Effect of fiber length on thermomechanical properties of short carbon fiber reinforced polypropylene composites

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A R T I C L E   I N F O

Article history:
Received 1 December 2007
Accepted 1 May 2008
Available online 8 May 2008

Keywords:
- Polypropylene
- Thermoplastic
- Composites
- Carbon fibers
- Thermogravimetric analysis (TGA)
- Dynamic mechanical analysis (DMA)

A B S T R A C T

Carbon fiber reinforced composites have all the ideal properties, leading to their rapid development and successful use for many applications over the last decade. In this paper, short carbon fiber reinforced polypropylene (SCF/PP) composite were prepared with melt blending and hot-pressing techniques. The thermomechanical properties of this composite were investigated taking into account the combined effect of mean fiber length. Thermal stability of the composite was studied via the thermal gravimetric analysis (TGA) and dynamic mechanical analysis (DMA) was used to measure the damping properties of the composites. Finally it can be shown that an increase in fiber length can enhance the thermal stability of SCF/PP composites and improve the damping properties as well.

1. Introduction

Carbon fibers are widely used in polymer–matrix composites owing to their good mechanical, thermal and electrical properties [1,2]. Due to these good mechanical, thermal, and electrical properties of conventional PAN and pitch-based carbon fibers, much effort has been devoted to the use of these fibers to improve and optimize the properties of various structures [3]. Although the majority of fiber reinforced resins contain glass fibers, the attractive properties of carbon fibers have made them a material of choice in various applications [4]. Furthermore, thermoplastic matrix composites offer property advantages, such as enhanced toughness and an unlimited shelf-life. Furthermore, their intrinsic recyclability is rapidly being recognized as a strong driving force for their application [5,6]. Short fiber reinforced polymers (SFRPs) were developed to fill the mechanical property gap between the continuous-fiber laminates used as primary structures by the aircraft and aerospace industry and the unreinforced polymers used in non-load-bearing applications [7–9]. SFRP composites are very attractive because of their ease of fabrication, economy and superior mechanical properties. Although SFRP composites are often made with conventional techniques, namely extrusion compounding and injection molding, for processing polymers [10,11], however compression moulding is a relatively simple and inexpensive process to make short fiber composites. Thermal analysis methods can provide a useful approach to characterize and investigate the interaction between fibers and polymers [12]. In this investigation, carbon fibers in different sizes were used to reinforce polypropylene (PP). PP was chosen as this polymer is produced in large quantities and it is not very sensitive to chemical stress cracking.

There are current or potential applications for SCF/PP composites in body structures for ‘passenger cars’ (e.g., car bonnet/hood [13] and interior trim), fuel cells, fuel tanks and several other niche uses. Combination of characteristics such as light-weight, corrosion resistance, low to moderate cost, thermal stability and easy processability, make them attractive for many applications especially in automotive industry [14].

Since nowadays, carbon fiber thermoplastic composites are widely used in various applications, it is essential to know about the thermal properties of these materials [15]. Thermogravimetry analysis (TGA) and dynamic mechanical analysis (DMA) were applied in this study. TGA techniques were used to determine the thermal decomposition and stability of SCF/PP composites with different CF lengths. DMA was used to determine the viscoelastic properties of SCF/PP composites with different CF lengths. The use of DMA to investigate the fiber–matrix interphase in polymer composites has been explored since last decade [16]. Here it will demonstrate that DMA offers a direct approach to evaluating the fiber–matrix adhesion based on the contribution of the interphase to the tan δ damping peak [17].

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doi:10.1016/j.matdes.2008.05.005
2. Materials and methods

2.1. Materials

The materials employed in this investigation were isotactic polypropylene (Titanpro SM950 Polypropylene Copolymer, Titan Chemical® Co., Malaysia) as the matrix and carbon fiber (Composite Oracle®, Torayca T700S 12 K, Toray Co., Japan) as the reinforcing fiber. The mechanical and physical properties of these materials are listed in Table 1 [18,19].

2.2. Specimen preparation

Chopped carbon fibers were prepared from continuous carbon fiber using universal cutting mill machine (Pulverisette 19) in five sizes: 10, 5, 2, 1, and 0.5 mm. Chopped fibers descended with the help of vacuum operation. The composites were prepared by blending carbon fiber (10 wt.%), and polypropylene in pellets form using Thermo Haake PolyDrive R600/610. The temperature and the rotor speed were set to 170 °C and 50 rpm, respectively. At first, PP pellets were melted for 5 min and then chopped carbon fibers were added to the melted PP. All of the specimens were hot pressed using HSINCHU Hot Press Machine. Hot press temperature was set to 170 °C, cooling temperature 60 °C, heating time 5 min, cooling time 3 min and pressure 150 × 10^4 kg/m^2. The pressing technique is the most common method for making carbon fiber reinforced thermoplastics [20]. Composite sheets (15 × 15 cm) with 1 mm and 3 mm thickness were fabricated.

2.3. Thermogravimetric analysis (TGA)

TGA was used to determine the thermal stability and degradation of SCF/PP composites. The analysis was conducted by Perkin Elmer TGA-7 from ambient temperature to 500 °C at a heating rate of 10 °C/min.

2.4. Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis was carried out using Q800 TA Instrument analyzing machine in single cantilever mode. Specimens were tested under the condition of static force 110 N, dynamic force 100 N, frequency 1 Hz with 17.5 mm span length was used. The scan was done from 0 to 120 °C at 5 °C/min rate under cryogenic environment. Specimen dimension was 12 mm width, 3 mm thickness and 35 mm length.

3. Results

3.1. TGA

Thermal stability of CF composites for many applications is necessary in determining their end use. The effect of different lengths of CF on the thermal degradation of PP was investigated. A TGA curve of SCF/PP composites (10% fiber content) is given in Fig. 1. A sudden drop in the mass of the sample indicated the thermal degradation of the material. The materials started to thermally degrade at 300 °C, and decomposed at 472 °C where substantial loss in their weights was observed. The curve also shows that thermal degradation began to occur only after the materials have absorbed certain amounts of heat energy. The heat initiated the degradation processes and the breaking down of the fibers and matrix structure by causing molecular chain ruptures or scission.

3.2. DMA

Storage modulus for SCF/PP composites with different fiber lengths as a function of temperature at 1 Hz stress frequency are demonstrated in Fig. 2. The dynamic mechanical data of the unfilled PP was also included for comparison purposes. The storage modulus, $E'$, of the SCF/PP was compared for the samples with fiber sizing of 0.5, 1, 2, 5 and 10 mm. Comparing the $E'$ spectra of the composites with the unfilled PP at −25, 25 and 75 °C, it was observed that the incorporation of 10% CF to PP with 10 and 5 mm length resulted in the increase of the stiffness of the material within the temperature range taken into consideration.

The loss modulus, $E''$, of the SCF/PP composites and unfilled PP are presented in Fig. 4. The $E''$ of unfilled PP increased with the addition of CF for composites with 5 and 10 mm CF length. This indicated a higher viscosity as a result of the molecular movement restriction due to the presence of the fibers.

Table 1

<table>
<thead>
<tr>
<th>Materials</th>
<th>Tensile strength (MPa)</th>
<th>Young's modulus (GPa)</th>
<th>Density (g/cm^3)</th>
<th>Diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon fiber</td>
<td>4900</td>
<td>230</td>
<td>1.8</td>
<td>6.8671</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>18.35</td>
<td>1.47</td>
<td>0.9</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 1. TGA curves of PP Matrix and SCF/PP composites with 10% fiber content.

Fig. 2. Storage modulus ($E'$) of unfilled PP and SCF/PP composites with different fiber length.

Fig. 3. SEM micrograph of tensile fracture of the SCF/PP composite with 10 wt.% carbon fiber.
Table 2
Percentage weight loss in SCF/PP composites at different temperatures

<table>
<thead>
<tr>
<th>Weight loss(%)</th>
<th>PP</th>
<th>Degradation temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SCF/PP composites</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5 mm</td>
<td>1 mm</td>
</tr>
<tr>
<td>10</td>
<td>362</td>
<td>400</td>
</tr>
<tr>
<td>20</td>
<td>378</td>
<td>409</td>
</tr>
<tr>
<td>30</td>
<td>399</td>
<td>421</td>
</tr>
<tr>
<td>40</td>
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<td>424</td>
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<tr>
<td>50</td>
<td>413</td>
<td>429</td>
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<tr>
<td>60</td>
<td>425</td>
<td>432</td>
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<td>70</td>
<td>428</td>
<td>437</td>
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<td>80</td>
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<tr>
<td>90</td>
<td>445</td>
<td>450</td>
</tr>
<tr>
<td>93</td>
<td>441</td>
<td>463</td>
</tr>
</tbody>
</table>

Fig. 5 shows tanδ versus temperature plots for unfilled PP and the SCF/PP composites with different fiber lengths. Tanδ indicates the relative importance of both viscous and elastic behaviors of materials.

4. Discussion

4.1. TGA

Details of the thermal degradation of PP, and SCF/PP composites with different CF lengths are given in Table 2. According to these data, the introduction of CF fibers to the PP matrix, in general, increased the degradation temperature of the composites. This is due to the fact that heat absorption capacity of CF is higher than PP. As the length of fibers increased, the fibers in the composites absorbed more heat, thus higher temperature was therefore required to achieve the threshold energy for commencement of the degradation process. Thus, as CF lengths increased, there was a shift upward of the degradation temperature. According to Bryk [21], the introduction of fillers into polyalkanes results in an increase of the thermal stability of the polymer.

4.2. DMA

DMA looks at the modulus of elasticity or the ratio of mechanical stress to relative deformation. PP can change shapes as the result of external force. In DMA test, the storage modulus, E’, was measured. E’ is proportional to the energy stored elastically and is reversible. The loss modulus E” on the other hand, measures the energy transferred to heat and is irreversibly lost. In semi-crystalline polymers, the presence of amorphous and crystalline region gives different response to dynamic loading at a given temperature profile. Fibers would also change the morphology of CF composites as the crystallization character surrounding the fibers can be drastically altered. Crystallinity increases as the storage modulus increases in quantum for similar material tested [22]. Tg was expected to increase as the covalent bond increases the crystallinity in composite. The range at −10 to 20 °C is associated to the relaxation of unrestrained amorphous phase in PP of β relaxation [23].

The E' spectra of the SCF/PP composite with 2 mm length at −25 °C was close to PP. For this category, at 25 and 75 °C it was observed that E’ increased significantly. Storage modulus of SCF/PP composites with 1 and 0.5 mm fiber length, decreased at −25 °C, but at 25 and 75 °C the stiffness of composite improved. These curves indicated that the E’ of these composites have been improved compared to that of unfilled PP with the exception of the composite with 0.5 mm fiber lengths. In general, addition of 10% CF with 2, 1, and 0.5 mm lengths to the PP did not change the E’ of the composite significantly.

At these fiber sizes, the matrix was no longer continuous as elucidated in the SEM micrograph (Fig. 3) of the composite surface. The fibers rather than the PP matrix, impart a greater controlling influence. The fibers can no longer impart stiffness to the matrix when the size was too small, thus the storage modulus was low. As the temperature of the composite samples was raised, the E’ decreases gradually. At sub-ambient temperatures, the magnitude of the decrease was less. The E’ is high when molecular mobility is limited or restricted. As the temperature approaches the glass transition temperature region, there is a large drop in the storage modulus values indicating the phase transition, from the rigid glassy state where molecular motions are restricted to a more flexible rubbery state where the molecular chains have greater freedom to move. E’ is the most important property to assess when determining the load bearing capability of a composite material.

E’ indicates the material’s ability to dissipate energy, often in the form of heat or molecular rearrangements when there is deformation. It indicates the viscous nature of the polymer [24]. As longer fibers were incorporated, the slower the flow and the higher the E’. Generally, as the temperature increases, the viscosity of the materials decreases gradually. Broad peaks were observed on the curves within the temperature range of −20 to 40 °C representing the transition region from the glassy state to the rubbery state. The maximum dissipation of heat per unit deformation occurred at the temperature where E’ is maximum. Above the phase transition region, the decrease in the E’ is sharper indicating a sharp decrease in their viscosity. At −25 °C the E’ of 10 mm composites showed a
small change as compared to unfilled PP but at 25 and 75 °C $E'$ increased significantly. As can be seen from Fig. 4, at 25 °C the $E'$ of SCF/PP composites with 10, 5 and 2 mm was higher than the $E'$ of PP and as the $E'$ peak temperature is very close to $T_g$ of the composite [25], hence, it may be concluded that the composites prepared from CF and PP shift the $T_g$ value to a higher temperature.

In Fig. 5, broad peaks of the tan $\delta$ curves were shown scattered within the range of –20 to 40 °C. Since the tan $\delta$ peaks are not precisely defined and are rather scattered, quantitative assessment and detailed analysis on the peaks to relate the peaks with respect to the fiber length was not carried out. Furthermore, the incorporation of stiff fibers reduced the tan $\delta$ peak height by restricting the movement of polymer molecules [26]. The value of peak of tan $\delta$ is commonly taken to be the glass transition temperature, $T_g$, of the material. $T_g$ values of 10% SCF/PP composites with 0.5, 1, 2, 5 and 10 mm according to the value of peak of tan $\delta$ were 17.6, 18.3, 18.2, 19.1 and 22 °C, respectively. The $T_g$ of PP was measured to 18.4 °C. As can be seen, the $T_g$ of SCF/PP composites with 5 and 10 mm improved compared to $T_g$ of PP, while for other sizes of CF, no considerable change was observed.

5. Conclusions

This study suggests that longer CFs show better thermomechanical properties than shorter CFs in SCF/PP composites. The TGA results have shown that thermal stability of SCF/PP composites increased with the increase of carbon fiber length. Overall, the thermal degradation of SCF/PP composites with different sizes improved compared to unfilled PP. DMA results showed that the storage and loss modulus of SCF/PP composites improved with incorporation of 5 and 10 mm length but for 1 and 2 mm length, no considerable change was observed. The $T_g$ of composites with 5 and 10 mm length increased compared to unfilled PP. Successive studies will be conducted using various CF loading to investigate both effects of CF content and size on thermomechanical properties of SCF/PP composites.

Acknowledgements

The authors are indebted to SIRIM and MOSTI (Ministry of Science, Technology and Innovation) for providing financial support for this Project.

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