EFFECT OF CNTs ON THE ELECTRICAL AND MECHANICAL PROPERTIES OF POLYMERIC COMPOSITE AS PEM FUEL CELL BIPOLAR PLATE

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Graphical abstract

Characterizing raw materials

Pre-mixing G/CB/CNTs

Mixing G/CB/CNTs/PP

Compression molding

Testing

Abstract

The use of Carbon Nanotubes (CNTs) as a reinforcement in conductive polymer composite (CPCs) of bipolar plates nowadays attracts a great deal of attention. Therefore, the aim of this study was to identify the most effective and suitable ratio of CNTs loading in multi filler Graphite (G), Carbon Black (CB) composite using a medium crystallinity and low crystallinity Polypropylene (PP) denoted as MC-PP and LC-PP respectively. The composite were developed through compression molding technique with dry mixing method using a ball mill to investigate the influence of crystallinity on the dispersion of CNTs in PP matrix. Incorporating CNTs as a third filler in G/CB/CNTs/PP nanocomposites produces a synergistic effect that enhances the electrical conductivity is 158.32 S/cm with 6 wt.% CNTs content. The flexural strength of CNTs/MC-PP increased from 22.95 MPa (3 wt.%) to 29.86 MPa (5 wt.%) with the increment of CNTs content. The results indicated that CNTs was given more affect in MC-PP than LC-PP due to better electrical conductivity and mechanical properties of G/CB/CNTs/PP composite as bipolar plate.

Keywords: Nanomaterial fillers, carbon nanotube, conductive polymer composites, dry mixing method, crystallinity

Abstrak

Penggunaan karbon nanotub (CNTs) sebagai penguat dalam konduktif polimer komposit (CPCs) plat dwikutub pada masa kini telah menarik banyak perhatian. Oleh itu, tujuan kajian ini adalah untuk mengenal pasti nisbah paling berkesan dan sesuai kandungan CNTs dalam beberapa Graphite (G), Carbon Hitam (CB) komposit menggunakan penghabluran sederhana dan penghabluran rendah Polipropilena (PP) yang ditandakan masing-masing sebagai MC-PP dan LC-PP. Komposit yang dihasilkan melalui teknik pengacuan mampatan dengan kaedah campuran kering menggunakan ball mill adalah untuk menyiasat pengaruh penghabluran mengenai peningkatan kandungan CNTs dalam PP matriks. Menggabungkan CNTs sebagai pengisi ketiga dalam G/CB/CNTs/PP komposit menghasilkan kesan sinergi yang meningkatkan kekonduksian elektrik adalah 158.32 S/cm dengan kandungan CNTs 6 wt.%. Kekuatan lentur MWCNTs/MC-PP telah meningkat daripada 22.95 MPa (3 wt.%) kepada 29.86 MPa (5 wt.%) dengan peningkatan kandungan CNTs. Keputusan menunjukkan bahawa CNTs telah memberi kesan lebih baik dalam MC-PP berbanding LC-PP kerana kekonduksian elektrik dan sifat-sifat mekanik yang lebih baik G/CB/CNTs/PP komposit sebagai plat dwikutub.

Kata kunci: Pengisi bahan nano, karbon nanotub, Konduktif polimer komposit, kaedah campuran kering, penghabluran

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1.0 INTRODUCTION

Polymer electrolyte membrane fuel cell or proton exchange membrane fuel cell (PEMFC) is a very promising power source candidate for portable applications because of its high efficiency, light weight, low operating temperature, and fast startup mechanism [1, 2]. Hence, the PEMFC has received intensive research from both alternative energy and environmental considerations. There are four main components of PEM fuel cell: Membrane Electrode Assembly (MEA), Bipolar Plate (BP), End Plate and Current Collector. Among these components, the bipolar plate is the main component of PEMFCs stack, which takes a large portion of stack cost [3, 4]. They can contribute 70-80% of the stack weight and up to 45% of the cost. Hence, the investigation of cost/performance materials of bipolar plates has become a critical research issue [3]. The bipolar plates provide the following main functions within the fuel cell stack. The bipolar plates provide a distribution of fuel gases within the cell, promote water management over the whole cell, separate the individual cells in the stack and carry electrical current away from membrane electrode assemblies (MEA) [3].

Traditionally, the most commonly used BP material is graphite, both natural as well as synthetic, because it has excellent chemical stability to survive the fuel cell environment. It also has a very low resistivity, resulting in highest electrochemical power output. However, it is plagued with problems of high cost, low mechanical strength and the need for machining to form the flow channels [5, 6]. Therefore, the CPC development is a promising and growing field of research due to its highly resistant to corrosion, low cost and low densities that might result in the materials replacing metal bipolar plate in Proton Exchange Membrane Fuel Cell (PEMFC) [7-9]. However, CPCs would not be suitable to improve conductivity and mechanical performance simultaneously for the reason that high filler concentration improves on conductive performance but it deteriorates on mechanical performance. In order to obtain better electrical conductivity of the composite, a combination of multi fillers have been used as bipolar plate materials [10]. The commonly used reinforced fillers include graphite, carbon nanotube, carbon fiber, and carbon black which have been incorporated into the composites to enhance overall performance of composite bipolar plates by conventional polymer processing technique [3, 11].

In general, there are two different types of polymeric resins including thermoplastics and thermosets in order to fabricate composite bipolar plate. To compare both types of materials, PP has the advantages of low cost, good processability, well-balanced properties of physical and mechanical [11-13]. It has been used to fabricate composite bipolar plates in the past few years. Owing to the nonpolar functional groups in polypropylene backbone, it is difficult to improve the interfacial compatibility between additive filler and polymer matrix, thus, limiting the improvement and usefulness of PP composite bipolar plates in fuel cells [13]. However, according to Liou et al. [12], a lower degree of crystallinity of polymer would provide a significant influence on the filler-polymer interfacial adhesion, and provide a better dispersion of fillers within the polymer matrix. This phenomenon implies that introducing a lower degree of crystallinity of polymer into the composite materials may be a possible method to further improve the properties of composite bipolar plates.

Additionally, among various reinforcements introduced into the polymer composites, CNTs which possess outstanding mechanical and electrical properties have been applied to a great number of fields [14, 15]. However, two critical issues arise when CNTs are used as reinforcements in polymer composites [16]. First, CNTs tend to aggregate into ropes or bundles due to the strong intrinsic Van der Waals forces between them, thus, causing poor dispersion in polymer matrix. Moreover, smooth surface of CNTs and lack of interfacial bonding will result in weak interfacial adhesion between CNTs and matrix [17, 18]. These two major problems would limit the improvement of the electrical or mechanical properties of composites by CNTs. A common approach reported so far is the surface modifications or functionalizations of CNTs [18, 20]. However, this process may damage the molecular framework of CNTs such as breaking their sidewall and turning into amorphous carbon, reducing the mechanical properties and decreasing the electrical conductivity of composites [12]. Several studies have indicated that the physical method related to melt blending is one of the most promising routes [12]. When composite materials are prepared by melt blending, the high shear force leads to better interactions between CNTs and the polymer matrix without damaging the structure of CNTs, resulting in good processability and better performance of the composites [17]. Hence, melt blending method would be considered as an effective method to enhance the dispersion of CNTs in polymer [16].

The CPCs used as bipolar plate must meet the U.S. DOE requirement because of its multiple responsibilities and the challenging environment in which the fuel cell operates. Materials/composite properties must be considered for a fuel cell application specifically electrical and thermal conductivity, gas permeability, mechanical strength, corrosion resistance and low weight [9]. An ideal bipolar plate should meet the target properties specified by U.S. DOE. The property requirements shown in Table 1 should be fulfilled for the fabrication of a bipolar plate.

In this study, G/CNTs/PP nanocomposite bipolar plates to be used in PEM fuel cells were developed by a ball mill as a mixing process. Two different degrees of crystallinity of PP in powder form were introduced into G/CNTs/PP nanocomposite as bipolar plates to investigate the interfacial compatibility between PP and CNTs. Furthermore, the effects of CNTs incorporated into two types of PP on in-plane electrical conductivity and mechanical properties such as flexural strength, shore hardness, bulk density and
surface morphology of nanocomposite bipolar plates were also investigated.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical conductivity</td>
<td>&gt; 100 [Scm$^{-1}$]</td>
</tr>
<tr>
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<td>&gt; 10 [W/(mK)$^{-1}$]</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>&gt; 25 [MPa]</td>
</tr>
<tr>
<td>Shore hardness</td>
<td>&gt; 50</td>
</tr>
<tr>
<td>Bulk Density</td>
<td>&lt; 5 [g/cm$^3$]</td>
</tr>
</tbody>
</table>

### 2.0 METHODOLOGY

#### 2.1 Materials

Two types of commercial grade polypropylene (PP) in powder form were purchased from Polypropylene (PP) g/Malaysia Sdn. Bhd and used as the polymer matrix. The second conductive filler was graphite powder and the third filler was Carbon Black powder purchased from Asbury Carbon, New Jersey. The fourth conductive filler used in this study was Multiwalled carbon nanotubes (MWCNTs, type NC 7000) purchased from Nonocyl (Belgium). The μm was reported to have purity of 90% by the manufacturer. All conductive fillers were used as received without any further purification. Figures 1(a) and (b) show scanning electron microscopic image of graphite and carbon black. Furthermore, Figure 1 (c) shows transmission electron microscopic (TEM) image of MWCNTs. The comparison of physical-chemical properties among PP, MWCNTs, CB and G is shown in Table 2.

Table 1 Requirement properties for the bipolar plate (U.S. DOE target) [1, 6, 20 and 21]

<table>
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</tr>
<tr>
<td>Bulk Density</td>
<td>&lt; 5 [g/cm$^3$]</td>
</tr>
</tbody>
</table>

#### 2.2 Preparation of Polymer Nanocomposites

The multi filler materials were mixed using ball mill as a pre-mixing process at a speed of 200 rpm for 1 and half hour. The weight percentage (wt.%) compositions of G/CB/CNTs/PP nanocomposite are shown in Table 3. The ratio of fillers and binder was fixed at 80:20. Then, the ball mill was used again to mix the materials from the previous stage with binder at a speed of 200 rpm for 1 hour. A hot press machine was used to shape the samples before the property measurements. The mixture of all material was then preheated for 20 minutes in a mold placed in the hot pressing machine before it was pressed at a temperature of 185 ºC and pressure of 85 kg/cm$^2$ for 15 min. The dimension of this sample was 140 mm x 60 mm x 3 mm.

Table 2 Physical-chemical properties of MWCNTs, graphite and polypropylene used in this study a

<table>
<thead>
<tr>
<th>Material</th>
<th>MWCNTs</th>
<th>CB</th>
<th>G</th>
<th>MC-PP</th>
<th>LC-PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade</td>
<td>NC7000</td>
<td>5303</td>
<td>3243</td>
<td>Titan (600)</td>
<td>Goveaan Fibres</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>1.0</td>
<td>1.7~1 .9</td>
<td>1.74</td>
<td>0.91-0.92</td>
<td>0.855</td>
</tr>
<tr>
<td>Thermal stability (°C)</td>
<td>&gt;700</td>
<td>3000</td>
<td>350-400</td>
<td>175-220</td>
<td>130-171</td>
</tr>
<tr>
<td>Size (µm)</td>
<td>9.5nm</td>
<td>≤5</td>
<td>≤60</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>(diameter)</td>
<td>1.5nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(length)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resistivity (Ωcm)</td>
<td>Unknown</td>
<td>0.314</td>
<td>0.036</td>
<td>$1(10^{-14})$</td>
<td>$1(10^{-14})$</td>
</tr>
</tbody>
</table>

aThe powder properties are from manufacturers
Table 3: The composition of composite G/CB/CNTs/PP (Based on wt.%)

<table>
<thead>
<tr>
<th>Filler</th>
<th>Binder</th>
</tr>
</thead>
<tbody>
<tr>
<td>G %</td>
<td>CB%</td>
</tr>
<tr>
<td>52.0</td>
<td>25</td>
</tr>
<tr>
<td>51.0</td>
<td>25</td>
</tr>
<tr>
<td>50.0</td>
<td>25</td>
</tr>
<tr>
<td>49.0</td>
<td>25</td>
</tr>
<tr>
<td>48.0</td>
<td>25</td>
</tr>
<tr>
<td>47.0</td>
<td>25</td>
</tr>
</tbody>
</table>

2.3 Characterization of CNTs/PP Nanocomposite Bipolar Plates

2.3.1 Electrical and Mechanical Testing

In this study, two types of PP in powder form with low and medium degree of crystallinities were denoted as LC-PP and MC-PP respectively. The in-plane electrical conductivity of the sample was measured using Jandel Multi Four Point Probe technique at a constant current supply of 1 mA. While the flexural strength of nanocomposite bipolar plates with 140 mm length, 13 mm width and 3 mm thickness dimension was measured by the three-point method using the Instron Universal testing machine (model 4411 series IX Automated material testing System1.38) according to ASTM D790, shore hardness was measured using scleroscopic hardness tester (Type D) according to ASTM C886. The nanocomposite bipolar plates were cut with a Proxxon Table Saw into 20mm x 13mm x 3mm dimension to measure the bulk density by means of the well-known dry bulk density measurement method provided in ASTM C559.

2.3.2 Morphological Analysis

Morphological characterization of the composite surface was carried out using Scanning Electron Microscopy (SEM), an electron microscope that produced images of a sample by scanning it with a focused beam of electrons (JEOL, JSM 840). The electrons in the beam interacted with the sample, producing various signals that can be used to observe the dispersion of the conductive fillers in the polymer matrix and other microscopic features of the fracture surfaces. The cross sections of all the samples were coated with a thin film of platinum using Polaron SC 7640 Sputter in order to improve the conductivity and avoid electron charging effects during the examination.

3.0 RESULTS AND DISCUSSION

3.1 Effect of CNTs/PP on Electrical Conductivity

A number of reports have indicated that the incorporation of graphite into other conductive materials, especially carbon nanotubes, is considered as an effective method to develop higher electrical conductivity of the nanocomposite bipolar plates due to 3D conductive networks [15, 23]. As shown in Figure 2, two types of CNTs/PP nanocomposite bipolar plates had promising electrical conductivity, above the U.S. DOE target value of 100 Scm⁻¹. The results also showed that the electrical conductivities of both nanocomposite bipolar plates increased with the increment of CNTs content (from 3 wt.% up to 6 wt.%) and then decreased slightly with higher CNTs loading (7 wt.% up to 8 wt.%). Hence, the incorporation of a small quantity of CNTs into polymer composites could exhibit higher electrical conductivity due to the formation of extra effective electrical conducting paths [12, 24]. However, higher CNTs loading in polymer composites may cause serious CNTs agglomeration, and the electrical conductivity will be decreased [4].

In addition, electrical conductivity for CNTs/MC-PP nanocomposite always showed higher value than CNTs/LC-PP nanocomposite. At 6 wt.% CNTs content, the electrical conductivity values of CNTs/LC-PP and CNTs/MC-PP were 125.4 S/cm and 158.32 S/cm respectively. This phenomenon might be attributed to the better dispersion of CNTs in MC-PP than LC-PP [4]. Based on the SEM micrographs, the probability of self-agglomeration in the conductive materials would be reduced in MC-PP, thus, more electrical conducting paths were built up by the binary conductive materials system (which was assumed to consist of CNTs, G and CB throughout the nanocomposite bipolar plates).

Figure 2: Effect of CNTs contents on the electrical conductivity of the nanocomposite bipolar plate
3.2 Effect of CNTs/PP on Flexural Strength

In general, the flexural strengths of both nanocomposite bipolar plates increased with the increment of CNTs content as shown in Figure 3. However, CNTs/MC-PP nanocomposite always showed higher value than CNTs/LC-PP nanocomposite. The flexural strength of LC-PP increased up to 7 wt.% CNTs content while the flexural strength of MC-PP increased up to 5 wt.% CNTs. These may be due to the fact that PP resin cannot be wetted well especially LC-PP; with an excess of CNTs, agglomeration occurs, which deteriorates the flexural strength of the nanocomposites [3, 17]. Furthermore, the optimum content of CNTs is different due to homogeneous dispersion and alignment of CNTs in the polymer matrix [18].

As CNTs content was at 5 wt.%, the flexural strength of CNTs/MC-PP increased from 22.95 MPa (3 wt.%) to 29.86 MPa (5 wt.%) whereas at 7 wt.% of CNTs, flexural strength of CNTs/MC-PP nanocomposite decreased. Even though at 8 wt.% the flexural strength was slightly increased, the value was still lower compared to the values at 4 wt.% and 6 wt.% of CNTs. This can be attributed to the higher content of CNTs which are in agglomerated form and poor bonding of CNTs with other constituents in the composites [2]. The higher content of CNTs may also give barrier or inhibiting dislocation movement and transferring the load to the reinforcement through the reinforcement-matrix interface [14]. Overall, it is found that the flexural strength of nanocomposites at 4 wt.% up to 6 wt.% CNTs content shows some improvements whereas others are not greatly improved with the addition of CNTs.

Moreover, the flexural strength of CNTs/LC-PP increased with an increment of CNTs contents up to 7 wt.% (18.81 MPa) and decreased slightly as the CNTs content was further increased. However, all the values of CNTs/LC-PP flexural strength have not achieved the requirements stated by the U.S. DOE for bipolar plate (<25 MPa). This phenomena can be attributed to the lack of LC-PP capability to bind the filler during the fabrication process so that the fillers act as insulators and defects in the structure [23].

Better interfacial compatibility between CNTs and MC-PP matrix will promote the formation of a filler-polymer network structures, thus, enabling nanocomposite bipolar plate to transfer the load from the polymer matrix to CNTs more efficiently. Hence, the CNTs/MC-PP nanocomposite bipolar plates with a better compatibility between fillers and polymer resin have the greater reinforcement [12].

3.3 Effect of CNTs/PP on Shore Hardness

The values of shore hardness of CNTs/MC-PP nanocomposite bipolar plates were much higher than CNTs/LC-PP as shown in Figure 4. As 8 wt% of CNTs was incorporated into the LC-PP and MC-PP nanocomposites bipolar plates, the hardness increased to 72 (SH) and 81.3 (SH) respectively. Thus, the compactness of multifiller increased the interconnectivity and interactions between the reinforcing constituent [6, 25]. Moreover, the enhancement of the shore hardness for the nanocomposite bipolar plates increased in the order of CNTs/MC-PP>CNTs/LC-PP. These results postulated that better dispersion and good compatibility between CNTs and MC-PP will induce stronger adhesion [12].
3.4 Effect of CNTs/PP on Density

As shown in Figure 5, the density of CNTs/LC-PP and CNTs/MC-PP nanocomposite bipolar plates showed no significant differences on the increment of the CNTs content. An average value of CNTs/LC-PP and CNTs/MC-PP density was 1.616 g/cm³ and 1.635 g/cm³ respectively which achieved the requirements stated by the U.S. DOE for bipolar plate (<5 g/cm³).

![Figure 5](image)

**Figure 5** Effect of CNTs contents on density of the nanocomposite bipolar plate

3.5 Morphological Analysis

The micrographs of the fractured surfaces of CNTs/MC-PP nanocomposites were performed to study the dispersion of CNTs in the nanocomposite materials, as exhibited in Figure 6. The bright area represented CB and CNTs whereas dark area represented G [26]. Based on each micrograph, the fracture was occurring at the grain boundary as indicated by the dimples. For SEM images of CNTs/MC-PP, CNTs were well dispersed into polymer matrix. This would increase the conductive filler networks through the bipolar plate to enhance electrical conductivity and mechanical properties. Moreover, CNTs/LC-PP showed a decrease in electrical conductivity and flexural strength of nanocomposites which could be attributed to the formation of CNT agglomerates which degraded the mechanical properties as shown in Figure 6.

![Figure 6](image)

**Figure 6** SEM micrograph of G/CB/CNTs/MC-PP nanocomposite with: (a) 3 wt%, (b) 5 wt%, and (c) 8 wt% of CNTs content at 3kX magnifications

Based on both PP (MC-PP and LC-PP) as binders in nanocomposite properties, both nanocomposites optimum content of CNTs are different especially the electrical conductivity and flexural strength. This condition may be attributed to CNT agglomeration, voids and dispersion in the nanocomposite materials.
Through SEM micrograph of both nanocomposites with CNTs contents of 3 wt%, 5 wt%, and 8 wt%, the LC-PP binder showed more CNT agglomeration, voids and not well dispersion in the nanocomposite materials.

Figure 7 SEM micrograph of G/CB/CNTs/LC-PP nanocomposite with: (a) 3 wt%, (b) 5 wt%, and (c) 8 wt% of CNTs content at 3kX magnifications

4.0 CONCLUSION

In this study, a novel polymer nanocomposite bipolar plate comprises graphite, carbon black, CNTs and PP powder has been prepared successfully by ball mill mixing process and compression molding. Incorporating CNTs as a third filler in G/CB/CNTs/PP composites produces a synergistic effect that enhances electrical conductivity, flexural strength, bulk density and hardness of the composite which exceeds the U.S. DOE requirement. In terms of MC-PP, the dispersion of CNTs in nanocomposite bipolar plates is enhanced effectively, consistent with the micrographs by SEM. The addition of CNTs (6 wt.%) in MC-PP leads to a significant improvement with high electrical conductivity and mechanical properties which can be used when developing polymer composite as bipolar plate.

Acknowledgement

The authors would like to thank the Ministry of Higher Education, Malaysia and Ministry of Science, Technology and Innovation for sponsoring this work under PJP/2013/FKM (6A)/S01181 and Universiti Teknikal Malaysia Melaka (UTeM) for financial support for this study.

References
