MECHANICAL INVESTIGATION IN WHISKERIZED CARBON FIBER/POLYPROPYLENE COMPOSITE

Mahta Sadeghvishakei\textsuperscript{1}, Robiah Yunus\textsuperscript{2}, Mohamad Amran Mohd Salleh\textsuperscript{2}, Alain Pignolet\textsuperscript{1}

\textsuperscript{1}Institut National de la Recherche Scientifique, Centre Énergie Matériaux & Télécommunications (INRS-EMT), Varennes, Québec, J3X 1S2 CANADA
vishkaei@emt.inrs.ca
pignolet@emt.inrs.ca

\textsuperscript{2}Department of Chemical and Environmental Engineering, University Putra Malaysia, 43400 Serdang, Selangor, Malaysia
robiah@eng.upm.edu.my
asalleh@eng.upm.edu.my

ABSTRACT

The effects of whiskerized carbon fibers (WCF) embedded as filler into polymer matrix were investigated. In this respect, pure polypropylene as well as polymer-composites consisting of carbon fiber (CF)/polypropylene (PP) and whiskerized carbon fibers (WCF)/polypropylene (PP) were fabricated and compared. The polypropylene matrix was reinforced with 2\% of CF or WCF and prepared by a melt-mixing method. The tensile test indicated that the addition of 2\% WCF enhanced the tensile strength and Young’s modulus by 38.1\% and 28.2\%, respectively. Moreover, the elongation was decreased. Dynamic mechanical analysis showed an increase of 39.2\% in the stiffness of the WCF/PP composite and an improvement in the storage modulus.

Keywords: whiskerization, carbon fibers, surface treatment, carbon nanoparticles, composite.
INTRODUCTION

It has been established that polymer-based composites reinforced with a small percentage of fillers improve the mechanical and thermal properties of unfilled polymer matrix drastically [1]. The rod-shaped fillers, like carbon fiber, increase the mechanical strength and stiffness in axial direction due to their high surface area. Accordingly, they are considered as the most interesting fillers for advanced applications of composites [2]. For example, composites embedded with rod-shaped fillers are mainly utilized in aerospace, marine and automobile industries, as they offer high specific strength and stiffness, lower density, high damping and low thermal coincident, etc. [3]. However, the performance of these kinds of composites depends on the aspect ratio and degree of interfacial adhesion between the fiber and the resin binder. Adhesion is generally controlled by either chemical bonding or mechanical interlocking. Chemical bonding is attributed to the functional groups and mechanical interlocking is due to the surface morphology. Accordingly, researchers’ endeavours are towards developing a number of surface treatments that could improve the fiber matrix polymer interfacial bonding. Some researchers have investigated the effects of fiber content and fiber lengths on the mechanical and thermal properties of carbon fiber-reinforced polypropylene [4–8]. They indicated that fiber loading plays a major role in the strength of composites, as this material has much higher strength than the PP matrix. Their results showed that composite strength, stiffness, and thermal stability increase with increment of carbon fiber content and carbon fiber length. However, embedding the carbon fibers may cause some defects in polymer matrix composites such as: fiber breaking, fiber–matrix debonding, matrix fracture, fiber pull out, matrix wear related to fiber movement, peeling of the matrix, shear deformation of the fibers, and deformation of the edges of the wear track [6–8].

Surface modifications of carbon fibers have been suggested to enhance the interfacial bond strength, because carbon fibers have a large active specific surface area, low surface energy, and surface lipophobicity [9, 10]. Moreover, the feeble cohesive force between carbon fibers and the matrix makes the shear strength and the bending strength of the composites low. On the other hand, the surface-bound functional groups can enhance the wettability, dispersibility, and surface reactivity of the carbon fibers surface. Chemical method, [11,12] electrochemical method, [13,14] plasma treatment, [15,16] and fiber coating surface treatment [17–20] have been developed to spread a quantity of functional groups on the fiber surface and thus enhance the ability to create strong interactions between fibers and matrix. The whiskerization of a carbon fiber increases inter laminar shear strength (ILSS) of the resulting carbon fiber composite significantly. There are a large number of contact points for fiber matrix bonding where they bond more firmly to the various matrix filler materials and form high strength composites [21–24]. Kowble et al. [25] introduced a whiskerization process that provided the highest increase in ILSS (an improvement of 200–300%). It is believed that growing the carbon nanoparticles on surface of carbon fiber may create a uniform roughness on the surface [9]. The whiskerization of carbon nanoparticles on short carbon fiber could lead to similar improvement of the composite quality as demonstrated by the whiskerized long carbon fiber. The process of whiskerization of short carbon fiber in a continuous manner cannot be the same as the long fiber. Therefore, fluidized bed was considered for this study as it could provide good mixing between the carbon source and the fibers as well as the possibility of continuous discharge of product once the process is established.
EXPERIMENTS

Materials
In this experiment, polypropylene pellets (PP 600G) were purchased from PETRONAS Polymer Marketing and Trading Division, Malaysia and used as the polymer matrix. The synthesis of WCFs was carried out by catalytic reaction of $\text{C}_2\text{H}_2$ over Fe/CF catalyst in a stainless steel reactor with 55 cm height and a 5.2 cm internal diameter [26–28].

Composite preparation
Hot melt mixing of the components for the preparation of composites was carried out using an internal mixer equipped with a pair of roller-type blades. Polypropylene was introduced into the mixer and warmed up for 10 minutes, and the required amount of WCF was subsequently added to the melted PP. The rotor speed and temperature were set at 120 rpm and 180°C, respectively, and mixing was continued for another 10 minutes. The WCF/PP obtained from the melt blending was then compressed using Hot and Cold Press machine. For this purpose, composite was placed in a mould of size 15×15 cm$^2$ and 1mm or 3mm deep, allowed to melt for 5 minutes (preheating) with upper and lower platen temperature set to 180°C. Breathing time of 10 second was allowed releasing the bubbles and reducing voids. The products were then pressed for 5 minutes under a pressure of 150kg/cm$^2$. The sheets were immediately cooled at room temperature between two plates of a cold press for a cooling cycle of 3 minutes.

Mechanical Testing
Tensile Test: Tensile testing was performed to evaluate the mechanical properties of PP, CF/PP and WCF/PP composites. Dog-bone tensile bars (ASTM D638) with a parallel section of 15 mm and a rectangular cross-section of 2×4 mm$^2$ were prepared from the injection-molded plaques. Tensile properties were determined using 5 replicates for each composition with an Instron 4302 testing machine at a constant cross-speed 5.00 mm/min in the range of -20 to 100N load. Five specimens at each cross-head speed and fixed temperature were tested, and the average values were recorded.

Dynamic Mechanical Analysis (DMA): DMA offers information on storage modulus, loss modulus and damping factor properties of the materials tested. In a DMA test, the sample is subjected to a sinusoidal mechanical deformation at a fixed frequency of 1 Hz. Specimens with length of 62 mm and thickness of 12 mm and 3 mm thickness were tested under the condition of a static force of 110 N, and a dynamic force of 100 N. At least three samples were used for each measurement in order to obtain the reproducibility for test results. The scan was done from -30 to 70°C at a heating rate of 5°C/min under cryogenic environment. During the test, the storage modulus and loss modulus were measured. For pointing out similarities and differences between the different composites compositions, dynamic mechanical data for the unfilled PP and for CF/PP were also collected are included in the discussion.
RESULTS AND ANALYSIS

Although increasing the length of carbon fiber enhances the composite properties [5, 23], this parameter was kept in this study as it is the CF were used as substrate for growing nanoparticles on their surface. Therefore, carbon fibers of 2 mm length was utilized as support and coated by iron nanometal particles. Figure 1 shows the carbon fiber surface before and after growing the nanoparticles on it. The distribution of whiskers on the surfaces must be uniform to obtain maximum improvement.

Fig. 1: SEM images of CF after Fe nanoparticle deposition (a) and CF surface after growing carbon nanoparticles (b)

Tensile Properties

According to Table 1, adding the CF and whiskerized carbon fibers (WCFs) enhances the tensile strength of composites by 18% and 38% respectively when compared with pure PP. This improvement was attributed to the addition of adhesive filler into the matrix. The Young modulus of the composites also was increased by 28.2% and 38.1%, respectively compared to that of unfilled PP. Bao and Tjong [29] have reported that filler with higher stiffness than the matrix increases the modulus of the composite, hence the stiffness of a material. It is also noted that the most prominent effect of the fillers is the increase in modulus of the resultant composites. The improvement in tensile strength and Young’s modulus can be related to the several parameters, such as the inherent stiffness of the carbon fibers, the quality of their dispersion as well as the adhesion of the nanoparticles to the matrix.

Table 1 shows the elongation at break for pure PP and for two composites adding CF or WCF. A reduction in elongation at break is observable that implies that the ductility of PP was decreased in presence of CF and WCF. This result is in agreement with other reports [5-8], who explained that the elongation at break of composite reduces with adding fillers [13-15].
It could be pointed to the fact that ductility declines when rigidity is increased by reinforcement. Generally, micro failure at the interface between the fiber and matrix are responsible for the composite failure with short CF; hence a good adhesion at the interface is necessary for an improvement in composites properties.

Dynamic mechanical analysis (DMA)

Figure 2 shows the variation of composites’ storage modulus as a function of temperature at 1 Hz stress frequency. These curves indicate that the storage modulus of the composites was significantly improved when CF and WCF were embedded into the material, especially at lower temperatures. As the data in Table 2 shows, the storage modulus was increased by 3510 and 4690 MPa, respectively, with addition of 2wt% CF and WCF. CF and WCF enhanced the stiffness of the composites by 18.8% and 39.2%. Joseph et al. [30] explained that if the filler loading increased, the stress is more consistently dispersed, and therefore it improved the storage modulus.

![Fig. 2: Storage Modulus for PP, CF/PP and WCF/PP composite](image-url)

<table>
<thead>
<tr>
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<th>Tensile stress at Yield (MPa)</th>
<th>Young’s modulus (MPa)</th>
<th>Percentage of elongation at break</th>
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<tbody>
<tr>
<td>PP</td>
<td>21.6±0.3</td>
<td>569.8±18.7</td>
<td>66±0.00</td>
</tr>
<tr>
<td>CF/PP</td>
<td>26.5±0.5</td>
<td>712.7±24.5</td>
<td>23.3 ±0.01</td>
</tr>
<tr>
<td>WCF/PP</td>
<td>34.9±0.8</td>
<td>794.2±30.5</td>
<td>12.6±0.01</td>
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The loss modulus indicates the viscous nature of the polymer and gives information about the viscous or energy dissipation during flow \[13\]. The plastic flow is controlled by the cooperative motion of the chain segments. However, the incorporation of filler into PP leads to a reduction of its activation volume. The activation volume of composites appears to decrease with increasing filler content \[17\]. It is believed that the motion of PP molecular chain segments is restricted by WCFs because of the curving and coiling nature of whiskerized carbon fiber. As Figure 3 illustrates, the loss modulus of the composites was increased with adding the fillers due to an increase in the viscosity of composites when the fillers present. According to Figure 3 and Table 2, there is a slight change in the loss modulus of CF/PP and WCF/PP composite compared to that of unfilled PP.

![Fig. 3: Loss Modulus of Unfilled PP, CF/PP and WCF/PP Composite](image)

Broad peaks are evident on the curves in the temperature range of -30 to 30°C depicting the transition region from the glassy state to the rubbery state. Above the phase transition region [5-7°C], decrease in the loss modulus is sharper revealing a sharp reduction in their viscosities.

**Table 2:** DMA results for unfilled PP, CF/PP and WCF/PP composite

<table>
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<th>Storage Modulus (MPa)</th>
<th>Loss modulus (MPa)</th>
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<tbody>
<tr>
<td>PP</td>
<td>2850</td>
<td>121</td>
</tr>
<tr>
<td>CF/PP</td>
<td>3510</td>
<td>147</td>
</tr>
<tr>
<td>WCF/PP</td>
<td>4690</td>
<td>50</td>
</tr>
</tbody>
</table>
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20. Li, J. The Tribological Properties of Polypropylene Composite Filled with DBD Treated Carbon Fiber, Polymer-Plastics Technology and Engineering 2010, 49 (2): 204 — 207