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Effect of Carbon Nanotubes on Properties of Graphite/Carbon Black/Polypropylene Nanocomposites

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Abstract. High chemical corrosion, low manufacturing cost and light of total mass of bipolar plate in Proton Exchange Membrane Fuel Cell (PEMFC) lead most of the PEMFC's researchers over the world attracted their interest to replace pure graphite or metal based bipolar plate with conductive polymer composites (CPCs) bipolar plate. CPCs is fabricate from the mixed of conductive fillers such as and Graphite (G) andCarbon Black (CB) had been incorporated in Polypropylene (PP) matrix for fabrication of electrical conductive polymer composite plate. Most researchers reported only at high loading of fillers (more than 90 wt.%), are gave electrical conductivity above 100 S/cm, which is target from Department of Energy (USA). Higher loading of fillers cause change in rheological properties and increase the difficulties in polymer processing. Thus will decreasing the electrical and mechanical properties of CPCs as bipolar plate. Therefore, in this study carbon nanotubes (CNTs) which have 1000 time electrical conductivity than copper wire are introduced into G/CB/PP composite to compensate above problems. But the main problems of CNTs, at high loading it tend to agglomerate and thus will affect the properties of CPCs. So that, small amount of CNTs which is 0.2, 0.4, 0.6 and 0.8 wt.% will be added into G/CB/PP composite. But weight percentage of CB and PP has been fixed which is 25 wt.% and 20 wt.% respectively and the weight percentage of G will various from 55 wt.% to 54.2 wt.% according to CNTs loading. The result shows that the G/CB/CNTs/PP composite with 0.2 wt% CNTs has the higher electrical conductivity 295.78 S/cm.

Introduction

In the recent years, the Polymer Electrolyte Membrane Fuel Cell (PEMFC) has received intensive researches from both alternative energy and environmental consideration owing to their attractive features of high power density, low operating temperature and converting fuel to water as the only byproductof fuel cells [1,2]. Especially for bipolar plate (which accounts for nearly 38% in a fuel cell stack cost) [3], it is one of the most costly components in PEMFCs. Hence, the investigation on cost/performance materials of bipolar plates has become a critical research issue. The conventional materials for fabricating bipolar plate are based on either graphite materials or metals. The most commonly used bipolar plate material is graphite plates due to their advantages of high electrical conductivity, excellent corrosion resistance and lower density than those of metals. However, the disadvantages of graphite plates including the high cost resulted from machining channels into the surface and their brittleness would cause the fuel cell stack to be heavy and voluminous [4,5 & 6].

However CPCs bipolar plates are an attractive option for PEMFC. This composite not only offer advantages of low cost, but also has a lower weight and easy to be manufacture as compare to traditional graphite. In addition their properties also can be tailored through changes of reinforcements and the resin systems. Meanwhile the weakest of CPCs bipolar plates is their low electrical conductivity compared to conventional graphite or metallic bipolar plates. In order to obtain the better electrical conductivity of the composite, the combinations of multi fillers have been used as bipolar plate materials[7,8 & 9].The reinforced fillers used commonly including 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 &10]. Since the discovery of single-walled carbon nanotubes (SWCNT) and subsequently of multi-walled carbon nanotubes (MWCNT) and their exceptional mechanical properties, the idea of using them as reinforcing fibers in composite materials has been a driving force for composite design [10,11 & 12]. Since the Young's modulus of any material is related to the cohesion of the atoms and molecules that make up the solid [13], the adhesive forces between the matrix and the filler will similarly determine the properties of the composite. It is assumed that composites reinforced with carbon nanotubes (either SWCNT or MWCNT) could be stronger and lighter than reinforced with carbon black, metallic powders and glass fibers with metal coatings [3 & 14].

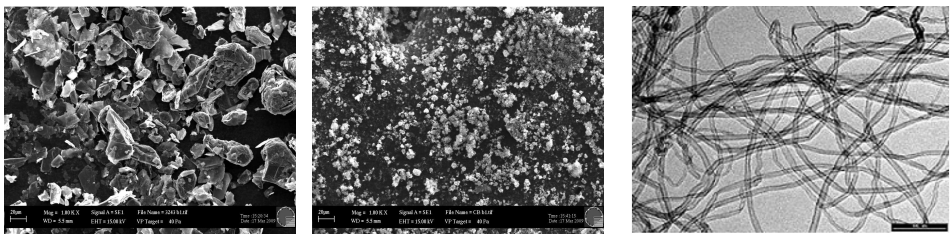
The CPCs to be used as bipolar plate must meet U.S. DOE requirement because of its multiple responsibilities and the challenging environment in which the fuel cell operates. Materials/composite properties must be considered for achievable design for a fuel cell application, specifically, electrical and thermal conductivity, gas permeability, mechanical strength, corrosion resistance and low weight [9]. The ideal bipolar plate should meet the target properties specified by DOE. 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) [9,15 & 16]

Properties	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]

Methodology

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. Comparison of properties between PP, MWCNTs, CB and G are shown in Table 2. Figure 1 (a) shown digital image of MWCNTs powder. Figure 1 (b) shown scanning electron microscopic image of graphite. Figure 1 (c) shown transmission electron microscopic (TEM) image of MWCNTs used in this study, which clearly indicate MWCNTs with fewer impurities.



(a) (b) (c)

Fig. 1 : (a) and (b) SEM image of graphite and carbon black, and (c) TEM image of MWCNTs

Table 2 : Properties of MWCNTs, graphite and polypropylene used 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)	≤5 um	≤60μm	Flakes
Resistivity	Unknown	0.314 Ωcm	1295 (10^{-8}Ωm)	1(10^{14}Ωm)

A Rheomix mixer (Haake-PolylabTM) with banburry type rotor and 50 cm^3 mixing chamber was used for composites compounding. The process sequences in obtaining composite sample start with the multi filler material are mixed in pre-mixing process. Followed with the melt compounding process and in this stage, Rheomix mixer Haake-Polylab TM with roller type rotors is used and the material from the previous stage is mixed and the composition as shown in Table 3. The nanocomposite obtained by melt compounding was crush and pulverized into powders in order to improve homogeneity of the specimen for next forming process. Liquid nitrogen had been used to assist pulverization process. A 50 Ton high precision hydraulic molding machine was used to prepare the samples for electrical conductivity measurements. The granules or powders was then preheated for 10 min in a mould placed in the hot pressing machine before it pressed into 25 mm diameter, 2 mm thick disk sample at a temperature of 200 ºC and a pressure of 75 kg/cm^2 for 3 min. The mould was placed in a water bath for 5 min to be cooled and the sample was then released from the mould.

Table 3 : Mixing composition between graphite, polypropylene and MWCNTs

Specimen	wt.%			
	G	CB	MWCNT	PP
1	55	25	0	20
2	54.8	25	0.2	20
3	54.6	25	0.4	20
4	54.4	25	0.6	20
5	54.2	25	0.8	20

Fig. 4 : Four-point Probe for electrical conductivity measurement

The effect of CB and CNTs loading on the properties of G/CB/CNTs/PP composite such as electrical conductivity, shore hardness and bulk density were observed. The electrical conductivity was measured using Jandel Multi Height Four Point Probes, shore hardness is measured by using Shoredurometer and bulk density measured by using weight balance tests (Densimeter) according to ASTM D792.

Results And Discussion

Effect of CB on Electrical Conductivity. Figure 5 has shown the electrical conductivity of G/CB/PP composite with various contents of CB. The result shown that the electrical conductivity is increase as CB contents increase until 25 wt.% CB. Thus shows that CB particles gives synergetic affects of composite G/CB/PP system, as CB contents increase the value of electrical conductivity also increases. The value of electrical conductivity for G/CB/PP has increasing sharply from 0 wt.% (7.6 S/cm) of CB to 25 wt.% CB (193.4 S/cm) than the value has decreasing sharply from 25 wt.% CB to 30 wt.% CB (119.5 S/cm). The conductivity has increase for CB contents below 25wt% CB because the sizes of filled space are smaller and thus forms synergetic effect between G and CB particles. As compare to 30 wt.% CB contents is less the synergetic effect between G and CB particles because the size of filled space is large. This due to when the CB contents are 5 wt.% to 25 wt.%, the conductivity of composite improves with increasing CB contents over the whole ranges of G contents. The smaller size of CB particles compare to G particles forming conductive bridges and make more conducting tunnels between the G particles thus increase the conductivity. Meanwhile for CB contents is 30 wt.% the electrical conductivity of composite decreases with increasing CB loading. Here when CB contents above the critical loading, the additional CB will not be wetted well with PP resin and its will deteriorate the conductivity of the composite because of incomplete compaction.

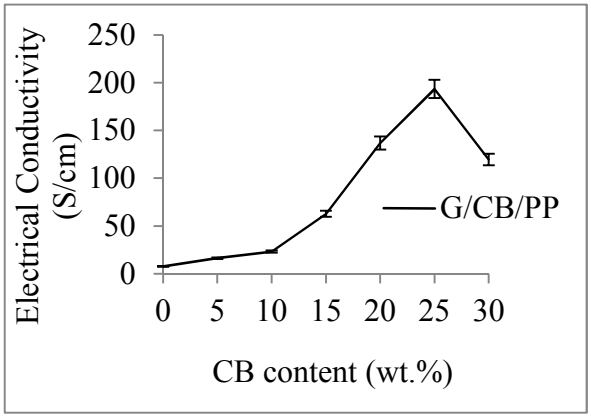


Fig. 5 : Electrical conductivity of various content of CB

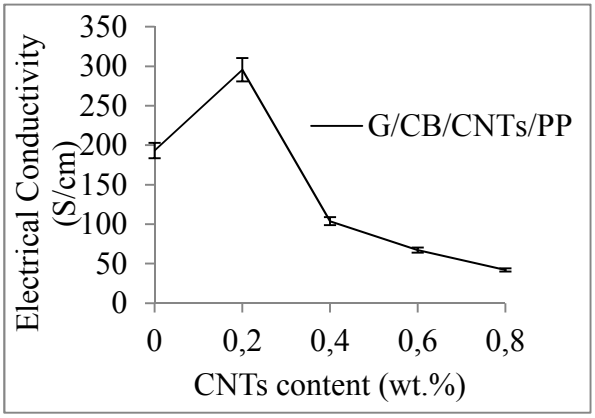


Fig. 6 : Electrical conductivity of various content of CNTs

Effect CNTs on Electrical Conductivity. The variations of electrical conductivity of G/CB/CNTs/PP nanocomposites as function of MWCNTSs loading are plotted in Figure 6. From the graph electrical conductivity against CNTs weight percentage, it shows that the electrical conductivity was increased after the CNTs was added in to the composition at 0.2 wt.% and has decreased constantly as the value of CNTs has increased. The electrical conductivity was measured started with the specimen has no CNTs until 0.8 wt.% CNTs. The result shows that the value of electrical conductivity is 179.42 S/cm with no CNTs, 0.2 wt.% CNTs the electrical conductivity is 285.78 S/cm and 0.8 wt.% CNTs the electrical conductivity is 42.09 S/cm. The result shows that, the optimum ratio for CNTs in G/CB/CNTs/PP composite is 0.2 wt.% CNTs as a result shown the highest electrical conductivity. Thus due to synergistic effects of combining CNTs and G, which are produces higher electrical conductivity. However, the electrical conductivity decreases as the CNTs contentsincreases because the PP resin cannot be wetted well; with an excess of CNTs, agglomeration occurs, which deteriorates the electrical conductivity of the nanocomposites [17].

Effect CNTs on Bulk Density. Figure 7 shows the variation in bulk density of composites of bipolar plate with increasing CNTs weight percentage. Due to lower density of CNTs, bulk density of composites has decreases with the increasing of CNTs content. Thus because due to the reducing of Graphite weight percentage. G has the highest value of density, so that the decreases the value of G, the value of bulk density of the specimens also decreases. Initially, at 0 CNTs weight percentage, the bulk density is 1.488 g/cm^3 and it was slightly increased when 0.2 wt.% of CNTs was added.

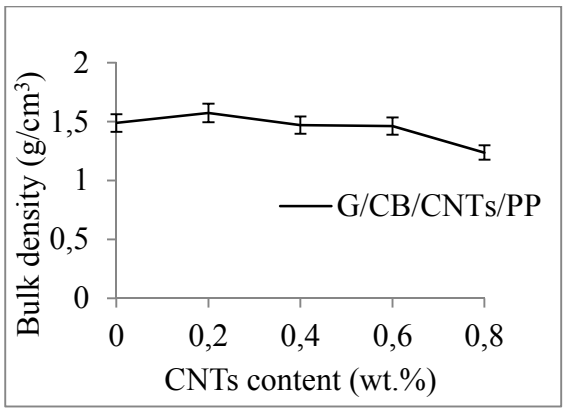


Fig. 7 : Bulk density of various content of CNTs

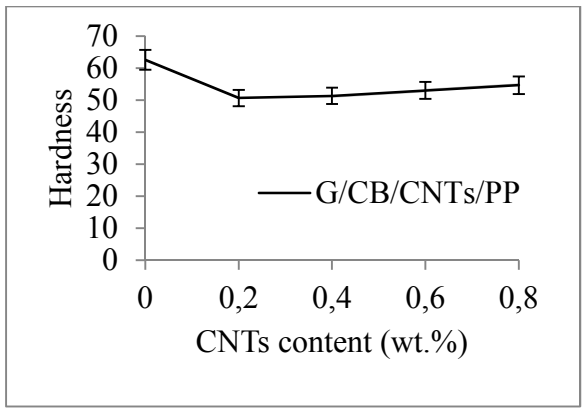


Fig. 8 : Shore Hardness of various content of CNTs

The value of bulk density with 0.2% CNTs content is 1.573 g/cm^3. But, it started to moderately decrease with increasing the CNTs content and the minimum value of bulk density is 1.237 g/cm^3 at 0.8 wt.% of CNTs.

Effect of CNTs on Hardness. Figure 8 shows the variation in shore hardness with increasing CNTs content. The shore hardness increases with increasing the content of CNTs except for specimen with 0% wt. CNTs. The value of shore hardness for specimen with 0 wt.% CNTs is 62.60 and decreased to 50.67 with 0.2 wt.% CNTs. Then the value increased constantly until 0.8 wt.% CNTs which is 54.67. Thus due to the compactness of multifiller, that increases the interconnectivity and interactions between the reinforcing constituent.

Summary

The result shown that the addition of CNTs in G/CB/PP composite with 0.2 wt.% has increase electrical conductivity of G/CB/CNTs/PP composite become more conductive about 53% higher compare to G/CB/PP composite. The hardness of G/CB/CNTs/PP composite has been increases with the increases of weight percentages of CNTs. For the bulk density of the G/CB/CNTs/PP composite has also decreases with the increasing of CNTs contain. However for the electrical conductivity of G/CB/CNTs/PP composite after CNTs contain more than 0.2 wt.%, the value has been decreases is due to agglomeration of CNTs has affect the electrical conductive pathway in polymer matrix. 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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