CHARACTERIZATION OF UNTREATED AND TREATED RECYCLED COPPER POWDER FILLED EPOXY/POLY (METHYL METHACRYLATE) COMPOSITES

by

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LIST OF ABBREVIATIONS

CPC	Conducting Polymer Composites
EMI	Electromagnet Interference
ESD	Electrostatic Discharge
LC	Liquid Crystalline
PTFE	Polytetrafluoroethlyene
ASTM	American Society for Testing and Materials
PEEK	Polyethereetherketone
IC	Infinite Conductive Cluster
PVC	Polyvinyl Chloride
ER	Epoxy Resin
LLDPE	Linear Low Density Polyethylene
LDPE	Low Density Polyethylene
HDPE	High Density Polyethylene
SEM	Scanning Electron Microscope
CTE	Coefficient of Thermal Expansion
MWS	Maxwell-Wagner-Sillars

LIST OF SYMBOLS

ϕ	Filler content
vol%	volume percentage
ρ	Density (g/cm^3)
ρ	Resistivity (Ωcm)
T_g	Glass transition temperature
F	Fahrenheit
μm	micrometer
rpm	ram per minute
MPa	Mega Pascal
nm	nanometer
mm	milimeter
ppm	part per million
Fe	Ferum
Cu	Copper
Zn	Zinc
SiC	Silicon carbide
Al_2O_3	Aluminium trioxide
σp	Conductivity
ϕc	Critical value
phr	per hundred resin
V_f	Filler volume fraction
W_f	Weight of filler
ρ_f	Density of filler
W_m	Weight of matrix

ρ_m	Density of matrix
A	Area
R	Resistance
h	thickness
σ_f	Stress in outer fibers at midpoint (MPa)
E_f	Flexural modulus of elasticity, (MPa)
P	Load at a given point on the load deflection curve, (N)
L	Support span, (mm)
b	Width of test beam, (mm)
d	Depth of tested beam, (mm)
m	The gradient of the initial straight-line portion of the load deflection curve, (N/mm)

CHAPTER 1

INTRODUCTION

1.1 Background

Polymer blends have long commercial history in rubber, coatings and adhesives industries applications. Polymer blends have gained significant commercial growth in the two last decades outpacing the growth rate of existing polymer by at least 2-5% (Utracki, 2002). Approximately 10% of thermoplastics and 75% of elastomers are processed as blends and 3% of thermoset was manufactured (4 million tonnes) worldwide and 120,000 tonnes of resins are used in adhesive application (Gardziella & Pilato, 1999). Initially polymer blends were used to manufacture materials with improved toughness and processability, such as heat distortion temperature, stress-cracking resistance, better adhesion, electroplating and fire resistance. The most command blends are the rubber-modified polystyrenes (Young & Lovell, 1991).

There are some reasons that contributed to the continued commercial interest in the polymer blends. First, the effective methods of developing a new material that appropriate the market requirement and customer desire as conflicting to develop totally new polymer blends which involved awfully high research, development and resources cost. Second, the highly cost of engineering polymer can be reduced by polymer blends. Numerous of properties can be united in a blend that a single polymer cannot present. Lastly, polymer blends offer economic and useful means advance recycled off specification polymers (Al-Salem et al., 2009).

Polymer blends contribute an economic incentive from synthesizing new materials. The outstanding comprehensive performance from polymer blend contributed to the excellent properties of each component involved (Huang et al., 2014). Phase behaviour is the main characteristic of polymer blends of two or more copolymer. Polymer blends can exhibit miscibility or phase separation at various levels of mixing in between partial miscibility (Robeson, 2007). The major factors that lead to miscibility in low molecular weight materials is the combinatorial entropy contribution which is very large compared to high molecular weight polymers (Utracki, 2002). Generally, polymer blends contain homogenous or heterogenous mixture of structurally different homopolymer or copolymer to obtain fiber for specific uses by tailoring one or more properties with minimum sacrifice of other properties (Ryan & Anthony, 2002).

Blends develop many of their beneficial properties from the interactions between the phases. Improved properties can be conveyed to certain polymers by blending the polymers with immiscible polymers in the right proportion with the purpose of producing a blend with much desirable stability of physical and mechanical properties (Scheirs, 2000). A beneficial blend has the characteristics of a uniform dispersion with fine distinct particles of one component being homogenously dispersed through the matrix of the other component. The polymer blend would be valuable when the size and size distribution of the dispersed phase remain unchanged from the condition of blending to under which the blend is required to perform (Ghosh, 2001).

Conductive polymer have received considerable interest as a solder replacement in flip chip packaging because there is a significant reduction in pitch, weight and volume and increased environmental compatibility (Sun, 2001). Conductive polymer materials, which have both strong conductivity and the properties of polymers, are widely used in electronics and biosensors (Glouannec et al., 2008). Polymer materials are often used as insulators because of their low thermal and electrical conductivity. This has led to limitations of the use of polymer in electrical and electronic applications (Boudenne et al., 2005).

However, the introduction of Conducting Polymer Composites (CPCs) has initiated the application of polymers in many fields of engineering especially in the electrical and electronic applications. Indeed, conducting polymer composites have shown its crucial importance in many useful and high end applications since few decades ago, and it continues to become choice of selection in various industries especially in electrical and electronic applications (Ramasubramaniam et al., 2003). Conducting polymer composites involves incorporating conductive filler into the polymer matrix. These composites are produced from the blending of an insulating polymer matrix with electrical conductive fillers (carbon black, carbon fibre, metal particles). They show many interesting features due to their electrical resistivity variation with thermal solicitations (Li et al., 2011).

A conductive polymer composite can be produced by loading an insulating polymer matrix with a sufficient volume of electrically conductive filler, so that interconnectivity of conductive pathways exists throughout the bulk material (Feller & Grohens, 2004). Factors such as the size, shape, chemistry and aggregation behaviour of filler particles must be considered in conjunction with the thermodynamic and rheological properties of the polymer matrix and the processing conditions employed (Burden et al., 1998). Polymer composites filled with metal are of interest for used, one main parameter determining CPC properties is the conductive pathways structure, depending on many parameters such as filler content (φ), surface free energy of the filler and the matrix, crystallinity, reticulation and exclusion volume, i.e. zones where carbon black is concentrated and filler distribution within the matrix (Gazotti et al., 1999 & Feller & Grohens, 2004).

Polymer-based electrically conducting composites have several advantages over their pure metal counterparts including lower cost, ease of manufacture, high flexibility, reduced weight, mechanical shock absorption ability, corrosion resistance and conductivity control of many fields of engineering, such as for electromagnet interference (EMI) shielding, safe packaging, corrosion protection, electrostatic discharge (ESD) control, conductive adhesive and etc. (Teh et al., 2011, Rupprecht, 1999). This interest arises from the fact that the electrical characteristics of polymer composites are closed to properties of metals, whereas the mechanical properties and processing methods are typical for plastics (Mamunya et al., 2002). In addition, since conducting polymer composites have the advantages of being less costly and lighter weight compared to metals, so they are positioned to play an increasingly important role in affairs of mankind, specifically in the area of electronic and electrical conductivity (Tavman, 1997).

Metal filled polymer composites are getting acceptance for the past few years, mainly due to concerns about the environment (Lira & Co'rdoba, 2005). The most general approach to describe the charge transport in conducting polymeric composites in relation to the content of conducting particles is provided by the percolation theory (Battisti et al., 2010). When a polymer matrix is filled with dispersed conductive filler, the composite prepared gains a conductivity value. When the filler volume fraction reaches a critical value, so-called percolation threshold, an infinite conductive cluster is formed and the composite shows a drastic increase in the conductivity value (Stauffer & Aharony, 1985). In such networks there is either direct contact between adjacent particles, or sufficiently small gaps between them, to enable a mechanism of quantum mechanical tunneling conductivity.

The percolation threshold is strongly influenced by the geometrical characteristics of the conductive filler, such as aspect ratio and particle size distribution, so that an increase in their value may dramatically drop the filler concentration required to achieve conduction in a given polymeric matrix (Rupprecht, 1999). The transfer conditions of the electric charge and heat flow determine the electrical and thermal conductivity level in the heterogeneous polymer-filler system, in which the conductive phase is formed by dispersed metallic or carbon filler (Jaafar, 2008).

An important feature of metal-filled polymeric materials is a transition from insulating to conducting behaviour over a narrow range of the volume fraction of conducting filler. The critical volume fraction of filler associated with the transition has been variously reported to range from about 5 to 40 vol% metal filler. The value of the critical concentration depends on the shape, size, and orientation of the filler and on the method of fabrication of the composite material (Micheal et al., 1985). Since metals are the quintessential conductors of electricity, it is not surprising that they have been used as fillers to create conductive plastic composites (Luyt et al., 2006). In comparison to conductive carbon, the resistivity of metals is much lower, while their densities are higher (Bhattacharya, 1986). However, density advantage is insignificant when the electrical conductivity is centered.

Generally, the metal with high electrical conductivity will become the choice of selection in producing conductive composites. Table 1.1 shows the density and electrical resistivity for some common metal fillers which are used to produce conductive composite. Among the frequently used metals, silver is the most conductive with the lowest resistivity value as shown in Table 1.1. Although silver is a better electrical conductor than copper, copper has been preferred owing to its more economical reason compared to costly copper (Bhattacharya, 1986).

Table 1.1: Density and electrical resistivity for some common metal filler (Gazotti et al,1999).

Metal	Density (g/cm³)	Resistivity (Ωcm)
Copper	8.82	1.7×10^{-6}
Nickel	8.90	6.84×10^{-6}
Aluminum	2.70	2.8×10^{-6}
Iron	7.86	10×10^{-6}
Stainless Steel	7.80	74×10^{-6}
Silver	10.50	1.59×10^{-6}

Copper is 100 % recyclable. Virtually all products made from copper can be recycled. Due to high product value and some related environmental issues, copper is recycled where possible. Using recycled copper can save energy as copper extraction is very energy-consuming. Consequently, it can save landfills by reducing the amount of waste copper (Clevend, 2004). Electrical conductivity of recycled copper may differ from the pure one. In fact, there are many sources of recycled copper ranging from copper piping of the air conditioning units, scrap electrical wiring to door and window frames. Besides, many machining operations such as milling, grinding, drilling, and etc. produce waste which can be recycled. In this research, waste copper from milling machine is collected and recycled to produce copper filled epoxy composite.

The epoxy resins have been extensively used in many industrial fields such as adhesives, constructions, coating and insulation materials for electric devices due to their good balance of properties such as excellent moisture, solvent and chemical resistance; low shrinkage after cure; superior electrical and mechanical properties; good adhesion to many substrates (Tao et al., 2007). The main drawback of an epoxy matrix is its inherent brittleness, which makes it notch sensitive and leads to composites with low toughness. Epoxy matrix composites are prone to impact damage which includes failure modes such as transverse cracking, delamination, fibre/matrix debonding and fibre fracture, all limiting their uses for many structural applications (Wong et al., 2010). Consequently, many techniques have been developed to modify the epoxy backbone in an effort to improve the thermal and flame retardancy characteristics of epoxy polymers (Ho et al., 2008). Among these work, introducing silicon and its groups into epoxy was attractive for its significant improvement on the electrical properties of the epoxy resins, thermal stability, and flame retardancy (Wu et al., 2002). An effective approach to enhance thermal properties of epoxy resins is introducing various aromatic ring structures into the skeleton of epoxy or curing agent, such as biphenyl, naphthalene, fluorene, heterocyclic ring, etc. (Dai et al., 2009). One effective method for offsetting these deficiencies of pure epoxy resins is incorporation of reinforcing fillers (Yang et al., 2007).

Poly (methyl methacrylate) (PMMA) is an atactic thermoplastic polymer and it is the most widely used acrylics (Mantia, 2002). PMMA is an important thermoplastic material. Among the ways more widely known in this research orientation and usable at an industrial scale, is the incorporation of inorganic flame retarding particles in the burning of the polymer (A. Laachachi et al., 2004). It is synthetic chemically from its monomer, methyl methacrylate (MMA). PMMA is a transparent material, completely amorphous but has high strength and excellent dimensional stability due to rigid polymer chains (Odian, 2004). PMMA with its intrinsic high mechanical properties, high transparency, UV resistance and long-term stability is a serious candidate for mixing with bio-based thermoplastic to produce a product especially in packaging industry (Cedric et al., 2013). The cost efficiency and property relation of the transparent thermoplastic polymer PMMA make it one of the most frequently employed matrices for the composite materials with wide applications in modern science. PMMA based materials have been utilised in many fields, like bio-medical technologies, implants and also in microelectronics (Himel et al., 2013). It also has high strength and excellent dimensional stability due to rigid polymer chains. It also has a very good weatherability, impact resistance and resistant to many chemicals although attacked by organic solvents (Odian, 2004).

1.2 Problem Statement

Copper is an expensive material and it is known as a ductile metal with excellent electrical conductivity. It is extensively used as an electrical and heat conductor or as a component in an alloy. By using recycled copper as conductive filler, the epoxy composite can gain electrical conductivity value. In addition, the replacement of pure copper with recycled copper can minimize the energy needed for copper extraction. Thus, by using recycled copper in epoxy composite, it can also save energy and cost. The study of different particle size will identify the best result since the different particle size will give different outcome. Epoxy resin offers numerous advantages including lower temperature processing, greater flexibility, creep resistance, energy damping, more flexible and simpler processing. Additionally, lower assembly temperatures negate the need for mold materials that can withstand high temperatures. These advantages bring lower processing costs, allow the use of lower cost components and substrates, and facilitate size reduction in devices. However, epoxy resin does have some limitations and drawbacks. Some reliability issues including limited impact resistance, increased contact resistance upon thermal cycling, and weakened mechanical strength in various climatic environmental conditions, lack of reworkability, conductivity fatigue and limited current carrying capability. Poly (methyl methacrylate) (PMMA) is an atactic thermoplastic polymer and it is the most widely used acrylics. The cost efficiency and property relation of the transparent thermoplastic polymer PMMA make it one of the most frequently employed matrices for the composite materials with wide applications in modern science. The usage of PMMA will produce a threshold percolation effect and reduce the amount of recycled copper used. Treatment of recycled copper is necessary to remove the oxidation and improve the compatibility.

1.3 Objectives of Study

The objectives of this study are:

I. To compare the effect of coarse, fine and mixed particle size of recycled copper on the properties of epoxy composites.

II. To study the effect of PMMA loading on the properties of epoxy composites using mixed particle size recycled copper.

III. To study the effect of surface treatments of copper by using hydrochloric acid and silane on the properties of epoxy/PMMA/recycled copper composites.

1.4 Scope of Work

In this study, recycled copper filled epoxy composites were characterized based on its mechanical, electrical and thermal properties. The effects of different particle sizes of recycled copper were filled with epoxy to investigate the effect of mechanical, electrical and thermal properties. Testing such as morphology, mechanical testing, coefficient of thermal expansion determination, thermogravimetric analysis and electrical conductivity measurement were done to study the properties of the composites. The particle size of recycled copper was determined by using particle size analysis. X-ray diffraction (XRD) analysis was performed in order to analyse the element of the recycled copper. Flexural test was carried out to investigate the flexural properties: flexural strength and flexural modulus of epoxy composites. Besides that, Vickers hardness and density testing were performed to study the physical properties of epoxy composites. Furthermore, coefficient of thermal expansion (CTE) analysis was carried out to investigate the thermal property of epoxy composites. The electrical property was performed in order to measure the electrical conductivity of epoxy composites.

1.5 Organization of the Thesis

Chapter 1 presented the overview of utilization and potential of recycled copper in polymer composites. This chapter also described the problems and several methods to overcome the problems of recycled copper used as reinforced filler in polymer composites. The objectives of this research were discussed in details in this chapter.

Chapter 2 reviewed the literature on the materials, properties and applications of recycled copper as reinforced filler in polymer matrix composites. Several methods enhanced the compatibility of recycled copper reinforced polymer matrix have been discussed in details in this chapter.

Chapter 3 discussed the experimental methods, including the preparation of PMMA/epoxy composites and modification methods apply on recycled copper to improve the compatibility and adhesion among recycled copper and PMMA/epoxy blends.

Chapter 4 presented the results and discussion based on the effect of different recycled copper sizes, addition of PMMA and different modification on recycled copper filled epoxy composites. In this chapter, it contains of five parts, to discuss the effect of coarse particle size of recycled copper followed by the effect of fine particle size of