analysis of in-situ composites based on MFCs. Most of the studies were oriented towards blend composition or the effect of compatibilizer. In PP/PA66 MFCs [1], as the PA66 content increases the tensile strength of the in-situ composites increase until PA 66 weight fraction reaches 15% and then decreases, whereas the Young’s modulus increases up to a plateau level. The impact strength continuously rises with PA66 weight fraction.

Li et al [2] reported the reinforcing effect of the PET microfibres was significant at 15wt % PET concentration, at which the tensile strength and tensile modulus of the composite were significantly increased when compared with the neat polyethylene and the conventional PET/PE blend with no microfibres. However, the tensile strength and modulus of the composite generally increased with the PET concentration, and were higher than the conventional PET/PE blend. Pesneau et al [3] obtained in-situ composites from PP/PA 6. The MFCs were found to have high Young’s moduli and an improvement of the tensile strength in comparison with the pure PP. However, PP-g-MA addition for compatibilization was not found to be effective for mechanical properties of the composite in comparison with the effect induced by the addition of PP-g-MA in polymer blends.
Evstatiev et al [4] reported that the modulus of MFC based on rPET/LDPE (50/50 w/w%) is about tenfold higher than that of LDPE and about three times that of glass sphere–reinforced LDPE, approaching the value of LDPE with 30 wt% GF. The tensile strength is at least twice that of LDPE or of glass sphere reinforced LDPE and similar to that of LDPE with 30% GF. The elongation at break is seven times lower than that of LDPE and half that of LDPE reinforced with glass fibres or glass spheres.

The studies on PP/PET 60/40 MFCs by Friedrich and co-workers [5] gave the following results. The compression moulded samples possess better mechanical indices (than the injection moulded specimens) and even than those of the PP + GF, because of the uniaxial orientation of the PET fibrils (when being oriented in the samples length direction). The impact energy of the injection moulded unmodified PET/PP blend is lower than that of the neat PP because of the incompatibility between PET and PP samples but it increase with increasing amount of the compatibilizer. Taepaiboon et al [6] reported that the flexural modulus, tensile modulus, and tensile strength of iPP/ rPET iMFCs were improved by the presence of rPET microfibres. Addition of PP-g-MA as the compatibilizer in the range of 2–7 wt % for this system was most suitable for the 85/15 w/w% iPP/rPET iMFCs.

Lei et al [7] found that the toughness of HDPE/recycled PET (75/25 w/w%) MFC was significantly enhanced by E-GMA compatibilizer. The impact strength increased from about 7 kJ/m² to about 60kJ/m² when 5% E-GMA was introduced, and the tensile fracture elongation increased by 83%. The mechanical properties of the samples injection moulded at 185 °C were usually higher than those of the samples injection moulded at 270 °C. In
their studies Evstatiev et al [8] reported that the tensile strength and impact strength of the PET/PP/TiO$_2$ MFC are lower when compared with the PET/PP MFC, because the incorporated TiO$_2$ particles either damage the PET fibrils or resulted in defects at the interface. However, an increase in tensile modulus for the PET/PP/ TiO$_2$ MFC was observed.

Only very few reports are seen in the literature on the effect of draw ratio on the properties of the MFCs. In a study involving hot stretched PE/PET blends [9] the tensile modulus and strength of PET/PE blends were significantly enhanced with increasing hot stretching ratio, indicating that the microfibres provided good reinforcement. However, too high a hot stretching ratio was not desirable for reinforcement of PET. Results from elongation tests showed that the ultimate elongation was greatly decreased with higher hot stretching ratio and there is a critical hot stretching ratio above which ductile-brittle transition occurred.

In this study the influence of draw ratio on the static mechanical properties of MFCs are studied. The effect of draw ratio on the mechanical properties is not reported widely in the literature. The significance of this study is that draw ratio employed during cold drawing has a significant role to play in the conversion of dispersed phase morphology into fibrillar type. Moreover, the stretch ratio employed decides the transverse dimensions of the fibrils which in turn decides the aspect ratio of the microfibrils after isotropization (injection moulding). From the morphology analysis it was clear that considerable variation in the microfibril diameter occurs on altering the draw/stretch ratio. Hence the optimization of draw ratio can be achieved only after analyzing the mechanical properties of the corresponding samples.
4.2. Results and discussion

The tensile, flexural and impact properties of PP, PET, neat blend and MFCs are given in Table 4.1.

Table 4.1. Static mechanical properties of PP, PET, neat blend and MFCs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (MPa)</th>
<th>Elongation at break (%)</th>
<th>Flexural strength (MPa)</th>
<th>Flexural modulus (MPa)</th>
<th>Impact strength (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>29.2 ± 0.6</td>
<td>1470 ± 32</td>
<td>33.9 ± 1.1</td>
<td>36.4 ± 1.7</td>
<td>742 ± 22</td>
<td>26.1 ± 0.2</td>
</tr>
<tr>
<td>PET</td>
<td>61.7 ± 1.4</td>
<td>3250 ± 33</td>
<td>24.7 ± 0.7</td>
<td>80.9 ± 1.8</td>
<td>1450 ± 31</td>
<td>27.2 ± 0.8</td>
</tr>
<tr>
<td>NB</td>
<td>23.3 ± 0.7</td>
<td>1514 ± 27</td>
<td>24.2 ± 0.7</td>
<td>39.1 ± 1.3</td>
<td>673 ± 19</td>
<td>21.7 ± 0.5</td>
</tr>
<tr>
<td>MC2</td>
<td>27.9 ± 0.5</td>
<td>1662 ± 36</td>
<td>28.6 ± 0.9</td>
<td>41.9 ± 0.8</td>
<td>787 ± 24</td>
<td>25.6 ± 0.4</td>
</tr>
<tr>
<td>MC5</td>
<td>32.4 ± 0.2</td>
<td>2137 ± 28</td>
<td>34.1 ± 1.1</td>
<td>47.1 ± 0.7</td>
<td>1015 ± 17</td>
<td>30.6 ± 1.0</td>
</tr>
<tr>
<td>MC8</td>
<td>31.5 ± 0.4</td>
<td>1927 ± 19</td>
<td>32.1 ± 0.8</td>
<td>44.4 ± 1.0</td>
<td>837 ± 28</td>
<td>36.7 ± 0.8</td>
</tr>
<tr>
<td>MC10</td>
<td>27.1 ± 0.7</td>
<td>1642 ± 22</td>
<td>27.8 ± 0.5</td>
<td>38.3 ± 1.1</td>
<td>735 ± 24</td>
<td>25.2 ± 0.6</td>
</tr>
</tbody>
</table>

4.2.1. Tensile properties

The influence of stretch ratio on the tensile strength and tensile modulus of the blend is presented in Figures 4.1 and 4.2. The properties of NB corresponds the values obtained at draw ratio 1. The low tensile strength of NB in comparison with PP can be attributed to the spherical
domains of the PET phase in the blend which remain incompatible with the PP phase. The tensile strength of MC2 is slightly higher than NB but still lower than PP. The tensile strength of MC5 is the maximum amongst all the samples analyzed. MC8 shows a slight reduction in the tensile strength in comparison with MC5. Further increase in stretch ratio leads to reduction in the tensile properties. The tensile modulus is found to be maximum for MC5. There is an increase of 41% in the tensile modulus of MC5 when compared to that of NB. MC8 also exhibits good tensile properties but slightly lower than MC5. It can be inferred that the tensile strength and tensile modulus of the in-situ composites increases with stretch ratio, reaches a maximum value between stretch ratios 5 and 8 and then reduces.

Figure 4.1. Variation of Tensile strength of MFCs with stretch ratio
Figure 4.2. Variation of Tensile modulus of MFCs with stretch ratio

The tensile response of the samples could further be analyzed using the stress-strain plots. The stress-strain curves of NB, MC2, MC5, MC8 and MC10 are plotted in Figure 4.3. It could be seen from the plot that the neat blend (NB) yields and fails at a low stress indicating that PET phase in the form of spherical particles are not able to act as reinforcement for the PP matrix. MC2 yields and fails at a higher stress in comparison with MC10. It should be remembered that the microfibrils obtained in the case of MC2 were longer than those obtained in the case of MC10. MC5 and MC8 exhibit a relatively ductile failure in comparison with NB, MC2 and MC10. From the Figure 4.3, one could see that necking is appreciable in the case of MC5 and MC8 as evident from the strain these samples are able to take up beyond the yield stress before failure. High yield stress followed by a pronounced necking region makes MC5 and MC8 samples stiffer and tougher. MC10 exhibits poor tensile properties, which may be attributed to the low aspect ratio of the fibrils as evidenced from the micrographs. In an earlier study [2]
involving PE/PET MFC system it was observed that the increase in hot stretch ratio made the composites more brittle.

In the case of neat blend the interfaces between the dispersed phase and the matrix debond and produce slippage due to the lack of the adhesion and interactions. When the specimens contain well defined reinforcing fibres, the interface area between the fibres and the matrix is very large because of the extremely small diameter of the fine fibres, and hence considerable interfacial contact exists compared to the spherical particles. As elongation increases, the slippage can go on until the specimen is broken.

![Stress-strain plots for NB and MFCs prepared at different stretch ratios](image)

**Figure 4.3.** Stress-strain plots for NB and MFCs prepared at different stretch ratios
The tensile moduli of all the in-situ composites are found to be higher than PP and NB. It was reported recently [9] that the tensile properties of HDPE/PET microfibrillar composites increased as the stretch ratio increases and then tends to decrease at very high stretch ratios. High tensile modulus coupled with high elongation at break as exhibited by MC5 and MC8 indicate the improvement in the toughness of the composites in comparison with NB. The length of the PET microfibrils were maximum in the case of MC5 and MC8 as evident from the corresponding SEM images. They are acting as excellent stress transfer agents, which contribute to the enhancement in the toughness of MC5 and MC8.

![Graph](image.png)

**Figure 4.4.** Variation of Elongation at break with stretch ratio

The elongation at break of the neat blend is the lowest as observed from Figure 4.4 owing to the spherical or elliptical shape of the PET phase.
Figure 4.5. Variation of Flexural strength with stretch ratio

Figure 4.6. Variation of Flexural modulus with stretch ratio
There is an increase in the elongation at break for the MFCs especially for MC5. It is generally reported that the incorporation of short fibres (especially inorganic ones) makes the composites more brittle. Here in this case the presence of PET microfibrils does not make the composite brittle as expected. They rather yield and break at higher stress levels since MC5 and MC8 possess longer microfibrils. Fibril tips in composite materials act as defects. Longer the fibrils the number of defects are less and higher the strength and elongation of the composite. At higher draw ratios (MC10) the elongation at break reduces which is due to the reduction in the length of the fibrils.

4.2.2. Flexural and impact properties

There is considerable improvement in the flexural properties of the in-situ composites in comparison with PP and NB as observed from Figure 4.5 and 4.6. The flexural strength of MC5 is found to increase by 20% and flexural modulus by 50% when compared to NB. There is an improvement in the flexural properties of the in-situ composites with stretch ratio. However, beyond stretch ratio 5, flexural strength and modulus decrease. MC10 exhibits poor flexural properties, which indicates the ineffectiveness of short PET microfibrils as reinforcement for PP.
Figure 4.7. Variation of Impact strength with stretch ratio

The impact strength of the samples are shown in Figure 4.7. The impact strength of MC8 is the maximum amongst all the samples followed by MC5. For MC8, microfibrils with the least diameter were obtained as observed from the micrographs. Further, the relatively continuous nature of fibrils allow better stress transfer from the matrix polymer (PP) during impact. MC10 exhibits poor impact properties since the short fibrils cannot act as effective stress transfer agents. It should also be mentioned that the impact strength is the lowest for NB, which is indicative of the immiscibility of the two polymers.

The reinforcing effect in a composite (matrix and fibre) system is related to amount of fibre, length of the fibre, the length/diameter ratio, length distribution of the fibre, direction of the fibre, amount of entangling points of the fibres, and the adhesion between the fibre and the matrix. There is a strong possibility for the formation of a transcrystalline
layer of PP around PET in the case of MC5 and MC8. The long microfibrils of PET in MC5 and MC8 act as nucleating agents for the transcrystallization of PP which improves the adhesion between the two phases.

The cavitation formation [9] between the two phases is significant in the case of MC2 and MC10 because of the short PET microfibrils they possess. The cavitation effect might lead to the debonding and failure of the composite without appreciable yielding. In the case of MC5 and MC8 the higher aspect ratio and the abundance of the PET microfibrils reduces the cavitation formation and brittle failure of the MFC. The longer microfibrils available in the case of MC5 and MC8 yield to higher levels before failure. The shorter fibrils which are randomly oriented in the case of other samples does not elongate much and exhibit a brittle failure.

4.2.3. Theoretical prediction of tensile properties

Halpin-Tsai equation has been proved useful in predicting the longitudinal modulus of aligned short fibre composites, e.g., in-situ composite with liquid crystalline polymer [10-12]. Li et al [13] and Fuchs et al [14] tried to apply this equation in predicting the tensile properties of MFCs. Here, both the fibre modulus \( E_f \) and the fibre aspect ratio \( L/D \) are dependent on the stretching ratio and the dispersed phase content of the extrudate.

According to Halpin-Tsai model [15], the Young’s modulus, \( M_c \), and the tensile strength, \( T_c \), of a composite are given by equations 4.1 and 4.2.

\[
M_c = M_n \left[ \frac{1 + A \eta_1 V_f}{1 - \eta_1 V_f} \right] \quad (4.1)
\]


\[ T_c = T_m \left[ \frac{1 + A \eta_2 V_f}{1 - \eta_2 V_f} \right] \]  \hspace{1cm} (4.2)

Where \( \eta_1 \) and \( \eta_2 \) are calculated using equations 4.3 and 4.4.

\[ \eta_1 = \frac{M_f - 1}{M_m} \left( \frac{M_f + A}{M_f} \right) \]  \hspace{1cm} (4.3)

\[ \eta_2 = \frac{T_f - 1}{T_m} \left( \frac{T_f + A}{T_f} \right) \]  \hspace{1cm} (4.4)

The terms \( M_c \), \( M_m \), \( M_f \) and \( T_c \), \( T_m \), \( T_f \) are the tensile modulii and tensile strengths of the composite, matrix and fibre, respectively, and \( V_f \) is the fibre volume fraction. The value of \( A \) is twice the aspect ratio of the fibres.

Halpin and Kardos [15] modified equations 4.1 and 4.2 by including the term \( \varphi \) which in turn is dependent on \( \Phi_{\text{max}} \), maximum packing fraction, of the reinforcement in the following manner.

\[ M_c = M_m \left[ \frac{1 + A \eta_1 V_f}{1 - \varphi \eta_1 V_f} \right] \]  \hspace{1cm} (4.5)

\[ T_c = T_m \left[ \frac{1 + A \eta_2 V_f}{1 - \varphi \eta_2 V_f} \right] \]  \hspace{1cm} (4.6)
The value $\Phi_{\text{max}}$ is 0.78 for square arrangement of fibres, 0.91 for hexagonal array of fibres and 0.82 for random packing of fibres. The value of $\Phi_{\text{max}}$ in this case was taken as 0.82 since the PET microfibrils are distributed randomly in the PP matrix. The value of $A$ estimated using SEM images were 12.5,64,60 and 10 respectively for MC2,MC5,MC8 and MC10. The tensile strength and tensile modulus of PET fibrils were taken as 61.7 MPa and 3250 MPa respectively for the calculations. The tensile strength and tensile modulus of PP (matrix) was experimentally obtained as 29.2 MPa and 1470 MPa.

**Table 4.2.** Experimental and theoretical tensile strength, tensile modulus values obtained for in-situ composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Halpin Tsai</th>
<th>Modified Halpin Tsai</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tensile Strength (MPa)</td>
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<td>34.0</td>
</tr>
<tr>
<td>MC10</td>
<td>27.1</td>
<td>1642</td>
<td>33.7</td>
</tr>
</tbody>
</table>
The tensile strength and modulus values obtained using Halpin-Tsai and modified Halpin-Tsai equations along with corresponding experimental results are given in Table 4.2. The theoretical values obtained by using both the equations are almost same for the in-situ composites at a particular stretch ratio. The tensile strength value obtained by theoretical prediction for MC8 shows a positive deviation of 8% from the experimental value, whereas in the case of MC5, the deviation is reduced to 5%. The tensile strength obtained experimentally for MC2 and MC10 are much lower than the values estimated theoretically. The tensile modulus values obtained theoretically are in close agreement with the experimental values obtained for MC2 and MC10. In the case of MC8, the theoretical value for the tensile modulus shows a negative deviation of 12%, whereas in the case of MC5 the negative deviation increases to 17%. The theoretical equations were found to be useful to model the tensile strength of MC5 and MC8 and tensile modulii of MC2 and MC10.

4.3 Conclusion

The tensile, flexural and impact properties of the MFCs are found increase with stretch ratio. However, too high a stretch ratio is not desirable for the reinforcement of PP. Neat blends, MC2 and MC8 exhibit a brittle failure in comparison with MC5 and MC8. In the case of MC5 and MC8 the higher aspect ratio and the abundance of the PET microfibrils reduces the cavitation formation and the brittle failure of the MFC. The impact strength of MFCs are found to be higher for MC8 on account of the fine (low diameter) microfibrils they possess. The experimental values for tensile strength and tensile modulus are compared with those obtained from the theoretical equations. The theoretical
equations are useful to model the tensile strength of MC5 and MC8 and tensile moduli of MC2 and MC10. Based on the above studies it can be concluded that microfibrils of PET obtained at draw ratios between 5 and 8 can effectively reinforce PP.

Reference


