IMPROVEMENT OF SCREEN PRINTABLE ANISOTROPIC CONDUCTIVE ADHESIVE WITH POLYETHYLENE GLYCOL AS DILUENT

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ปพิชญา แม้นด้วง : การปรับปรุงกาวนำไฟฟ้าในทิศทางเดียวซึ่งสกรีนได้ด้วยการเติมสารเจือจางพอลิเอทิลีนไกลคอล. (IMPROVEMENT OF SCREEN PRINTABLE ANISOTROPIC CONDUCTIVE ADHESIVE WITH POLYETHYLENE GLYCOL AS DILUENT) อ.ที่ปรึกษาหลัก : รศ. ดร.อนงค์นาฏ สมหวังธนโรจน์

เป้าหมายหลักของงานวิจัยนี้คือการปรับปรุงกาวนำไฟฟ้าที่สามารถพิมพ์สกรีนได้ โดยลดความหนืดของกาวนำไฟฟ้าที่ผสมด้วยอิพ็อกซี EPN/PPGDE/CTBN ด้วยการเติมพอลิเอทิลีนไกลคอลที่มีมวลโมเลกุล 400 งานวิจัยนี้ทำการศึกษาผลของปริมาณการเติมอนุภาคเงินโดยเปรียบเทียบอนุภาคเงินเชิงพาณิชย์และอนุภาคเงินจากการสังเคราะห์พบว่าความต้านทานไฟฟ้าของอนุภาคเงินเชิงพาณิชย์มีค่าน้อยกว่าอนุภาคเงินจากการสังเคราะห์เนื่องจากความเป็นออกไซค์ของอนุภาคเงินจากงานวิจัยนี้จึงเลือกใช้ปริมาณอนุภาคเงินเชิงพาณิชย์ที่น้อยที่สุดคือ ร้อยละ1 โดยน้ำหนักของอิพ็อกซี เพื่อให้กาวนำไฟฟ้ามีค่าความต้านทานไฟฟ้าไม่เกิน 1 Ω•cm ส่วนการศึกษาผลของปริมาณการเติมพอลิเอทิลีนไกลคอลในระบบกาวนำไฟฟ้าของอนุภาคเงินเชิงพาณิชย์ที่อัตราส่วนร้อยละ 1 ถึง 5 โดยน้ำหนักของอิพ็อกซี พบว่าระบบกาวนำไฟฟ้าเหล่านี้มีพฤติกรรมการไหลแบบนิวโตเนียน และเมื่อเพิ่มอัตราส่วนของพอลิเอทิลีนไกลคอลในกาวนำไฟฟ้าส่งผลให้ความหนืดลดลง จากสมบัติเชิงความร้อนของกาวนำไฟฟ้าเหล่านี้สามารถทำปฏิกิริยาการบ่มสมบูรณ์ได้ที่อุณหภูมิ 157 องศาเซลเซียส ภายในระยะเวลาไม่เกิน 30 นาที โดยใช้สารบ่มชนิด m-PDA จากสมบัติเชิงกลของกาวนำไฟฟ้าพบว่าการเติมพอลิเอทิลีนไกลคอลร้อยละ 3 โดยน้ำหนักของอิพ็อกซี เป็นอัตราส่วนที่แสดงค่ามากที่สุดคือ 1.358 N/mm เนื่องจากการเติมพอลิเอทิลีนไกลคอลทำให้กาวนำไฟฟ้ามีความหนืดลดลงส่งผลให้มีความสามารถชอบน้ำมากขึ้น ซึ่งทำให้การยึดเกาะของกาวนำไฟฟ้ากับแผ่นทองแดงดีขึ้น

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The primary aim of this research is to improve screen printable anisotropic conductive adhesive by reducing the viscosity of anisotropic conductive adhesive which is EPN/PPGDE/CTBN epoxy adhesive with polyethylene glycol 400. This research compared the conductivity of commercial and synthesized silver particles. As a result, the volume resistivity of commercial silver particles was lower than the synthesized silver particle due to silver oxide of silver particles. 1 phr of commercial silver particle was added in anisotropic conductive adhesive in which its volume resistivity was less than 1 Ω·cm. The effect of addition polyethylene glycol in the anisotropic conductive adhesive with commercial silver particle by various concentrations of 1 - 5 phr was studied. As a result, the flow behavior of anisotropic conductive adhesive was Newtonian fluid and the viscosity decreased when the content of PEG increased. The anisotropic conductive adhesive was fully cured at 157 °C within curing time less than 30 minutes by using m-PDA as a curing agent. The highest peel strength of anisotropic conductive adhesive is 1.358 N/mm, it is obtained from 3 phr of PEG-modified anisotropic conductive adhesive system because the addition of polyethylene glycol decreased the viscosity and the adhesive become more hydrophilic which affect the adhesion of anisotropic conductive adhesive and copper substrate.

Field of Study:	Chemical Engineering	Student's Signature ....
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Papitchaya Manduang

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1 Introduction

A flexible printed circuit (FPC) has been used in many electronic devices such as laptop, desktop computer, monitor and screen TVs. The FPC is a component to connect with other electronic devices by an anisotropic conductive paste (ACP) for an alternative to lead-solder. In the assembly process, the ACP is used in the screen-printed process since ACP offers the benefits of low production costs, fewer steps in the manufacturing process, and reduced production times.

The most common materials used are epoxy resins as an adhesive whose properties are high mechanical strength and good chemical resistance for the application of a flexible print circuit. For the screen-printed process, the factor in producing adhesive is the rheology. The commercial epoxy novolac resin is usually used as the epoxy base. The state of epoxy novolac resin is semi-solid or solid resins which is not suitable for screen-printed process. The advantage of epoxy novolac resin over DGEBA-based epoxy resins is the multiplicity of epoxy groups thus these resins can achieve increased crosslink density. Flexible epoxy resin can be blended with the commercial epoxy novolac resin; however, their strength of structure may decrease, especially bond strength. Toughness consists of high elongation and tensile strength with minimal change in the crosslink density. Carboxyl-terminated butadiene-acrylonitrile (CTBN) is chosen as the elastomer because of its miscibility in many epoxy resins. The degree of toughness is determined by the crosslink density of the matrix [1]. The conductive particles in the adhesive is generally a silver particle due to higher electrical and thermal conductivity than metal others. However, the silver particle can agglomerate and result in poor dispersion in the epoxy matrix [2]. Diluents are added in the mixture in order to improve the mixing capacity. Polyethylene glycol (PEG) is a common diluent to modify epoxy systems. Because of PEG’s low viscosity, it is important in good adhesion by penetration on porous substrates and faster wetting; therefore, it can increase the peel strength between materials [3].

In this research, the flow behavior and mechanical properties of an anisotropic conductive adhesive for screen printed process were studied Epoxy systems consisting of epoxy resin matrix based on epoxy novolac resin and polypropylene glycol diglycidyl ether resins, carboxyl-terminated butadiene-acrylonitrile as a toughener, metaphenylene diamine as curing agent, silver particle as a conductor in epoxy and polyethylene glycol as a diluent with various concentration were selected to use for screen printed process.

1.2 Objectives

1.2.1 To improve the flow behavior, peel strength, mechanical strength and electrical properties of anisotropic conductive adhesive paste for the screen print process by the addition of polyethylene glycol.

1.2.2 To study the curing kinetics of anisotropic conductive adhesive paste for the screen print process.

1.3 Scopes

1.3.1 The content of polyethylene glycol was varied at 0, 1, 3 and 5 phr of epoxy systems.

1.3.2 Size of synthesized and commercial silver particle was 1.26 μm and 1.03 μm, respectively.

1.3.3 EPN was mixed with PPGDE at a ratio of 1:1 w/w as well as 5 phr of CTBN and 1 phr of triphenylphosphine (TPP) for pre-reaction.

1.3.4 The resistance of ACP should be less than 1 Ω.

CHAPTER II

Theory and literature reviews

2.1 Flexible printed circuit

Flexible printed circuit (FPC) is used with many electronic devices such as laptop, monitor and screen TVs because flexible print circuit have varied designs and shapes which can be used in an electronic device. This technology is led popular for electronic industries.

2.2 Primary materials of flexible printed circuit

Figure 2.1 The three main materials of flexible printed circuit

2.2.1 Conductor materials

The conductor materials of FPC must provide enough electricity for electric devices. The main conductor material extensively used in the flexible printed circuit is copper substrates because it is commonly bonded with epoxy adhesive. But copper is difficult to be bonded if high shear and peel strengths are desired due to the oxide that rapidly forms on copper. Therefore, for copper in which low to medium bond strengths are acceptable there should be pretreatments. The surface treatment is the process to clean the attached copper oxide layer from the base metal. However, there are several problems with metal substrates which are as follows:

- Environment of the substrate surface and interface of the adhesive joint

- the surface chemistry depending on metal, processing, and preconditioning.
- high thermal expansion coefficient and low thermal conductivity of epoxy adhesive.

Moreover, it should consider the nature of the adhesive force between the base metal and oxide that can be determined by:

- The cohesive strength of the material
- The forces between the adhesive and the metal oxide
- The strength of the metal-oxide bond to the base metal.

Therefore, surface treatment can improve adhesive bonding by removing oxide layers and providing a more consistent surface than untreated metal [4].

2.2.2 Insulators

An insulator from a part of the flex circuit is used for preventing moisture, contamination, and abrasion. In addition, the insulator can prevent the damage from heat during operation. The most common materials used to cover are polyimide film. Polyimide can be bonded with epoxy adhesive because of its great resistance to solvents and thermal stability. However, the bonding can be improved, if there is the surface preparation by solvent cleansing the before operation [4].

2.2.3 Electrically conductive adhesives (ECAs)

Electrically conductive adhesives are used for the flexible print circuit because it can serve as the bridge to interconnect the integrated circuits (IC) and other components into the system-level board to form the electronic products. Moreover, the electrically conductive adhesives are used essentially to attach the metal conductor firmly onto the insulators for electronics packaging. There are two types of ECAs which are isotropic conductive adhesive (ICA) and anisotropic conduction adhesive (ACA). The difference between ICA and ACA is an isotropic conductive adhesive that is conductive equally in all directions; however, anisotropic conductive adhesive conducts in only one-direction (vertical axis). The anisotropic conductive adhesive can prevent short circuits in the horizontal axes. The difference between ICAs and ACAs is particle loadings which are based on the percolation theory. Metal-filled electrically conductive adhesives offer an alternative to typical lead–tin soldering with the advantages of being simple to process at lower temperatures without toxic lead or corrosive flux. The disadvantage of conventional metal-filled conductive adhesives is that a high loading of filler decreases the mechanical impact strength, while a low filler loading results in poor electrical properties.

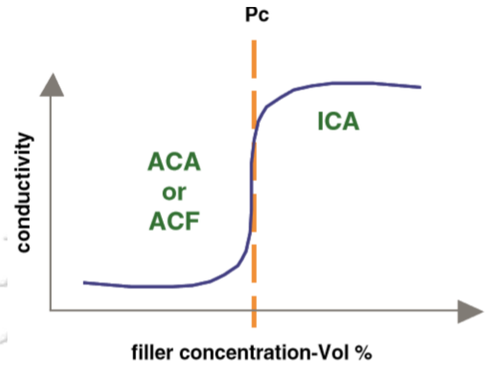


Figure 2.2 Typical percolation curve of conductive adhesive [5]

Percolation theory can explain the electrical properties of ECAs by electrical conductivity through contact between the conductive particles in an insulator in which an insulator can transform into a conductor when a critical volume fraction of conductive particles is the percolation threshold. The volume fraction of conductive particles has affected the resistivity of ECAs. If the volume fraction of conductive particles equal or above the percolation threshold, the resistivity decreased due to all the conductive particles that are contacting an all-direction network which can transform into ICA. However, it can decrease the mechanical of ICA so the volume fraction of the conductive particles that are limited conductive particles content for high electrical conductivity and is not affecting the mechanical properties of ICA [6].

2.3 Anisotropic conduction adhesive (ACA)

There are two types of anisotropic conductive adhesives that are anisotropic conductive film (ACF) and anisotropic conductive paste (ACP). The effectiveness of process of ACAs usage is influenced by the loading and distribution of conductive particles in an adhesive. Because the ACF has to be in the B-stage, semi-solid stage, there is no movement of conductive particles while curing. However, ACP must be mixed before using in a process for the good distribution of conductive particles due to agglomeration. Therefore, ACP has not been used in screen-printing process [7].

2.3.1 Epoxy

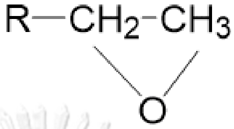


Figure 2.3 The epoxy ring or oxirane structure

Generally, the properties of the adhesive should be high mechanical strength and good chemical resistance for the application of a flexible print circuit; therefore, the most common materials are epoxy resins. Due to the low-stress property of epoxy, it can be used for the conductive adhesive in which the commercial epoxy is bisphenol A resins. Another commen commercial epoxy is novolac resin which is semi-solid resins with epoxy equivalent weight (EEW) in the range of 170 to 230 equivalentgrams that there is a low-viscosity epoxy novolac resin (18,000 to 28,000 cP) and it is easy to be used in screen-printed process. The difference between epoxy novolac resin and DGEBA-based epoxy resins is that the novolac resin has multiplicity of epoxy groups and these resins can increase crosslink density. When cured with curing agents, the properties of epoxy novolac, such as performance, chemical resistance, and adhesion, are better than bisphenol A-based resin. Because of the phenolic groups in the novolac, they are cured with a hydroxyl group on the epoxy; therefore, epoxy novolac resin is widely used in structural adhesive systems due to high-temperature performance.

Flexible epoxy resin can be prepared by incorporating the commercial epoxy novolac resin with large groups of molecular chain, such as to change from an aromatic structure to aliphatic hydrocarbon, reducing the multiplicity of epoxy groups and insertion of long hydrocarbon side chains which increases the distance between crosslinks.

The epoxy resins which can be used to modify the flexibility of resin are as follows:

- Epoxy resins are derived from acid functional oils (dimer acid, cashew nut oil, and castor oil).
- Epoxy resins are derived from polyalkylene glycol (polyethylene or polypropylene glycol).
- Epoxy resins with longer molecular weight while it can maintain the same number of reactive sites.

In addition, the reduction in crosslink density would increase the flexibility of epoxy which decreases the glass transition temperature resulting in a decrease in tensile and shear strength as well as a decrease in other properties, such as chemical and heat resistance [4].

2.3.2 Curing agent

Normally, epoxy resin is in a liquid form. When the curing agent is introduced and cured under heat, the three-dimensional cross-linked structure of epoxy resins is formed. Therefore, the adhesive is transformed into a rigid solid but when the adhesive is transformed, it cannot be reversibly cured reaction. There are generally two types of curing agent in the epoxy system, i.e., anhydrides, and amines. When the epoxy is cured with a curing agent, the viscosity, and reactivity of epoxy increase because of the degree of cross-linking and the formulation of chemical bonds in the epoxy with a curing agent. The curing agents will then react with the epoxy groups or hydroxyl groups followed the stoichiometric ratio of resin to curing agent. In flexible printed circuit, it usually uses amine curing agents because these curing agents provides low brittleness [1]. Therefore, the aromatic amines has been selected in this study which are widely used as curing agents for epoxy resins. The advantage of aromatic amines curing agents is to provide higher heat resistance and greater chemical resistance than aliphatic amine curing agent. The disadvantages of this curing agent are that they are solids at room temperature. Metaphenylene diamine (mPDA) is the common curing agent of the aromatic amine used to cure epoxies that is mixed with epoxy resin at melting temperature (65 °C) [4].

2.3.3 Tougheners

The structure of epoxy resins tends to have poor resistance to crack initiation and growth, which results in poor impact and peel properties. Toughness has both high elongation and tensile strength by the minimal change in the crosslink density. The elastomeric, particulate phase is used as a “crack stopper” for improving fracture toughness. Generally, CTBN is a choice for using the elastomer because of it can be miscible with many epoxy resins. The degree of toughness is determined by the crosslink density of the matrix, the particle size and size distribution of elastomer, the volume fraction of the elastomeric phase, and the degree of adhesion between the epoxy matrix and the particle. In general, the elastomer must be prereacted with the epoxy for the toughening effect. Also, the solubility of the elastomer in the uncured resin system. For CTBN the reaction is carried out at high temperatures (150 to 160 °C) by the catalyst, such as tris dimethylamino phenol or piperidine. After the cure is complete, the adhesive consists of an epoxy matrix with embedded rubber particles [4, 8].

2.3.4 Diluents

Diluents are used to lower the viscosity of epoxy resins system to ease compounding with other or to aid in the application of the adhesive onto a substrate because diluents are low molecular weight liquid compounds which is chemically and physically compatible with epoxy resins and their curing agents. Two distinct classes of diluents are nonreactive diluents and reactive diluents. Reactive diluents have crosslink reaction with the primary resin, while nonreactive diluents act as plasticizers due to low-molecular-weight structure for the epoxy composition. Diluents that have high molecular weight are added in the epoxy adhesive to lower the viscosity and modify processing conditions. Also, in order to easily mix fillers in epoxy and to improve filler loading capacity, the low-viscosity diluent provides good adhesion by penetrating into porous substrates and faster wetting. Moreover, most diluents decrease the reactivity of the epoxy system because of the dilution of the resin; however, diluents may increase the exotherm due to the heat release from epoxy groups. If small content of diluents are used, these effects on reactivity exotherm are generally minor. Also, diluents containing alcoholic hydroxyl groups accelerate the curing rate of epoxy with amine curing agents. The presence of diluents will decrease the degree of crosslinking of the cured epoxy which increases flexibility of epoxy because nonreactive diluents are relatively mobile, and it reduces tensile strength. The degree of effects depend on the type of diluents which is epoxy's reactive diluent or nonreactive diluent. Generally, reactive diluents have been used more than nonreactive diluents because reactive diluents are chemically linked into the epoxy network. However, reactive diluents also reduce the physical properties because degree of functionality is lower than that of the resin. An example of diluents is polyethylene glycol (PEG) which is one of the common diluents used to modify epoxy systems because it contains many ether groups and having dipole interaction between the PEG chain and ester group in the epoxy network [4].

2.3.5 Conductive particles

The factors of conductive particles that affect the performance of epoxy are type, size, shape, amount, and distribution of conductive particle in the epoxy matrix. Example of conductive particles are nickel (Ni) copper (Cu) and silver (Ag). Nickel and copper do not have good conductivity because these are easily oxidized under high-temperature and humidity conditions resulting in the increase of volume resistivity. However, silver has higher electrical and thermal conductivity than other metal because silver is highly concentrated on the surface's particle which is exposed to around 100ppm of oxygen content in a nitrogen atmosphere without oxidation. So silver is the most popular conductive particle. Size of conductive particle was to be considered. If the micro-sized and nano-sized silver particles are still not connected in the matrix, the volume resistivity would be high. Silver particles has to be added more to interconnect between the conductive particles as network The addition of nano-sized silver colloids increase the relative contribution of contact resistance between the particles which increased the conductivity. Shape of conductive particle also affect the conductivity of adhesive. The flake shape is the most common for conductive particles because silver flakes have large surface area. As a result, more electrical paths than spherical particles would occur, so the flake-shaped particles are appropriate for ICAs. Effect of addition of conductive particles are to increase the modulus, glass transition temperature and dielectric properties such as voltage in the epoxy matrix due to the strong interaction between the conductive particles and the epoxy matrix. However, problems related to the conductive particles in ACP are the oxidation phase separation, aggregation, poor dispersion of particles in the epoxy matrix. Thus surface treatment on particles has to be performed to protect conductive particles to obhtain good adhesion of adhesive [9]. Silver, particles have a thin layer of capping agent on their surface to improve their dispersity, thus adhesive with treated silver had lower resistivity than the ECAs with untreated Ag flake due to interaction between the capping agents and the silver flake surface. Meanwhile, the curing temperature of these ECAs is lower than the capping agent because the capping agent did not decompose due to the high boiling point of a low molecular weight polyethylene glycol. So, the diluents are either dissolved or reacted with the epoxy resin or remained on the Ag flake surface after epoxy resin are cured when adhesive is heated to an onset temperature decomposition of capping agent, as a result, Ag particles are agglomerated in which the particle-particle contact resistance decreased and the viscosity of an ACA paste may increase [10, 11].

The concentration of filler is limited by viscosity and negative effects on some properties. The effect of filler in epoxy depends on the type of filler, particle size, shape, size distribution, concentration, surface chemistry, dispersion characteristics, and compatibility with other components. Particle interactions resulting in aggregates of particles will affect dispersion thus, surface treatments reduce aggregation forces. For particles with large aspect ratios, such as fibrous fillers, and particles with large size are difficult to disperse. In addition, high filler loading makes wetting of the filler more difficult because of the increased viscosities. Thus, the diluents are added in epoxy resin which is the method of lowering the viscosity so that fillers can be added to the epoxy adhesive which affects the reduction in crosslinking density and thermal or chemical properties [2].

Table 2.1 Volume resistivities of metals and various insulation materials [2]

Material	Specific gravity (g/cm^3)	Volume resistivity (Ω•cm)
Silver	10.5	1.6×10^{-6}
Copper	8.9	1.8×10^{-6}
Gold	19.3	2.3×10^{-6}
Aluminum	2.7	2.9×10^{-6}
Unfilled epoxy adhesive	1.1	10^{14} - 10^{15}

2.4 Anisotropic conductive paste

Anisotropic conductive paste (ACP) is a viscous material consisting of conductive particles uniformly dispersed within an adhesive component. A functional material, ACP process produces an anisotropic conductive film through application and drying by the screen-printed process resulting in original print fabics, as shown in Figure 2.4. After the screen printing and drying steps, the original print fabics are used to assemble with other electronic parts, such as a liquid crystal display (LCD), a heat seal connector and a touch panel. Advantages of the ACP process are the benefits of low production costs, fewer steps in the manufacturing process, and reduced production times, as can be seen in Table 2.2.

Table 2.2 Comparison of the characteristics of ACP and ACF [12]

Item	ACP	ACF
Facility	Screen print machine Drier Heat press machine	Preliminary pressure bonding Separator winding unit Heat press machine
Number of steps	(1) Screen printing (2) Drying (deposition) (3) Final pressure bonding	(1) Cutting (2) Pasting (3) Preliminary pressure bonding (4) Separator peeling (5) Final pressure bonding
Storability of film	3 to 6 months	Three days at room temperature after application
Pressure bonding temperature	120 to 160 °C	150 °C or above

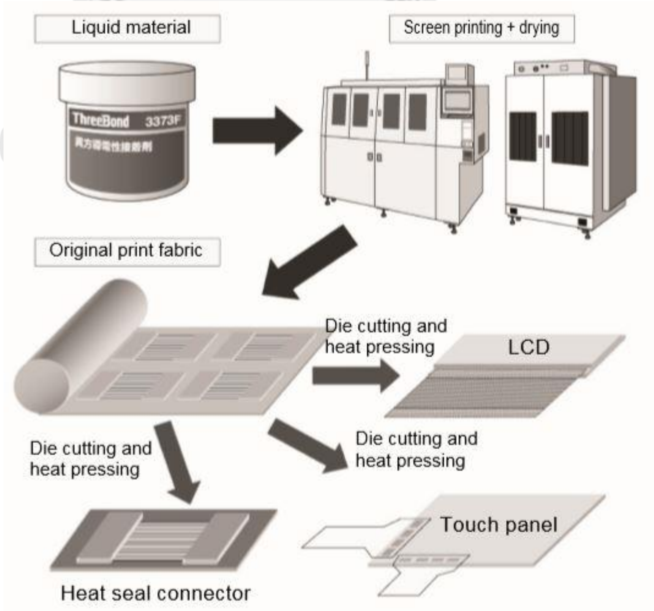


Figure 2.4 Step of ACP process [12]

2.5 Screen printable anisotropic conductive paste

Thick-film circuits are produced primarily by the screen-printing process in which the mesh choices are synthetic fibers such as Dacron (polyester) or Nylon (polyamide). The basic concept in screen-printing is to force a viscous paste through apertures of a stencil screen to deposit a pattern onto a substrate by the squeegee. That is made from a rubber blade. The advantages of the process are cleaner and easier to handle (no spraying or handling of liquids). An important factor in producing thick-film circuits is the rheology of the paste which can explain the flow behavior of the thick-film paste. Thixotropy is the fluid with high viscosity. However, when thixotropic fluid is subjected to shear force, viscosity decreases sharply which can rapidly flow in screen printing. Then, when the fluid is not subjected to shear force the viscosity of the fluid increases again. Also, Other important factors which affect the performance of the screen-printed process are screen tension, screen angle, squeegee speed, squeegee pressure, angle of the squeegee, and snap-off distance [13].

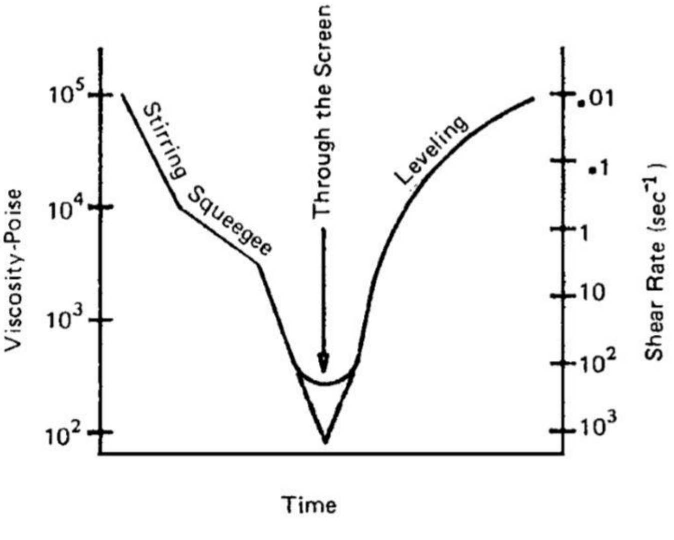


Figure 2.5 The flow changes that occur in the paste during screen-printing process [14]

2.6 Properties of the uncured epoxy system

The viscosity of the epoxy can be used to determine the final viscosity of the formulated system. Some curing agents can have a significant effect on the viscosity. Adding fillers usually increase viscosity of system while diluents can be used to decrease viscosity. Controlling viscosity is an important part of the adhesive process. If the viscosity of the epoxy system cannot flow easily before curing and to entrap air at the interface, the final product would have defects. Therefore, the viscosity of epoxy has to be modify to obtain the optimal value. The addition of fillers such as fibrous fillers could increase viscosity of epoxy more than particulate fillers. Small-sized particle having a large surface area generally but not always increase the viscosity of epoxy. This property is called thixotropy that provides a shear-thinning effect when it has a shear force which the viscosity decrease. Thixotropy behavior of fluid results from the ability of the dispersed particles to come together and form network structures by van der Waals forces between molecules. Thus, low shear forces would slightly affect viscosity due to the breaks down of structure. The surface chemistry of filler is important because of its influence on the rheological behavior. Three types of chemical groups can be formed on the surface of the particle which are

- Isolated hydroxyl
- Hydrogen bonded hydroxyl
- Siloxane

Moreover, wetting is measured by the contact angle in which the adhesive wets the surface of the substrate.

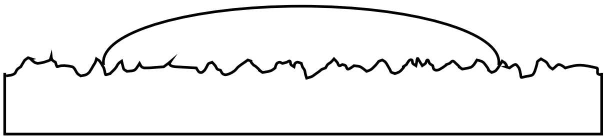


Figure 2.6 Good wetting by an adhesive spreading over a surface

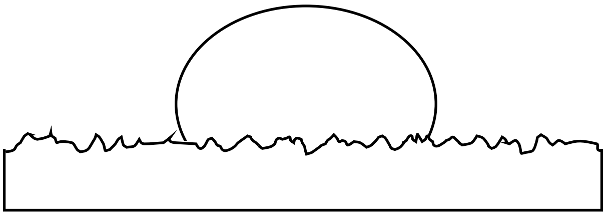


Figure 2.7 Poor wetting by an adhesive spreading over a surface

In the liquid state, the adhesive must “wet” the substrate surface. Wetting can be explained from the adsorption theory of adhesive that adhesion results from molecular contact between two materials and the surface forces are usually van der Waals forces. From Fig2.6. good wetting is the greater contact area between adherend and adhesive. The critical surface tension of various subtrate materials is tabulated in Table 2.4. The surface free energy of the liquid (γ_{LV}) must be less than the critical surface tension of the adherend solid (γ_C) which can be explained by the attribution of the adhesive to interfacial hydrogen bonding, which occurs along the molecular chain to crosslinking which are strongly adsorbed onto oxide and hydroxyl of surfaces that are characteristic of the surface roughness. The poor wetting of epoxy resin is caused by less actual area of contact between the adhesive and adherend and the small air pockets along the interface which lower overall joint strength [4, 15-18].

Table 2.3 Shows the surface tension of several liquids [4]

Adhesive	Surface tension (dyn/cm)
Epoxy resin	47
Fluorinated epoxy resin	33
Epoxy resin + DETA	44
Epoxy resin + DEAPA	33
Silicone	24
Polyolefins	31
Water	72

Table 2.4 Critical surface tension of various substrate materials [4]

Substrate	Critical surface tension (dyn/cm)
Aluminum	~500
Copper	~1000
Glass	~1000
Epoxy	47
Polycarbonate	46
Polyimide	40
Polyethylene	31
Silicone	24
Nylon	46

2.7 Properties of the cured epoxy system

Epoxy polymers are network polymers with three-dimensional molecule which are crosslinked throughout the bulk polymer which relate to properties such as rigidity, heat resistance, strength, and chemical resistance. Generally, the rigid structural adhesive shows some problems such as peel, flexibility, and toughness that can be controlled by the parameters shown in Table 2.5.

Table 2.5 Effect of various formulation parameters on the flexibility of an epoxy adhesive [4]

Increasing parameter	Effect on flexibility
Molecular weight	Generally, increases
Crosslinks density or reactive	Decreases
Chain branching	Generally, increases
Glass transition temperature	Decreases
Filler concentration	Decreases
Plasticizer concentration	Increases

The adhesion properties of epoxy depend on the crosslink density. It is dependent on the number of reactive sites, the molecular distance and chain mobility between functional sites, and the percentage of these sites that react with other molecules. In addition, the crosslinks density defines the rheological and mechanical properties. Moreover, glass transition temperature (T_g) is a thermal property of a polymer that depends on its chemical composition and the degree of crosslinking or molecular interaction. T_g affects bond strength due to the increased of degree of crosslinking. However, flexibility and peel strength at room temperature will be low if the T_g is high.

Table 2.6 Glass transition temperature of the common polymer [4]

Adhesive type	Glass transition temperature, °C
Silicone elastomer	-90
Natural rubber	-70
Neoprene	-50
Polyamide thermoplastic	60
Epoxy	100

CHAPTER III

EXPERIMENTS

3.1 Materials

Epoxy phenol novolac resin (EPN) which is a multifunctional epoxy resin that has aromatic epoxy as the main structure (EEW = 172.7 g/eq.) was obtained from Aditya Birla Chemical (Thailand) Ltd. Poly(propylene glycol) diglycidyl ether (PPGDE) which is a flexible aliphatic epoxy resin (EEW = 455 g/eq.) was obtained from Aditya Birla Chemical (Thailand) Ltd. Carboxyl-terminated butadiene-acrylonitrile (CTBN) which was used as toughener which must be pre-reacted with epoxy mixture by using Triphenylphosphine (TPP) as a catalyst. Poly(ethylene) glycol (PEG) was used as diluent (MW = 400 g/mol.). The amine curing agent is 1,3-phenylenediamine (m-PDA). Silver powder is the conductor in the adhesive. The chemicals were purchased from Sigma-Aldrich chemical company. The chemical structures of the epoxy resins, curing agents, CTBN, PEG, and catalysts are shown in Figure 3.1-3.6.

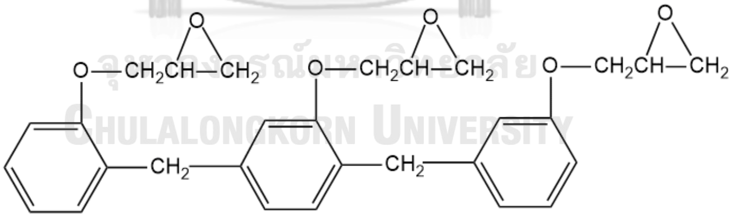


Figure 3.1 Epoxy phenol novolac resin (EPN)

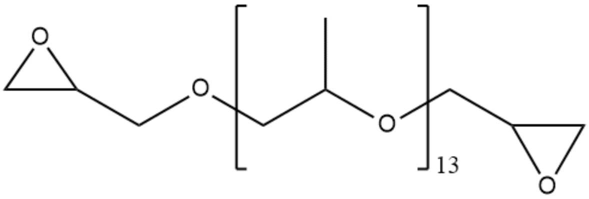
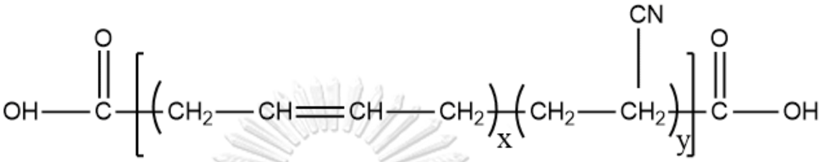


Figure 3.2 Poly(propylene glycol) diglycidyl ether (PPDGE)



$$HO-\overset{\overset{O}{\|}}{C}-\left[\left(CH_2-CH{=}CH-CH_2\right)_x\left(CH_2-\overset{\overset{CN}{|}}{CH_2}\right)_y\right]-\overset{\overset{O}{\|}}{C}-OH$$

Figure 3.3 Carboxyl-terminated butadiene-acrylonitrile (CTBN)

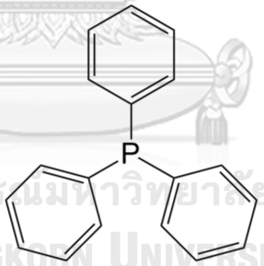


Figure 3.4 Triphenylphosphine (TPP)

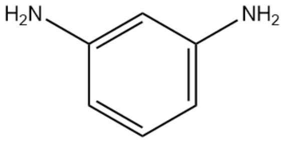


Figure 3.5 1,3-Phenylenediamine (m-PDA)

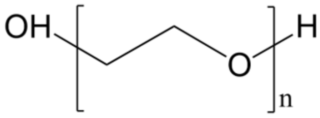


Figure 3.6 Poly(ethylene) glycol (PEG)

3.2 Sample preparation

3.2.1 Surface preparation of copper substrates

In this research, copper alloys containing over 95% of copper are used to study the adhesion between epoxy adhesive and copper alloys. The surface preparation of copper alloys was performed by chemical treatment followed ASTM D2651 standard. In the first step, copper was immersed for 30 seconds at room temperature in the following solution by volume 30 parts of nitric acid to 70 parts of water. In the second step, Copper alloy was rinsed on running cold tap water. In the third step, the copper alloy was immersed for 2 to 3 minutes at 93 to 102 °C in the following solution: 31.6 g/l sodium chloride, 10.5 g/l trisodium phosphate, 5.3 g/l sodium hydroxide. In the fourth step, Copper alloy was rinsed thoroughly in running water until the pHD of the water was neutral. Finally, the copper alloy was dried. All prepared samples are kept in a desiccator before using, for preventing corrosion on samples.

3.2.2 Synthesis of silver particles

In the first step, silver nitrate ($AgNO_3$) 1 M 10 ml, ascorbic acid ($C_6H_8O_6$) 1 M 2 ml and polyethylene glycol 0.1 wt% 200 ml was mixed for 2 hours at room temperature in the dark. The silver particle was them filtered with filter paper by a vacuum pump. Finally, silver particles was dried in a vacuum oven for 30 minutes at 60 °C. The silver particles were kept in a desiccator to prevent silver oxide on the samples.

3.2.3 Pre-reaction of epoxy-CTBN adhesive

In the first step, the EPN was mixed with PPGDE at a weight ratio of 1:1 using a magnetic stirrer at room temperature until the mixture becomes homogeneous. In the second step, 5 phr of CTBN was mixed with the epoxy mixture at room temperature until it was homogeneous. In the third step, 1 phr of triphenylphosphine (TPP) which is a catalyst for pre-reaction was added into the mixture. Then it was heated to 190 °C and continually mixed for 2 hours. In the final step, the epoxy-CTBN was rapidly cooled down to stop the pre-reaction and it was kept at temperature of -40°C for further use.

3.2.4 Preparation of anisotropic conductive paste

In the first step, the epoxy-CTBN was mixed with the silver particles at 60 °C until it was homogeneous. In the second step, the polyethylene glycol (PEG) was added and continuously mixed for 15 minutes at 60 °C. In the final step, the m-PDA at a stoichiometric molar balance of hydrogen of amine to epoxide ring of 1:1 was added and continuously mixed at 60 °C for 15 minutes.

The content of silver particles affected volume resistivity of the ACP. According to the company’s requirement, the volume resistivity of ACP must be less than 1 Ω·cm. The content of silver particle was varied from 1 – 10 phr as shown in Table 3.1. After that, the PEG content which was used to adjust the viscosity of ACP was varied from 0 – 5 phr as shown in Table 3.2.

Table 3.1 Formulation of ACP with various content of silver particles

Formula	EPN	PPGDE	m-PDA*	CTBN	TPP	Commercial Silver Particles	Synthesized Silver Particles
	(wt%)	(wt%)	phr*	phr	phr	phr	phr
1AgC	50	50	12	5	1	1	-
3AgC	50	50	12	5	1	3	-
5AgC	50	50	12	5	1	5	-
10AgC	50	50	12	5	1	10	-
1AgS	50	50	12	5	1	-	1
3AgS	50	50	12	5	1	-	3
5AgS	50	50	12	5	1	-	5
10AgS	50	50	12	5	1	-	10

*Amount of m-PDA was calculated from EEW which was shown in Appendix A.

Table 3.2 Formulation of ACP with various content of PEG

Formula	EPN	PPGDE	m-PDA*	CTBN	TPP	Commercial Silver Particles	Synthesized Silver Particles	PEG
	(wt%)	(wt%)	phr*	phr	phr	phr	phr	phr
1AgCPEG0	50	50	12	5	1	1	-	0
1AgCPEG1	50	50	12	5	1	1	-	1
1AgCPEG3	50	50	12	5	1	1	-	3
1AgCPEG5	50	50	12	5	1	1	-	5
3AgSPEG0	50	50	12	5	1	-	3	0
3AgSPEG1	50	50	12	5	1	-	3	1
3AgSPEG3	50	50	12	5	1	-	3	3
3AgSPEG5	50	50	12	5	1	-	3	5

3.3 Characterization

3.3.1 Differential scanning calorimetry (DSC)

Differential scanning calorimetry is the techniques to evaluate the glass transition, melting, and boiling temperatures as well as, curing temperature and time, heats of reactions, specific heat capacity, rate and degree of cure, and reaction kinetics. Both non-isothermal and isothermal temperature scanning is observed by using differential scanning calorimeter (DSC, model DSC1 module, Mettler-Toledo, Thailand). Temperature range is performed from 25°C to 250°C at a heating rate of 10°C/min for non-isothermal to obtain onset temperature (T_o), the highest reactions at peak temperature (T_p), and heat of reaction (ΔH). Moreover, the temperature range is scanning from 0°C to 250°C at a heating rate of 10°C/min to obtain a glass transition temperature (T_g). The isothermal scanning is explored at a temperature of 157°C. All measurements are performed under nitrogen atmosphere.

3.3.2 Thermogravimetric analyzer (TGA)

The thermogravimetric analyzer is the measurement of a change in weight loss when temperature is ramped. For anisotropic conductive adhesive, TGA has used to determine the conductive particle loadings, thermal stability, and degradation of a cured epoxy matrix due to decomposition temperature on a particle which is the oxidation stability of conductive particle. The thermal stability of epoxy adhesive is analyzed by a thermogravimetric analyzer (model SDT Q600 manufactured by TA instruments). The samples were heated from 25°C to 700°C at a heating rate of 10°C/min under a nitrogen atmosphere.

3.3.3 Rheometer

The rheometry is the measurement of the viscosity and flow properties of fluids. It is widely used to test the visco-elastic properties of adhesive. The rheometer can be used to evaluate yield stress, kinetic properties, complex viscosity, and modulus. The adhesive sample is performed on the rheometer (model AR-G2 manufactured by TA instruments). A 25 mm diameter parallel plate is used, and the instrument settings are as follows: viscosity is measured as a shear rate ramp mode, a gap of 1,000 μm, at temperature 25±2°C, and a varying shear rate of 0.0005 – 50 s^{-1}.

3.3.4 Fourier transform infrared spectroscopy (FTIR)

Infrared absorption spectroscopy is the measurement of the major functional groups and a particular compound in the anisotropic conductive adhesive. FTIR can be used to evaluate the curing reaction of epoxy resin, optimize the ratio of anisotropic conductive adhesive and crosslinking in reactions. Besides, the surface properties of conductive particles of anisotropic conductive adhesive can also be evaluated such as the interaction between epoxy and conductive particles. The curing reaction is further confirmed by Fourier transform infrared spectroscopy (model Spectrum GX manufactured by PerkinElmer, Transmission mode). FTIR spectra of the uncured epoxy, CTBN rubber, epoxy-CTBN blend and cured epoxy are measured in a spectral range of 4,000 - 200 cm^{-1} with 128 scans at a resolution of 4 cm^{-1}. All samples are placed on KBr plates.

3.3.5 X-Ray diffraction (XRD)

X-ray diffraction technique is the measurement of the chemical composition and crystal structure of a particle. It can characterize the geometry or shape of crystals including nanoparticles such as silver nanowires and silver power.

3.3.6 Scanning electron microscopy (SEM)

Scanning Electron Microscopy can be used to evaluate the size, distribution, and surface of the particle. The particle in the adhesive is explored by the scanning electron microscope with a Hitachi S3400 instrument.

3.3.7 Electrical resistance

Electrical conductivity is characterized by measuring the volume resistivity of cured ACP specimens according to ASTM D2739. The electrical contact resistance of the ACP joints is measured by a four-point probe method, in which the currents are varied by a power supplier, a Keithley 6221 DC and AC current source, and the voltage of the interconnect joints are measured by a Keithley 2182A nanovoltmeter. The thickness of the cured ACP is 30 µm.

3.3.8 Peel strength

Peel strength is always tested because it is easy to measure. Peel strength can be used to indicate the adhesion of anisotropic conductive paste. The 90° peel strength (ASTM D1876) is measured by a universal testing machine (Instron, model 5567, Thailand). The epoxy mixture was applied on the surface of copper substrates with controlled adhesive thickness about 30 µm and then laminated with the polyimide film. Finally, the sample was cured in an oven at curing temperature of 157 °C for 17 minutes. Five specimens (5 mm width of a peel test specimen) of the adhesive joints between copper substrates and polyimide film are evaluated with a peel rate of 50 mm/min. The peel strength is the average peel force divided by specimen width.

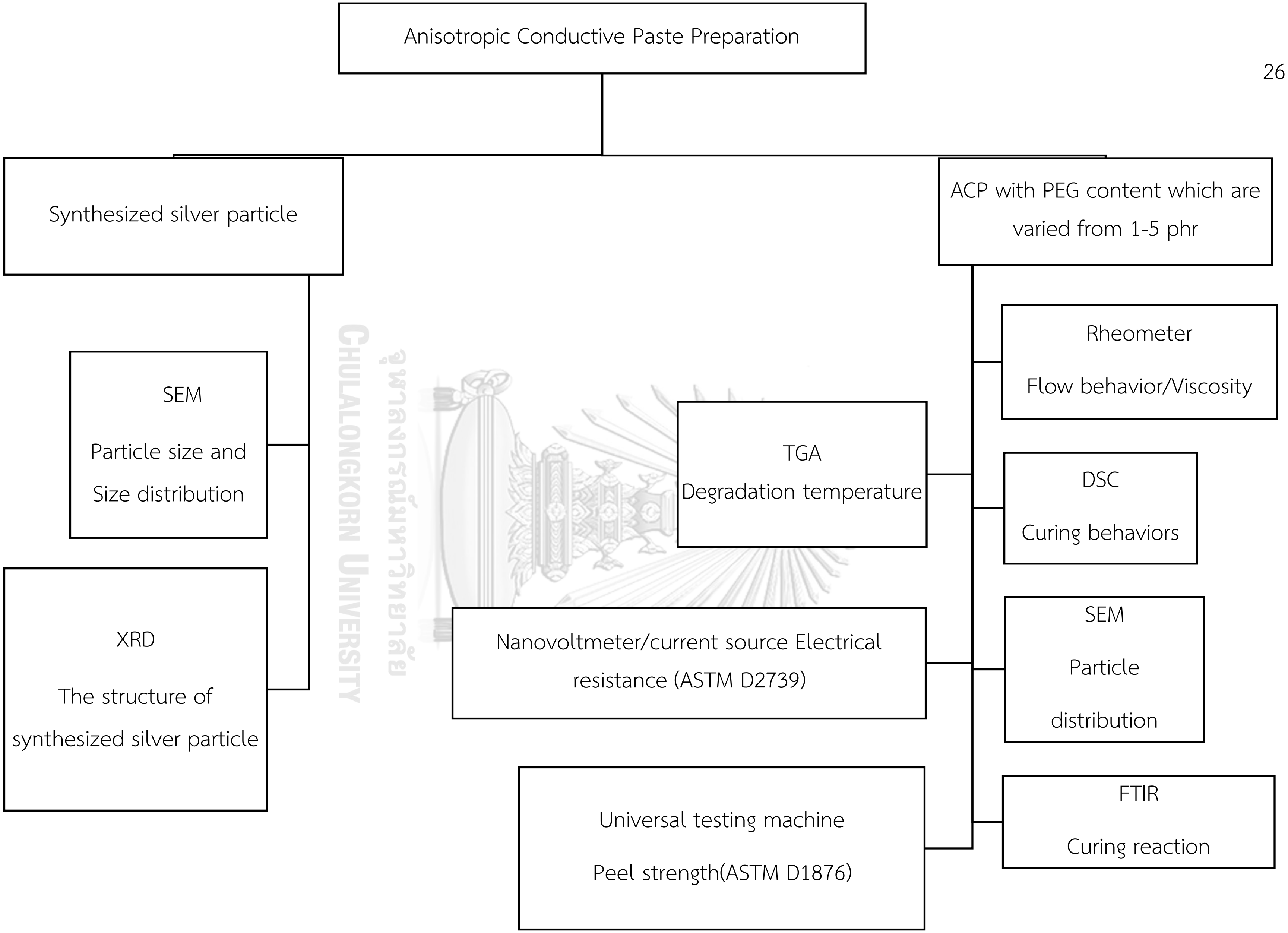


Figure 3.7 Methodology research

CHAPTER IV

RESULTS AND DISCUSSION

4.1 The properties of silver particle

In this work, the silver particles were synthesized via the reduction reaction between the silver solution and ascorbic acid. The X-ray diffraction (XRD) technique was used to analyze the structure of the synthesized silver particle. The appearance and element composition of silver particles were observed by scanning electron microscope with energy dispersive X-ray analysis (SEM-EDX). The XRD pattern of the synthesized silver particle was shown in Figure 4.1. The diffraction peaks at 2θ were observed at 38.14°, 44.37°, 64.58° and 77.50° which correspond to (111), (200), (220), and (311) plane of silver metal [19]. It was confirmed that the silver particles were successfully synthesized.

Figure 4.2 shows the appearance of commercial and synthesized silver particles. It was found that the diameters of commercial and synthesized silver particles were around 1.03 μm and 1.26 μm, respectively. Moreover, the element composition of commercial and synthesized silver particles obtained from EDX analysis was summarized in Table 4.1. Synthesized silver particles contained more oxygen element than the commercial silver particles. The more oxygen element can imply the more silver oxide in the silver particle [20, 21]. Therefore, the electrical conductivity of synthesized silver particles might be lower than that of commercial silver particles. The commercial and synthesized silver particles were used to prepare anisotropic conductive paste (ACP) and evaluated the suitable content of silver particles.

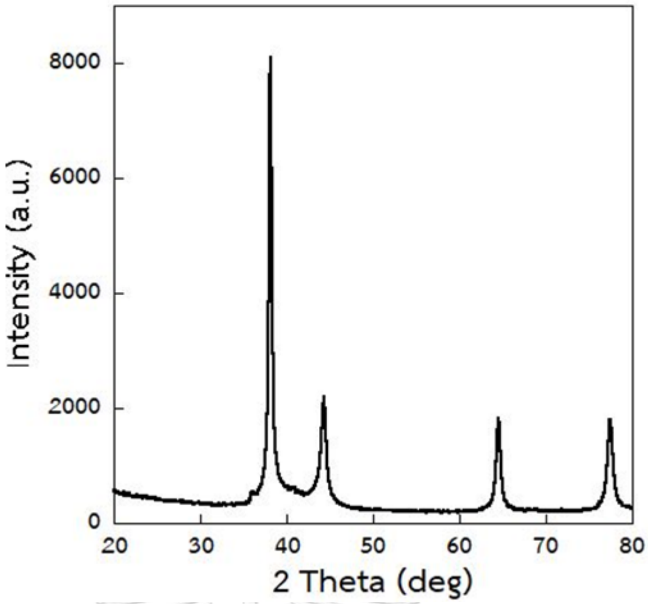
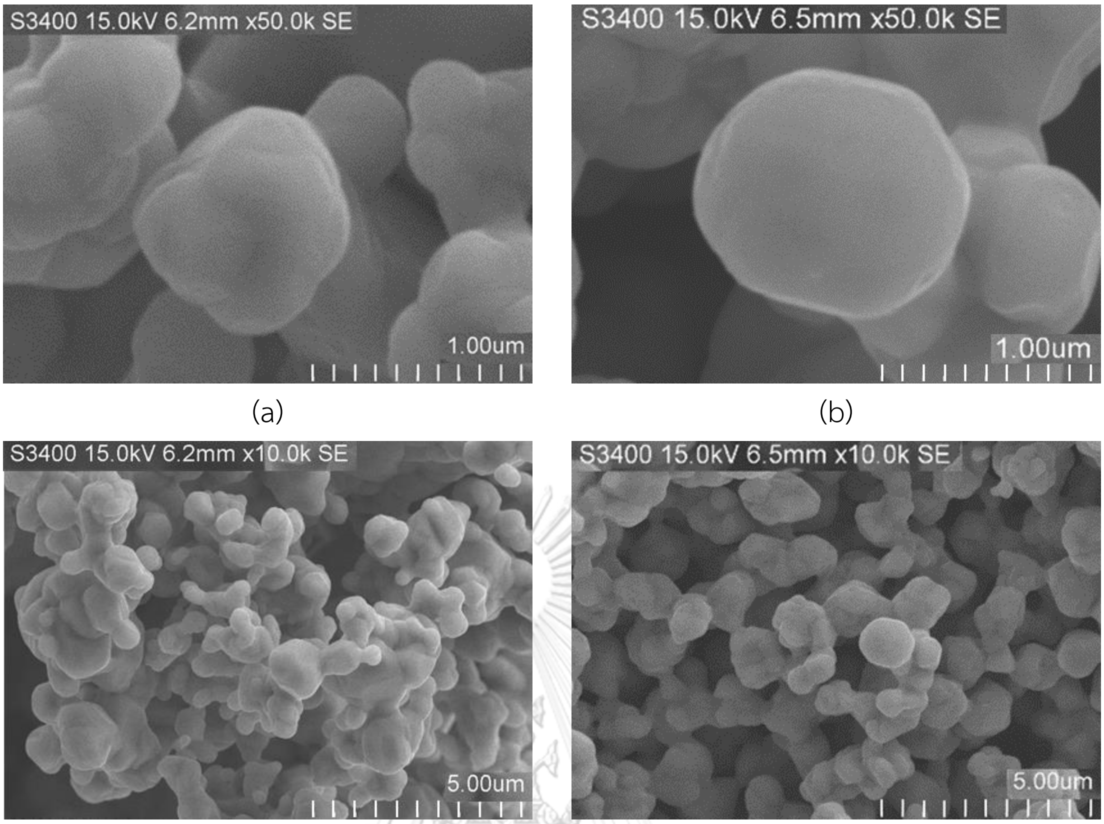


Figure 4.1 X-ray pattern of the synthesized silver particle

Table 4.1 Element composition of commercial and synthesized silver particles

Element	Commercial silver particle	Synthesized silver particle
Oxygen (wt%)	16.27	25.65
Silver (wt%)	83.73	74.35



(a) (b) (c) (d)

Figure 4.2 SEM micrographs of the silver particles with magnification of 50k and 10k (a), (c) commercial silver particles (b), (d) synthesized silver particles

4.2 Electrical properties of ACP

The electrical properties of the ACP were evaluated as a volume resistivity in the thickness direction of the ACP. A four-point probe method following ASTM D2739, as shown in Figure 4.3, was used. The samples were prepared by applying the ACP between two copper substrates and was cured at 157 °C for 17 minutes. The thickness of ACP was controlled at around 30 µm. According to the literature regarding conductive adhesive [6, 22, 23], silver particles was more agglomerated in the thickness direction (z-axis) than surface direction (x and y-axis).

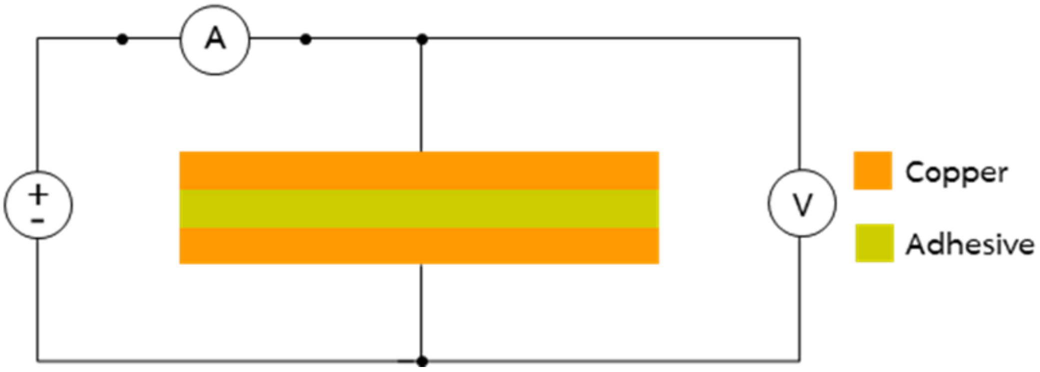


Figure 4.3 Test method for volume resistivity measurement of ACP

The volume resistivity of ACP with various amounts of the silver particles was demonstrated in Tables 4.2 and 4.3. It was found that the volume resistivity decreased with an increase in the content of silver particles. According to the company's requirement, the volume resistivity of ACP must be less than 1 Ω·cm. Therefore, the minimum contents of silver particles were selected at 1 phr of commercial and 3 phr of synthesized silver particles, respectively. However, the excess content of conductive particles causes the anisotropic conductive adhesive to become isotropic conductive adhesive [6].

Figure 4.4 shows the SEM micrographs of ACP containing 1 phr of the commercial and synthesized silver particle, as well as 3 phr of synthesized silver particles. It was found that the silver particle distribution of commercial (Figure 4.4 (a)) and synthesized (Figure 4.4 (b)) particles were not different at 1 phr, whereas the 3 phr of the synthesized silver particle (Figure 4.4 (c)) exhibited more agglomeration of silver particles. Therefore, the distribution of silver particles in ACP did not affect the volume resistivity of ACP.

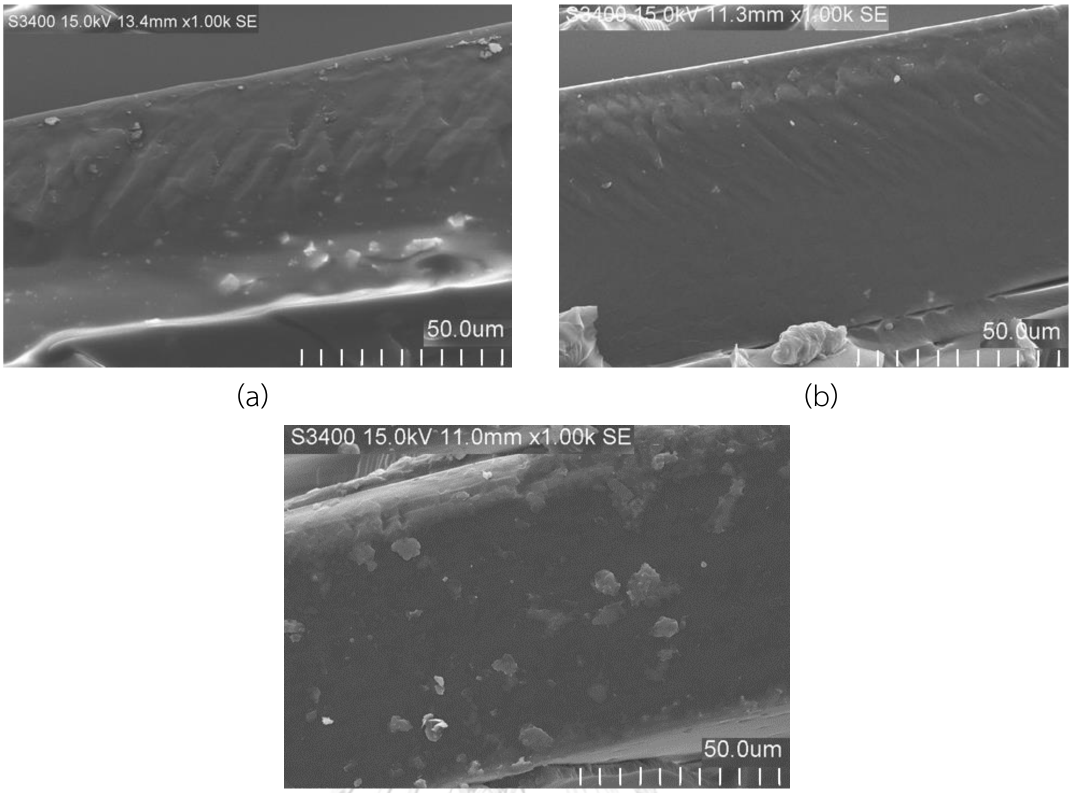
Table 4.2 Measured volume resistivity of ACP with commercial silver particle systems

Silver particle content (phr)	**1 phr**	**3 phr**	**5 phr**	**10 phr**
Volume resistivity (Ω•cm)	0.60±0.081	0.08±0.006	0.08±0.003	0.08±0.002

Table 4.3 Measured volume resistivity of ACP with synthesized silver particle systems

Silver particle content (phr)	**1 phr**	**3 phr**	**5 phr**	**10 phr**
Volume resistivity (Ω•cm)	1.11±0.039	0.84±0.087	0.15±0.013	0.03±0.001

*The resistance of ACP was less than 1 Ω•cm, which passed the company's requirement.



(a) (b)

(c)

Figure 4.4 SEM micrographs of ACP with silver particle (a) 1 phr commercial silver particles (b) 1 phr synthesized silver particles and (c) 3 phr synthesized silver particles

At the same content of silver particle, the volume resistivity of ACP contained commercial silver particle was lower than that of ACP contained synthesized silver particles due to low silver oxide content, as described in section 4.1. In general, the metal oxide has higher electrical resistivity than the pure metal. Consequently, the content of synthesized silver particles was more than that of commercial silver particles to achieve a similar volume resistivity.

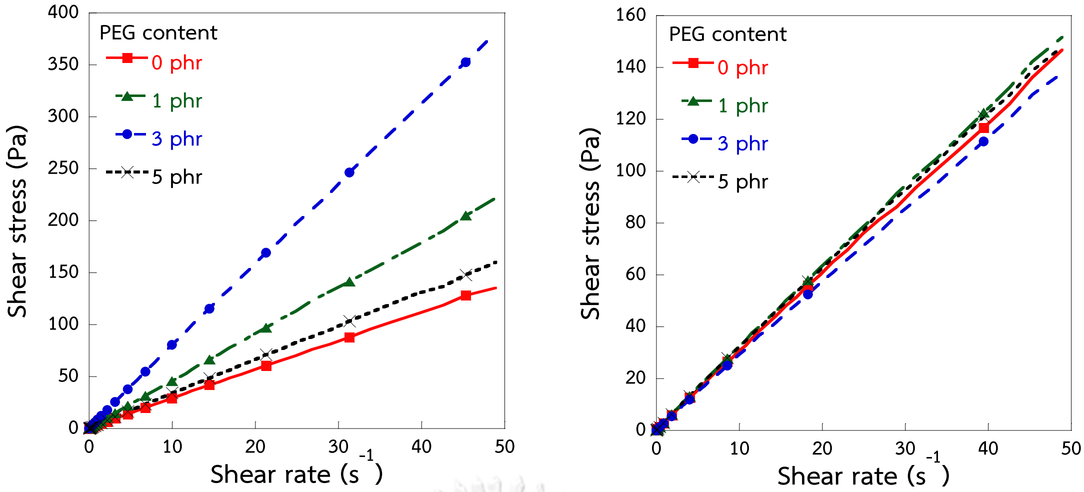
4.3 Effect of PEG content on the properties of ACP

In this section, the PEG content was varied to suitably adjust the viscosity of ACP for the screen-printing process. The ACP system with 1 phr of commercial silver particles and 3 phr of synthesized silver particles were chosen according to the company's requirement which described in the previous section. However, the content of PEG might affect the properties of ACP. Thus, flow behavior, pot-life, cure behavior, cure kinetics, mechanical properties, and thermal stability of the ACP were investigated.

4.3.1 Flow behavior of ACP

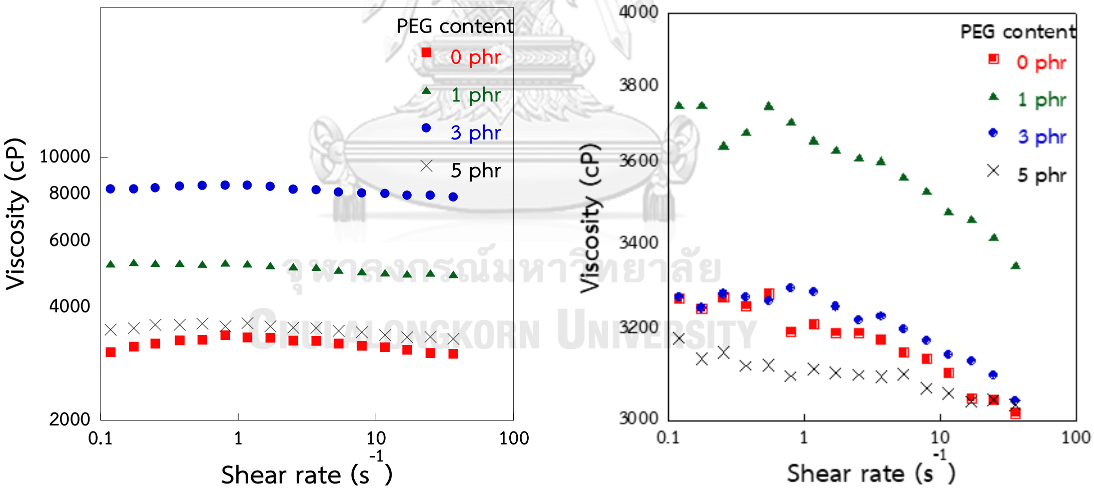
The flow behavior of ACP is an important factor for the screen printing process. The rheological properties such as shear stress and viscosities of ACP with various PEG contents were measured by using the parallel plate rheometer at various shear rates. Figure 4.5 shows that the shear stress was linearly correlated to shear rate for every ACP samples, showing that the flow behavior of the ACP was a Newtonian fluid at the tested condition. The shear rate of the screen-printing process in this work was in the range of 0.1 - 0.2 s^{-1} in which the flow behavior of ACP was Newtonian fluid.

Figure 4.6 shows that the viscosity of the ACP system at various PEG content remained constant at the shear rate range of 0.0005 – 50 s^{-1}. The viscosity of the ACP system with 1 phr commercial silver particles and 3 phr synthesized silver particles with 1 phr PEG were increased from the ACP system without PEG. At 3 phr of PEG, the viscosity of the ACP system with 1 phr commercial silver particles increased while that of the ACP system with 3 phr synthesized silver particles decreased. At 5 phr of PEG, the viscosity of both the ACP system decreased. It might be due to a small amount of PEG having hydrogen bonds between the hydroxyl groups of PEG and ether oxygens of epoxy which increase the viscosity. However, high content of PEG decreased the viscosity of ACP because PEG acted as a diluent that adds free volume between molecules of polymer which increase the mobility of network chain [3].



(a) (b)

Figure 4.5 Relationship between shear stress and a shear rate of ACP with silver particle by varying PEG 0, 1, 3 and 5 phr (a) 1 phr commercial silver particles and (b) 3 phr synthesized silver particles



(a) (b)

Figure 4.6 Viscosity behavior as a function of shear rate (0.0005 – 50 s^{-1}) of ACP with silver particle by varying PEG 0, 1, 3 and 5 phr (a) 1 phr commercial silver particles and (b) 3 phr synthesized silver particles

4.3.2 Pot-life time

Pot life is defined as the amount of time before the viscosity of ACP changes substantially viz., an initial viscosity is doubled, for lower viscosity products at room temperature. The amount of time the ACP remains low enough viscosity in which it can still be easily applied to screen printing techniques. The viscosity of the ACP systems with various PEG contents was studied under a constant shear rate of 0.1 s^{-1} for 2 hours, as shown in Figure 4.7. When the time passed by, it was found that the viscosity of the ACP system by all content of PEG significantly increased due to the curing reaction of ACP at room temperature. The presence of PEG could increase the crosslink density due to hydrogen bonding between the hydroxyl groups of PEG and the ether oxygens of the ACP system. This inceases the crosslink density of the ACP and decreases the mobility of the network chain [24].

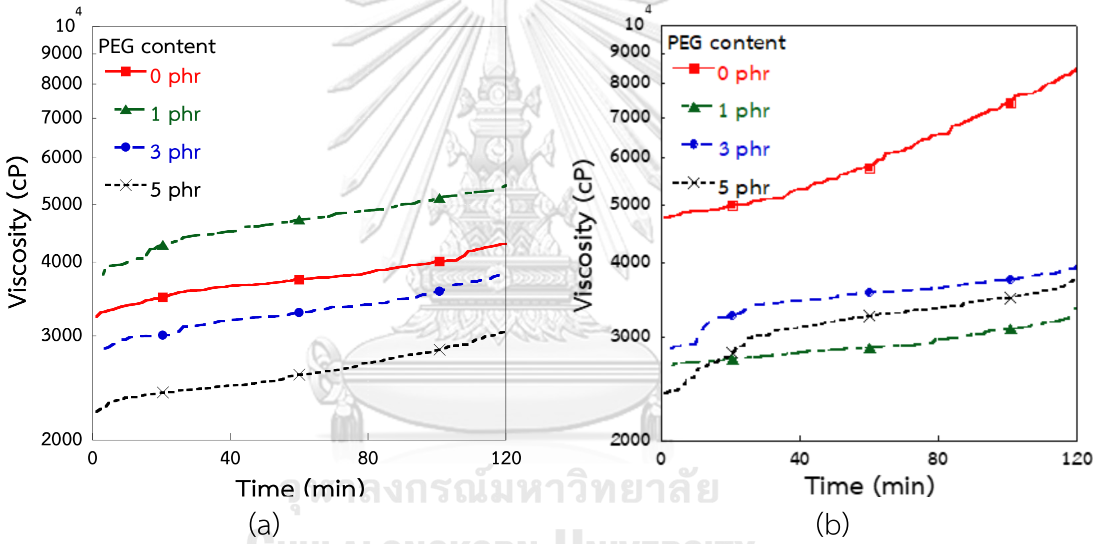


Figure 4.7 Viscosity profile of ACP with silver particle by varying PEG 0, 1, 3 and 5 phr at a constant shear rate of 0.1 s^{-1} for 2 hours (a) 1 phr commercial silver particles and (b) 3 phr synthesized silver particles

The ACP system with 1 phr commercial silver particles at 3 phr of PEG was selected to study pot-life time at room temperature under a constant shear rate of 0.1 s^{-1} for 8 hours, as shown in Figure 4.8. This measurement was studied to obtain the working time of screen printable ACP from the viscosity of ACP to increase to double values. The initial viscosity transformed to more viscous which indicates that the cross-linking reaction between the aromatic diamine curing agent and epoxies gradually proceeded at ambient condition, hydrogen bonding between the hydroxyl groups of PEG and the ether oxygens of the ACP system. That increases the crosslink density of the adhesive. As a result, the initial viscosity was about 2,722 to 5,507 cP, this one-part ACP had a pot-life of 3 hours and 3 minutes at room temperature.

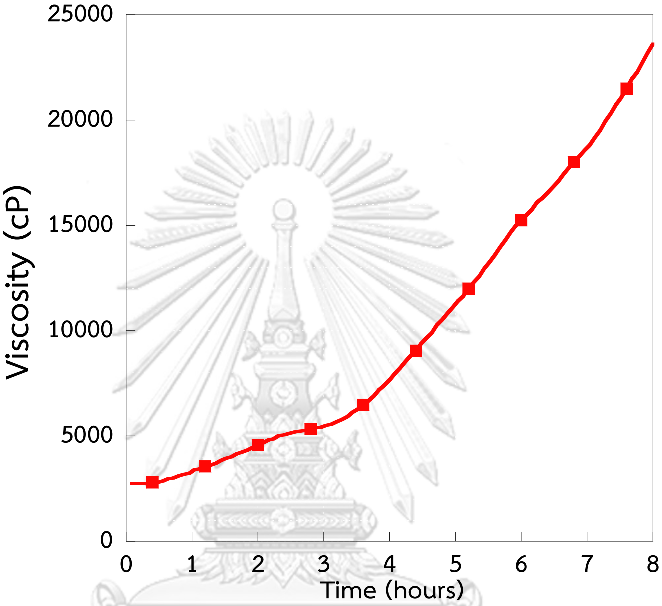


Figure 4.8 Viscosity profile of ACP with 1 phr commercial silver particle and 3 phr of PEG at a constant shear rate of 0.1 s^{-1} for 8 hours

4.3.3 Curing behavior of ACP

The curing behaviors of ACP with synthesized silver particles with varying PEG 0, 1, 3 and 5 phr were investigated by non-isothermal DSC using a heating rate of 10 °C/min to raise temperature from 25 °C to 250 °C. Figure 4.9 shows the initial curing reactions at onset temperature (T_o) of ACP with commercial silver particle by varying PEG 0, 1, 3 and 5 phr were 105.53 °C, 103.27 °C, 108.20 °C and 106.96 °C, respectively and those of synthesized silver particle by varying PEG 0, 1, 3 and 5 phr were 113.05 °C, 109.04 °C, 111.70 °C and 108.12 °C, respectively. The highest reactions at peak temperature (T_p) of ACP with commercial silver particle by varying PEG 0, 1, 3 and 5 phr were 155.32 °C, 155.61 °C, 155.32 °C and 157.82 °C, respectively and those of synthesized silver particle by varying PEG 0, 1, 3 and 5 phr were 161.49 °C, 156.97 °C, 156.82 °C and 154.82 °C, respectively. The heat of reaction (ΔH) of ACP with commercial silver particle by varying PEG 0, 1, 3 and 5 phr were 240.64 J/g, 249.90 J/g, 229.09 J/g, and 228.01 J/g, respectively and those of synthesized silver particle by varying PEG 0, 1, 3 and 5 phr were 274.95 J/g, 248.28 J/g, 210.46 J/g, and 214.19 J/g, respectively. Moreover, the DSC thermograms with temperature scanning from 0 °C to 160 °C at a heating rate of 10 °C/min reported glass transition temperature (T_g) of ACP with silver particles after the curing process as shown in Figure 4.10. T_g of ACP with commercial silver particle by varying PEG 0, 1, 3 and 5 phr were 115.21 °C, 121.09 °C, 119.92 °C and 109.30 °C, respectively and those of synthesized silver particle by varying PEG 0, 1, 3 and 5 phr were 118.54 °C, 135.40 °C, 117.34 °C and 110.14 °C, respectively.

After adding 1 phr PEG in ACP with a commercial silver particle, the heat of reaction increased because PEG can act as the catalyst of crosslink reaction in epoxy system. Moreover, the glass transition temperature tended to increase due to from high crosslink reaction resulting in high crosslink density. However, adding 3 and 5 phr PEG in ACP with the commercial silver particle, the heat of reaction decreases because PEG prevents the reaction in which PEG increases the flexible chain in the system and the glass transition temperature tends to decrease.

For ACP with a synthesized silver particle containing 1 phr PEG, it was found the heat of reaction decreased because of epoxy-CTBN content to decrease. The glass transition temperature increase because PEG can act as a catalyst. However, adding 3 and 5 phr PEG in ACP with synthesized silver particle, the heat of reaction decreased because PEG prevents the crosslink reaction by increasing the flexible chain in the system and resulting in the decrease of glass transition temperature [3].

Table 4.4 Curing data obtained from thermal curves of ACP with 1 phr commercial silver particles by various PEG content

PEG content (phr)	T_0 (°C)	T_p (°C)	T_g (°C)	ΔH (J/g)	**Time curing at 157 °C (min)**
0 phr	105.53	155.32	115.21	240.64	17.43
1 phr	103.27	155.61	121.09	249.90	20.85
3 phr	108.20	155.32	119.92	229.09	20.51
5 phr	106.96	157.82	109.30	228.01	23.35

Table 4.5 Curing data obtained from thermal curves of ACP with 3 phr synthesized silver particles by various PEG content

PEG content (phr)	T_0 (°C)	T_p (°C)	T_g (°C)	ΔH (J/g)	**Time curing at 157 °C (min)**
0 phr	113.05	161.49	118.54	274.95	13.73
1 phr	109.04	156.97	135.40	248.28	12.77
3 phr	111.70	156.82	117.34	210.46	15.63
5 phr	108.12	154.82	110.14	214.19	20.79

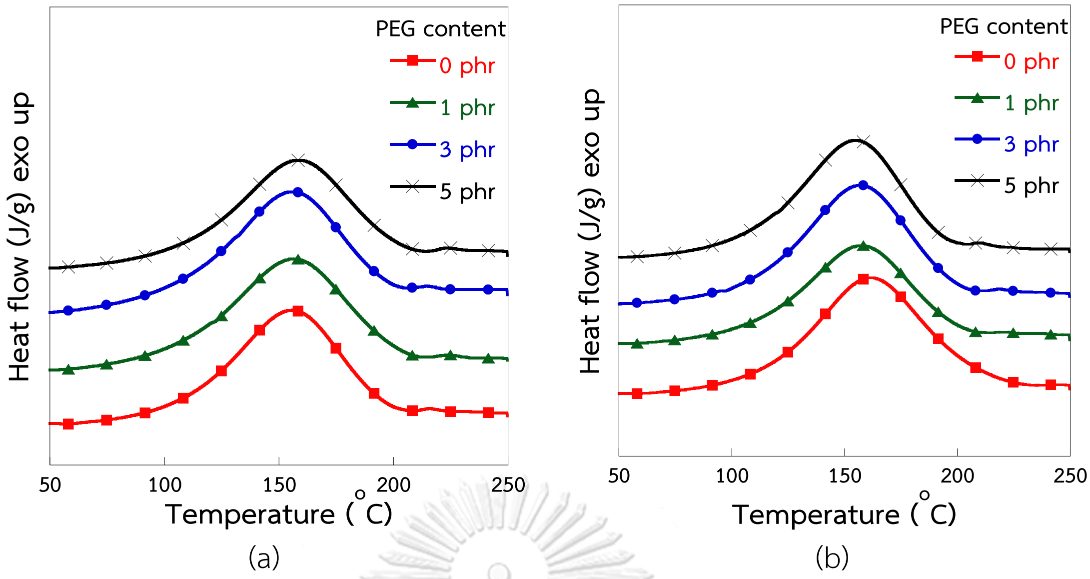


Figure 4.9 Non-isothermal DSC curves of ACP with silver particle by varying PEG 0, 1, 3 and 5 phr (a) 1 phr commercial silver particles and (b) 3 phr synthesized silver particles

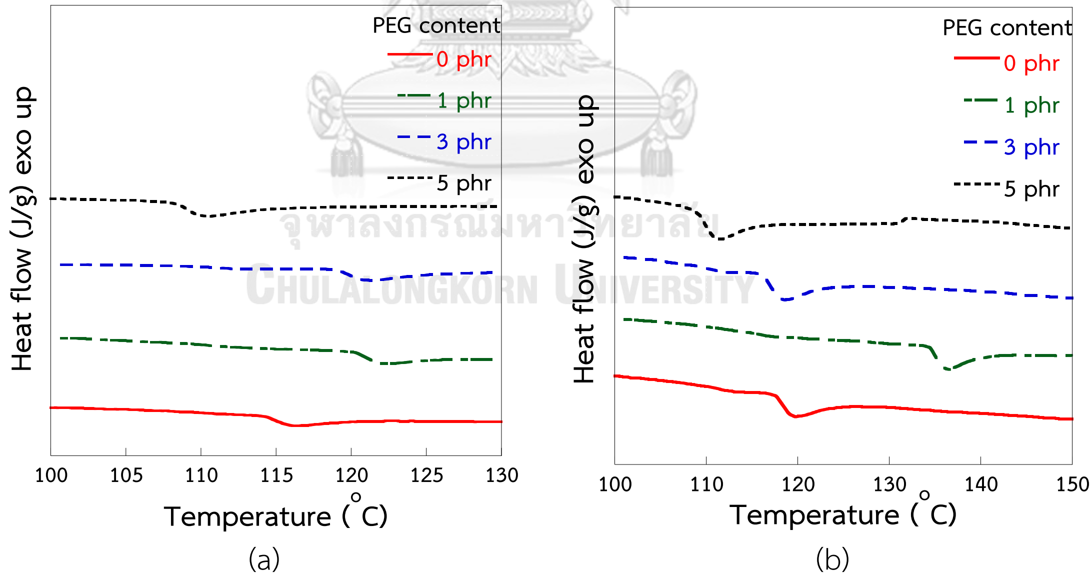
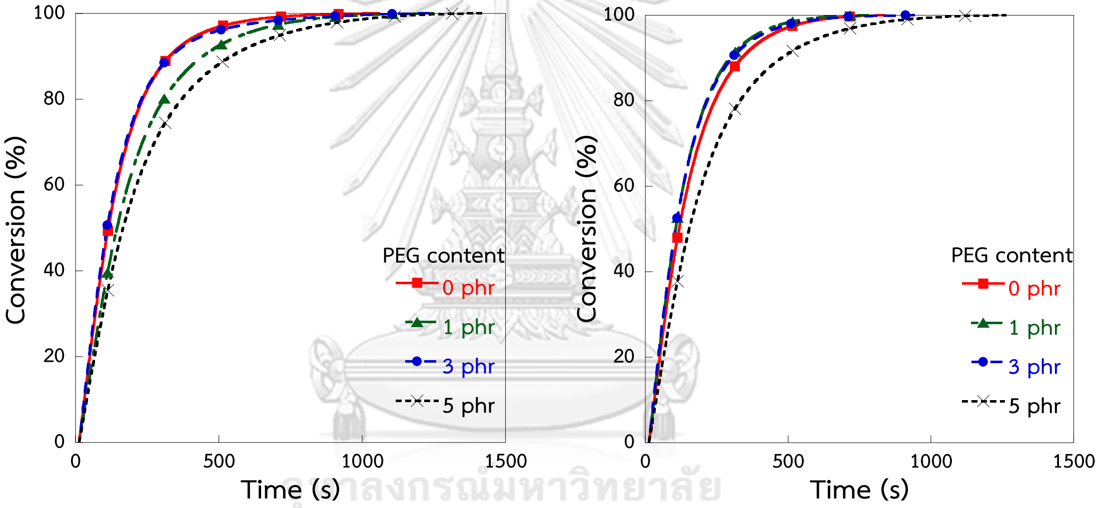


Figure 4.10 Glass transition temperature of ACP with silver particle by varying PEG 0, 1, 3 and 5 phr (a) 1 phr commercial silver particles and (b) 3 phr synthesized silver particles

4.3.4 Cure kinetics

The curing time of these ACP with silver particle systems was investigated by isothermal DSC at a curing temperature of 157 °C, as shown in Figure 4.11 and Tables 4.4–4.5. At 100% conversion (degree of cure of 1), the curing times of the systems with 0, 1, 3, and 5 phr PEG in ACP with the commercial silver particle were 17.43 min, 20.85 min, 20.51 min, and 23.35 min, respectively. The curing times of the systems with 0, 1, 3, and 5 phr PEG with the synthesized silver particle were 13.73 min, 12.77 min, 15.63 min, and 20.79 min, respectively. When the content of PEG increased, the curing time increases, as expected.



(a) (b)

Figure 4.11 Isothermal DSC profiles of ACP with silver particle by varying PEG 0, 1, 3 and 5 phr at 157 °C (a) 1 phr commercial silver particles and (b) 3 phr synthesized silver particles

The reaction rate of ACP with commercial silver particle and synthesized silver particle by varying PEG 0, 1, 3, and 5 phr was found that the addition of PEG into the ACP system decreased the reaction rate because PEG prevented reaction of ACP system.

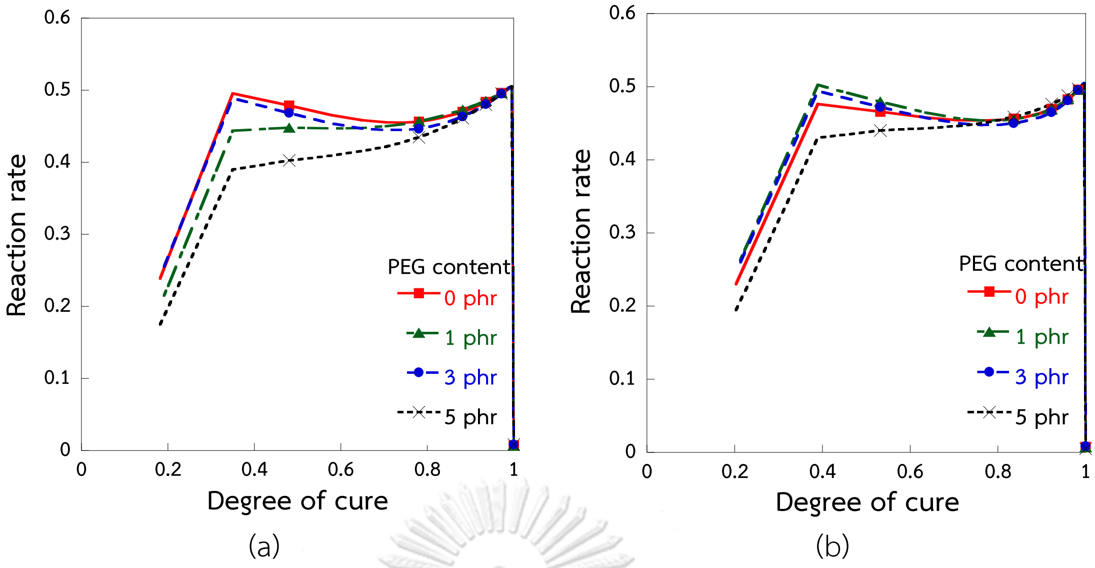


Figure 4.12 The reaction rate of ACP with silver particle by varying PEG 0, 1, 3 and 5 phr at 157 °C (a) 1 phr commercial silver particles and (b) 3 phr synthesized silver particles

4.3.5 Mechanical properties of ACP

The peel strength of ACP with silver particle by varying PEG 0, 1, 3 and 5 phr was obtained from the highest peel strength, as shown in Figure 4.13. The highest average peel strengths of ACP with commercial silver particle and synthesized silver particle were found at PEG content of 3 phr (1.358 N/mm) and 1 phr (0.558 N/mm), respectively. Because the interactions between the hydroxyl groups of PEG and the ether oxygens of the ACP system have an interaction force between molecular or surface energy. That effect can improve the adhesion between ACP and copper substrates. However, excessive PEG content could decrease peel strength because PEG chain increased steric hindrance resulting in obstructing the curing reaction. Yet, the results conformed to that the values of the heat of reaction and the glass transition temperature decreased. The peel strength of ACP with 3 phr synthesized silver particle was lower than that with 1 phr commercial silver particle because more content of silver increases the contact area of silver with copper but surface energy of metal decrease the adhesion between ACP and copper [3].

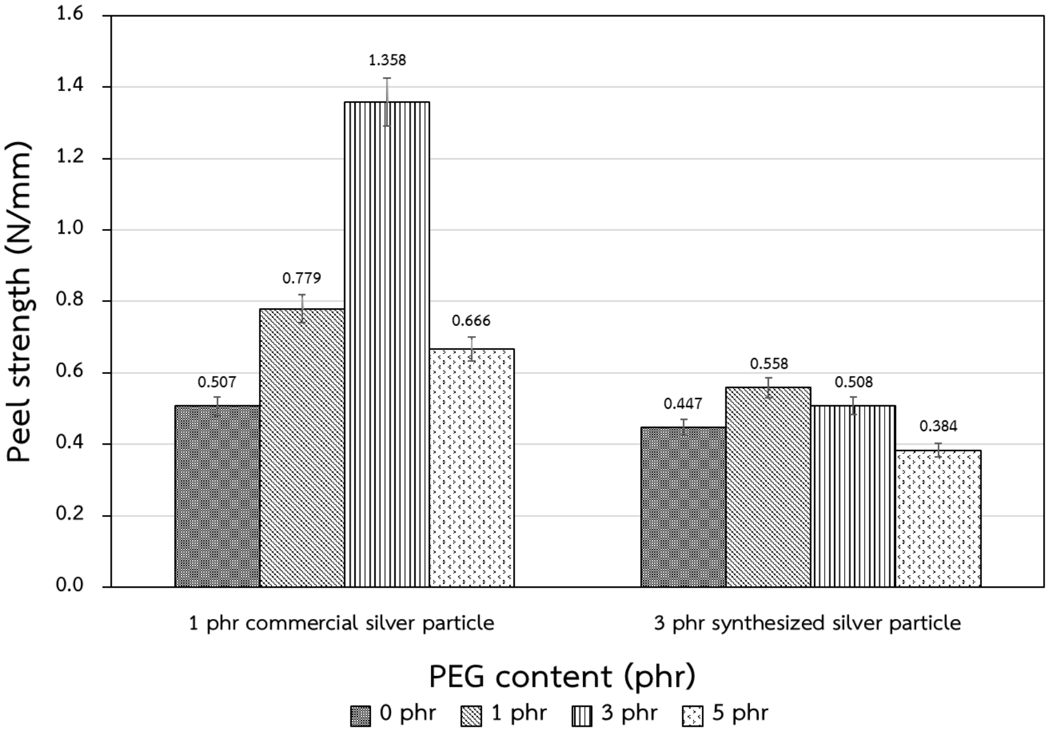
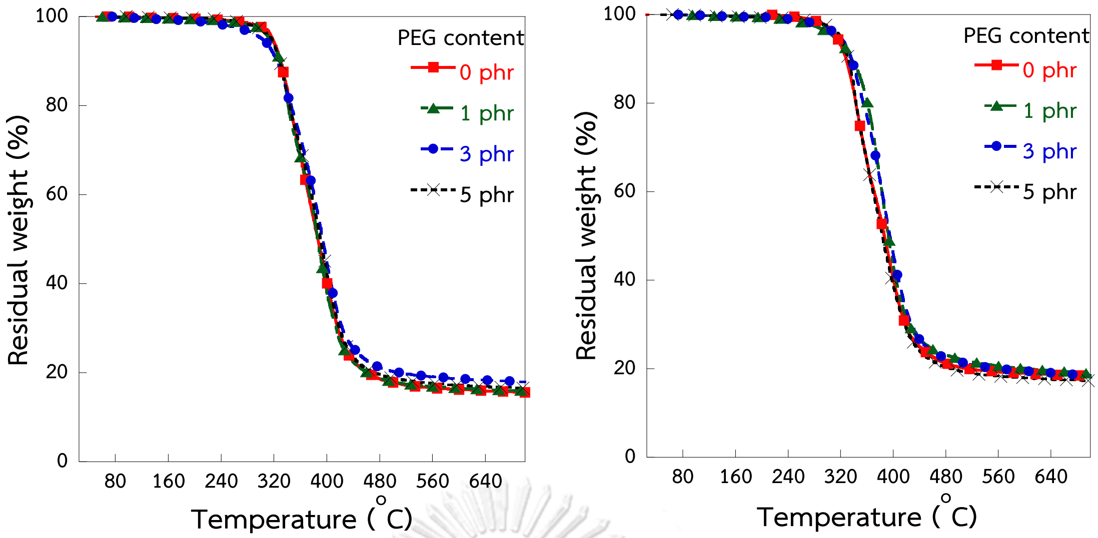


Figure 4.13 Peel strength of ACP with silver particle by varying PEG 0, 1, 3 and 5 phr

4.3.6 Thermal degradation properties of ACP

The degradation temperature profiles of ACP with silver particle by varying PEG 0, 1, 3 and 5 phr were studied by a thermogravimetric analyzer (TGA). According to Figure 4.14 and Tables 4.6–4.7, the degradation temperature (T_d) at 5 wt% loss ($T_{d,5}$) of ACP with commercial silver particle by varying PEG 0, 1, 3 and 5 phr were 317.58 °C, 314.10 °C, 302.04 °C, and 316.45 °C, respectively and those with synthesized silver particle by varying PEG 0, 1, 3 and 5 phr were 302.29 °C, 310.56 °C, 317.75 °C, and 319.32 °C, respectively. As a result, it was found that degradation temperature at 5 wt% loss ($T_{d,5}$) increased with increasing in PEG content. As a result, %weight loss shows the same content as to the content of silver in the ACP system.



(a) (b)

Figure 4.14 TGA Thermogram of ACP with silver particle by varying PEG 0, 1, 3 and 5 phr (a) 1 phr commercial silver particles and (b) 3 phr synthesized silver particles

Table 4.6 TGA results of ACP with 1 phr commercial silver particle

PEG content (phr)	0 phr	1 phr	3 phr	5 phr
$T_{d,5}$	317.58	314.10	317.80	316.45
%weight loss ที่ T 700 °C	15.59	15.93	16.33	16.54

Table 4.7 TGA results of ACP with 3 phr synthesized silver particle

PEG content (phr)	0 phr	1 phr	3 phr	5 phr
$T_{d,5}$	313.60	310.56	317.75	319.32
%weight loss ที่ T 700 °C	18.38	18.88	18.45	17.29

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

The viscosity and surface tension of Anisotropic conductive paste for screen printable process was improved by adding PEG400. At first, commercial and synthesized silver particles content were varied to select the lowest contents of silver particle in which the ACP has volume resistivity less than 1 Ω•cm. It was found that the content of commercial and synthesized silver particles was 1 phr and 3 phr, respectively. Then, the PEG content of ACP with commercial and synthesized silver particles was varied at 0, 1, 3, and 5 phr. It was found that all uncured ACP showed Newtonian flow behavior at a constant shear rate of 0.2 s^{-1}. The viscosity of ACP increased with time due to curing reaction at room temperature. It was found that the addition of PEG affects the viscosity of uncured ACP. The viscosity of ACP increased with increasing PEG content from 1 phr for synthesized silver particles and that from 1 and 3 phr of commercial silver particles which might be due to hydrogen bonding between the hydroxyl groups of PEG and the ether oxygens of the ACP. However, higher content of PEG tends to decrease the viscosity of ACP because PEG could form free volume between molecules of polymer that increases the mobility of the network chain which can be interpreted from the heat of reaction and glass transition temperature of ACP. The addition of PEG can prevent crosslink reaction in ACP and increase curing time as observed from the decreasing of curing rate. From the mechanical properties of ACP with peel strength of adhesion between copper and polyimide film, it was found that ACP with 3 phr PEG and 1 phr commercial silver particle has the highest peel strength. It was due to the interaction between PEG and ACP systems that increase adhesion with copper. Adding high silver content provided low viscosity and low adhesion due to more mobility of molecules and low difference of surface energy between copper substrate and ACP with silver particles, respectively. Moreover, small voids occur at the metal/polymer interface, which supports crack formation and delamination on a macroscopic scale. Finally, the ACP with 3 phr of PEG and commercial silver particle was the optimal formulation to use with copper substrate and polyimide film because it provided low volume resistivity, highest peel strength and low viscosity.

Recommendations

1. The particle shape of the silver particle in the ACP system should be studied.
2. The viscosity affects the screen-printed process so it should be taken to understand the actual working temperature of the process.

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APPENDIX A

Calculation of ACP formula

Calculation of equivalent weight of epoxy mixtures:

To calculate the desired stoichiometric quantity of amine in weight parts per gram epoxy resin the following formula can be used:

$$\text{Amount of amine needed (g)} = \text{AHEW} \times \frac{\text{1 g mass of epoxy resin}}{\text{EEW}}$$

Where Amine hydrogen equivalent weight, AHEW refers to as equivalent weight per active hydrogen of the amine as followed by:

$$\text{AHEW}\left(\frac{\text{grams}}{\text{equivalent}}\right) = \frac{\text{Molecular weight of hardener}}{\text{number of active hydrogen per molecule}}$$

Whereas Epoxy Equivalent Weight, EEW is the amount of resin (grams) that contains one molecule of an epoxy group as calculated by:

$$\text{EEW}\left(\frac{\text{grams}}{\text{equivalent}}\right) = \frac{\text{Molecular weight of epoxy resin}}{\text{number of epoxide ring}}$$

For the epoxy mixtures,

$$\text{EEW of epoxy mixture } = \frac{\text{total weight of epoxy mixture}}{\frac{\text{Weight 1}}{\text{EEW 1}} + \frac{\text{Weight 2}}{\text{EEW 2}}}$$

For example: 50/50 with m-PDA system on basis 1 gram mass of the epoxy mixture

$$\text{EEW of epoxy mixtures } = \frac{1}{\frac{\text{0.5 g of EPN}}{172.7} + \frac{\text{0.5 g of PPGDE}}{335.8}} = 228.1$$

Hence,

$$\text{Amount of m} - \text{PDA (g)} \quad = \; 27.035 \; \times \frac{1 \text{ g (mass of epoxy resin)}}{228.1}$$

$$= 0.12 \text{ g mass of m} - \text{PDA}$$

APPENDIX B

Data of SEM-EDX

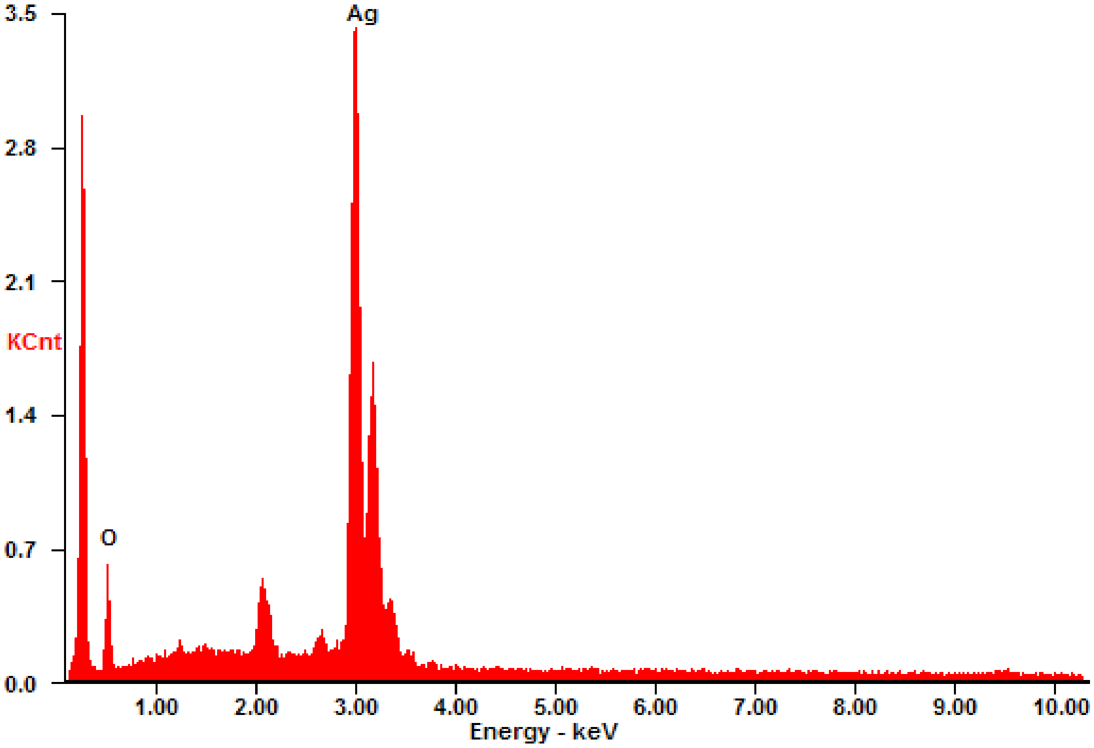

Figure B.1 EDX graph of the commercial silver particles

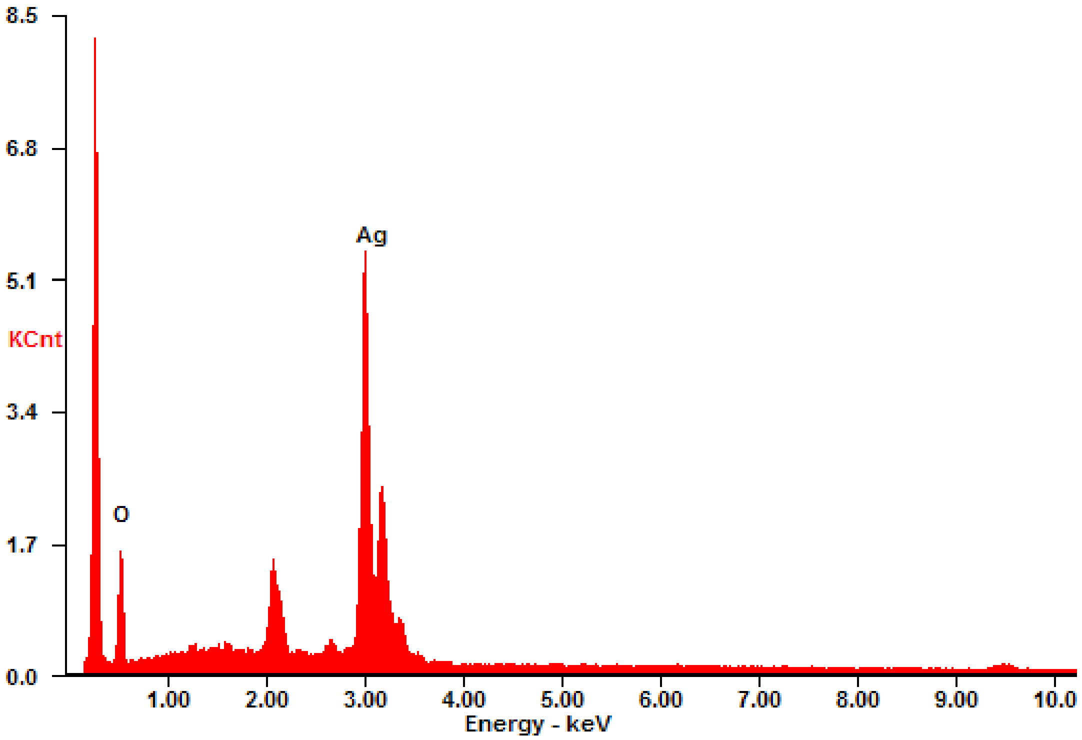

Figure B.2 EDX graph of the synthesized silver particles

APPENDIX C

Data of isothermal DSC

Table C.1 Degree of cure and cure rate of various PEG-modified ACP with a commercial silver particle at curing temperature of 157 °C

Time	AgCPEG0		AgCPEG1	
(min)	dx/dt	x	dx/dt	x
1	0.238889	0.258068	0.201641	0.208749
2	0.495498	0.477778	0.443742	0.403282
3	0.47888	0.624532	0.448113	0.548116
4	0.465328	0.717769	0.447103	0.649754
5	0.458286	0.777594	0.447634	0.721161
6	0.455566	0.81717	0.449922	0.772511
7	0.455277	0.844363	0.453168	0.810503
8	0.456447	0.863862	0.456763	0.839424
9	0.458712	0.878629	0.46037	0.862015
10	0.461519	0.890643	0.463835	0.880082
11	0.464398	0.900834	0.467103	0.894842
12	0.467258	0.90972	0.470166	0.907144
13	0.470096	0.917675	0.473024	0.917587
14	0.472903	0.924956	0.475701	0.926596
15	0.475695	0.931741	0.478227	0.934494
16	0.478464	0.938173	0.480624	0.941525
17	0.481173	0.944335	0.482914	0.947872
18	0.483791	0.950259	0.485136	0.953677
19	0.48631	0.955959	0.487305	0.959072
20	0.48881	0.961439	0.489506	0.964144

Table C.1 Degree of cure and cure rate of various PEG-modified ACP with a commercial silver particle at curing temperature of 157 °C (cont.)

Time (min)	AgCPEG0		AgCPEG1	
	dx/dt	x	dx/dt	x
21	0.491298	0.966789	0.491747	0.969042
22	0.493732	0.972018	0.493981	0.973819
23	0.496109	0.977126	0.496213	0.978501
24	0.498444	0.982118	0.498435	0.983122
25	0.50074	0.987007	0.500639	0.987686
26	0.503006	0.991799	0.502826	0.9922
27	0.5041	0.99651	0.5039	0.996669
28	0.00698	1	0.006663	1

Table C.1 Degree of cure and cure rate of various PEG-modified ACP with a commercial silver particle at curing temperature of 157 °C (cont.)

Time (min)	AgCPEG3		AgCPEG5	
	dx/dt	x	dx/dt	x
1	0.241927	0.26824	0.175182	0.181926
2	0.489041	0.483854	0.389927	0.350363
3	0.468229	0.623161	0.402503	0.48089
4	0.453927	0.710157	0.409172	0.577685
5	0.446965	0.765507	0.415326	0.649617
6	0.444514	0.802043	0.421772	0.704169
7	0.444619	0.827268	0.428308	0.74658
8	0.446456	0.84564	0.434687	0.780392
9	0.449531	0.860089	0.440749	0.807977
10	0.453015	0.872351	0.446448	0.830945
11	0.45649	0.883059	0.451751	0.850437

Table C.1 Degree of cure and cure rate of various PEG-modified ACP with a commercial silver particle at curing temperature of 157 °C (cont.)

Time (min)	AgCPEG3		AgCPEG5	
	dx/dt	x	dx/dt	x
12	0.459954	0.892665	0.456676	0.867223
13	0.463448	0.901483	0.461255	0.881894
14	0.466976	0.90978	0.465537	0.894867
15	0.470491	0.917717	0.469547	0.906484
16	0.473931	0.925381	0.473307	0.91698
17	0.477241	0.932789	0.476846	0.926549
18	0.480395	0.939931	0.480175	0.935336
19	0.483395	0.94679	0.483331	0.943449
20	0.486371	0.953361	0.486435	0.950999
21	0.489338	0.959766	0.48949	0.958159
22	0.492253	0.966018	0.492472	0.964989
23	0.495137	0.972136	0.495373	0.971551
24	0.498	0.978147	0.498204	0.977867
25	0.500833	0.984068	0.500986	0.98398
26	0.503649	0.989906	0.503726	0.98992
27	0.505047	0.995683	0.50504	0.995716
28	0.008634	1	0.008569	1

Table C.2 Degree of cure and cure rate of various PEG-modified ACP with a synthesized silver particle at curing temperature of 157 °C

Time (min)	AgSPEG0		AgSPEG1	
	dx/dt	x	dx/dt	x
1	0.229911	0.251314	0.249262	0.276636
2	0.47627	0.459822	0.502461	0.498524
3	0.465995	0.601927	0.479797	0.640779
4	0.457938	0.695906	0.464477	0.729059
5	0.454332	0.758901	0.456896	0.784867
6	0.453653	0.802286	0.45403	0.821426
7	0.454558	0.833103	0.453938	0.846464
8	0.456306	0.855701	0.455606	0.864651
9	0.458571	0.872857	0.458047	0.878838
10	0.461208	0.886421	0.460663	0.890372
11	0.463993	0.897637	0.463389	0.900082
12	0.466728	0.907203	0.466201	0.908575
13	0.469417	0.915547	0.469081	0.916241
14	0.472079	0.923019	0.471999	0.923369
15	0.474716	0.929853	0.474908	0.930119
16	0.477338	0.936225	0.477788	0.936592
17	0.479948	0.942264	0.480614	0.942848
18	0.482548	0.94806	0.48334	0.94891
19	0.485134	0.95368	0.485953	0.954764
20	0.487788	0.959164	0.488541	0.960408
21	0.490478	0.964628	0.491089	0.965923
22	0.493133	0.970059	0.493561	0.971293
23	0.495761	0.975447	0.495979	0.976522
24	0.49834	0.980791	0.498357	0.981626

Table C.2 Degree of cure and cure rate of various PEG-modified ACP with a synthesized silver particle at curing temperature of 157 °C (cont.)

Time (min)	AgSPEG0		AgSPEG1	
	dx/dt	x	dx/dt	x
25	0.500838	0.986064	0.500718	0.986618
26	0.503247	0.991233	0.503075	0.991531
27	0.504383	0.996279	0.504235	0.996384
28	0.007443	1	0.007231	1

Table C.2 Degree of cure and cure rate of various PEG-modified ACP with a synthesized silver particle at curing temperature of 157 °C (cont.)

Time (min)	AgSPEG3		AgSPEG5	
	dx/dt	x	dx/dt	x
1	0.246722	0.27632	0.194842	0.202641
2	0.494327	0.493445	0.430696	0.389684
3	0.472258	0.632487	0.44004	0.532016
4	0.457525	0.71898	0.443101	0.634882
5	0.450256	0.773768	0.446222	0.709109
6	0.447652	0.809746	0.450147	0.763663
7	0.44801	0.834537	0.454429	0.804702
8	0.450144	0.852883	0.458774	0.836261
9	0.452817	0.867412	0.462911	0.861125
10	0.455621	0.879259	0.466727	0.881042
11	0.458606	0.889327	0.470238	0.89729
12	0.461756	0.898236	0.47342	0.910759
13	0.465035	0.906419	0.47633	0.922065
14	0.468372	0.914153	0.479004	0.931709
15	0.471688	0.921582	0.481464	0.940036

Table C.2 Degree of cure and cure rate of various PEG-modified ACP with a synthesized silver particle at curing temperature of 157 °C (cont.)

Time	AgSPEG3		AgSPEG5	
(min)	dx/dt	x	dx/dt	x
16	0.474945	0.928765	0.483759	0.947319
17	0.478088	0.935736	0.48591	0.953777
18	0.481092	0.94247	0.487931	0.959569
19	0.483975	0.94896	0.489856	0.96482
20	0.48684	0.95521	0.491772	0.969641
21	0.489711	0.96132	0.493636	0.974181
22	0.49254	0.967316	0.49543	0.978457
23	0.495335	0.9732	0.497182	0.982521
24	0.498087	0.978993	0.498904	0.98641
25	0.500804	0.984687	0.500602	0.990165
26	0.50352	0.9903	0.502287	0.993808
27	0.50485	0.995864	0.503096	0.997369
28	0.008273	1	0.005262	1

When, x : degree of cure

dx/dt : cure rate

t : cure time (min)

APPENDIX D

Data of flow behavior of ACP

Table D.1 Viscosity of PEG-modified ACP with a commercial silver particle (cP) and shear rate (s^{-1})

Shear rate (s^{-1})	0 phr	Shear rate (s^{-1})	1 phr
0.01132	621.8	0.01123	4554
0.01224	414.5	0.01209	4983
0.01318	646.4	0.01306	4901
0.0141	1406	0.01418	4906
0.01521	1402	0.01518	4981
0.01662	1288	0.01653	4659
0.01803	1530	0.01775	5196
0.01898	1390	0.01919	4859
0.02067	1620	0.02076	5099
0.022	1566	0.02245	4631
0.0239	2056	0.02422	5010
0.02574	2179	0.02605	4891
0.02776	2012	0.02816	4690
0.03007	2479	0.03043	4863
0.0326	2573	0.03278	5037
0.03524	2619	0.03537	4648
0.03787	2775	0.03768	4812
0.04085	2699	0.0406	4962
0.04423	2743	0.04371	5074
0.04782	2666	0.0472	5250
0.0514	2522	0.05149	5250

Table D.1 Viscosity of PEG-modified ACP with a commercial silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	0 phr	Shear rate (s^{-1})	1 phr
0.05544	2882	0.05527	5010
0.06006	2576	0.06	5566
0.065	2927	0.06413	5427
0.06972	3156	0.0697	5100
0.07494	3108	0.07541	4946
0.08127	3103	0.08113	5028
0.0883	3005	0.08723	5309
0.0951	2910	0.09512	5213
0.1002	2991	0.1014	5170
0.1092	2995	0.1103	5170
0.1182	3036	0.1193	5212
0.1271	3036	0.1282	5270
0.139	3097	0.1372	5233
0.1481	3165	0.1491	5185
0.1597	3177	0.161	5192
0.1747	3152	0.1758	5259
0.1896	3141	0.1877	5222
0.2028	3146	0.2011	5250
0.2149	3148	0.2189	5234
0.2329	3134	0.2368	5220
0.2565	3185	0.2547	5233
0.2744	3202	0.2726	5209
0.2982	3177	0.2963	5200
0.3221	3199	0.32	5220
0.3457	3224	0.3436	5215
0.3755	3204	0.3731	5231

Table D.1 Viscosity of PEG-modified ACP with a commercial silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	0 phr	Shear rate (s^{-1})	1 phr
0.397	3264	0.4016	5205
0.4333	3218	0.4372	5199
0.4686	3277	0.4729	5244
0.5045	3250	0.5087	5209
0.5491	3262	0.5449	5205
0.5866	3277	0.5937	5188
0.6338	3270	0.6408	5201
0.6936	3246	0.6877	5209
0.7402	3261	0.7472	5224
0.7915	3279	0.7988	5242
0.865	3368	0.859	5211
0.9416	3292	0.9331	5213
1.009	3297	1.015	5143
1.097	3215	1.085	5194
1.168	3307	1.175	5213
1.272	3325	1.258	5241
1.357	3312	1.363	5218
1.476	3320	1.483	5172
1.602	3324	1.582	5166
1.708	3345	1.716	5163
1.853	3317	1.863	5138
2.007	3305	2.016	5151
2.174	3315	2.15	5144
2.32	3291	2.331	5116
2.513	3283	2.523	5123
2.723	3259	2.733	5101

Table D.1 Viscosity of PEG-modified ACP with a commercial silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	0 phr	Shear rate (s^{-1})	1 phr
3.144	3249	3.153	5088
3.402	3261	3.414	5098
3.68	3247	3.69	5104
3.982	3250	3.995	5082
4.306	3255	4.325	5074
4.658	3251	4.604	5063
5.036	3182	4.977	5039
5.362	3217	5.385	5017
5.8	3200	5.818	5020
6.266	3195	6.294	5021
6.776	3195	6.809	5023
7.327	3196	7.357	5001
7.914	3178	7.948	4972
8.555	3159	8.594	4963
9.24	3155	9.142	4973
9.984	3159	9.881	4983
10.79	3140	10.68	4947
11.66	3115	11.53	4937
12.41	3127	12.46	4960
13.41	3126	13.46	4941
14.48	3090	14.54	4920
15.64	3109	15.71	4953
16.9	3084	16.96	4905
18.26	3080	18.33	4936
19.73	3076	19.8	4904
21.3	3065	21.38	4932

Table D.1 Viscosity of PEG-modified ACP with a commercial silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	0 phr	Shear rate (s^{-1})	1 phr
24.86	3068	24.95	4930
26.84	3021	26.95	4897
29	3025	29.1	4866
31.32	3049	30.95	4916
33.82	3038	33.43	4904
36.53	3019	36.1	4882
39.45	3007	38.98	4871
42.6	3007	42.11	4868
46.01	2939	45.47	4877
48.93	3003	49.11	4875

Table D.1 Viscosity of PEG-modified ACP with a commercial silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	3 phr	Shear rate (s^{-1})	5 phr
0.01109	5331	0.01127	1069
0.01194	5558	0.01209	1513
0.01306	5251	0.01323	1795
0.01397	5993	0.01413	1691
0.01516	5974	0.01519	1942
0.01644	5716	0.01647	1971
0.01769	6441	0.01803	1766
0.01901	5959	0.01888	2021
0.02048	6783	0.02077	1982
0.0222	5918	0.02205	2119

Table D.1 Viscosity of PEG-modified ACP with a commercial silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	3 phr	Shear rate (s^{-1})	5 phr
0.02574	6844	0.02582	2757
0.02791	6944	0.02782	2468
0.03042	6882	0.03002	2645
0.03262	7630	0.03268	2819
0.03513	7727	0.03516	3092
0.03785	7833	0.03788	3288
0.04107	7855	0.04098	3375
0.04433	7954	0.04441	3435
0.048	7858	0.04765	3278
0.05155	7646	0.05104	3489
0.05579	8194	0.05583	3475
0.06041	7645	0.05974	3523
0.06537	7929	0.06507	3178
0.07007	8107	0.07029	3455
0.0755	7980	0.07585	3492
0.08158	8095	0.08182	3501
0.0884	8329	0.08855	3392
0.09617	7782	0.09485	3371
0.1007	8197	0.1002	3477
0.1096	8259	0.1092	3453
0.1187	8233	0.1182	3480
0.1276	8174	0.1271	3517
0.1394	8198	0.1391	3542
0.1484	8208	0.148	3534
0.1603	8310	0.1598	3446
0.1751	8233	0.1747	3514

Table D.1 Viscosity of PEG-modified ACP with a commercial silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	3 phr	Shear rate (s^{-1})	5 phr
0.2034	8295	0.2028	3561
0.2153	8265	0.2147	3559
0.2331	8335	0.2329	3572
0.2511	8297	0.2505	3587
0.2749	8294	0.2745	3570
0.2987	8332	0.2981	3574
0.3224	8359	0.3218	3579
0.3461	8370	0.3454	3601
0.3756	8393	0.3753	3590
0.3979	8411	0.3974	3609
0.4337	8383	0.4333	3596
0.4693	8394	0.4689	3617
0.5052	8414	0.5048	3599
0.5493	8407	0.5489	3616
0.587	8363	0.5864	3574
0.6343	8371	0.6334	3612
0.6931	8429	0.6925	3620
0.7405	8429	0.7397	3643
0.8073	8428	0.8073	3558
0.8666	8417	0.8662	3636
0.9411	8397	0.9407	3602
1.008	8426	1.007	3569
1.079	8418	1.078	3596
1.169	8426	1.169	3622
1.273	8414	1.273	3553
1.358	8404	1.357	3585

Table D.1 Viscosity of PEG-modified ACP with a commercial silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	3 phr	Shear rate (s^{-1})	5 phr
1.602	8339	1.601	3603
1.708	8365	1.709	3559
1.853	8313	1.852	3550
2.008	8270	2.007	3555
2.175	8257	2.176	3546
2.32	8209	2.32	3519
2.512	8226	2.513	3527
2.723	8187	2.723	3512
2.949	8192	2.95	3520
3.146	8171	3.142	3507
3.403	8208	3.404	3510
3.68	8203	3.681	3521
3.983	8185	3.981	3511
4.306	8191	4.306	3499
4.658	8152	4.66	3493
5.036	8118	4.958	3478
5.362	8081	5.363	3461
5.798	8074	5.798	3456
6.27	8082	6.267	3455
6.779	8102	6.778	3451
7.328	8088	7.324	3444
7.92	8046	7.915	3426
8.558	8041	8.558	3407
9.249	8058	9.242	3416
9.994	8069	9.983	3414
10.8	8019	10.79	3380

Table D.1 Viscosity of PEG-modified ACP with a commercial silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	3 phr	Shear rate (s^{-1})	5 phr
12.42	8037	12.41	3386
13.42	8015	13.4	3369
14.49	7960	14.48	3344
15.65	8007	15.65	3369
16.91	7933	16.9	3326
18.27	7963	18.26	3347
19.73	7920	19.73	3317
21.32	7939	21.31	3334
23.03	7866	23.02	3293
24.87	7924	24.86	3330
26.85	7857	26.84	3294
29.01	7817	29	3271
31.33	7861	31.32	3300
33.83	7864	33.82	3305
36.54	7839	36.52	3294
39.47	7821	39.46	3284
42.62	7811	42.61	3205
45.32	7782	45.31	3265
48.94	7788	48.94	3269

Table D.2 Viscosity of PEG-modified ACP with a synthesized silver particle (cP) and shear rate (s^{-1})

Shear rate (s^{-1})	0 phr	Shear rate (s^{-1})	1 phr
0.01111	3534	0.01209	3273
0.01194	3767	0.01282	2963
0.01308	3517	0.0142	3354
0.0141	3277	0.01512	3273
0.01526	3699	0.01631	3231
0.0166	3180	0.01779	3198
0.01759	3765	0.01893	3206
0.01919	3353	0.02051	3141
0.02083	3707	0.02199	3537
0.02226	3515	0.02396	3285
0.02422	3624	0.02593	3722
0.02609	3365	0.02793	3618
0.02824	3268	0.03019	3443
0.03038	3542	0.03278	3295
0.03277	3488	0.03537	3434
0.03522	3483	0.03813	3491
0.03798	3575	0.04107	3521
0.04121	3561	0.04432	3415
0.04453	3448	0.04776	3499
0.04825	3411	0.05179	3853
0.0512	3305	0.05599	3475
0.05493	3161	0.06016	3777
0.05981	3451	0.06512	3633
0.06409	3309	0.07057	3613
0.0698	3054	0.07626	3774

Table D.2 Viscosity of PEG-modified ACP with a synthesized silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	0 phr	Shear rate (s^{-1})	1 phr
0.08121	3101	0.08887	3421
0.08727	3303	0.09524	3916
0.09492	3311	0.1008	3750
0.1013	3269	0.1097	3753
0.1102	3329	0.1187	3704
0.1192	3297	0.1276	3670
0.128	3292	0.1395	3715
0.1368	3290	0.1484	3749
0.1488	3247	0.1602	3732
0.1608	3262	0.1752	3694
0.1756	3287	0.1871	3625
0.1874	3324	0.2033	3637
0.2008	3299	0.2153	3644
0.2188	3272	0.2331	3672
0.2366	3305	0.251	3701
0.2546	3304	0.2748	3680
0.2724	3301	0.2985	3706
0.2961	3295	0.3222	3678
0.3198	3253	0.3462	3695
0.3495	3306	0.3755	3731
0.3735	3283	0.398	3731
0.401	3305	0.4344	3722
0.4369	3282	0.4691	3748
0.4727	3280	0.5051	3698
0.5085	3272	0.5491	3716
0.5441	3281	0.5867	3652

Table D.2 Viscosity of PEG-modified ACP with a synthesized silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	0 phr	Shear rate (s^{-1})	1 phr
0.6407	3250	0.6938	3705
0.6883	3195	0.7399	3745
0.7473	3234	0.8072	3636
0.7987	3246	0.8673	3674
0.8737	3239	0.9417	3656
0.9338	3232	1.008	3658
1.015	3211	1.079	3648
1.086	3209	1.168	3689
1.175	3239	1.274	3660
1.258	3246	1.358	3638
1.364	3203	1.476	3632
1.483	3192	1.602	3638
1.581	3197	1.709	3627
1.715	3213	1.853	3606
1.863	3181	2.008	3621
2.017	3186	2.176	3613
2.15	3191	2.319	3600
2.33	3173	2.514	3607
2.523	3175	2.723	3596
2.734	3177	2.95	3602
2.91	3178	3.193	3605
3.155	3176	3.403	3594
3.412	3191	3.682	3600
3.689	3180	3.981	3584
3.996	3178	4.307	3569
4.326	3160	4.66	3565

Table D.2 Viscosity of PEG-modified ACP with a synthesized silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	0 phr	Shear rate (s^{-1})	1 phr
4.976	3135	5.361	3558
5.383	3127	5.798	3560
5.82	3122	6.272	3544
6.294	3133	6.779	3530
6.806	3133	7.328	3515
7.357	3116	7.917	3515
7.949	3095	8.561	3515
8.593	3090	9.252	3502
9.143	3092	9.992	3478
9.883	3102	10.8	3475
10.67	3076	11.49	3481
11.53	3063	12.42	3463
12.46	3078	13.42	3440
13.46	3063	14.49	3458
14.54	3048	15.66	3434
15.71	3066	16.91	3428
16.97	3032	18.27	3429
18.33	3050	19.74	3409
19.8	3027	21.32	3415
21.39	3043	23.03	3403
23.1	3011	24.88	3375
24.96	3038	26.86	3407
26.96	3016	29.01	3380
30.96	3023	31.33	3348
33.44	3015	33.84	3347
36.12	3002	36.54	3355

Table D.2 Viscosity of PEG-modified ACP with a synthesized silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	0 phr	Shear rate (s^{-1})	1 phr
42.12	2990	42.63	3335
45.49	2993	46.04	3294
49.13	2989	48.96	3303

Table D.2 Viscosity of PEG-modified ACP with a synthesized silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	3 phr	Shear rate (s^{-1})	5 phr
0.01214	2649	0.01212	2717
0.01323	2804	0.01286	3196
0.01414	2729	0.014	3270
0.01526	2648	0.01522	2910
0.01614	3074	0.01618	3392
0.01752	3034	0.01778	3182
0.01893	3194	0.01915	3183
0.02041	2823	0.0207	2891
0.02222	2677	0.02213	3354
0.02376	2818	0.02407	2790
0.02568	2541	0.02609	2977
0.02798	2949	0.02805	3192
0.03002	3181	0.03024	2852
0.03261	3081	0.03273	2834
0.03505	3051	0.03551	2839
0.03771	3174	0.03834	2840
0.04083	3196	0.0414	3019

Table D.2 Viscosity of PEG-modified ACP with a synthesized silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	3 phr	Shear rate (s^{-1})	5 phr
0.04785	3292	0.04791	3087
0.05174	3024	0.0518	3352
0.0555	3125	0.05633	3096
0.06031	3165	0.06031	3337
0.06455	3270	0.06509	3041
0.06997	3181	0.06942	3396
0.07571	3176	0.07465	3309
0.08185	3024	0.08068	3290
0.08762	3312	0.0874	3345
0.09585	3283	0.09476	3072
0.1006	3274	0.1011	3216
0.1094	3274	0.11	3216
0.1183	3248	0.119	3180
0.1274	3211	0.1279	3139
0.1391	3217	0.1369	3138
0.1481	3248	0.1487	3150
0.16	3293	0.1606	3153
0.1748	3297	0.1755	3133
0.1897	3293	0.1871	3156
0.203	3280	0.2007	3159
0.215	3280	0.2185	3138
0.2328	3283	0.2364	3100
0.2507	3324	0.2541	3148
0.2746	3267	0.2721	3138
0.2986	3297	0.296	3100
0.3219	3272	0.3199	3113

Table D.2 Viscosity of PEG-modified ACP with a synthesized silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	3 phr	Shear rate (s^{-1})	5 phr
0.3753	3310	0.3729	3118
0.3976	3313	0.4016	3102
0.4337	3294	0.4369	3116
0.4697	3265	0.4727	3096
0.5038	3323	0.508	3106
0.5486	3320	0.5437	3120
0.5861	3328	0.5923	3102
0.634	3320	0.6394	3094
0.6937	3293	0.6885	3065
0.7411	3298	0.747	3112
0.8081	3289	0.7991	3096
0.8669	3293	0.858	3113
0.9404	3288	0.9316	3118
1.008	3285	0.9965	3076
1.097	3288	1.084	3100
1.17	3278	1.175	3112
1.273	3259	1.26	3095
1.357	3263	1.364	3096
1.476	3251	1.482	3094
1.603	3250	1.581	3119
1.709	3239	1.715	3103
1.852	3231	1.862	3097
2.008	3234	1.984	3093
2.176	3220	2.152	3095
2.319	3220	2.328	3098
2.514	3218	2.523	3098

Table D.2 Viscosity of PEG-modified ACP with a synthesized silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	3 phr	Shear rate (s^{-1})	5 phr
2.949	3222	2.912	3102
3.144	3229	3.153	3093
3.403	3225	3.413	3091
3.683	3217	3.692	3094
3.983	3214	3.993	3087
4.305	3205	4.324	3085
4.658	3199	4.606	3089
5.04	3191	4.977	3090
5.363	3196	5.383	3099
5.801	3196	5.821	3098
6.269	3186	6.297	3093
6.776	3174	6.806	3080
7.323	3164	7.355	3069
7.919	3162	7.951	3069
8.554	3168	8.591	3029
9.249	3159	9.141	3084
9.994	3141	9.877	3070
10.8	3135	10.68	3056
11.67	3144	11.53	3059
12.41	3134	12.46	3068
13.41	3114	13.46	3048
14.49	3128	14.54	3049
15.65	3110	15.71	3058
16.91	3102	16.97	3040
18.27	3111	18.33	3056
19.73	3087	19.8	3036

Table D.2 Viscosity of PEG-modified ACP with a synthesized silver particle (cP) and shear rate (s^{-1}) (cont.)

Shear rate (s^{-1})	3 phr	Shear rate (s^{-1})	5 phr
23.02	3083	23.1	3033
24.87	3067	24.95	3044
26.85	3088	26.95	3038
29	3063	29.11	3026
31.32	3041	31.44	3027
33.83	3047	33.44	3038
36.54	3053	36.11	3032
39.47	3049	39	3028
42.62	3038	42.12	3026
45.33	3042	45.49	3026
48.95	3014	49.13	3019

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