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Original Article

Enhance the electrical conductivity and tensile strength of conductive polymer composites using hybrid conductive filler

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Abstract

This paper focused on using a hybrid conductive filler to enhance the conductive polymer composite (CPCs) properties, especially the electrical conductivity and tensile strength. CPCs can be used for various applications in electronic devices; however, CPCs have low electrical conductivity. Therefore, a hybrid filler was chosen because it has the potential to produce higher electrical conductivity compared with a single filler. In this study, the CPCs were prepared by compounding using a mechanical mixer followed by a casting process. Graphite (10 wt%) with a particle size of 5µm (G5) as the secondary filler resulted in an electrical conductivity of 0.029 S/cm and tensile strength of 3.6 MPa. These results succesfully improved the electrical conductivity of the CPCs more than 100% compare with a single filler CPCs at the same amount of 50 wt% conductive filler.

Keywords: hybrid conductive filler, conductive polymer composites, electrical conductivity

1. Introduction

The materials of conductive polymer composites (CPCs) are from the combination of a matrix that serves as a binder and filler as a conductive material. Graphite is a good conductive material due to its high electrical conductivity. The other properties are easy to make using conventional processes such as compression molding and injection molding for various shapes and sizes (Marthur, Dhakate, Gupta, & Dhami, 2008; Mohd Radzuan *et al.*, 2016; Yen-Chuang *et al.*, 2006; Zhang *et al.*, 2017). Kuan, Ma, Chen, and Shih (2004) investigated the effect of graphite particle size on the electrical conductivity of vinyl ester (VE) for composite bipolar plates. The graphite used in that research had diameter sizes from 53µm to 1000µm. They reported that the minimum diameter of graphite which had the highest resistivity was 53µm.

Other research was performed by Heo, Yun, Oh, and Han (2006) which investigated the effects of graphite particle sizes (7, 10, 15, and 25 µm for sphere and 25 µm for flake-like shaped types) on the electrical conductivity of phenol resin for composite bipolar plates. That experiment was carried out using a single filler with a conductive filler of 85 wt%. They found that sphere shaped graphite with diameter sizes of 7-25 µm produced relatively similar electrical conductivity. The highest electrical conductivity was produced by the flake-shaped particles (25 µm).

Derieth *et al*. (2008) investigated the effect of different geometrical shapes of graphite used in the electrical conductivity of polypropylene (PP) for bipolar plates at a fixed loading concentration of 78 wt%. The research results showed that the electrical conductivity of flake-like particles was higher than spherical particles. This was because flake-like particles have a higher surface area compared with spherical particles, which results in a better conductivity network formation. Chunhui, Mu, and Runzhang (2008) used single and hybrid conductive fillers to improve the electrical conductivity of conductive polymer composites. The effects of the hybrid conductive fillers with different particle sizes and

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shapes on the electrical conductivity of conductive polymer composite for bipolar plate's material were investigated in that research. The research found that the appropriate size of hybrid conductive fillers within a polymer matrix could enhance the compactness of the conductive polymer composites, which thereby increased the electrical conductivity.

Dhakate, Marthur, Sharma, Borah, and Dhami (20 09) used a combination of expanded graphite (EG) with different particle sizes as the secondary filler on a phenolic resin conductive polymer composite for bipolar plates. The research found that the conductive polymer composite of 50 µm EG in 300 µm based composite at 10 wt% obtained the highest electrical conductivity.

Hui, Bo, Li, Xin, and Li (2010) investigated the effect of graphite particle size on the electrical conductivity of a conductive polymer composite for bipolar plates. This research used natural graphite particles and novolac epoxy resin. They found that the electrical conductivity of the conductive polymer composites increased as the graphite particle size increased.

Further investigations are still needed in the incorporation of flake-like and spherical graphite with variations in the size and loads of the second filler to increase the electrical conductivity and tensile strength at low loads.

2. Experiments

2.1 Materials and fabrication process

Graphite powder (G74) as primary filler has electrical resistivity of 0.03 ohm-cm, average diameter particle size of 74 µm, and density of 1.74 g/cm^3. It was purchased from Asbury Carbons, NJ, USA. Other particle sizes of graphite as secondary fillers were purchased from FRIway Industry, China. They were G25 (density 1.9 g/cm^3), G13 (density 2.01 g/cm^3), and G5 (density 2.12 g/cm^3). The particle sizes were 25 µm (G25), 13 µm (G13), and 5 µm (G5) and the electrical resistivity was 10.5×10^6 ohm-m as reported by the manufacturer. The epoxy resin was a bisphenol-A based epoxy resin (635 types), purchased from US Composites with a viscosity of 6 Poise and density of 2.25 g/cm^3.

G25/G74/Epoxy, G13/G74/Epoxy, and G5/G74/ Epoxy composites were prepared by adding G25, G13, and G5 at different loading concentrations (2.5 to 10 wt%) into the G74/Epoxy mixture. A 10 wt% was selected as the maximum loading concentration of the second conductive filler because the electrical conductivity of CPCs decreases if the secondary conductive filler loading concentration exceeds 10 wt% due to agglomeration (Dhakate *et al.,* 2009). The mixture was prepared using a mechanical mixer (IKA-RW-20 digital, Germany), stirred at 250 rpm for 10 min. The specimens were made using a casting process at a fixed molding temperature (150 °C) and 30 to 90 min formation time.

2.2 Characterizations

The electrical conductivities of G25/G74/Epoxy, G 13/G74/Epoxy, and G5/G74/Epoxy composites with different loading concentrations of conductive fillers were measured by the ASTM C 61 method (Kakati, Sathiyamoothy, & Verma, 2010). The tensile strengths of the CPCs were measure according to ASTM D3039 with dimensions (250×25×3 mm). Scanning electron microscopy (SEM) was used to observe the dispersion of the conductive fillers in the polymer matrix through fractured surfaces of G25/G74/Epoxy, G13/G74/ Epoxy, and G5/G74/Epoxy composites using Hitachi S-3400 N. Table 1 and Table 2 show the compositions of the single and hybrid conductive fillers. The compositions of graphite as a conductive filler and epoxy resin as the matrix are shown based on weight percentage (wt%). The maximum composition of conductive filler and matrix were 50 wt% because this research focused on producing CPC materials with conductive filler contents from 20 to 50 wt%.

Table 1. Composition of single filer composites.

Graphite/epoxy	Graphite (wt%)	Epoxy (wt%)
50/50	50	50
40/60	40	60
30/70	30	70
20/80	20	80

Table 2. Composition of hybrid fillers composites.

(G74/G5/Epoxy)	Graphite (74 µm) (wt%)	Graphite (5 µm) (wt%)	Epoxy (wt%)
47.5/2.5/50	47.5	2.5	50
45/5/40	45	5	50
42.5/7.5/40	42.5	7.5	50
40/10/50	40	10	50
(G74/G13/Epoxy)	Graphite (74 µm) (wt%)	Graphite (13 µm) (wt%)	Epoxy (wt%)
47.5/2.5/50	47.5	2.5	50
45/5/40	45	5	50
42.5/7.5/40	42.5	7.5	50
40/10/50	40	10	50
(G74/G25/Epoxy)	Graphite (74 µm) (wt%)	Graphite (25 µm) (wt%)	Epoxy (wt%)
47.5/2.5/50	47.5	2.5	50
45/5/40	45	5	50
42.5/7.5/40	42.5	7.5	50
40/10/50	40	10	50

3. Results and Discussion

3.1 Characterization of conductive fillers

This study used three types of conductive filler materials of different sizes and shapes. This distinction is intended to observe the influence of each conductive filler type on the conductive polymer composite properties. The differences of the shapes and sizes of the conductive materials are shown in Figure 1. SEM images showed G74 as the primary filler. G13 and G5 as secondary fillers were flake-shaped, and G25 also as a secondary filler was sphere-shaped.

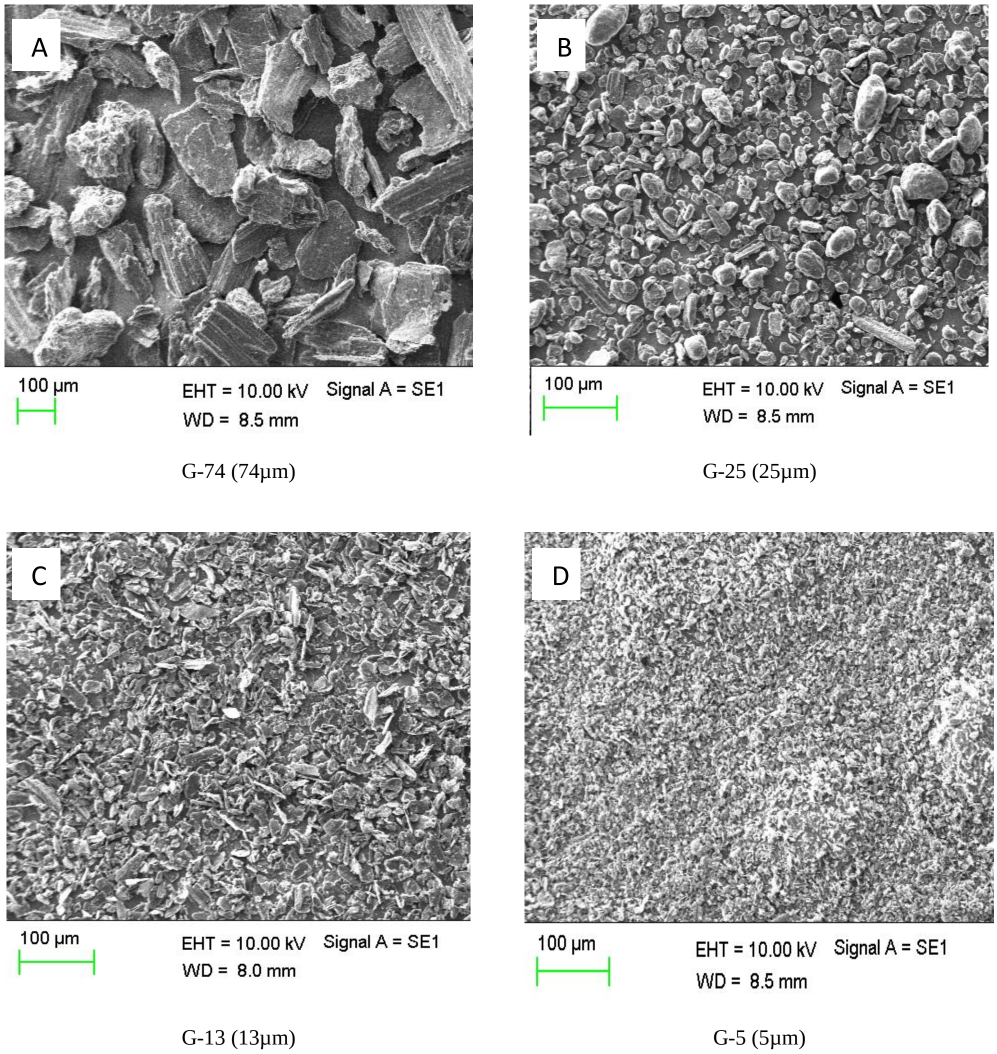


Figure 1. SEM images of conductive fillers (A) G74, (B) G25, (C) G 13 and, (D) G5.

3.2 Electrical conductivity of single filler conductive material

Figure 2 shows the effect of adding 20 to 50 wt% of conductive fillers to the electrical conductivity of G74/Epoxy composites. The filler contents were selected as 20 to 50 wt% because these observations focused on the low content (≤50 wt%) of graphite as the conductive filler. The electrical conductivity of the G74/Epoxy composite increased significantly by the addition of conductive fillers. The electrical conductivity of G74/Epoxy composites increased as 0.001 S/cm at 20 wt% conductive filler loading concentration and continued to increase to 0.013 S/cm at 50 wt%. This occurred because the addition of conductive filler to the matrix increased the conductive network within the polymer matrix and produced high electrical conductivity. (Chen, Xia, Yang, He, & Liu, 2016; Hu-Ning *et al.*, 2008).

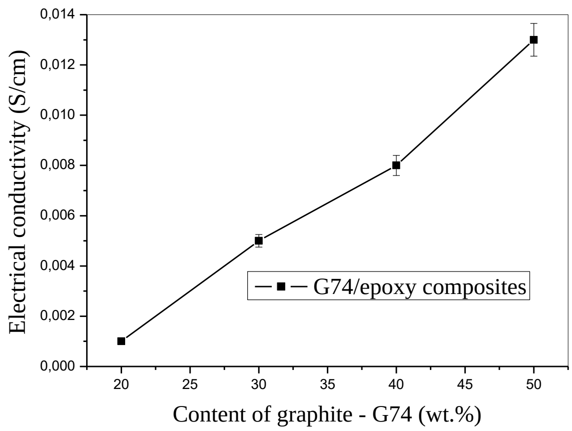


Figure 2. Effect of adding graphite (wt%) on the electrical conductivity.

Figure 3 shows SEM images of G74/Epoxy composite at conductive filler loading concentrations of 20 and 50 wt%. Figure 3 shows a very clear distinction in the amount of conductive filler loading concentrations (red circles) in the polymer matrix.

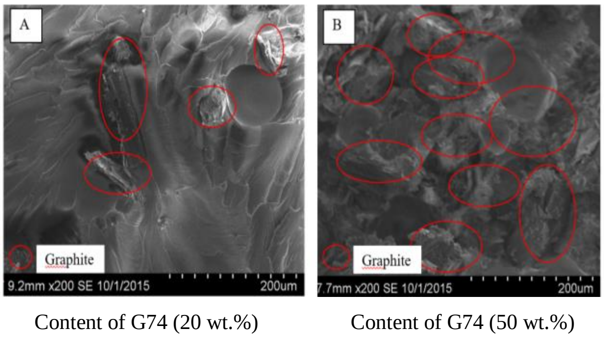


Figure 3. SEM images of fracture surfaces of G74 (a) 20 wt% and (b) 50 wt%.

3.3 Electrical conductivity of hybrid conductive fillers

Hybrid conductive fillers are used in an attempt to improve the electrical conductivity of CPC materials. The combination of two conductive filler materials results in a better conductive network, especially if the conductive material has a different particle size (Chunhui *et al.*, 2008; Ma *et al.*, 2009; Suherman *et al.*, 2010).

The effects of the second filler materials (G25, G13, and G5) on the electrical conductivity of G25/G74/Epoxy, G 13/G74/Epoxy, and G5/G74/Epoxy composites are shown in Figure 4. Figure 4 shows the electrical conductivities of these three CPC materials produced from different sizes and shapes of the second conductive filler material. Overall, the epoxy composite materials showed almost the same tendencies at conductive filler loadings of 7.5 wt%. The 5 µm graphite particles as a second filler produced higher electrical conductivity compared with the other graphite sizes (13 µm and 25 µm). This occurred because smaller secondary conductive fillers are able to fill the voids formed by the primary conductive filler which results in the formation of more conductive networks which increases the electrical conductivity (Nishata, Sulong, Sahari, & Suherman, 2013; Suherman, Sulong, & Sahari, 2013).

The electrical conductivity of G25/G74/Epoxy and G13/G74/Epoxy composites decreased as the filler loading exceeded 7.5 wt%. The conductive fillers were no longer uniformly dispersed in the whole matrix which reduced the formation of a conductive network.

The G5/G74/Epoxy composites showed different phenomena. The electrical conductivity still increased at 10 wt% of secondary conductive filler. This occurred because the G5 has a different size but it is similar in shape to the G74. The G5 is small (5 µm) and flake-shaped and is more effective as a secondary filler material compared with G25 and G13 (Dhakate *et al.*, 2009). Although the electrical conductivity of the 10 wt% secondary conductive filler composite (5 µm) was higher, the electrical conductivity decreased when the secondary conductive filler exceeded 10 wt% (Dhakate *et al.*, 2009; Suherman *et al.*, 2013). Therefore, the maximum content of the secondary conductive filler was set at 10 wt%.

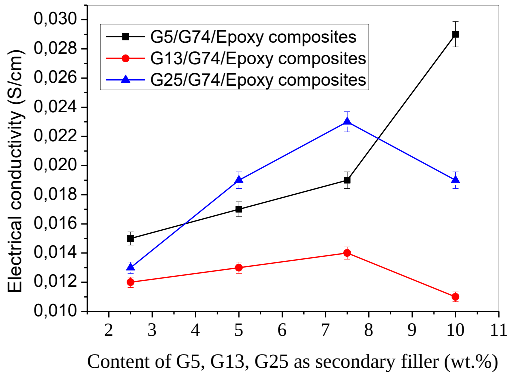


Figure 4. Effects of G25, G13, and G5 on the electrical conductivity.

3.4 Effect of molding time on the electrical conductivity of the hybrid conductive filler

Molding time plays an important role in making CPCs material. The forming of a conductive net-work depends on the formation time of CPC materials within polymer matrix (Ganglani *et al.*, 2002; Hu *et al.*, 2008). The effect of molding times on the electrical conductivity of G25/G74/Epoxy, G13/G74/Epoxy, and G5/G74/Epoxy composites are shown in Figure 5. Figure 5 shows that increasing the molding time from 30 to 90 min also increased the electrical conductivity for all secondary conductive filler materials at different sizes and shapes. The highest electrical conductivity of the conductive filler material (0.029 S/cm) was demonstrated at the size of 5 µm, flake-shaped, and a molding time of 90 min.

The formation time has a significant effect on the conductive network formed. A longer formation time is required for the conductive filler to be distributed and dispersed more evenly within the matrix. A longer formation time also reduces the viscosity of the matrix to improve the movement of different particle sizes and shapes of the graphite in the matrix. This condition produces a better conductive network within the polymer matrix to increase the electric conductivity (Ganglani *et al.*, 2002; Hu *et al.*, 2008).

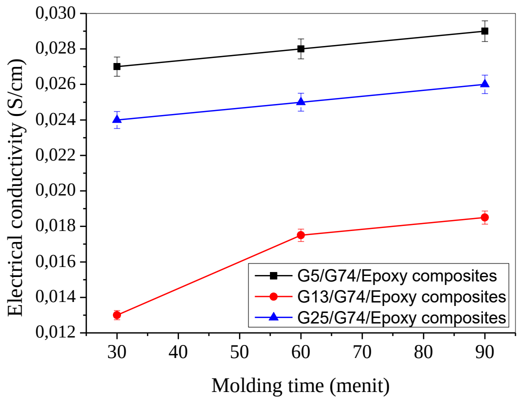


Figure 5. Effect of molding time on the electrical conductivity.

3.5 Tensile strength of G74/epoxy composites

Figure 6 shows that a small addition of conductive filler (20 wt%) was able to increase the tensile strength from 1.55 MPa (pure epoxy resin) to 3.3 MPa (20 wt%). The tensile strength of G74/Epoxy composites was lower when the conductive filler exceeded 20 wt% due to agglomeration of the conductive filler whithin the polymer matrix. The agglomeration significantly decreased the tensile strength of the G74/ epoxy composites which was even lower than the epoxy resin without the conductive filler material (Ma *et al*., 2009).

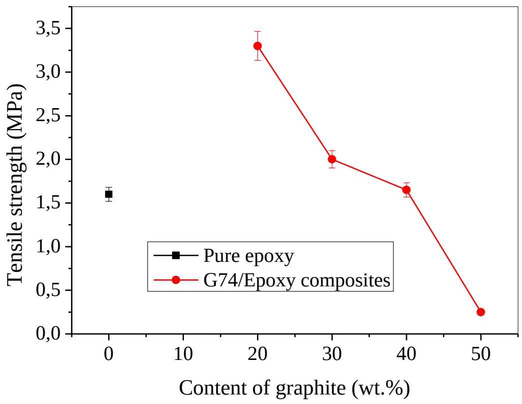


Figure 6. Effect of adding graphite on the tensile strength.

3.6 Tensile strength of hybrid filler composites

Figure 7 shows the effect of adding hybrid fillers on the tensile strength of G25/G74/Epoxy, G13/G74/Epoxy, and G5/G74/Epoxy composites. The addition of the secondary conductive filler at different sizes and shapes in the amounts of 2.5 to 10 wt% showed an interesting phenomenon (Figure 7). The tensile strengths increased in both of the G13/G74/ Epoxy and G5/G74/epoxy composites at a filler loading concentration of 5 wt%. The tensile strength increased significantly in the G5/G74/Epoxy composites. This condition was caused by the characteristic flake-shape and the 5 µm size of the secondary fillers which was able to synergize with the primary filler material that was also flake-shaped. At 5 wt% of secondary conductive filler, the maximum tensile strengths of the G5/G74/Epoxy and G13/G74/Epoxy composites were 3.8 MPa and 1.3 MPa, respectively. A different phenomenon occurred with the G25/G74/Epoxy composite. The tensile strength decreased with the addition of secondary conductive filler material from 2.5 to 7.5 wt%. This indicated that the smaller amount of secondary conductive filler was more effective in increasing the tensile strength, because it was well dispersed in the whole polymer matrix. This condition is similar with the results obtained by Chunhui *et al.* (2008), which showed that a single conductive filler material was more effective if it is large, but in the case of hybrid fillers, the secondary conductive filler should have a smaller size than the primary conductive fillers.

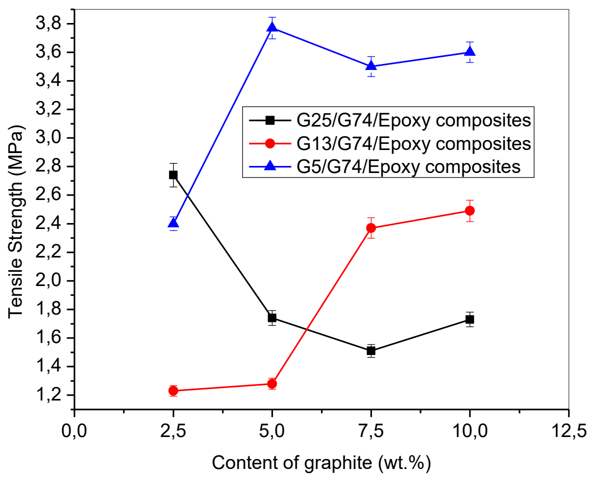


Figure 7. Effect of adding hybrid fillers (wt%) on the tensile strength.

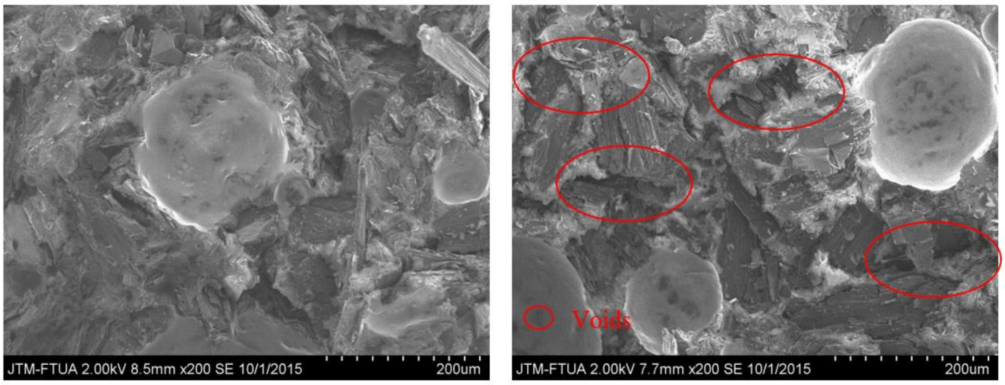
3.7 Dispersion of G25/G74/Epoxy, G13/G74/Epoxy, and G5/G74/Epoxy composites

The dispersion of conductive filler material within the polymer matrix is very important in determining the conductive polymer composite properties. Figures 8a, 8b, and 8c show the SEM fracture surfaces of the G25/G74/Epoxy, G13/ G74/Epoxy, and G5/G74/Epoxy composites.

The SEM fracture surfaces in Figures 8a, 8b, 8c show that all of the different shapes and sizes of the secondary conductive fillers were well dispersed. Voids occurred in the secondary filler concentration of 10 wt% in the G25 (Figure 8a) and G13 (Figure 8b) which decreased the electrical conductivity. However, the electrical conductivity increased up to the addition of 10 wt% of the second conductive filler material G5 (Figure 8c). This occurred because the smaller particle size (5 µm) and the flake-shape was similar to the primary conductive material and was more synergistically effective in this condition (Antunes *et al.*, 2011; Ma *et al.*, 2009).

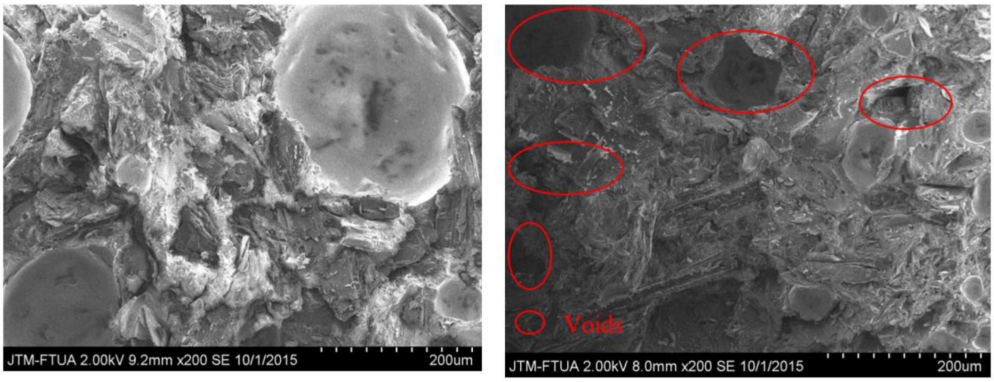
4. Conclusions

Three CPC materials were produced: G25/G74/ Epoxy, G13/G74/Epoxy, and G5/G74/Epoxy. The electrical conductivity of G74/epoxy composites increased by increasing the amount of conductive filler from 20 to 50 wt% within polymer matrix. The electrical conductivity of the hybrid filler composites increased as the amount of conductive fillers increased within polymer matrix to 7.5 wt%. After 7.5 wt% the electrical conductivity of the G25/G74/Epoxy and G13/G74/Epoxy composites decreased, except the G5/G74/ Epoxy composite. This was because G5 as the secondary filler could fill the gaps between the primary filler of a larger particle size. The maximum tensile strength obtained was 3.8 MPa from the G5/G74/epoxy composite with a 5 wt% composition of G5 as the secondary filler. The smaller size and similar shape of the secondary filler material was more effective in generating the higher electrical conductivity and better tensile strength of the hybrid composites. This was caused by the contact area between the primary filler and the secondary filler having the same shape. It could fill the voids effectively and produce a better conductive network.



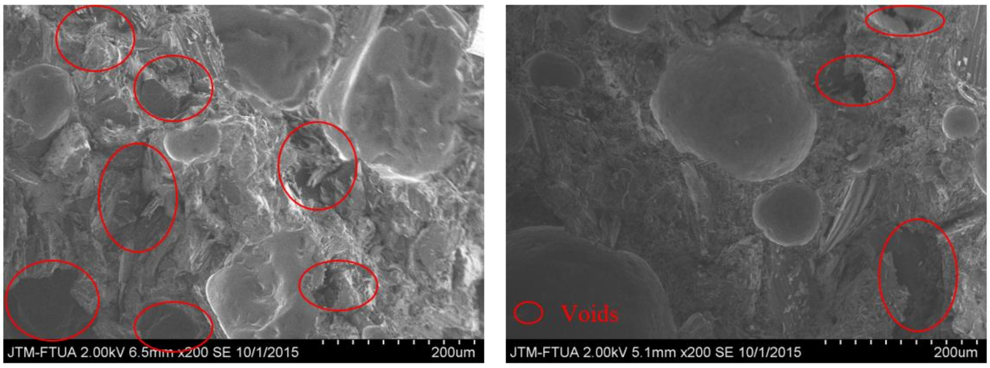
7.5 wt.% 10 wt.%

Figure 8a. SEM images of fracture surfaces of G25 with addition of 7.5 and 10 wt%.



7,5 wt.% 10 wt.%

Figure 8b. SEM images of fracture surfaces of G13 with addition of 7.5 and 10 wt%.



7.5 wt% 10 wt%

Figure 8c. SEM images of fracture surfaces of G5 with addition of 7.5 and 10 wt%.

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