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Effect of carbon nanotubes loading in multifiller polymer composite as bipolar plate for PEM fuel cell

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Abstract

In this study, bipolar plates for Proton Exchange Membrane Fuel Cell (PEMFC) were developed by compression molding technique using Polypropylene (PP) as a polymer matrix and Graphite (G), Carbon Black (CB) and Carbon Nanotube (CNTs) as reinforcements. United Stated Department of Energy (US DOE) target values were taken as the benchmark for the development and investigation of the bipolar plate properties. The effects of CNTs loading on the electrical and mechanical properties of G/CB/PP composite were investigated. By adding small amount of CNTs such as 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 wt% into G/CB/PP composite thus will give synergy effects on electrical conductivity and mechanical properties. It was found that, using CNTs as a third filler at a loading of 6 wt% in a G/CB/PP composite, shown the higher result of in-plane electrical conductivity is 158.32 S/cm, the density and shore hardness 1.64 g/cm^3 and 81.5 (SH) respectively. Meanwhile, the optimum value of flexural strength obtained was 29.86 MPa at 5 wt% of CNTs.

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Keywords: nanomaterial fillers; electrical conductive polymer composite; carbon nanotube.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) is a good contender for portable and automotive propulsion applications because of their advantages of high power density, solid state construction, high efficiency of conversion of chemical to electrical energy, near zero environmental emissions and low temperature operation[1]. The bipolar plate is a main component of PEMFCs stack, which takes a large portion of stack cost[2,3]. They can contribute 70-80% of the stack weight and up to 45% of the costs[4]. Thus, the investigation on cost/performance materials of bipolar plates has become a critical research issue. Bipolar plates can be made from many different materials, such as pure graphite, metal or polymer composites with carbon or metal conductive as a main filler. Pure graphite is one of the more traditional materials used to produce bipolar plates due to their advantages of good thermal and electrical conductivity, excellent chemical compatibility and good corrosion resistant. However, some problems with pure graphite is during fabrication process is too costly and time consuming, especially the machining process of gas flow channels into the plate surface and yet graphite has low mechanical strength properties[5-7].

Although there were many researches about Conductive Polymer Composite (CPCs) as bipolar plates for PEMFCs, only few of them focused on CNTs as reinforced filler. So it is necessary to do deep research on the combinations of multi fillers bipolar plate materials to obtain the better electrical conductivity of the composite[8-10]. Therefore, some conductive fillers like carbon black, graphite, carbon nanotubes and carbon fiber are commonly used as reinforced filler to enhance overall performance of CPCs as bipolar plates[11,12]. The interaction between fillers and polymer chains are the most important aspect need to be improved in CPCs as bipolar plates by conventional polymer processing technique[13,14].

Since Carbon nanotubes (CNTs) have good electrical and mechanical properties due to its high aspect ratio [15], the idea of using them as reinforcing fibers in composite materials has been a great potential for composite design [14,16]. However, the dispersion of CNTs in the polymer matrix is a challenging operation since they tend to agglomerate due to their high surface energy, thus impeding the formation of conductive paths that allow for the buildup of enhanced conductivity[17]. One of the most widely used methods to prevent the agglomeration of CNT in polymer matrix is melt mixing via internal mixer technique[18]. CNTs is a good candidate to produce nanocomposite with polymers due to its high Young‘s modulus, aspect ratio and electrical properties[19]. It is assumed that composites reinforced with carbon nanotubes could be stronger and lighter than reinforced with carbon black, metallic powders and glass fibers with metal coatings[11,20,21].

The aim of the present work is to investigate the effects of CNTs loading in multi filler G/CB/CNTs/PP composite for bipolar plate PEMFC. The paper also explores the electrical and mechanical properties of using more than one conducting fillers in CPCs. To achieve the requirements stated by the U.S. DOE for bipolar plate, materials/composite properties of the CPCs must be considered for achievable design for a fuel cell application, specifically, electrical and thermal conductivity, gas permeability, mechanical strength, corrosion resistance and low weight[10]. The properties requirements shown in Table 1 should be satisfied for the fabrication of a bipolar plate.

Table 1 Requirement properties for the bipolar plate (DOE target)[10,16,22]

Property	Value
Electrical conductivity	> 100 [Scm^{-1}]
Thermal conductivity	> 10 [$W(mK)^{1}$]
Flexural strength	> 25 [MPa]
Shore hardness	>50
Bulk Density	<5 [g/cm^3]

2. Experimental

2.1 Material

The polymer matrix used in this research was polypropylene (PP) grade Titan 600 which was purchased from Polypropylene (PP) Malaysia Sdn. Bhd. The second conductive filler is graphite powder and the third filler is Carbon Black powder purchased from Asbury Carbon, New Jersey. The fourth conductive filler used in this study is Multiwalled carbon nanotubes (MWCNTs, type NC 7000) purchased from Nonocyl (Belgium). It had been reported to have 90% of purity by manufacturer. Both conductive fillers used as received condition without any further purification. The comparison of properties between PP, MWCNTs, CB and G are presented in Table 2. Fig. 1 shows the photograph of the raw material for CNTs, G, CB and PP as powder forms which are used in this experiment.

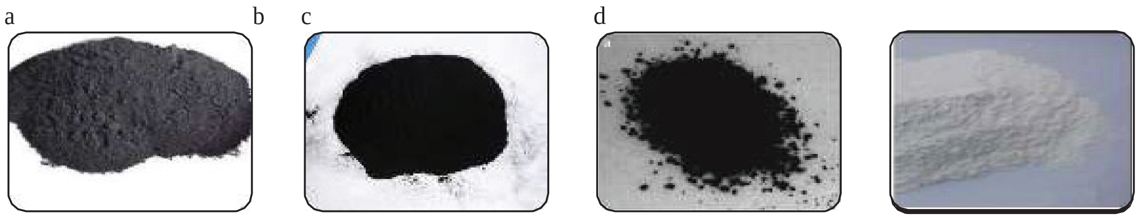

Fig. 1. (a) Graphite; (b) Carbon Black; (c) Carbon Nanotube; (d) Polypropylene.

Table 2 Properties of MWCNTs, graphite and polypropylene used in this study

Material	MWCNTs	Carbon Black	Graphite	Polypropylene
Grade	NC7000	5303	3243	Titan (600)
Density	1.0 g/cm^3	1.7~1.9 g/cm^3	1.74 g/cm^3	0.91-0.92 g/cm^3
Thermal stability	>700°C	3000°C	350-400 ºC	175-220 ºC
Size	9.5 nm (diameter) 1.5 um (length)	≤η µm	≤θ0µm	250 µm
Resistivity	Unknown	0.γ14 Ωcm	1295 (10^{-8}Ωm)	1(10^{14}Ωm)

2.2 Fabrication of polymer nanocomposites

The process sequences in obtaining composite sample start with produce the polypropylene (PP) powder. The granule PP was compressed by using hot press machine at a temperature of 190 ºC and pressure of 15 ton for 15 min pre-heat and 15 min pressed to form PP sheet. Then, the PP sheet were crushed, pulverized and sieved to form powder of 250 µm. After that, the multi filler materials are mixed used ball mill as pre-mixing process at a speed of 200 rpm for 1 and half hour. After that the wt% compositions of G/CB/CNT/PP are shown in Table 3 has been prepared. Again, a ball mill was used 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 for properties measurements. The mixture of all material was then preheated for 20 min in a mould placed in the hot pressing machine before it pressed at a temperature of 185 ºC and a pressure of 85 kg/cm^2 for 15 min. Then, the heater is off and let cool down at the machine until temperature decrease below 100 ^oC. The mold is then carried out from hot press space and carefully placed in the cold press space for 15 min to be cooled and the sample was then released from the mould.

Table 3 The composition of composite G/CB/CNTs (Based on weight %)

	Filler		**Binder**
G %	**CB%**	**CNTs%**	**PP%**
54.0	25	1.0	20
53.0	25	2.0	20
52.0	25	3.0	20
51.0	25	4.0	20
50.0	25	5.0	20
49.0	25	6.0	20
48.0	25	7.0	20
47.0	25	8.0	20
46.0	25	9.0	20
45.0	25	10.0	20

The effect of CNTs loading on the properties of G/CB/CNTs/PP composite such as electrical conductivity, flexural strength, bulk density and shore hardness were observed. The electrical conductivity was measured using Jandel Multi Height Four Point Probe while flexural strength was measured by the three-point method using the Instron Universal Testing Machine. Shore hardness is measured by using Shoredurometer (Type D) and bulk density measured by using weight balance tests (Densimeter) according to ASTM D792.

3. Result and discussion

3.1 Effect CNTs on Electrical Conductivity

The electrical conductivity of G/CB/CNTs/PP composites has increased initially with the increment of CNTs content from 1.0 wt% to 6.0 wt% as showed in Fig. 2. Thus, finding provides the evidence that using CNTs as a third filler with a high surface area and nano-sized diameter was giving a synergistic effect on the electrical conductivity of G/CB/CNTs/PP composites[17]. This is because the gaps between the synthetic graphite particles, which exhibit a flake-like geometry, were filled effectively with CNTs, which have a smaller diameter and a tubular geometry and thus, conducting networks were formed between the CNTs/G/CB and PP matrix[21]. However, the electrical conductivity of G/CB/CNTs/PP composites has been decreased slightly as the CNTs filler loading concentration increased. This due to higher CNTs loading in the polymer composites may cause critical CNTs aggregation and the electrical conductivity will be leveled off, even decreased[7]. The present finding also in line with researches have been done by Suherman (2013) and Selamat (2013) which concluded that electrical conductivity has decreased as the CNTs contents have been increased because agglomeration occurs with excess CNTs which deteriorates the electrical conductivity of nanocomposites[17,21]. Thus also similar with the findings by Dhakate (2010), we found that the value of electrical conductivity decreases when further increasing CNTs and this may be due to agglomeration of CNTs in the composite[23]. The maximum value of electrical conductivity is at loading of 6 wt% of CNTs with the value of 158.32 S/cm.

3.2 Effect CNTs on Flexural Strength

The graph flexural strength against weight percentage of CNTs of the G/CB/CNTs/PP composite has been plotted as shown in Fig. 3. The flexural strengths of the G/CB/CNTs/PP composite tend to increase gradually with increasing CNTs content. The optimum value of flexural strength obtained was 29.86 MPa at 5 wt% of CNTs. This showed an increment of imperfection binding between the fillers and PP with increasing of CNTs content. The decreasing of flexural strength after adding CNTs loading at 5 wt% can be attributed due to the poor dispersion of CNTs and a lack of PP powder to bind the conductive filler[17].

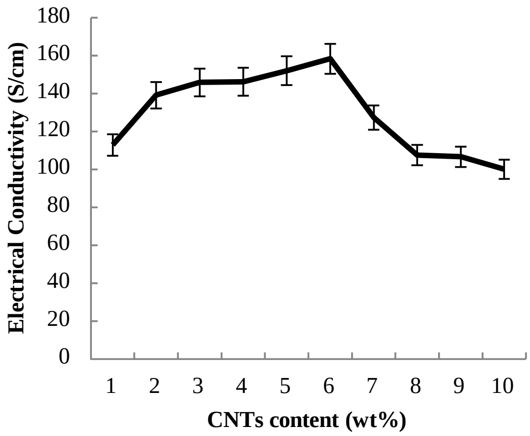

Fig. 2. Electrical conductivity of various content of CNTs.

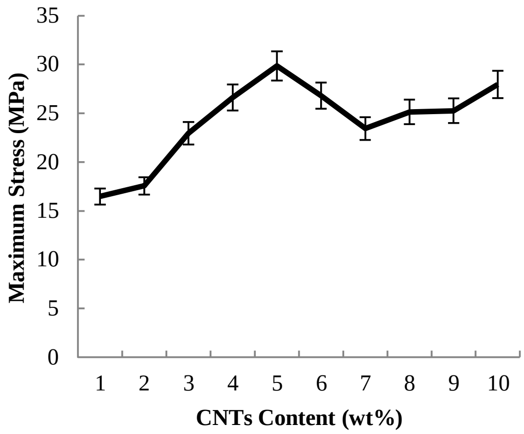

Fig. 3. Flexural strength of various content of CNTs.

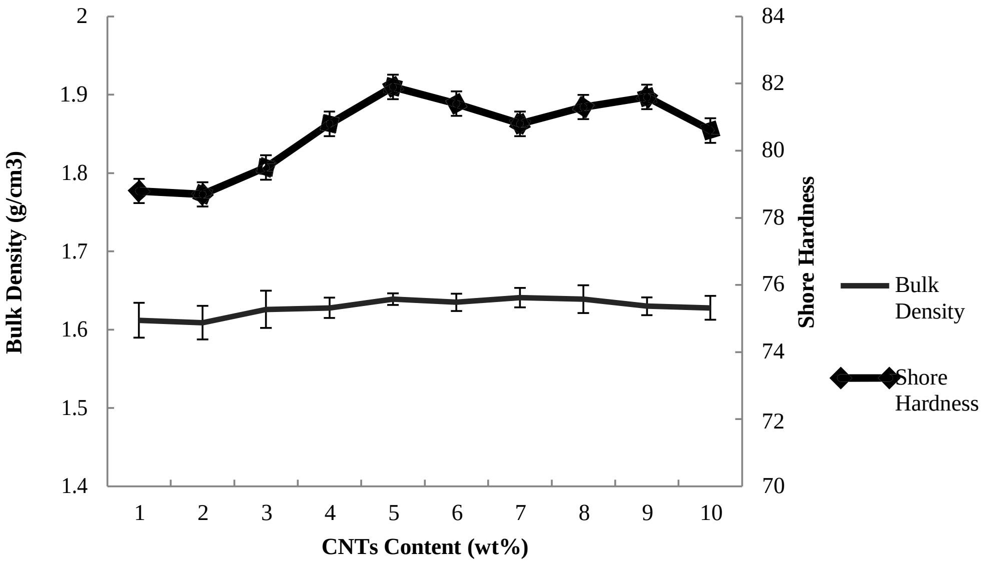

Fig. 4. Bulk density and shore hardness of various content of CNTs.

3.3 Effect of CNTs on Bulk Density and Shore Hardness

As showed in the graph in Fig. 4, the density of the composite bipolar plate is shown no significant effects of increasing of the CNTs content. An average value of density is 1.629 g/cm^3 and it achieve the requirements stated by the U.S. DOE for bipolar plate (<5 g/cm^3). However, the shore hardness of the composite had been increased with the increment of CNTs loading. The value of shore hardness has increased from 78.8 at 1 wt% of CNTs to 81.4 at 5 wt% of CNTs. After that, the hardness value has been decreased as the increment of wt% CNT. The decreased in hardness of the composite can be attributed to the fact that on the poor bonding of CNTs with other constituents in composite[23].

4. Summary

The effects of CNTs loading in multi filler G/CB/CNTs/PP composite for bipolar plate PEMFC are investigated. Incorporating CNTs as a third filler in G/CB/CNTs/PP composites produces a synergistic effect that enhances the electrical conductivity, flexural strength, bulk density and hardness of the composite which are exceeded of US-DOE requirement. With increasing of the CNTs content, electrical conductivity of G/CB/CNTs/PP composites is increase at maximum value 6 wt% of CNTs. It was observed that the critical weight percentage of the flexural strength and shore hardness G/CB/CNTs/PP composites was at a 5 wt% CNTs concentration as the third filler. Further study on agglomeration and the mechanical properties such as flexural strength and surface morphology need to be studied and further investigated.

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