Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

A Development and a Physical Properties Characterization of a Conductive Polymer Composite Reinforced with Metallic Particulates and Short Wire Fillers

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Abstract

Metallic particles polymer composites exhibit a remarkable development in electrical conductivity. Polymers conductivity has been improved by inclusion different metallic materials, the development has been found to be filler characteristics dependent. This study uses copper (Cu), zink (Zn), tin (Sn) particles, as well as copper short wires (CSW) to develop composites with different weight fractions, and evaluate their electrical conductivity, mechanical properties, and density. The results showed positive effect of the filer weight fraction on the conductivity. The CSW composites demonstrated almost double electrical conductivity compared to particulate composites. Up to 15% and 57% development in the ultimate tensile strength was achieved in the particulate and the CSW composites, respectively. However, an adverse effect for the CSW filler was recognized at a weight fraction higher than 33%. Microstructure investigation revealed some inhomogeneous distribution of the CSW in the matrix at the higher filler fraction, which could be the reason behind the achieved reduction in mechanical properties.

Keywords: Conductive polymers; particulate composites; metallic fillers

1. Introduction

By nature, plastics are very good insulators. This inherent attitude gives the plastics good tendency towards holding electrostatic charges while allowing the electromagnetic and radio frequency to pass through. With the great development in electronic technology, of the past few decades, plastics have become excellent option for electronic components such as cell phones and computers. Due to their desired low density, color ability, cost effectiveness, and design flexibility, plastics have become strong competitive for metals. However, dielectric materials exhibit low thermal conductivity, the property that limits their implementation in some electronic technologies, such as integrated circuits, diode lamps, computer chips, and intelligent circuits. These applications require high heat dissipation rate to maintain their high performance, which is not achievable with the dielectric plastics. To solve this issue, a considerable research attention has been dedicated to develop the thermal- and electrical-conductivity of the plastics [1]. Conductive plastics (CPs) are characterized by a tunable conductivity, low density, affordable cost, and easy to fabricate, these aptitudes make them excellent option multifunctional sensors [2]. They are not only excellent materials for structural applications but also they can be functional materials [3]. According to Wang, et al. [4], polymer with improved electrical conductivity can provide excellent performance in a variety of applications, including the charge storage, electromagnetic interference shielding (EMI), and electrical sensors. Because of their smart response to different body tissues' electrical fields such as nervous, muscles, and epithelium, CPs have become excellent potential for numerous biomedical applications [5]. They have vast clinical applications, and can help fulfill a variety of the presently unmet medical requirements, such as nerve conduits development to motivate regeneration of the nerve which is very essential in organ transplantation. Moreover, CPs can play a significant rule in scaffolds synthesis which contributes to efficacious myocardial tissue regeneration. They are also applicable for neurological syndromes treatment, like Parkinson's illness. More importantly, biocompatible CPs are anticipated to replace the metallic implants, which demonstrate low biocompatibility and develop an integration with the body tissues [5].

The implementation of the CPs in electrical-linked applications has witnessed evolving demand in the resent years. It is predicted that the global market need for the CPs will reach USD 5.7 billion by 2027. This is basically powered by the escalating demand for anti-static packaging which is particularly required in electronics industry [6]. CPs also can

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Receive Date: 20 January 2023, **Revise Date:** 26 March 2023, **Accept Date:** 10 April 2023, **First Publish Date:** 10 April 2023
DOI: 10.21608/EJCHEM.2023.188561.7485

provide effective shielding against the electromagnetic interference (EMI) to minimize the wave transmittance and to improve the reflectance and absorption of the radiation which makes them excellent material in electronic industry [7]. Due to their fascinating characteristics and high potential in critical engineering and biomedical applications, researchers have considered the CPs on both academic and industrial levels. Ighalo and Adeniyi [8] prepared a Polystyrene-based resin from polystyrene waste and mixed it with aluminum particles of 150 μm. Composites with different aluminum weight fraction 0 %, 10 %, 20 %, 30 %, and 40 % were tested to evaluate the electrical properties. The study reported an electrical resistivity of 1.32×107 ohm-cm and 1.38×106 ohm-cm for the 10 wt% aluminum and 40 wt% aluminum, respectively, compared to 1.3×108 ohm-cm for the neat plain polystyrene. The study also pointed that when the weight fraction increases from 0 to 40 wt%, the density of the composite increases from 0.81 g/cm3 to 1.20 g/cm3. Good aluminum dispersion in the polystyrene matrix was also reported in the study. McGhee, et al. [9] conducted an electric characterization for three conductive 3D printing filaments to check the visibility of using them in functional devices. The compositions of the filaments were carbon dispersed polylactic acid, carbon dispersed acrylonitrile butadiene styrene, and graphene dispersed polylactic acid. Extrusion and printing methods were used to prepare the samples, which were reported as piezoresistive. The study concluded that these materials are able to perform as a low cost strain gauge. More recently, Adeniyi, et al. [10] employed the aluminium, iron, and copper waste metallic particulates to develop conductive plastic composites using a polystyrene resin. Electrical conductivity, density, and microstructure of the composites were evaluated. The results revealed that the aluminium-based composite is the most conductive compared to others. Also, the composites' density and conductivity increase with the filler concentration increase. The aluminium-based composite showed the best homogeneity, with excellent dispersion in the matrix compared to other composites. In another study, Lam, et al. [11] developed a conductive, bio-based, flexible film by combining silver nanowires with polyethylene terephthalate (PET). PET is known by its interesting renewable biomass features, and high transparency (90% in the visible wavelength). The study evaluated the visibility of using the developed conductive film in fabricating organic photovoltaic and organic thin-film flexible transistor. The implementation of the developed film in a photovoltaic device demonstrated a 6.7% conversion efficiency which higher than the indium tin oxide based device.

More importantly, the development in the plastics' electrical conductivity is sometimes associated with a development in the thermal conductivity, which is a preferable feature in some electronic and biomedical applications. In this context, Guo, et al. [12] adopted the filler dispersion technique to design a nanocomposites with outstanding electrical and thermal conductivity. For this objective, the graphene was dispersed in biodegradable polymer. The study reported a high thermal conductivity of 3.15 W/m.K and electrical conductivity of 338 S/m for the developed nanoparticle composite of 40 wt% graphene powder loading. The study also reported high mechanical properties for the developed composite even with such high filler loading, which is attributed to the robust interaction between the graphene powder and the employed biodegradable polymer. Another study by Li, et al. [13] provided a fabrication process for a high-density polyethylene/carbon nanotubes porous scaffolds. The results showed that the carbon nanotubes improved the electrical conductivity 2.94 times and 13 orders of magnitude, and increased the phase change enthalpy. The study concluded that the polyethylene/carbon nanotubes composite is a promising material in electro-to-thermal conversion, thermal energy storage, and light-to-thermal conversion applications.

In this study, metal filler materials and short copper wires were added to an epoxy resin to create particulate composites with a developed electrical conductivity. The added filler materials are copper (Cu), zink (Zn), tin (Sn) powders, and copper short wires (CSW). Samples with different filler weight fraction and different filler combinations are prepared and investigated to evaluate their mechanical properties, electrical conductivity, and density.

2. Materials and methods

2.1. Materials

A Nitofill EPLV is the trade name of an epoxy resin supplied by Fosroc / Jordan, was used as a composite matrix in developing the composites. It is a low viscosity epoxy resin system with low creep characteristic and range of chemical resistance. The physical properties of the epoxy resin are provided in

Table 1. Table. 1 The physical properties of the Nitofill EPLV epoxy resin

Physical property	Value
Tensile strength (N/mm2)	26
Youngs modulus in compression (GPa)	16
Specific gravity	1.04
Viscosity	1.0 poise @ 35°C
Density (g/cm3)	1.2
Electrical conductivity	10E-9 (ohm.m)-1

Different conductive metal filling materials were used to improve the electrical conductivity of the developed composites. These filling materials were divided into two groups; the first group includes Tin (Sn) and Zinc (Zn) powders, while the second group comprises a hybrid mixture of copper powder (CP) and copper short wires (CSW). The physical properties of the filler materials are given in Table 2.

Table. 2 Properties of the added metallic powder fillers

Property	Sn	Zn	Cu	CSW
Modulus of elasticity (MPa)	41.6	96.5	210	210
Tensile strength ultimate (MPa)	220	37	110	110
Density (gm/cm^3)	5.76	7.1	7.76	7.76
Thermal conductivity	63.2	112.2	385	385
Particle size (µm)	<5	<5	12	12
Wire diameter / length (mm)				1×2

2.2. Preparation of the composite samples

Two hybrid filler mixtures were prepared using the tin, zinc, copper powder, and copper short wires. First mixture comprises 50 wt% Sn powder and 50 wt% Zn powder whereas the second mixture contains the CP and the CSW at the same weigh fractions. Two sets of samples were prepared using the two filler mixtures, samples prepared using the first mixture where coded as (A), while samples prepared using the second mixture were coded as (B). Each set was cast with different filler contents (15, 25, 35, and 45%), Table 3 demonstrates the design of the samples. The Casting was done by mixing the resin with the filler using an electric mixer to achieve uniform distribution of the filler materials within the resin. The mixing process was done for 20 minutes before the mixture was put in an ultrasonic device for half an hour to remove the air bubbles that have been trapped inside the mixture during the mixing process. Then, the hardener was added to the mixture at a ratio of 1:2, and thoroughly mixed by hand. Finally, two types of samples were cast by purring the mixture into an aluminum molds. The first type has a cylindrical configuration with a 10 mm diameter and 20 mm height, and it has been used for the electrical conductivity test, SEM investigation, and the density measurement.

The second type has a dog bone configuration, according to EN ISO 527-2 standard, for the tensile test, as shown in Fig. 1.

Fig. 1 The configuration of the prepared composite samples

2.3. Experimental testing

Prepared specimens were evaluated to characterize their physical properties development due to the addition of the conductive metal fillers. This was done using a universal tensile machine, to evaluate the mechanical properties. The electrical conductivity measuring apparatus was used to evaluate the electrical conductivity, whereas a sensitive electronic balance was used to calculate the density. A scanning electron microscopy (SEM) was used to assess the dispersion of the fillers inside the matrix, the composite morphology, and the development of the conductive network inside the matrix.

2.3.1. Tensile test

The tensile test was done at the materials characterization laboratory of the University of Technology / Baghdad. The test was performed using Larry Universal Tensile Testing Machine with maximum capacity of 50 KN shown in Fig. 2. The test was done according to the EN ISO 527-2 testing standard at 25°C room temperature, with a tensile machine head speed of 10mm\min.

Table. 3 The codding and composition description of the prepared composite samples

Group A			Group B		
Filler (50 wt% Sn + 50% Zn)			Filler (50 wt% CP + 50% CSW)		
Sample	Epoxy resin (%)	Filler (%)	Sample	Epoxy resin (%)	Filler (%)
A1	85	15	B1	85	15
A2	75	25	B2	75	25
A3	65	35	B3	65	35
A4	55	45	B4	55	45

Fig. 2 Universal tensile machine used in tensile test

2.3.2. Electrical conductivity

Materials' electrical conductivity relies on the existence of free ions or electrons. In insulating materials, such as polymers, these ions and electrons are restricted due to the presence of strong bonding between atoms. This develops a large energy gap inside the material which results in static electrical conductivity. Polarization occurs in the insulator when it is placed between two conductive surfaces. The ability of a material to polarize and store electric charge is measured by relative permittivity or dielectric constant (εr) which, in turn, depends on the dielectric loss factor (tanδ). The characterization of the electrical conductivity was done using LCR Meter, LCR-8105G - GW Instek 100kH, 1F, 5MHz shown in Fig. 3.

Fig. 3 LCR Meter

2.3.3. The SEM test

The SEM characterization was done using VEGA-II Scanning Electron Microscopes available at the Materials Engineering Department / University of Technology.

2.3.4. The density determination

The cylindrical shaped samples having a diameter and height of 20mm and 50 mm, respectively, were used to determine the composite's density. A sensitive electronic scale was used to weight the samples, and then the density was calculated by divided the sample's weight by its volume.

3. Results and discussions

3.1. Mechanical properties

Fig. 4 shows the load-extension curves of the composite samples 4A and 4B. These two particular samples were selected because they have the highest filler fraction. The results revealed significant difference between the two samples' behavior. The samples that belongs to group A shows approximately 45% higher ultimate tensile load compared to the corresponding sample of group B. On the other hand, the 4B sample demonstrates 32% higher failure extension relative to 4A sample. This indicates that the filler of group A (50 wt% Sn + 50% Zn) surpasses the filler of group B (50 wt% CP + 50% CSW) in terms of enhancing the load carrying capacity. However, this enhancement is accompanied with a reduction in the extensionality.

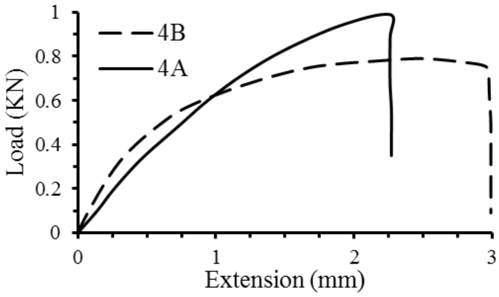

Fig. 4 The load–extension relation of the samples (4A) and (4B)

Fig. 5 demonstrates the effect of the filler weight fraction on the ultimate tensile strength (UTS) of the two groups of samples. The results show insignificant effect of the filler weight fraction on groups A samples' UTS. The percentage of change in UTS for samples A1, A2, A3, and A4 is about 15%, 11%, 7%, and 7%, respectively, compared to neat epoxy. On the other hand, the filler effect on samples in group B is much significant. The percentage of development in the UTS for samples B1, B2, compared to neat epoxy, is 61%, 57%, respectively. However, samples B3 and B4 demonstrated reduction in UTS by 7% and 1, respectively. Samples in group B have a higher UTS value than group A at a lower filler fraction, and lower UTS value than at a higher filler fraction. For group B, changing the filler percentage from 15% to 25% did not show important change in UTS. Though, at higher percentages, from 25 to 35%, a 70% reduction in UTS is recognized. At percentages higher than 34%, the samples in group B start demonstrate lower UTS than neat epoxy. These observations specify that the higher percentage of filler in group B has a negative effect on the mechanical properties which is not the case for group A. This could be due to the presence of the copper short fiber which provides discontinuous reinforcement. Another reason could be due to the weak interaction bonding between the copper and the epoxy resin.

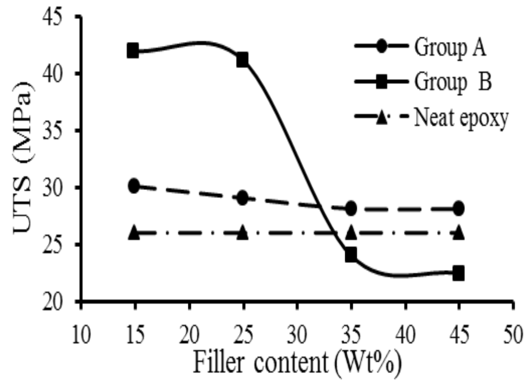

Fig. 5 the effect of the filler content on the ultimate tensile strength

3.2. Electrical conductivity

The conductivity test results of both sample groups are demonstrated in Fig. 6 and Fig. 7 below. The test measures a complex impedance *Z(f)* which depends on frequency (f), and represented as: $Z(f) = R(f) + jX(f)$. It is a sum of the real resistive term, *R(f)*, and of the complex capacitive term, *X(f)*, which both are frequency dependent. Figure 6 (A) shows the dielectric tangent loss factor (tan δ) of group (A) samples as a function of frequency. The results show a reduction in the tan δ value due to the inclusion of filler material, the reduction percentage is a filler fraction dependent. The reason why tan δ had this behavior is due to the principle of the classical physics, the electrical materials face a reduction in this value when the frequency increases because an external electrical filed that generated in the matrix. Figure 6(B) illustrates the AC conductivity of group (A) samples as a function of frequency. The results show improvement in conductivity due to the inclusion of the conductive filler. Also, the results show development in conductivity with the increase in the frequency, particularly in frequency range between 0 and 1 MHz.

Fig. 7 (A) shows the dielectric tangent loss factor (tan δ) of group (B) samples as a function of frequency. The results show a reduction in the tan δ due to the inclusion of filler material, the reduction percentage is a filler fraction dependent. Fig. 7 (B) illustrates the AC conductivity of group (B) samples, an improvement in conductivity is observed due to the inclusion of the conductive filler. Also, the results show development in conductivity with the increase in the frequency, particularly in frequency range between 0 and 0.5 MHz. The results in Fig. 6 and Fig. 7 revealed a higher development in group (B) conductivity compared to group (A). This might be due to the existence of the CSW in group (B), which contributes significantly to improve the conductivity by building active microstructure network.

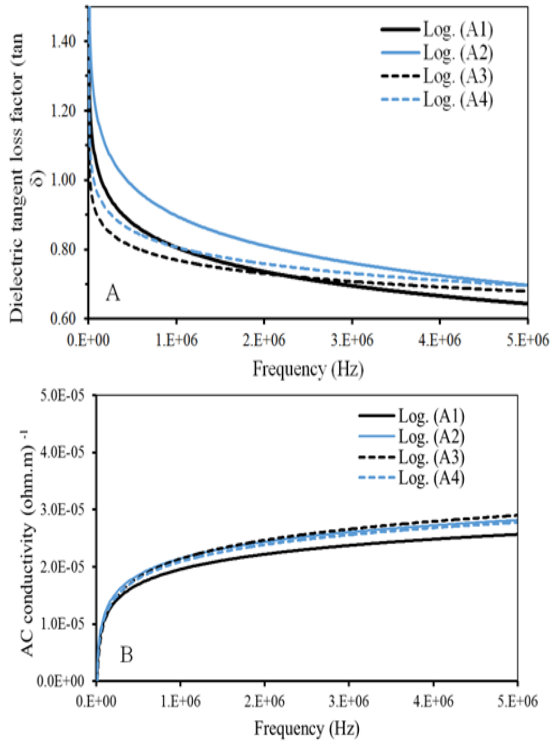

Fig. 6 The dielectric tangent loss factor (tan δ), and (B) the AC conductivity of group (A) samples as a function of frequency.

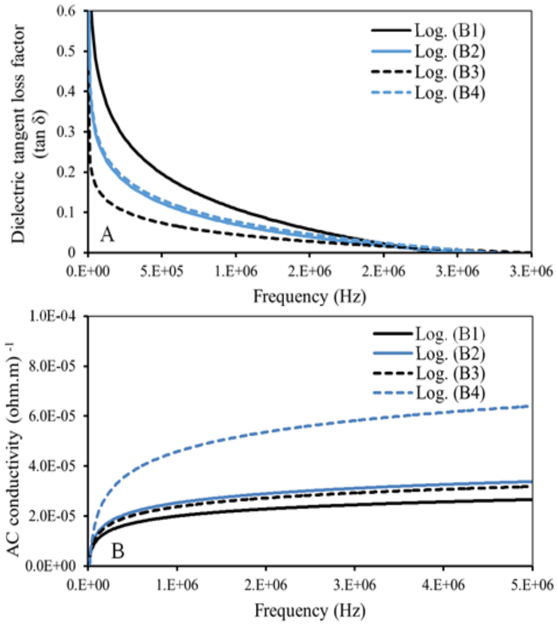

Fig. 7 (B) the Dielectric tangent loss factor (tan δ), and (B) the AC conductivity of group (B) samples as a function of frequency.

3.3. Material Density

Fig. 8 shows the density variation with the filler content for both composite. The results show that the density trend, for both composites, is directly proportional to the filler content. Also, the density of group B is 7% lower than group A.

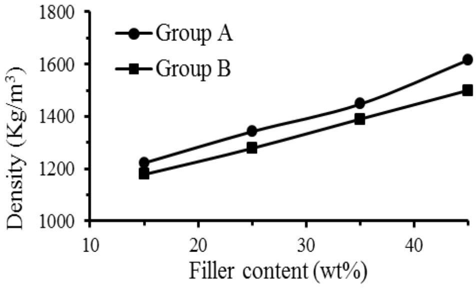

Fig. 8 Epoxy / meal powder composites' density variation with filler fraction

3.4. Microstructure investigation

Fig. 9 and Fig. 10 depicts the microstructure morphology of the 45% filler fraction composite of groups A and B, respectively. The bright parts with luster represent the filler, while the matt brown color refers to the polymer matrix. The SEM images if Fig. 9 demonstrates some of these bright spots which specify a sort of non-uniform distribution for the filler inside the matrix.

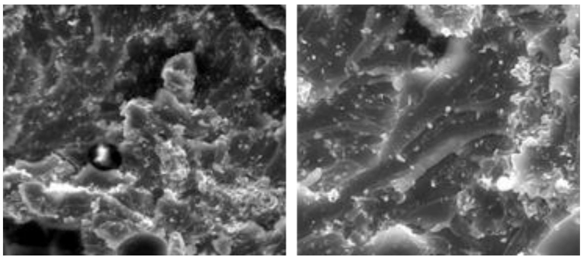

Fig. 9 SEM images of group (A) with filler content 45%

Fig. 10 shows the short Cu wires with metals powder and their spatial arrangement in the epoxy matrix. The light with luster phase represents the metals fillers phase. The images confirm that a composite with high filler fraction of 45% can be produced. Despite this has been proven to improve the composite electrical conductivity, the non-homogenous distribution of the short wires could lead to lower interaction between the matrix and metals phase. Which consequently results is poor mechanical properties and high brittleness in some spots than others.

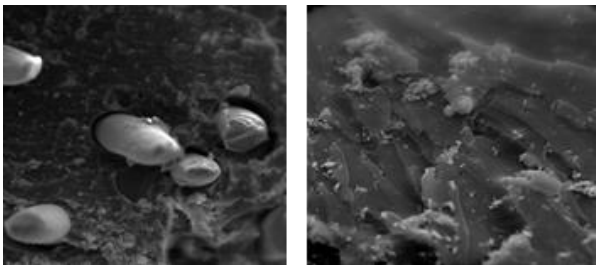

Fig. 10 SEM images of group (B) with filler content 45%

4. Conclusions

Metallic particles polymer composites have been proven to show significant electrical conductivity enhancement the feature that makes them attractive in a variety of electronic, telecommunication, and industrial technologies. Many polymers with diverse metallic additives materials have been proposed to improve the polymers' electrical conductivity. Factors like the filler volume fraction, particle size and shape, and the arrangement of the particles inside the matrix have been found to be of significant effect on the resulting composites. Different metallic particle fillers and short wires were proposed in this study as an attempt to improve the electrical conductivity of an epoxy resin matrix. The used filler includes copper (Cu), zink (Zn), tin (Sn) particles, as well as copper short wires (CSW). Different weight fraction and different combinations of the filler materials were used to prepare the composite samples. Then, electrical conductivity, mechanical properties, and density of the samples were evaluated. The results showed a positive effect of the filer weight fraction on the conductivity and adverse effect on the UTS. The CSW composites demonstrated almost double electrical conductivity compared to particulate composites. Up to 15% and 57% development in the UTS was achieved in the particulate and the CSW composites, respectively, compared to neat epoxy. However, at a higher weight fraction (33%), an important reduction in the UTS is recognized. The microstructure investigation revealed some inhomogeneous distribution of the CSW in the matrix at the higher filler fraction, which could be the reason behind the achieved reduction in the UTS.

5. Conflict of interest

The authors have no conflicts of interest to declare. All co-authors have seen and agree with the contents of the manuscript and there is no financial interest to report. We also certify that the submission is original work and is not considered for publication elsewhere.

6. References

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