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Investigation of conductive hybrid polymer composites reinforced with copper micro fibers and carbon nanotubes produced by injection molding

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1. Introduction

Conductive polymeric composites have proved themselves invaluable for novel manufacturing and applications. In this paper, production and properties of injection moldable conductive plastics to replace metal circuits especially in micro components are investigated. Polymeric composites containing conductive micro and nano fillers are designed and characterized experimentally and numerically. Results show that hybridization of Copper micro fibers and carbon nanotubes enhances the conductivity properties two orders of magnitude while reducing the weight and cost of the composites. Moreover, the new injection moldable conductive plastics show improved mechanical and surface properties. The research endeavors to provide novel multifunctional solutions for future components with complex geometries.
functionally improved components [2, 17].

This paper investigates production and properties of the injection molded Polyamide 12 based composites reinforced with micro and nano fillers. Micro copper fibers and carbon nanotubes as the best-known conductive materials are considered in the design and production to achieve the desired multifunctional properties in the composites. The evolution of features such as electrical, thermal, mechanical, surface, etc. as the functional of manufacturing and filler contents are discussed. Moreover, the involved mechanisms in the property variations are investigated through optical and scanning electron studies in combination with the injection molding simulations.

2. Experiments

2.1. Materials and manufacturing

The incorporated carbon nanotubes in this study were catalytic chemical vapor deposition produced thin MWCNTs (NC 7000 ™) by Nanocyl SA, Belgium, with the average diameter of 10.4 nm [18]. Electron mobility in carbon nanotube layers at room temperature could be as high as $2 \times 10^5 \text{cm}^2/\text{V s}$ leading to the highest known electrical conductivity at room temperature as high as $10^8 \text{S/m}$ [19–21]. The presence of the unlocalized electrons on the graphene surface leads to the exceptional electrical conductivity in the graphene plane. The powder conductivity of the used nano fillers was $10^5 \text{S/m}$. In addition, the used metallic micro fibers were Cu99 copper fibers (STAX, Germany) with the average diameter and length of 45 μm and 700 μm, respectively. The used metallic fibers showed excellent electrical conductivity values as $5.9 \times 10^7 \text{S/m}$. A polyamide 12 (PA12) was also selected as the base polymeric matrix in the produced composites ($T_g = 49.1 \degree C$).

PA12 based composite batches with different contents of micro and nanofillers were compounded between 215 and 240 \degree C to perform the melt mixing process a Twin Screw Extruder (Brabender TSE 20/40; Screw length (L : D) 40) was selected. Injection molding of the composite specimens was performed on an Arburg Allrounder 420C (Arburg, Germany) following the instructions of ISO 294-1. The pelletized compounded composites were injected at the nozzle temperature of 245 \degree C, injection speed of 55 mm/s, and holding pressure of 55 bar. The geometry of the produced parts is illustrated in Fig. 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature(℃)</th>
<th>Specific heat (J/g·℃)</th>
<th>Thermal conductivity (W/m·℃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA 12</td>
<td>25</td>
<td>2.149</td>
<td>0.37 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.453</td>
<td>0.36 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>2.926</td>
<td>0.34 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>3.364</td>
<td>0.34 ± 0.03</td>
</tr>
<tr>
<td>PA 12</td>
<td>25</td>
<td>1.93</td>
<td>0.42 ± 0.03</td>
</tr>
<tr>
<td>+ 4 vol. % CNT</td>
<td>50</td>
<td>1.99</td>
<td>0.41 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>2.51</td>
<td>0.41 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>2.98</td>
<td>0.39 ± 0.03</td>
</tr>
<tr>
<td>PA 12</td>
<td>25</td>
<td>0.72</td>
<td>1.38 ± 0.03</td>
</tr>
<tr>
<td>+ 30 vol. % Cu</td>
<td>50</td>
<td>0.794</td>
<td>1.26 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.916</td>
<td>0.93 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>1.042</td>
<td>0.84 ± 0.07</td>
</tr>
<tr>
<td>PA 12</td>
<td>25</td>
<td>0.69</td>
<td>1.69 ± 0.11</td>
</tr>
<tr>
<td>+ 30 vol. % Cu</td>
<td>50</td>
<td>0.74</td>
<td>1.67 ± 0.13</td>
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<tr>
<td>+ 2 vol. % CNT</td>
<td>100</td>
<td>0.86</td>
<td>1.43 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>0.94</td>
<td>1.21 ± 0.08</td>
</tr>
<tr>
<td>PA 12</td>
<td>25</td>
<td>0.62</td>
<td>1.85 ± 0.15</td>
</tr>
<tr>
<td>+ 30 vol. % Cu</td>
<td>50</td>
<td>0.70</td>
<td>1.68 ± 0.11</td>
</tr>
<tr>
<td>+ 4 vol. % CNT</td>
<td>100</td>
<td>0.82</td>
<td>1.49 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>0.92</td>
<td>1.39 ± 0.10</td>
</tr>
</tbody>
</table>

Table 1
Thermal properties of the produced specimens.

Table 2
Mechanical properties of the produced specimens.

Fig. 1. The geometry of the produced composite specimens.
Fig. 2. Mid-plane tensile strength and fibre orientation distributions in principal (x) direction of (a), (b) nanocomposites, and (c), (d) hybrid composites.

Fig. 3. The pull-out mechanism of copper fibers and the surface area of the holes in (a), (b) Copper filled composites, and (c), (d) PA 12 + 30 vol. % Cu + 2 vol. % CNT hybrid composites.
2.2. Characterization

The mechanical properties of the injection-molded specimens were characterized using uniaxial tensile experiments using a MTS 858, USA, according to ASTM D1708. The electrical conductivity experiments were performed on rectangular specimens (20 × 5 × 1.5 mm). Volume electrical resistivity was measured at room temperature using two copper electrodes contacting the two ends of the test specimen under constant pressure using a Hewlett Packard multimeter, US. In order to ensure the effective contact between the electrodes and the specimen surfaces, the contacting areas were sanded. Conductive carbon tapes were also placed between the contacts. In addition, a constant pressure (40–50 N) was applied from the holding screw.

In order to attain the required properties for the simulations, the thermal diffusivity of the specimens were determined using laser flash experiments using a LFA 1000 Laser Flash Apparatus. In addition, melt shear viscosity investigations were performed using a Discovery HR-2 (TA Instruments, USA). The oscillatory shear measurements were performed on 25 mm disc-shape polymeric specimens under nitrogen atmosphere with 1.0 mm gap between the plates. The capillary rheometry and PVT characterizations were conducted using a Göttfert Werkstoff-Prüfmaschinen GmbH Rheograph 25. The optical microscopy studies was performed using a LEXT (Olympus, Japan). Furthermore, in order to study the fracture and involved mechanism in electrical conductivity scanning electron microscopy (SEM) (Quanta FEG 200 ESEM) was employed on the fractured surfaces of the nanocomposites. In order to characterize the melting behavior and specific heat of the produced specimens, nonisothermal thermal studies were conducted on a Discovery DSC (TA instruments). A sample of 4–6 mg of the nanocomposites was cut from the middle section of the injection molded specimens, and placed in sealed aluminum pans. Differential scanning calorimetry (DSC) experiments were performed under Argon atmosphere in the temperature range of −5 °C to 180 °C with the rate of 10 °C/min.

Fig. 4. Electrical conductivity of the produced specimens.

Fig. 5. (a) Optical images of the fibre reinforced composite and the insulating micro gaps between the fibers, (b) the filled gaps with conductive nanofillers. (c) The SEM micrographs of the gap area between the two adjacent (5μm distance) copper fibers, in PA 12 + 30 vol. % Cu+ 2 vol. % CNT composites and (d) and the bridging mechanisms by carbonic nanofillers.
In addition, Autodesk Moldflow simulations were performed according to the performed characterizations on the compounded batches and the injection molding machine parameters.

3. Results and discussions

3.1. Thermal properties

Table 1 presents the thermal behavior of the produced specimens. As it can be noticed from the table, while the incorporation of conductive fillers decreased the specific heat values, the thermal conductivity values increased significantly. In fact, the hybrid composites containing both copper micro fillers and carbon nanotubes showed thermal conductivities four times higher than their base polymer. Inclusion of the two different fillers led to enhancement of thermal conductivities additionally. The involved mechanisms in thermal conductivity of the hybrid composites are intricate. In fact, the final thermal conductivity of polymeric composites is determined by the least thermal conductivity among the constituents [22]. Comparing to the thermal conductivity of Copper (400 W/ m K), structurally perfect carbon nanofiller could show very high thermal conductivities in the range of 4000–6000 W/m K. However, industrially produced nanofillers based on the level of defects and number of layers show diminished conductivity values. In fact, while the heat is mostly transformed by phonons in graphene layers, the heat transfer mechanism in the metallic fillers is controlled by electrons. Combination of the parameters such as the short bond length between carbon atoms, the periodicity of the structures, and the delocalized electrons leads to the enhanced phonon propagation through graphene layers in carbon nanotubes. As the atoms in the composite structure are exposed to a heat source, they start to vibrate. These vibrations with regard to the compact structure of the reinforcements are passed to the neighboring atoms [23]. However, as the temperature rose, the average distance between the phases increased. Therefore, the chances of direct contact between fillers in a homogenous dispersion are decreased. The elevated motion of polymer chains also reduced the stiffness of the structure and the atom vibration effects leading to longer distances for the phonon transport and lower thermal conductivities.

Moreover, it could be noticed that the specific heats of the composites are less than the neat PA12. In fact, the smaller contents of polymers within the structure of composites lead to lower values of specific heats among the produced composites. As the included polyamide reflects the highest specific heat properties among the constituents (compared to specific heats of copper and nanotubes are around 0.3 and 0.7, respectively), its reduction, would result into the decrease of the specific heats of the composites.

The importance of the observed synergic effect as the result of hybridization is more pronounced when the values is compared with metal filled composites. The traditional composites should contain more than 50 vol. % of conductive fillers to reach the achieved

Fig. 6. Cross section of the composites along the thickness: (a) PA 12 + 30 vol. % Cu, (b) PA 12 + 30 vol. % Cu + 2 vol. % CNT and (c) PA 12 + 30 vol. % Cu + 4 vol. % CNT.
Carbon nanotubes are among the strongest known materials. Benefiting from strong sp² interactions in their structure, they show higher stiffness and tensile strengths than diamond. Strong interactions between the carbon atoms within the unique atomistic structure of carbon nanotubes and graphene with shorter carbon-carbon length than diamond make them strong and stable under deformation. However, while their aspect ratios provide larger interfacial regions leading to enhancement of the properties, their processing is challenging. In fact, achieving more oriented within the hybrid composites. This anisotropy in the properties in the produced composites according to the specimen positioning direction. In order words, the nano fillers in the nanocomposites are mostly distributed randomly; however, in the hybrid composites, the fillers are oriented towards the flow direction. This phenomenon is due to higher aspect ratio of nanofillers and viscosity of the melts in combination with their lower thermal conductivities during the injection molding of the nanocomposites.

Moreover, the mechanical properties in the hybrid composites benefitted from the reinforcement of the polymeric fraction. Fig. 3 shows fractographs of the hybrid composites. The micrographs shows copper fibre pull-out as the main failure mechanisms. As it can be noticed, the pull-out holes are notably rough. This increased roughness is due to better interfacial adhesion between the copper microfibers and the surrounding nanocomposite as the results of the incorporation of the nanotubes. Therefore, more aligned fibers in combination with a strengthened plastic fraction lead to hybrid composites with enhanced mechanical properties.

3.2. Mechanical properties

In order to understand the produced composites and their application, their mechanical properties were investigated (see Table 2). Carbon nanotubes are among the strongest known materials. Benefiting from strong sp² interactions in their structure, they show higher stiffness and tensile strengths than diamond. Strong interactions between the carbon atoms within the unique atomistic structure of carbon nanotubes and graphene with shorter carbon-carbon length than diamond make them strong and stable under deformation. However, while their aspect ratios provide larger interfacial regions leading to enhancement of the properties, their processing is challenging. In fact, achieving dispersed or aligned nanofillers requires effective prior investigations [8,9,25]. Results showed that incorporation of 4 vol. % carbon nanotubes lead to 32 and 28% enhancement in elastic modulus and tensile strength, respectively. Moreover, while elongation at break decreased significantly, the nanocomposites with elongation at break values more than 80% show a ductile behavior. Moreover, the combination of copper fibers and carbon nanotubes increased the elastic moduli more than two times compared to the base polymer.

Fig. 2 shows the injection molding simulation results on tensile strength and fibre orientation distribution in nano and hybrid composites. As it can be clearly seen in the figures, the incorporated fillers are more oriented within the hybrid composites. This anisotropy in the final fibre configuration leads to variation of mechanical and electrical properties in the produced composites according to the specimen positioning direction. In order words, the nanofillers in the nanocomposites are mostly distributed randomly; however, in the hybrid composites, the fillers are oriented towards the flow direction. This phenomenon is due to higher aspect ratio of nanofillers and viscosity of the melts in combination with their lower thermal conductivities during the injection molding of the nanocomposites.

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3.3. Electrical conductivity

Fig. 4 shows the influence of conductive fibre incorporation and combination on the electrical properties of the produced composites. Despite the superior electrical properties of carbon nanotubes originating from their hybridization state, the polymeric nanocomposites could usually deliver up to 10 S/m [8]. On the other hand, conventional polymeric composites reinforced with metallic fillers could not be processed after certain filler contents levels. Therefore, further electrical conductivity enhancement could not be expected by adding more metal-based fillers. Therefore, nanofillers are incorporated to improve the properties by introducing novel mechanisms.

The idea behind designing hybrid composites originates from the fact that the micro gaps between metallic fillers are filled with an insulating plastic (see Fig. 5(a)). In other words, the network of conductive fillers are compromised in many locations due to the presence of these gaps. The microscopy investigations revealed the dominance of 3–40 μm gaps within the network of the metals. Therefore, incorporation of nanofillers could convert the trapped materials in the gaps between the metallic fillers into conductive mediums resulting into an enhanced electrical network (Fig. 5). Fig. 5(c) and (d) illustrates the constructed bridging mechanism within the hybrid composites. The carbon nanotubes construct a conductive network between themselves. The constructed nano networks enables the electrons to travel between adjacent micro fibers. As the result of combination of nano and micro networks, the electrical conductivities increased by more than two orders of magnitude compared to the metal filled composites [26,27]. It is
noteworthy to mention that while addition of 2 vol. % of nanofillers to metal filled systems led to significant improvement in conductivity of the composites, additional inclusion of nanofillers did not result in similar enhancement. In other words, it seems that a limit for nanofiller inclusion exists wherein the desired networks are constructed within the microstructure and further addition of nanofillers would not lead to effective enhancement. Therefore, the spent cost on the additional nanofiller following the discussed threshold just led to difficulties in mechanical or manufacturing performances.

Moreover, optical microscopy revealed reduction of the fibre depleted frozen layer by addition of nanofillers in the hybrid composites (see Fig. 6). As the nanotubes increased in the composite system, the number of copper fibers increased in the layer adjacent to the surface, which results in a more conductive surface layer and efficient application of the composites without the need for post-processing to remove this skin layer. This phenomenon is due to the flow-induced crystallization and the variation of rheological properties by addition of the nanotubes in the polymeric structure [8,9].

Moreover, incorporation of nanofillers changes the surface characteristics of the produced specimens effectively (see Fig. 7). By addition of the carbon nanotubes in the structure, the surface roughness decreases. The investigation showed that arithmetic average roughness (Ra) decreased from 170 to 100 nm by addition of nanofillers to the neat polymer. Moreover, Ra decreased 2.5 μm to 400 nm in the produced composites compared to copper filled specimens.

4. Conclusions

Production and characterization of novel conductive hybrid composites were investigated. The results showed the effectiveness of combination of the copper micro fibers and carbon nanotubes to achieve multifunctional composites. Hybridization of the fillers led to 220 and 26% improvement in elastic modulus compared to the neat polymer and the metal filled composite, respectively. Moreover, the electrical and thermal conductivities increased two orders of magnitude and 37% compared to the metal filled composites, respectively. The bridging mechanism of nanotubes between the micro fillers was recognized as the main mechanism of enhancement of electrical conductivities. Moreover, variation of thermal conductivity and viscosity by addition of nanotubes results in thinner skin layer devoid of copper filler and better surface finish. Therefore, not only the properties are enhanced but also the need for final polishing is eliminated.

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References