

**SYNTHESIS, CHARACTERISATION,
THERMAL AND ELECTRICAL BEHAVIOUR OF
COPPER AND
COPPER SULPHIDE-EPOXY NANOCOMPOSITES**

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ELECTRICAL BEHAVIOUR OF COPPER AND COPPER
SULPHIDE-EPOXY NANOCOMPOSITES**

by

NOR HASHILA MOHD HIRMIZI

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LIST OF SYMBOLS

2θ	Bragg angle
V_f^*	Critical volume concentration at the percolation threshold
μ	Dipole moment
Σ	Electrical conductivity
P	Electrical resistivity
T	Exponent determining the increase of the conductivity above V_f^*
T_g	Glass transition temperature
A	Linear coefficient thermal expansion
λ_{\max}	Wavelength at the maximum absorbance

LIST OF ABBREVIATIONS

AAO	Anodized aluminium oxide
AAS	Atomic Absorption Spectroscopy
ACA	Anisotropic conductive adhesive
Ar	Aromatic ring
C11-resorcinarene	C-undecylcalix[4]-resorcinarene
CNT	Carbon nanotube
CTAB	N-cetyl-N,N,N-trimethylammonium bromide
CTE	Coefficient of thermal expansion
DCM	Dichloromethane
DGEBA	Diglycidyl ether of bisphenol A
DSC	Differential Scanning Calorimetry
DTG	Differential Thermogravimetric
ECA	Electrical conductive adhesive
ENR	Epoxidised natural rubber
FTIR	Fourier transform infrared
Hr	Hours
ICA	Isotropic conductive adhesive
IPA	Isopropanol
L	Length
MDA	4,4'-methylenedianiline
Min	Minutes
MWNT	Multi-walled carbon nanotube
N	Refractive index
NR	Natural rubber
P3EBT	Poly(3-(ethyl-4-butanoate)thiophene)
PA	Polyamide
PANI	Polyaniline
PCB	Printed circuit board
PDA	Polydiacetylene
PEG	Poly ethylene glycol
PEO	Polyethylene oxide
PMMA	Poly(methyl-methacrylate)
PP	Polypropylene
PPy	Polypyrrole

PS	Polystyrene
PU	Polyurethane
PVA	Poly(vinyl-alcohol)
PVC	Poly vinyl chloride
PVP	Poly(N-vinylpyrrolidone)
R	Resistance
S	Seconds
SDS	Sodium dodecyl sulphate
SSSC	Solid state solar cell structure
T	Thickness
TAA	Thioacetamide
TEM	Transmission Electron Microscopy
TG	Thermogravimetric
TMA	Thermal Mechanical Analysis
TOAB	Tetra-n-octyl-ammonium bromide
TU	Thiourea
UV	Ultraviolet
UV-vis	Ultraviolet-visible
v/v	Volume to volume ratio
V_f	Volume fraction of the filler
vol. %	Volume percentage
W	Width
XRD	Powder X-Ray Diffraction

SINTESIS, PENCIRIAN, SIFAT TERMAL DAN ELEKTRIK NANOKOMPOSIT EPOKSI KUPRUM DAN KUPRUM SULFIDA

ABSTRAK

Nanozarah kuprum (Cu) dan kuprum sulfida (CuS) disintesis di dalam fasa akueus dan serta-merta dipindahkan ke fasa organik yang mengandungi epoksi melalui kaedah pemindahan fasa. Spektrum penyerapan UV-vis menunjukkan kehadiran Cu dan CuS. Penambahan diglisidil eter bisfenol A (DGEBA) ke dalam organosol masing-masing dan setelah penyingkiran pelarut memberikan nanokomposit Cu- dan CuS-epoksi. Komposit ini dimatangkan menggunakan 4,4'-metilenadianilina (MDA). Bagi Cu-epoksi, kecekapan pemindahan zarah yang tertinggi adalah $\approx 97.2\%$ apabila sampel disediakan menggunakan 5 mL isopropanol (IPA). IPA turut memberi kesan terhadap saiz purata zarah. Pada peratusan epoksi tertinggi, saiz zarah, taburan saiz serta penswabentukan zarah dikurangkan. Tambahan pula, saiz zarah adalah lebih kecil berbanding di dalam hidrosol. Bagi CuS, tempoh pengacauan memberi kesan terhadap bentuk zarah. Purata saiz zarah, taburan saiz dan penyebaran adalah berbeza apabila zarah dipindahkan ke dalam fasa organik dan juga bergantung kepada jenis pelarut organik yang digunakan. Kehadiran epoksi juga meningkatkan penstabilan terhadap zarah dan memberikan kawalan yang lebih baik terhadap saiz zarah. Bagi nanokomposit Cu-epoksi, komposit tersebut mempamerkan kestabilan terma yang lebih rendah berbanding epoksi matang disebabkan oleh kesan pecutan terhadap penguraian komposit oleh pengisi berkonduksi bersaiz nano. Walau bagaimanapun, penambahan pengisi Cu meningkatkan nilai suhu peralihan kaca (T_g) komposit daripada 114.9°C kepada 122.7°C , kesan daripada penurunan isipadu bebas dan pergerakan rantai polimer. Tambahan pula, ia juga menurunkan nilai pemalar pengembangan terma (CTE). Sebaliknya, bagi CuS-epoksi, dapat dilihat bahawa tahap proses pematangan diganggu oleh penambahan zarah CuS. Penambahan pengisi CuS merendahkan nilai T_g dan CTE tetapi mengekalkan kestabilan terma nanokomposit CuS-epoksi. Hal ini dikaitkan dengan saling tindak yang mungkin wujud diantara zarah CuS dan epoksida. Penambahan kedua-dua pengisi kedalam epoksi meningkatkan nilai kekonduksian elektrik bagi masing-masing komposit. Dengan pecahan isipadu bagi pengisi $< 10 \text{ vol.}\%$, nilai kekonduksian adalah dalam julat $10^{-2} \text{ S cm}^{-1}$, komposit yang diperolehi dalam kajian ini dikategorikan sebagai jenis pelekat konduktif anisotropi (ACA).

SYNTHESIS, CHARACTERISATION, THERMAL AND ELECTRICAL BEHAVIOUR OF COPPER AND COPPER SULPHIDE-EPOXY NANOCOMPOSITES

ABSTRACT

Copper (Cu) and copper sulphide (CuS) nanoparticles were synthesised in an aqueous phase and subsequently transferred into the organic phase containing epoxy *via* phase transfer technique. The UV-vis absorption spectra confirmed the existence of Cu and CuS. Incorporation of diglycidyl ether of bisphenol A (DGEBA) into the respective organosols and upon solvent removal afforded Cu- and CuS-epoxy nanocomposites. These composites were cured using 4,4'-methylenedianiline (MDA). In the case of Cu-epoxy, the highest particle transfer efficiency was at $\approx 97.2\%$ when the samples were prepared with 5 mL isopropanol (IPA). IPA also exerts influence on the average particle size. At higher percentage of epoxy, the particle sizes, size distributions as well as the particle self assembly were decreased. Moreover, the size of the particles was smaller as compared to in the hydrosol. For CuS, period of stirring affects the shape of CuS particles. The average particle size, size distribution and dispersion vary upon particle transfer into the organic phase as well as dependent on the types of organic solvent used. The presence of epoxy also enhanced the CuS particle stabilisation and exerts better particle size control. For the Cu-epoxy nanocomposites, the composites exhibit lower thermal stability as compared to cured epoxy due to accelerating effect on decomposition of the composites by the nano-sized conducting filler. However, addition of Cu filler increased the glass transition temperature (T_g) values of the composites from 114.9°C to 122.7°C as the result of decrement in free volume and the polymer chains mobility. Furthermore, it also decreased the coefficient of thermal expansion (CTE) values. On the contrary, for the CuS-epoxy, it is observed that the extent of curing has been disrupted by the addition of CuS particles. Addition of CuS filler decreased the T_g and CTE values but maintained the thermal stability of CuS-epoxy nanocomposites. This is attributed to the probable interactions between CuS particles and the epoxides. Addition of both fillers into epoxy increased the electrical conductivity of the respective composites. With the volume fraction of the fillers $< 10 \text{ vol.}\%$, the electrical conductivity values were within the range of $10^{-2} \text{ S cm}^{-1}$, the composites obtained in this work were categorised as the anisotropic conductive adhesive (ACA)-type.

CHAPTER 1

INTRODUCTION

1.1 Background and Issues

Epoxy resin is one of the most used polymers in industries. It provides a good balance between mechanical and thermal properties as well as exhibiting good chemical resistance. Epoxy is extensively applied in electronic packaging. One of the many applications of epoxy in electronic packaging is as conductive adhesives where metal fillers were incorporated into the epoxy. However, these were limited to certain metals viz. silver (Ag), gold (Au), nickel (Ni), aluminium (Al) and copper (Cu). Cu has high conductivity comparable to Ag but rather much cheaper. The Cu particles are prone to oxidation and coalescence. This can be overcome *via* incorporation of nanoparticles into polymer matrix.

In previous reported studies on the electrical properties of inorganic-polymer composites, several issues were raised which includes the dispersion, size and shape of fillers in the polymer matrix and filler-matrix interactions. Highly dispersed nano-sized metal fillers within a polymer matrix often afford better physical and chemical properties of metal-polymer nanocomposites. However, highly dispersed particles within a polymer matrix were seldom realised *via* conventional methods. One of the solutions to enhance the dispersing of fillers within a polymer is through colloidal formations.

Aqueous colloids or hydrosols are easily prepared. However, a majority of known polymers are insoluble in aqueous phase but are soluble in organic solvents. Thus by employing aqueous to organic phase transfer technique, metal-polymer matrix can be prepared in the form of organosols. The respective organosols afforded nanocomposites upon drying. The above technique was deemed suitable for application in electronic

packaging as the synthesised particles are often in certain uniform morphology, shape as well as in nano-size regime that disperses readily within the polymer matrix.

Beside metals particles, particles of metal oxides and chalcogenides may also be incorporated into the polymer matrix *via* the phase transfer technique. Thus apart from Cu-epoxy, others such as copper sulphide, CuS-epoxy can be prepared by employing similar technique. In the case of the latter, there is a possibility of chemical interactions occurring between the filler moieties with the polymer. This is expected to change the properties of the resultant composite and may further improve the conduction of the composite. Therefore, the thermal and electrical behaviours can be tailored to the desired applications. To date, there are barely any reports on the synthesis of Cu and CuS particles dispersed in epoxy matrix using phase transfer technique.

1.2 Aims

The aims of this work are to synthesise Cu and CuS nanoparticles in colloidal forms in the presence of various amount of epoxy *via* the phase transfer technique and the products obtained are cured, characterised and evaluated in term of their thermal and electrical characteristics.

1.3 Research Objectives

The objectives of the thesis are:

- (a) To synthesise and characterise the Cu and CuS nanoparticles with reasonable particle size and size distribution and those are dispersed in organic media containing epoxy using the phase transfer technique.

- (b) To study the effects of various parameters such as solvents and stabilisers on the particle size, size distribution and morphology of the synthesised Cu and CuS nanoparticles.
- (c) To study the extent of curing process of Cu- and CuS-epoxy nanocomposites.
- (d) To evaluate the thermal and electrical behaviours of Cu- and CuS-epoxy nanocomposites.

CHAPTER 2

LITERATURE REVIEW

2.1 Nanocomposites

Nanocomposite is defined as a material processed from a combination of two or more separate phases with at least one dimension of the phases is in nano-size regime (below than 100 nm) (Kumar et al., 2009). By combination of these “host” and “guest” phases, a superior performance leading to attractive physical properties of the nanocomposite can be achieved and thus widened its potential applications (Mallick et al., 2006). Nanocomposite is an alternative to the conventional composites. Unlike the conventional composites (macrocomposites), nanocomposites offer tremendous improvements in properties as a result of nano-metric dimensions. Each of the respective composites consists of three components, namely the reinforcement (filler), bulk (matrix) and interfacial region. These are described below. A comparative summary of the properties and morphology between the conventional composites and nanocomposites is shown in Figure 2.1 (Vaia & Wagner, 2004).

2.1.1 Fillers

Generally, fillers are often of various types of inorganic materials which include metals (Bozanic et al., 2010; Bai et al., 2007; Zhou, 2011), metal oxides (Liufu et al., 2005; Guo et al., 2007), carbon materials (Martin et al., 2004; Zhang et al., 2009) and ceramics (Teh et al., 2007; Lim et al., 2010; Uygun et al., 2009). The morphology of these fillers can be varied to manipulate the outcome properties of the resultant composites. These include size (Wu et al., 2007), shape (Burda et al., 2005), volume fraction (Bao & Tjong, 2008) and dispersion of fillers (Chen et al., 2007a). For example,

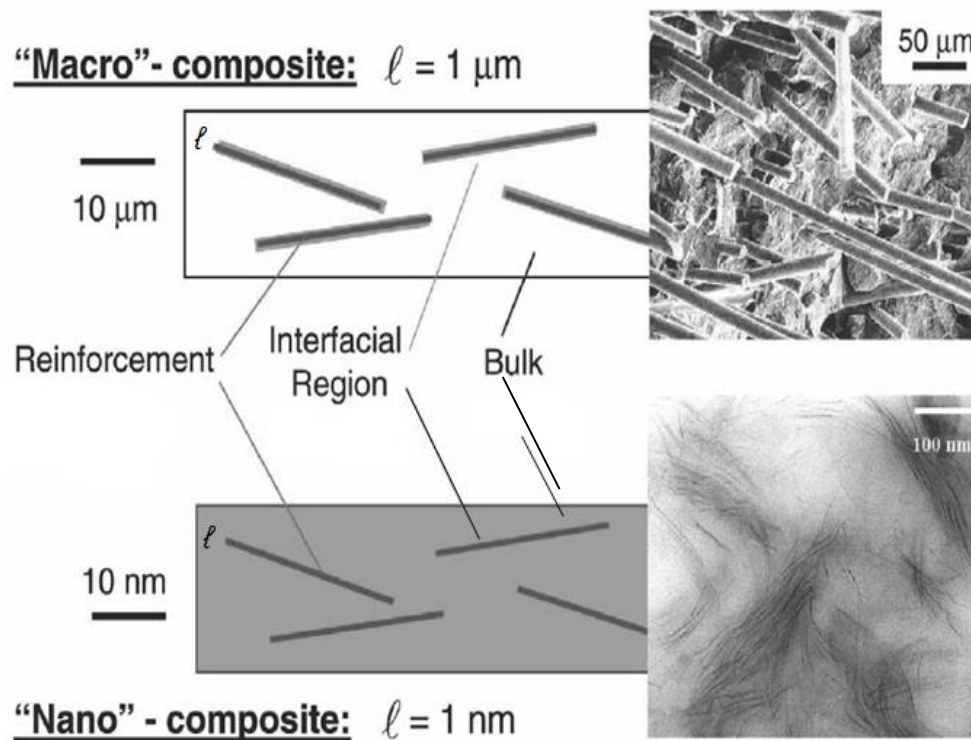


Figure 2.1: The comparative properties and morphology of macro-composites and nano-composites (Vaia & Wagner, 2004).

it was found that the geometry of alumina particles exert an effect towards the dispersion of the particle in epoxy that consequently affects the mechanical properties of the resultant composite (Lim et al., 2010). The shape of the fillers could be spheres, tubes, sheets, flakes, disks and ribbons. One of the ways to vary the morphology of the fillers is *via* the preparation protocols. There are numerous preparative routes that have been reported in the literature and could be divided into two approaches, which are “top-down” and “bottom-up” (Kumar et al., 2009). A “top-down” approach is basically the breaking down of bulk materials into smaller units. The “bottom-up” approach involves the self-assembly of basic units into larger configurations. The most common method for the former approach is milling (Ohara et al., 2010) while the latter is chemical synthesis (Le

et al., 2010). The “top-down” approach is able to produce nanoparticles in a large scale but it is very difficult to fully control the distribution of particle size (Le et al., 2010). On the other hand, “bottom-up” approach offers better ability in controlling the desired particle size and uniformity (Le et al., 2010). Thus, this latter approach has been widely used in the preparation of nanoparticles *albeit* in small scale.

2.1.2 Matrix

The matrix is the major component in the composite. Thus it categorises the types of composite. These are the metal-, ceramic- and polymer-based composites (Callister, 2003). For metal-based composites, Al (pure or alloyed) is the most frequent metal that has been used as the matrix. It has been widely applied in aerospace and automotive parts due to its notable mechanical properties such as improved strength, stiffness and wear resistance (Canakci, 2011). From the literature, various types of fillers have been incorporated into this type of matrix to tailor its properties to meet specific conditions. These includes silicon carbide (SiC) (Kurt et al., 2011), alumina (Al_2O_3) (Ahamed & Senthilkumar, 2010) and boron carbide (B_4C) (Canakci, 2011).

For the ceramic-based composites, there are various types of ceramics used as the matrix, such as silica (SiO_2) (Chen et al., 2011), SiC (Cocera et al., 2011), alumina (Bocanegra-Bernal et al., 2010) and titanium diboride (TiB_2) (Cheloui et al., 2011). The fillers that have been incorporated in this type of composites include zirconia (Bocanegra-Bernal et al., 2010), graphite (Colorado et al., 2011) and carbon nanotubes (CNTs) (Chen et al., 2011; Bocanegra-Bernal et al., 2010; Ahmad et al., 2010). Tremendous effort has been done to improve the properties of these ceramic-based composites for used in a wide range of applications such as medical, aerospace, structural and automobile industries.

Polymer-based composite is the most common type of composites. It has been used in flame retardant, electrical/electronic, cosmetics and anti-bacterial devices. The polymers as matrix in the composite can be divided into synthetic and natural polymers. Examples of synthetic polymer are polystyrene (PS) (Pang et al., 2011), epoxy resins (Zhang & Jiang, 2011), poly(methyl-methacrylate) (PMMA) (Logakis et al., 2011), poly(vinyl-alcohol) (PVA) (Bernabo et al., 2009), polyamide (PA) (Liu et al., 2011), polypropylene (PP) (Wang et al., 2011c) and polyurethane (PU) (Putson et al., 2011). Examples of natural polymers also include natural rubber (Wang et al., 2011b), starch (Pushpadass et al., 2010), cellulose (Vilela et al., 2010) and chitosan (Wang et al., 2010a). The type of polymer used often depends on the desired properties of the outcome composites and these are dictated by the intended applications.

2.1.3 Interfacial region

The interfacial region is defined as the area of “communication” between the matrix and filler (Vaia & Wagner, 2004). The relative volume fraction of interfacial region to volume of filler for conventional composites is smaller due to lower surface area of the filler. However, for the nanocomposites, the relative volume fraction of interfacial region to volume of filler is larger due to higher surface area of the filler and increment of the density of particles. The “communication” between the matrix and filler may range from weak interactions (van der Waals interaction) to chemical interactions where a large interface region allows for better contact between matrix and filler. Thus, this region is the core of the performance of the resultant composite.

2.1.4 Polymer-based nanocomposites

Table 2.1 lists some of the recently reported polymer-based nanocomposites and their properties and applications. From the Table, it can be seen that the polymer-based nanocomposites cover various types of polymers and fillers. Consequently, they exhibit various properties and have been applied in various applications.

The attempt to achieve nanoparticles filled polymer-based composites can be divided into four categories (Mallick et al., 2006) which are; i) *in-situ* preparation of the nanoparticles in the polymer where the reduction of metal salts were done in the polymer matrix, ii) polymerising the matrix around the nanoparticles, iii) mixing the pre-formed nanoparticles and pre-synthesised polymer, and iv) *in-situ* synthesis of composite materials where the metal nanoparticles and the polymer were produced from the respective ionic precursors and monomers. It is said that the latter attempt would provide better particle-polymer interactions due to the *in-situ* synthesis of both substances. However, variations of the above categories have also been reported. One example is the colloidal route (Bai et al., 2007).

2.2 Phase Transfer Technique

The colloidal route to polymer-based nanocomposites has emerged as the potential way to obtain a better dispersion of filler materials in a composite. However, one of the challenges to synthesise the nanoparticles in colloidal form is that the particles tend to slowly agglomerate and grow in size. This will consequently lead to poor particles dispersion within the matrix. To overcome these, the two-phase approach known as phase transfer technique was devised. This technique involves the transfer of metal ions or pre-formed particles from one phase to the other and *vice versa* (Misra et

al., 2006). Table 2.2 lists some of the advantages and disadvantages of nanoparticle preparations in aqueous and organic phases.

Table 2.1: Recently reported polymer-based nanocomposites, their properties and applications.

Matrix	Filler	Property	Application	Reference
Polydiacetylene (PDA)	zinc oxide (ZnO)	thermochromic behaviours	sensors	(Traiphol et al., 2011)
Diglycidyl ether of bisphenol A (DGEBA)	multi-walled carbon nanotubes (MWNTs)	thermostability	electronic and aeronautics industry	(Damian et al., 2011)
Polypropylene (PP) & Polypyrrole (PPy)	Montmorillonite	effective shielding	microwave absorber	(Moucka et al., 2011)
Dimethacrylate-based polymers	Ag	antibacterial	biomedical device	(Cheng et al., 2011)
Poly vinyl chloride (PVC)	single wall carbon nanotubes (SWNTs)	thermal conductivity	electronic	(Aljaafari et al., 2011)
Poly(3-(ethyl-4-butanoate)thiophene) (P3EBT)	Cadmium sulphide (CdS), lead sulphide (PbS) or zinc sulphide (ZnS)	photovoltaic	photovoltaic cells	(Maier et al., 2010)
Poly(N-vinylpyrrolidone) (PVP)	Ag	electrical conductivity	conductive adhesives	(Chen et al., 2009)
Polyurethane (PU)	Silica	shape memory	medical	(Lee et al., 2011)
Poly(lactic acid) (PLA)	CdS	optical properties	bio-imaging & biosensing	(Wang et al., 2011a)

Table 2.2: Some of the advantages and disadvantages of synthesising nanoparticles in aqueous and organic phases (Sastry, 2003).

	Aqueous-based synthesis	Organic-based synthesis
Advantages	<ul style="list-style-type: none"> • Single step reduction process as most of precursors, reducing and capping agents are soluble in water. • Shape controllable by suitable micelles as the template. • Bioconjugation towards the particles can be achieved. 	<ul style="list-style-type: none"> • High degree of controllable size, dispersity and surface functionalised. • Large scale production. • Spontaneous assembly into close packed and hexagonal monolayers upon solvent evaporation.
Disadvantages	<ul style="list-style-type: none"> • Small scale production. • Low degree of controllable size and dispersity. 	<ul style="list-style-type: none"> • Multi step reduction. • Bioconjugation towards the particles cannot be attained.

2.2.1 Transfer of metal ions

In this protocol, the metal ions are transferred prior to reduction or oxidation from an aqueous to an organic phase or *vice versa*. It was first reported by Brust and co-workers in 1994 (Brust et al., 1994). In their work, tetrachloroaurate(III) ion (AuCl_4^-) was transferred from aqueous solution to toluene with the help of tetra-n-octyl-ammonium bromide (TOAB). Then, it was reduced using sodium borohydride (NaBH_4) in the presence of dodecanethiol. This procedure affords better control on the particle size and monodispersity but is unable to control the particle shape.

2.2.2 Transfer of pre-formed particles

In this case, the pre-formed particles are transferred from aqueous to organic solution or *vice versa*. For example, it was reported that the previously synthesised Ag

nanoparticles were re-dispersed in distilled water and stabilised by sodium oleate in the presence of sodium chloride. The oleate-stabilised Ag nanoparticles were successfully transferred into three distinct non-aqueous solutions, which are cyclohexane, n-hexane and benzene (Hirai et al., 1992). The advantage of using this method is the elimination of any oxidised products from the reducing agent from the secondary phase (Sarkar et al., 2009). Thus it reduces the number of impurities in the final product. Besides that, this procedure also is relatively simple, inexpensive and provides better control on the shape of the particles by using suitable templates and most importantly it is reproducible.

2.2.3 Brief descriptions of phase transfer technique

The synthesis of nanoparticles *via* phase-transfer method offers several advantages (Bala et al., 2005). These are (i) better arrangement or self-assembly of nanoparticles, (ii) evaluation of several properties can be done due to the advent of various physicochemical environments of the particles, and (iii) provides routes to numerous applications.

Generally, the phase transfer technique needs a stabiliser and a phase-transfer agent (Zhao et al., 2004). A stabiliser is used to control the growth of the particles in aqueous and organic phase and also during the transferring process. Besides that, it is also needed to modify the surface of the particles to tailor the particles dispersibility in the other phase (Bala et al., 2005). Some of the common stabilisers are N-cetyl-N,N,N-trimethylammonium bromide (CTAB) (Abu Bakar et al., 2007), oleic acid (Bala et al., 2005), trisodium citrate (Misra et al., 2006), alkylamine (Wang et al., 2010b; Yang et al., 2004) and dodecanethiol (Brust et al., 1994).

Phase-transfer agent is needed to help the particles to cross over from one phase to the other *via* the inter-phase. Examples of phase-transfer agents are TOAB

(Brust et al., 1994), C-undecylcalix[4]-resorcinarene (C11-resorcinarene) (Misra et al., 2006), aromatic amine (Grace & Pandian, 2007), octadecylamine (Kumar et al., 2004; Sastry et al., 2001), dodecylamine (Yang et al., 2007), hydrochloric acid (Sarathy et al., 1997) and sodium hypophosphite (NaH_2PO_4) (Li et al., 2002). There are also some reports on the usage of alcohol as an intermediate solvent to improve the interfacial contact between two different media (Yang et al., 2007).

Figure 2.2 shows the schematic of phase transfer process of Ag nanoparticles from water to toluene using oleic acid as stabiliser. In the phase transfer process, oleic acid also acts as particle transfer agent due to the presence of hydrophobic and hydrophilic groups in the acid.

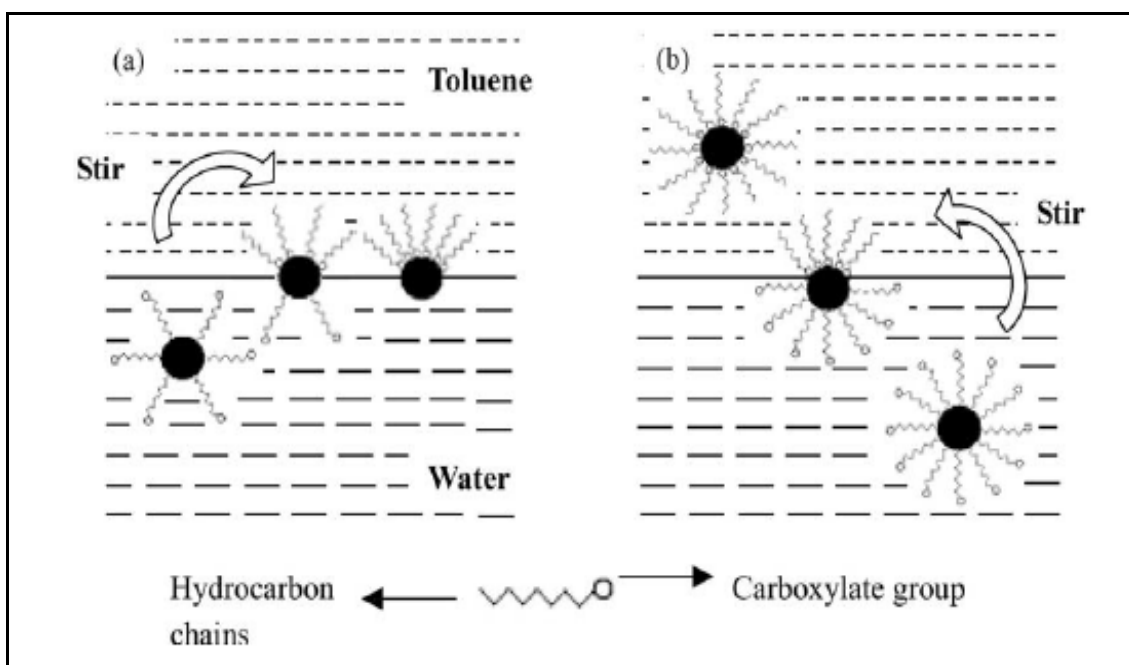


Figure 2.2: The schematic of phase transfer process (Li et al., 2002).

Several metals, metal oxides and chalcogenides and alloys have been successfully synthesised by using phase transfer method. For instance, Ag (Zhao et al.,

2004; Sarkar et al., 2009), Au (Misra et al., 2006), Pd (Yang et al., 2007), Ru (Yang et al., 2004), Pt (Yang et al., 2004), magnetite (Fe_3O_4) (Abu Bakar et al., 2007), cadmium selenide (CdSe) (Navarro et al., 2010), $\text{Ni}_{\text{core}}\text{Ag}_{\text{shell}}$ (Bala et al., 2005), Au-Ag alloy (Devarajan et al., 2004), maghemite (Fe_2O_3) (Meriguet et al., 2003) and copper monosulphide (Cu_2S) (Tian et al., 2005). Recently, there is a report on Cu particles synthesised *via* phase transfer technique (Dadgostar et al., 2010). The Cu nanoparticles with the average size of 6.06 nm were prepared in a water-toluene system in the presence of oleylamine, TOAB and NaBH_4 as the stabilising ligand, phase transfer and reducing agent, respectively. The obtained Cu nanoparticles were spherical in shape and non-agglomerated.

2.3 Copper Nanoparticles

Cu metal is abundant in the Earth's crust, which account to approximately 70 parts per million (Newton & Baker, 1999). It is reddish-brown in colour, fairly soft and ductile. Common Cu bearings minerals are as listed in Table 2.3. Cu is frequently used as a thermal and electrical conductors as well as alloys. One of the common alloys of Cu is bronze.

Table 2.3: Common Cu bearings minerals (Newton & Baker, 1999)

Common Name	Chemicals Name	Chemical Formula
Azurite	Basic copper carbonate	$\text{Cu}_2(\text{OH})_2\text{CO}_3$
Chalcoxite	Copper sulphide	Cu_2S
Chalcopyrite	Copper iron sulphide	CuFeS_2
Cuprite	Copper oxide	Cu_2O
Malachite	Basic copper carbonate	$\text{Cu}_2(\text{OH})_2\text{CO}_3$

The use of Cu is economical as it is widely available and environmental friendly compared to other noble and heavy metals. Cu nanoparticles offer further advantages such as, i) high stability, ii) low boiling point, iii) excellent electrical conductivity and catalytic properties due to the face-centred cubic with a full d-band (Ko et al., 2009). Nowadays, Cu in nano-scale is of world-wide interest as it exhibits special properties. The unique properties arise from the small size which is very well differs from the bulk. These will ascertain diverse and potential applications. However, Cu nanoparticles are easy to oxidise and congregate due to the particle's high surface energy. This inevitably limits its usage.

2.3.1 Method of preparations

Cu nanoparticles have been synthesised through different techniques. Those techniques can be divided into two categories, namely physical and chemical methods (Dadgostar et al., 2010). Examples of physical methods are laser irradiation (Teng et al., 2011) and ablation (Silva et al., 2010), electron beam irradiation (Park et al., 2010) and vacuum vapour deposition (Zhang et al., 2006c). While microemulsion (Qiu et al., 1999), sonochemical reduction (Dhas et al., 1998), chemical reduction (Cheng et al., 2006), and reverse micelle (Pileni, 2006) are examples of chemical methods. Physical methods produced metallic nanoparticles in large scale and are applicable to most common solid metals. However, the quality is inferior compared to those that are chemically synthesised. On the other hand, chemical methods are a small scale process and to date are applicable to certain metals. However, the growth and assembly of metallic nanoparticles produced by this latter method is controllable *via* optimising the reaction parameters. These include concentration of metal precursors, stabilisers, reducing

agents, reaction temperature and reaction chemistry. Below are the descriptions of few known methods to produce Cu nanoparticles.

(a) Laser irradiation (Silva et al., 2010)

When the sample containing Cu ions in silica glass was irradiated by a focused nanosecond near-infrared laser, there is a formation of plasma inside or on the surface of the glass. These generated free-electrons that are responsible for the reduction of metal ions to atoms.

(b) Microwave heating (Xu et al., 2006)

A solution containing Cu precursor, modifier and reductant was placed in a microwave reflux system under ambient air for 30 min at a power 365 W. Then, the sample was cooled to room temperature before being centrifuged, washed and dried.

(c) Thermal decomposition (Salavati-Niasari et al., 2008)

A mixture of copper oxalate and oleylamine was heated up to 140°C for 60 min under an argon atmosphere. The resulting metal complex was injected into triphenyl phosphine at 240°C. The reddish solution was heated for 45 min before being cooled to room temperature, washed and dried.

(d) Chemical reduction

This method is the most extensively used because it is simple with controllable size and shape of nanoparticles and the ability of water to solubilise a variety of salt precursors and stabilise the respective ions/particles. NaBH₄ (Chen et al., 2006), hydrazine hydrate (Vaseem et al., 2011), sodium formaldehyde sulfoxylate (Khanna et

al., 2007), glucose (Panigrahi et al., 2006) and ascorbic acid (Cheng et al., 2006) are some examples of reducing agents that have been employed. While, polymers (Singh et al., 2010), ligands (Kanninen et al., 2008), dendrimers (Jin et al., 2008) or surfactants (Vaseem et al., 2011) are normally used in this process as stabilisers to control the growth as well as to prevent the oxidation of the particles.

(e) Polyol method (Park et al., 2007)

A mixture of capping agent, PVP dissolved in diethyleneglycol (DEG) with the reducing agent, sodium phosphinate monohydrate was heated to reaction temperature ranging from 140-200°C. Then, the aqueous solution of Cu precursor was injected into the hot reaction medium. The sample was cooled to room temperature before being centrifuged, washed and dried.

2.3.2 Applications

Table 2.4 lists some of the reported applications of Cu nanoparticles. It shows that Cu nanoparticles have a wide range of applications due to the unique properties.

2.4 Copper Sulphide Nanoparticles

Copper sulphide (CuS) exists in various stoichiometries. The compositions vary from a copper rich, Cu_2S to copper deficient, CuS. These include CuS (covellite), $\text{Cu}_{1.96}\text{S}$ (djurleite), $\text{Cu}_{1.8}\text{S}$ (digenite), $\text{Cu}_{1.75}\text{S}$ (anilite) and Cu_2S (γ,β -chalcocite) (Jiang et al., 2000). Due to the CuS complex structures and valence states, it shows some unique properties. CuS is a p-type semiconductor due to copper vacancies within the lattice (Roy & Srivastava, 2007; Ou et al., 2005) and is of special interest because it shows metallic conductivity (Liao et al., 2003). Furthermore, it can be transform into a

Table 2.4: Some of the reported applications of Cu nanoparticles.

Application	Description	Reference
1. Catalysts	<ul style="list-style-type: none"> Alumina supported Cu nanoparticles as a catalyst for aziridination and cyclopropanation of olefins. Catalyst for hydroxylation of phenol by hydrogen peroxide. Mesoporous silica supported Cu nanoparticles as a catalyst for hydrogenation of carbonyl compounds. 	(Kantam et al., 2007) (Karakhanov et al., 2010) (Yoshida et al., 2010)
2. Heat Exchange Materials	<ul style="list-style-type: none"> Ethylene glycol-based nanofluids containing Cu nanoparticles. Cu-H₂O nanofluids. 	(Eastman et al., 2001) (Li et al., 2008)
3. Electrochemical Sensors	<ul style="list-style-type: none"> Cu nanoparticles and carbon nanotubes were used to modify GC/Cu electrodes to improve their electroactivity and selectivity. 	(Male et al., 2004)
4. Antimicrobial Agents	<ul style="list-style-type: none"> Polyurethane nanofibers contains Cu nanoparticles – kill the microorganisms by distort the cell wall. 	(Sheikh et al., 2011)

superconductor at 1.6 K (Ou et al., 2005). Besides that, it also has ability for chemical-sensing and solar energy absorption. However, these properties are highly dependent toward size and shape of the particles. Thus, it is crucial to control the size and shape of the particles in order to manipulate the resultant properties. Consequently, there are various shapes of CuS that have been synthesised. For instance; nanowires (Wang & Yang, 2000), hollow spheres (Chen et al., 2004b), flakes (Zhang et al., 2006a), disks (Zhang & Gao, 2003) and flower-likes (Gorai et al., 2005). Compared to other type of

chalcogenides, CuS offers several advantages such as cheap, less hazardous and exhibit similar performance as nonlinear devices (Haram et al., 1996).

2.4.1 Method of preparations

Various types of stabilisers have been used to control the morphology of CuS particles. These include PVP (Dutta & Dolui, 2008), PVA (Shen et al., 2009), poly ethylene glycol (PEG) (Ji et al., 2005), CTAB (Zhang & Gao, 2003), sodium dodecyl sulphate (SDS) (Liao et al., 2003) and Triton-X 100 (Haram et al., 1996). While, there are also a variety of sulphur (S) precursors that have been used such as thiourea (TU) (Ji et al., 2005), sodium sulphide (Na_2S) (Zhang & Zhang, 2008a), sulphur powder (Kuzuya et al., 2008), thioacetamide (TAA) (Xu et al., 2008) and carbon disulphide (CS_2) (Roy & Srivastava, 2007). Listed below are some reported methods to synthesise CuS nanoparticles.

(a) Water-in-oil microemulsions (Gao et al., 2004)

The microemulsion is generated by vigorous mixing of water, cyclohexane, CTAB and ethanol as co-surfactant. Volume ratio between water and cyclohexane is fixed to 2, while, the amount of CTAB was varied. TAA and copper chloride were used as the precursors.

(b) Solvothermal (Shen et al., 2009)

The all-in-one Cu-S precursor, $\text{Cu}(\text{S}_2\text{CNET}_2)_2$ together with surfactant and ethylamine as the solvent were transferred into a Teflon-lined autoclave. This was put in an oven for 11-21 hr at 150°C . The resultant products were centrifuged and wash repeatedly.

(c) Wet chemical method (Roy & Srivastava, 2007)

In this method, a solution containing Cu precursor, CS₂ as S-source and ethylenediamine were used. The later acts as an agent to release S²⁻. The temperature was increased slowly before refluxing at 105°C for 12 hr with continuous stirring.

(d) Sulphuring (Chen et al., 2008)

Anodised aluminium oxide (AAO) was used as the template. Arrays of Cu nanowires were then fabricated by electrochemical deposition. Later, the samples were annealed together with S powder in a vacuum sealed quartz tube for several hrs.

(e) Hydrothermal (Zou et al., 2007)

Firstly, the Cu salts were complexed with citric acid and TU in a mixture of ethanol (C₂H₅OH) and water solvents. Then, it is transferred into a Teflon-lined autoclave for hydrothermal processing at 160°C. The product was centrifuged and washed repeatedly.

2.4.2 Applications

Due to its unique properties, CuS particles have potential applications in various fields. Table 2.5 lists some of the reported applications of CuS nanoparticles.

2.5 Epoxy Resins

Epoxy basically consists of aliphatic, cycloaliphatic or aromatic backbones (Pham & Marks, 2004). Epoxy is a thermosetting resins and often widely used as the matrix for composites in structural applications, electrical insulating materials, adhesives and surface coatings (Budrugaac et al., 2008; Remiro et al., 1999; Rosu et al., 2004). Epoxy

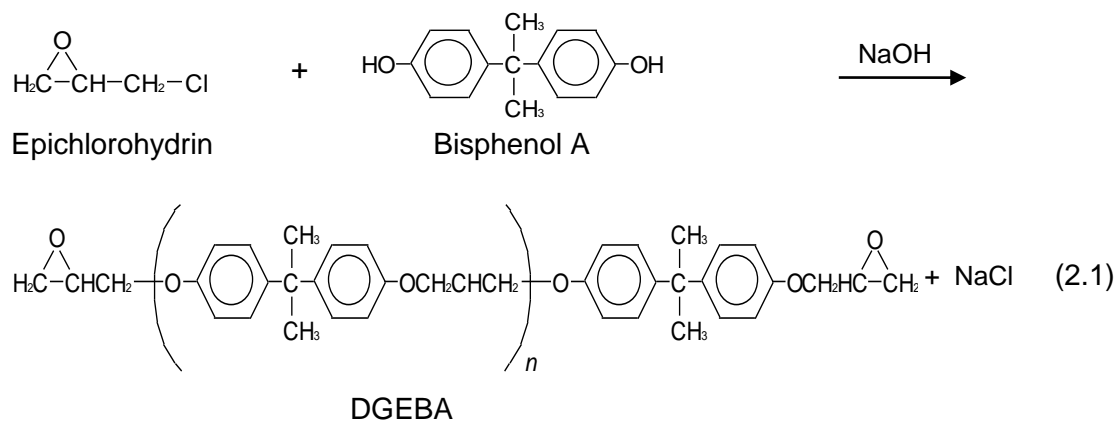
Table 2.5: Some of the reported applications of CuS nanoparticles.

Application	Description	Reference
1. Pollution control and environmental protection	<ul style="list-style-type: none"> • Good photocatalytic activity by degradation of eosin Y under UV-vis light irradiation. • Decomposition of Rhodamine in atmosphere. 	(Wang et al., 2009) (Ding et al., 2008).
2. Solar cells	<ul style="list-style-type: none"> • Solid state solar cell structures (SSSC) contains Cu_xS, TiO_2 and indium(III) sulphide (In_2S_3) prepared using automatic spray pyrolysis. However, the obtained photovoltaic response is very low. 	(Isac et al., 2010)
3. Catalysts	<ul style="list-style-type: none"> • Catalytic activity in the hydrosulphide air oxidation in aqueous solutions at atmospheric pressure and room temperatures. 	(Raevskaya et al., 2004)

has excellent chemical, electrical, moisture and corrosion resistance, good mechanical properties, high thermal stability, ease of processing (Teh et al., 2007) and cost effectiveness (Sarathi et al., 2007). However, there are few disadvantages of epoxy which include brittleness and poor resistance to crack propagation (Zhang & Vyazovkin, 2006b) but can be improved by incorporation of rubber (Remiro et al., 1999; Sanchez-Soto et al., 2007).

The most widely used epoxy is the diglycidyl ether of bisphenol A (DGEBA) which covers 75% of resins sales volume. It is a product of step-growth polymerisation reaction between epichlorohydrin and bisphenol A (equation 2.1) (Pham & Marks, 2004). The toughness, rigidity and elevated temperature performance arise from the bisphenol A while the chemical resistance arises from the ether linkages (Lin & Zhong, 2008). The

adhesive properties and formulation latitude, or reactivity with a wide variety of chemical curing agents are due to the hydroxyl and epoxy groups (Lin & Zhong, 2008).



2.5.1 Curing an epoxy

Curing an epoxy under specific conditions will form a three-dimensional (3D) cross-linked structure. The process is irreversible thus it will hinder disassembly and interconnection repair (Lin & Zhong, 2008). The curing techniques include heat, UV light and catalyst which correlates to the energy needed to initiate the chemical reaction. Basically, curing agents for epoxy can be divided into two types which are catalytic and co-reactive (Pham & Marks, 2004). The function of catalytic curing agents is to initiate the homopolymerisation of epoxy or accelerate the other curing agent such as boron trihalides and tertiary amines. The co-reactive curing agents, however, act as monomers in the polymerisation process. These include amines, phenols, thiols and carboxylic acids. The degree of curing and type of curing agent used will determine the outcome physical, electrical and mechanical properties of a cured epoxy. For example by using an aliphatic amine as the curing agent, the cured epoxy exists as low viscosity material and with little colour imparted (Pham & Marks, 2004). The process will take place at

ambient temperature but at a slower rate (Lin & Zhong, 2008). On the other hand, using aromatic amines, the cured epoxy generally presents good thermal and chemical resistance, long pot life and low moisture absorption. It is slowly cured at room temperature due to steric hindrance of aromatic rings (Hara, 1990). Table 2.6 lists some examples of curing agent for epoxy and their advantages and disadvantages.

2.6 Epoxy Nanocomposites

There are various types of fillers that have been incorporated into epoxy. The types of filler used are determined by the desired properties in certain applications. Below are some of the property enhancements affected by addition of fillers into epoxy (Pham & Marks, 2004).

- (a) Increase pot life and lower exotherm – Fillers such as metals and silica is often better conductor compared to the resin and this assists the system to dissipate heat readily.
- (b) Increase thermal shock resistance – This can be achieved by addition of fillers for instance metals (Zhou, 2011), silica and glass (Teh et al., 2008) which do not experience significant changes such as thermal expansion or thermal conductivity during heat treatment of the composite.
- (c) Reduce shrinkage – The use of fillers such as silica, metal and alumina decrease the shrinkage of the overall composite system.
- (d) Increase machinability and abrasion resistance – Increment in the hardness which will require higher energy for the composites to undergo any mechanical action. Furthermore, it will also give good finishing. This can be achieved by addition of rigid fillers for example clay (Yasmin et al., 2006), alumina (Lim et al., 2010) and silica (Baller et al., 2009).