DEVELOPMENT OF ENVIRONMENTAL FRIENDLY ELECTRICAL CONDUCTIVE ADHESIVES (ECAS) AS A REPLACEMENT TO LEAD BASED SOLDER MATERIALS IN ELECTRONIC MANUFACTURINGINDUSTRY

By

LAM WAI MAN

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ABSTRACT

DEVELOPMENT OF ENVIRONMENTAL FRIENDLY ELECTRICAL CONDUCTIVE ADHESIVES (ECAS) AS A REPLACEMENT TO LEAD BASED SOLDER MATERIALS IN ELECTRONIC MANUFACTURINGINDUSTRY

LamWai Man

Isotropic conductive adhesives (ICAs) have recently received a lot of focus and attention from the researchers in electronics industry as a potential substitute to lead-based solders. Numerous studies have shown that ICAs possess many advantages over conventional soldering such as environmental friendliness, finer pitch printing, lower temperature processing and more flexible and simpler processing. However, complete replacement of soldering by ICAs is yet not possible due to several limitations of ICAs which one of the properties mostly studied by researchers is the rheological behaviour of ICAs. A number of factors influence the rheology of ICAs, including filler size, particle size distribution, volume fraction of filler, shape and surface roughness of filler.

The stencil printing process is an important process in the assembly of Surface Mount Technology (SMT) devices. There is a wide agreement in the industry that the paste printing process accounts for the majority of assembly defects. Experience with this process has shown that typically over 60% of all soldering defects are due to problems associated with the rheological properties of solder pastes. Therefore, the rheological measurements can be used as a tool to study the deformation or flow experienced by the pastes during the stencil printing process.

The work reported here on the rheological characterisation of ICAs paste used in Microsystems assembly applications divided into four main parts. The first part concerns the study of theeffect of filler size and volume fraction on viscosity measurement of ICA pastes. The relationship between viscosities and volume fraction of ICAs is described by empirical models namely; Krieger-Dougherty model, Quemada model and Eilers model. The second part of the study concerns the visco-elastic behaviourof ICA pastes. The main focus of the work was to determine the linear visco-elastic region using oscillatory shear stress experiments. The third part of the work deals with the study of the thixotropic behaviour of ICA pastes using both hysteresis loop and constant shear rate tests. The final part of the study concerns the thermal properties of ICA pastes which study the curing effects of the pastes.

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FACULTY OF ENGINEERING AND SCIENCE
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PERMISSION SHEET

It is hereby certified that **LAM WAI MAN** (ID No: **08UEM08124**) has completed this report entitled **"DEVELOPMENT OF ENVIRONMENTAL FRIENDLY ELECTRICAL CONDUCTIVE ADHESIVES (ECAS) AS A REPLACEMENT TO LEAD BASED SOLDER MATERIALS IN ELECTRONIC MANUFACTURINGINDUSTRY"** under the supervision of **ASSISTANT PROFESSORRAJKUMAR DURAIRAJ"** from the Department of Mechanical and Material Engineering.

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Approved by:

Supervisor

____

(Associate Professor RajkumarDurairaj) Date:_________________

Supervisor

Department of Mechanical and Material Engineering

Faculty of Engineering Science

UniversitiTunku Abdul Rahman

DECLARATION

I hereby declare that the dissertation is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTAR or other institutions.

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LIST OF PUBLICATION

1. R.Durairaj, **Lam Wai Man**, N.N.Ekere and S. Mallik (2010).The effect of wall-slip formation on the rheological behaviour of lead-free solder pastes. ***Journal ofMaterials and Design***, 31, 1056-1062.

2. R. Durairaj and **Lam Wai Man.** (2010).Structural breakdown and build-up inSn/Ag/Cu paste suspensions.***Journal of Science and Technology in the Tropics***, 5, 125-131.

3. R.Durairaj, **Lam Wai Man**, S.Ramesh, Lim Chia Wea, EuPohLeng, N.N.Ekere, S. Mallik and A.Seman, "Investigation of Wall-slip Behaviour in Lead-free Solder Pastes and Isotropic Conductive Adhesives",presented at the *11th Electronics Packaging Technology Conference (EPTC)*,Singapore, 2009.

4. R. Durairaj, **Lam Wai Man**, S. Mallik and N.N.Ekere, "*Thixotropic Studies of Lead-based Solder, Lead-free Solder and Conductive Adhesive Pastes*", presented at the *11th International Conference on Electronics, Materials and Packaging Conference (EMAP)*,Penang, 2009.

5. R. Durairaj and **Lam Wai Man,** "Investigation of the thixotropic behaviour of solder pastes and isotropic conductive adhesives used in the assembly of high density electronic packaging", presented at the *10th Asian Conference on Analytical Sciences (ASIANALYSIS X)*, Kuala Lumpur, Malaysia, Aug.2009.

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LIST OF ABBREVIATIONS

ICAs	Isotropic Conductive Adhesives
Ag	Silver
ACA	Anisotropic Conductive Adhesive
CTE	Coefficient of Thermal Expansion
Cu	Copper
DGEBA	Diglycidyl Ether of Bisphenol-A
DSC	Differential Scanning Calorimetry
ECA	Electrical Conductive Adhesives
G’	Storage Modulus
G”	Loss Modulus
LMPA	Low-melting-point Alloy Fillers
LVER	Linear Visco-elastic Region
Ni	Nickel
Pb	Lead
PCB	Printed Circuit Board
PU	Polyurethane
SMT	Surface Mount Technology
SMA	Surface Mount Assembly
SMC	Surface Mount Components
Sn	Tin

SEM	Scanning Electron Microscopy
TMA	Thermo-mechanical Analysis
T_g	Glass Transition Temperature

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CHAPTER 1

INRODUCTION

1.1 Importance of isotropic conductive adhesives (ICAs)

The interconnect technology in electronics has been dominated by tin/lead based solders since the very beginning. However, as the environmental awareness increased, the toxicity of lead received universal attention and its overall adverse effect on human health is being closely monitored (Liu, 1999). In addition, the selection of ideal lead-based solder alternative appears to be a moving target, since the miniaturization trend of the electronic industry is constantly imposing new criteria and challenges on the solder materials. Isotropic conductive adhesives (ICAs) are considered as the most promising replacement to lead-based solders due to relatively low melting point, simple processing and fine pitch capability (Wong and Yi, 2006). In recent years there has been a lot of research going on throughout the globe to produce ICAs with desirable overall properties and one of the properties mostly being studies is the rheological properties of ICAs. Rheological properties such as the flow and deformation behavior of conductive paste directly affect the stencil printing process quality and behavior after printing (Bullard et al., 2009). The printing of pastes (solder paste and ICAs) through very small stencil apertures required for ultra-fine pitch and flip chip applications is known to result in

increased stencil clogging and incomplete transfer of paste to the printed circuit boards. At these very narrow aperture sizes, achieving consistent paste deposits from board to board becomes very difficult and the solder paste withdraws because for smaller paste volumes the surface tension effects become dominant over viscous flow. The paste (solder paste and ICAs) rheology is therefore considered to be one of the most important parameters which affect the paste printing process, the reflow soldering performance, and hence the resulting solder joint quality and reliability.

ICAs are comprised of polymeric binders (which provide mechanical strength) and conductive fillers (which act as channel for charge transport). ICA formulations usually include epoxy resin as the polymeric matrix. Epoxy based materials have been widely used in engineering components due to their outstanding mechanical and thermal properties. The most promising filler material for ICAs is silver (Ag) which has superior conductivity and chemical stability. Also, it is easy to precipitate into a wide range of controllable sizes and shapes, and silver oxide show high conductivity. The desirable properties may further be improved with suitable choice of solvents, plasticisers, curing agents and accelerators. While the solder paste consists of functional groups such as solder particles, resin, solvent, thickener and activators.

1.2 Introduction to Electrical conductive adhesives (ECAs)

Electrical conductive adhesives (ECAs) are gaining great interest as potential solder replacements in microelectronics assemblies. Basically, there are two types of ECAs, isotropic conductive adhesive (ICA) and anisotropic conductive adhesive (ACA) (Gilleo, 1995).

Although the concepts of these materials are different, both materials are composite materials consisting of a polymer matrix containing conductive fillers. Typically, ICAs contain conductive filler concentrations between 60 and 80 wt.%, and the adhesives are conductive in all directions. ICAs are primarily utilized in hybrid applications and surface mount technology (Perichaud et al., 2000). In ACAs, the volume fractions of conductive fillers are normally between 5 and 10 wt.% and the electrical conduction is generally built only in the pressurization direction during curing. ACA technology is very suitable for fine pitch technology and is principally used for flat panel display applications, flip chips and fine pitch surface mount devices (Wong and Lu, 2000).

Compared to conventional solder interconnection technology, conductive adhesives are believed to have the following advantages (Liu and Lai, 1998):

1). More environmental friendly than lead-based solder;

2). Lower processing temperature requirements;

3). Finer pitch capability (ACAs);

4). Higher flexibility and greater fatigue resistance than solder;

5). Simpler processing (no need to use of flux);

6). Non-solderable (inexpensive) substrates can be used (e.g., glass).

Despite the advantages of ECA technology, the replacement of solder by this technology has not been widely adopted by the electronics industry. Lower electrical conductivity than solder (Hvims, 1995), poor impact resistance and long-term electrical and mechanical stability (Liu et al., 1997) are several critical concerns that have limited wider applications of electrically conductive adhesive technology. Numerous studies are being conducted to develop a better understanding of the mechanisms underlying these problems and to improve the performance of conductive adhesives for electronic applications.

1.3 Conduction Mechanisms in Isotropic Conductive Adhesives

In general, there are two conductive pathways for isotropic conductive adhesives as shown in Figure 1.1. One is genuine conduction, caused by particle-to-particle contact within the polymer matrix. The other is percolation, which involves electron transport brought about by quantum-mechanical electron tunneling between particles close enough to allow dielectric breakdown of the matrix. Researchers has suggested that percolation is the dominant conduction phenomenon in the early stages of conduction, as the applied current polarizes the conductive adhesive system causing the electrical resistance to drop by charge effects (Ritter, 1999). As currents, especially high currents, continue to be applied, polarized particles migrate and further combine, and conduction by particle-to-particle contact overwhelms percolation and becomes the dominant conduction phenomenon.

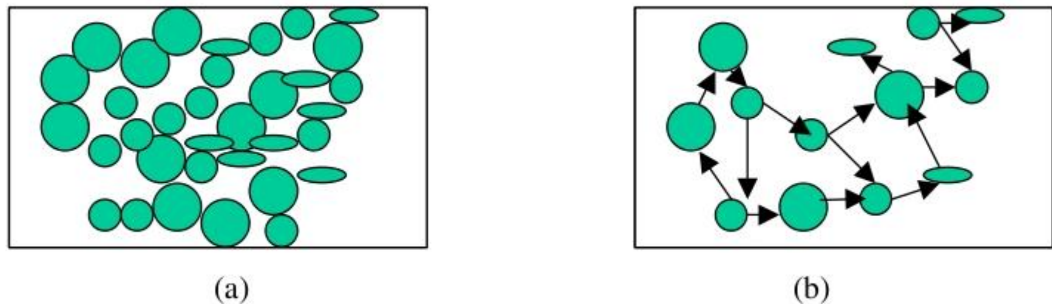


Figure 1.1: Conduction Mechanisms in conductive adhesives; (a) Particle-to-particle, (b) electron tunneling.

1.4 Main issues of ICAs application

Although electrically conductive adhesives have potential usage and various advantages over solder for surface mount technology (SMT) and microelectronics applications, issues and problems still remain to be solved in order to successfully implement ICAs for solder replacement in electronics assemblies. SMT requires short process times, high yield, high component availability, reliable joints for different components, visual inspection of joints, and capability of repair (Lundstrom, 1995). ECAs will not be a drop-in replacement for solder in the existing surface mount production lines. First, it will not be cost effective to do so. Special component lead plating and board conduction pad metallisations need to be optimized for conductive adhesives. Standard materials, components and assembly equipment for specific applications need to be developed combining the material vendors', research organizations', and application companies' efforts together. Mechanical bonding strength and electrical conductivity cannot be compromised for the new material development. Fine pitch and thinner lead trends have improved both the pick and placement machine accuracy and the stencil printing process (the laser etched or electroplated stencils and precise stencil printing machine). ICAs have more rigid process requirements for positioning due to their non-selective wetting and lack of self- alignment. Currently major concerns for using ICAs for SMT are the limited availability of components and substrates designed for adhesives, and the lack of methods to predict life-time reliabilities and their relationship to the accelerated life time tests

performed as solder joints. Different electrical and mechanical failure mechanisms require one to monitor these properties separately during life-time tests. There are difficulties to inspect the adhesive joints and judge the quality of the joints from visual and x-ray inspection methods, which work for solder joints perfectly. Repairability and reworkability of adhesive joints need to be investigated and improved.

1.5 Objectives

The aim of the research is to develop a conductive adhesive that have satisfactory rheological behavior that can be potentially used for solder replacement in the assembly of electronic devices. The aims of the research encompass the following measurable objectives:

1) To study the effect of filler size and volume fraction on viscosity measurement of ICA pastes.
2) To study the visco-elastic behaviour of pastes.
3) To study the thixotropic behaviour of pastes.
4) To investigate the thermal properties of ICA pastes.

In order to achieve the aims and objective of the research; the following research and development questions has been arouse as stated below:

1) How to relate ECAs formulation performance to rheological test methods?
2) What test methods used to characterise electrically conductive adhesives?
3) Comparison of flow behaviour between ICAs and solder pastes

1.6 Overview of the Thesis

Chapter 1 provides the introduction to the study, the aim and objectives of the work, and presents an overview of the thesis.Chapter 2 presents the results of the literature review on rheology of ICA pastes, linear visco-elasticity, thixotropic behaviour and thermal properties of the pastes. With regard to paste material, the volume fraction and the maximum volume fraction can also influence the viscosity of the paste. The relationship between viscosities and volume fractions of material paste can be described by some empirical models namely Krieger-Dougherty model, Quemada model and Eilers model (Agote et al., 2001). Therefore, in this study, the variation of viscosity and volume fraction of ICAs with three types of fillers (silver flakes, silver powder and mixture of silver flakes and silver powder) are investigated. The results obtained is benchmark against the commercial available solder paste and ICAs. Finally, the relationship between viscosities and volume fraction of ICAs is described by empirical models mentioned above. As the demand for lead-free pastes increases, hence, rheological measurements is needed in the formulation of new pastes.

Chapter 3 presents a description of the chemicals used, experimental equipment and parameters used for different parts of the study. In this study, the variation of rheology and volume fraction of ICAs with three types of fillers (silver flakes, silver powder and mixture of silver flakes and silver powder) are investigated. The investigation are divided into four parts. Chapter 4 presents the relationship between viscosities and volume fractions of material paste which described by using empirical models namely Krieger-Dougherty model, Quemada model and Eilers model (Agote et al., 2001).

The second part is the study of linear-viscoelasticity which presents in chapter 5. This study is characterised by using oscillatory stress and frequency sweep experiments. The third part presents an investigation of thixoptropic behaviour of the pastes which is discussed in Chapter 6. The final part which presents in chapter 7 is to study on the thermal properties of the pastes. The final chapter, Chapter 8 presents the summary of the study, the main conclusions from the study and the suggestions for the further work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter presents the relevant literature review on the rheological characterisation of solder pastes and ICAs used for Microsystem Assembly. The chapter is made up of three main sections; the first section gives a review on the rheological characterisation of solder pastes and ICAs used for Microsystem Assembly. In this section, a general literature search was carried out to identify the previous work on the rheology of solder pastes and ICAs. Based on the literature review, three main area were identified; firstly the visco-elastic behaviour of the paste, secondly the thixotropic behaviour of the paste materials and finally the relationship between viscosities and volume fraction of solder paste and ICAs. These areas of investigation are necessary for understanding the pastes behaviour during the stencil printing process.

The second section deals with the effect of filler size, volume fraction of filler and types of resins on rheology of the pastes. This area of investigation will allow for a better understanding of the rheological test methods that can be used in characterising the rheology of the pastes.

The final section gives a review on the thermal properties of the ICAs. This area of investigation is necessary because the physical, electrical and mechanical

properties of conductive adhesives depend to a large extent on the degree of cure of the epoxy composition in the ICAs.

2.2 Rheology

Rheology is defined as the science of the deformation and flow of matter and describes mainly the material properties of fluid and semi-solid materials. The term “rheology” was coined by Professor Bingham in 1929 and from then there has been a rapid development of the subject. Rheology is interdisciplinary and is used to describe the properties of a wide variety of materials such as oils, foods, inks, polymers, clays, concrete and asphalt. The common factor is that these materials exhibit some sort of flow and exhibit a rheological behavior that classifies them in a region somewhere between viscous and elastic. For example, the toothpaste that sits apparently motionless (elastic behavior) on the bristles of the toothbrush can be easily squeezed (viscous behavior) from the tube. Thus, toothpaste is said to be viscoelastic materials due to the ability to exhibit elastic and viscous properties simultaneously.

Fluid mechanics is the study of how fluids move and the forces on them. Fluid mechanics can be divided into fluid statics, the study of fluids at rest, and fluid dynamics, the study of fluids in motion. It is a branch of continuum mechanics, a subject which models matter without using the information that it is made out of

atoms. Fluid mechanics, especially fluid dynamics, is an active field of research with many unsolved or partly solved problems. A material can be classified as either a Hookean solid, a Newtonian liquid or as visco-elastic. In a perfect Hookean solid, material deforms when a force is applied and it relaxes on the removal of the force. The deformation energy is stored and is subsequently recovered on relaxation. In Newtonian viscous fluids, the deformation causes flow which ceases on the removal of the force, and the energy is dissipated as heat.

2.2.1 Basic terms associated with Rheology

(a) Newtonian and non-newtonian fluids

The simplest relationship between shear stress and shear rate for a fluid is one that is constant or directly proportional, as given by the equation below.

$$\tau = \eta \dot{\gamma} \tag{1}$$

The symbol η, is referred to as the Newtonian viscosity, and the flow curve (a plot of shear stress versus shear rate) is therefore a straight line passing through the origin, as can be seen Figure 2.1. In common terms, this means the fluid continues to flow, regardless of the forces acting on it. For example, water is Newtonian, because it continues to exemplify fluid properties no matter how fast it is stirred or mixed (Larson, 1999; Mewis and Wagner, 2009). Newtonian behaviour is rarely observed in suspensions (except in those non-interacting particles, which are fully dispersed – light concentrations in which particle collision rarely occurs).

The paste materials used in the studies reported in this studies are dense suspensions, exhibiting very densely packed particles which are in close contact with continuous interactions between particles – these pastes therefore exhibit non-Newtonian flow behaviour. In contrast, non-Newtonian fluid is one that does not exhibit a linear relationship between shear stress and shear rate. Therefore a constant coefficient of viscosity cannot be defined (Mewis and Wagner, 2009).

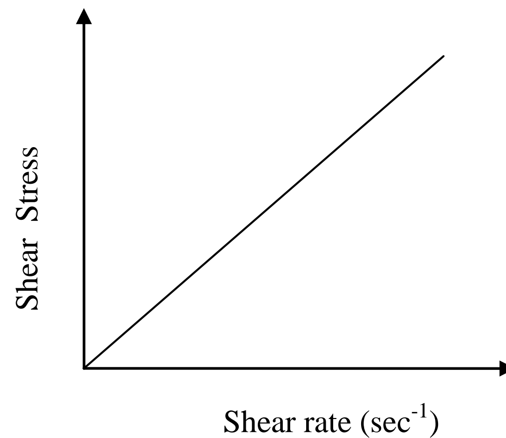


Figure 2.1: Flow curve of a Newtonian fluids

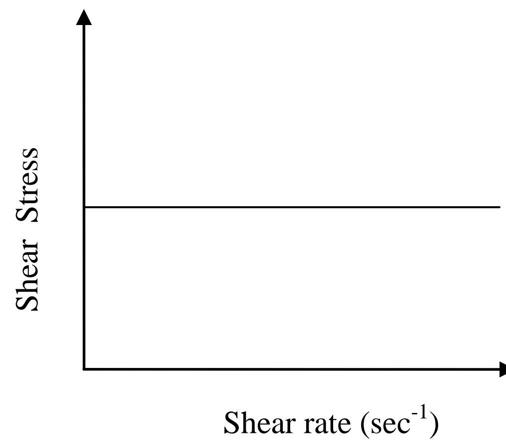


Figure 2.2: Flow curve of a Non-Newtonian fluids

(b) Visco-elasticity

Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. Viscous materials, like honey, resist shear flow and strain linearly with time when a stress is applied. Elastic materials strain instantaneously when stretched and just as quickly return to their original state once the stress is removed. Viscoelastic materials have elements of both of these properties and, as such, exhibit time dependent strain. Whereas elasticity is usually the result of bond stretching along crystallographic planes in an ordered solid, viscoelasticity is the result of the diffusion of atoms or molecules inside of an amorphous material (Bullard et al., 2009). Before making detailed dynamic measurements to probe the sample's microstructure, the linear visco-elastic region (LVER) must first be defined as the LVER can also be used to determine the stability of a suspension. This is determined by performing an amplitude sweep test. The length of the LVER of the elastic modulus (G') can be used as a measurement of the stability of a sample's structure, since structural properties are best related to elasticity. A sample that has a long LVER is indicative of a well-dispersed and stable system (Durairaj et al., 2008). Therefore, the oscillatory stress sweep is typically used to characterize the visco-elastic effect of emulsions, dispersions, gels, pastes and slurries (Mewis and Wagner, 2009). A frequency sweep is a particularly useful test as it enables the viscoelastic properties of a sample to be determined as a function of timescale. Within LVER, several segments might have the different visco-elastic properties, therefore,

frequency sweep test is performed to study the visco-elastic properties against time (Lapasin et al, 1997). Several parameters can be obtained, such as the Storage Modulus (G') and the Loss Modulus (G").

In terms of rheology, paste (solder paste and ICAs) can be classified as a visco-elastic fluid, the extreme described by Hooke's law of elasticity and Newton's law of viscosity (Jan et al., 2005). This means that solder paste has both viscous and elastic properties. The elastic properties is identified as the Storage Modulus (G'):

$$G' = \left(\frac{\tau_0}{\gamma_0}\right)\cos(\delta) = G^*\cos(\delta) \tag{2}$$

and the viscous properties as the Loss Modulus (G"):

$$G' = \left(\frac{\tau_0}{\gamma_0}\right)\sin(\delta) = G^*\sin(\delta) \tag{3}$$

The ratio between both properties is very important. It is expressed as the quotient of G" and G' and it is identified as the phase angle (tan δ):

$$\tan(\delta) = \frac{G''}{G'} \tag{4}$$

A structured system will gain energy from the oscillatory shear applied as long as the shear does not disrupt the structure. This energy is stored in the sample and is described as elastic modulus. However, the friction between the composition in the sample will cause energy to be lost as viscous

heating. Therefore, the loss modulus describes the part of the energy which is lost as viscous dissipation. Phase angle tan (δ) is associated with the degree of visco-elasticity of the sample. A low value in tan (δ) or δ indicates a higher degree of visco-elasticity (Durairaj et al., 2008).

During storage, transport and after printing the elastic properties in the solder paste (Storage Modulus) should dominate. Therefore tan (δ) should be < 1 and, more specifically, within certain maximum and minimum values (Lapasin et al., 1997). The accurate determination of the elastic fraction of a solder paste can only be carried out by sophisticated rheometry equipment according the principle of oscillation. A high G' value generally is an indication of a high resistance towards separation and slumping. The downside of a high G', however, may be paste hang-up on squeegees, limited print-speeds and ski sloping (Nachbaur et al., 2001).

2.2.2 Correlation of viscosity with volume fraction

In the rheological studies, several empirical models can be found that describe the relationship between the relative viscosity (η_r) of the suspension and the solids powder content expressed by volume fraction. The relative viscosity (η_r) is defined as the quotient of the apparent viscosity of the suspension ($\eta_{\text{material paste}}$) and the pure binder ($\eta_{\text{resin}}$). Einstein showed in 1906 that with increasing solids powder content the viscosity of the suspensions increases (Einstein, 1906):

$$\eta_r = 1 + 2.5\phi \tag{5}$$

The Einstein relationship is valid for diluted solutions and requires the solid particles to be spherical with an identical radius (Batchelor, 1970). With the integration and expansion of Einstein's equation, a large number of empirical models have been developed for a correlation of the relative viscosity with solids content, namely Krieger-Dougherty model, Quemada model and Eilers model (Eilers, 1941; Kriger, 1949; Quemada, 1977):

Krieger-Dougherty model:

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \tag{6}$$

Quemada model:

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-2} \tag{7}$$

Eilers model:

$$\eta_r = 1 + \left(\frac{1.25\phi\phi_m}{\phi_m - \phi}\right)^2 \tag{8}$$

With η_r relative viscosity, ϕ volume fraction, ϕ_m maximum packing factor, and $[\eta]$ intrinsic viscosity of the suspension ($[\eta]$=2.5 for spheres). And noted that ηr=ηsuspensionηmedium . The advantage of the Krieger-Dougherty model is, that it reduces to the correct Einstein equation in the limit of infinite dilution, whereas the Quemada and Eilers models give the right divergence for viscosity (η) as volume fraction (ϕ) approaches maximum packing factor (ϕ_m).

The viscosity of the suspensions, considering particles as rigid spheres, is directly related to the volume fraction. In suspensions with high-powder (fillers) concentration, the interactions between the particles affect the overall rheological behaviour. This is because, at high concentration ϕ, viscosities become sensitive to small variations in particle properties such as surface roughness, size distribution, shape and arrangement of the particles. In particular, when particles of two differing sizes are mixed, the viscosity can be much more lower than it is for suspensions containing the same volume fraction of monosized particles. Maximum packing factor ϕ_m is the highest volume of particles that can be added to a fluid until the flow of suspension is blocked (Barnes et al., 1989).

2.2.3 Introduction to thixotropic

All viscous fluids can exhibit thixotropy, because thixotropy reflects the finite time taken to move from any state of microstructure to another and back again. Certain materials behave as solids under very small applied stresses but under greater stresses become liquids. When the stresses are removed the material settles back into its original consistency. This property is particularly associated with certain colloids which form gels when left to stand but which become sols when stirred or shaken, due to a redistribution of the solid phase (Barnes, 1997; Mewis and Wagner, 2009).

Thixotropic describes the time dependence of the transient state viscosity at a given shear rate and the reversible and relatively slow breakdown of internal structure under shear. It is usually evaluated by measuring the area enclosed between the up-and-down curves obtained in a increasing and decreasing shear rate over time; named hysteresis loop test, as shown in Figure 2.2 (Barnes, 1997; Green and Weltmann, 1946). Green and Weltmann originally developed hysteresis technique in 1943. The area between the hysteresis loops is used as a measure of the 'amount' of thixotropy in the material and can be used as an indication of energy required to break down the material structure. However, the hysteresis area is a relative measure of thixotropic since it depends on the nature of the material and the parameters that define the hysteresis loop test: maximum shear rate and the times of duration of the linear increasing and decreasing of shear rate.

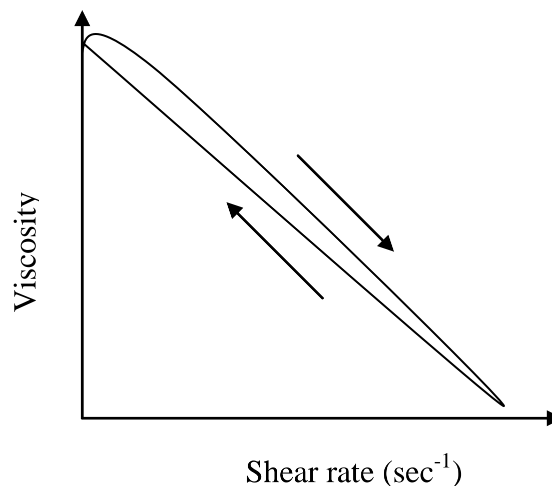


Figure 2.3: Hysteresis loop obtained by ramping 'up' and 'down' (Durairaj *et al*., 2004)

The complex rheological behaviour of thixotropic materials can be understood on the basis of a microstructure that depends on the shear. It is most often the result of relatively weak attractive forces between the particles. They will cause the formation of flocs, which normally evolve into a space-filling particulate network. The inter-particle bonds are, however, weak enough to be broken by the mechanical stresses that occur during flow. The result is that during flow the network breaks down in separate flocs, which decrease further in size when the strain rate is increased. Reducing the shear rate can cause a growth of the flocs, resisting the flow will allow the particulate network to rebuild. Kinetic coagulation is the driving mechanisms in this case. The stresses in the suspension depend on the microstructure and will vary accordingly during or after flow. When the structural changes require a finite amount of time, the same will apply to the stresses, resulting in thixotropic behaviour (Mewis and Wagner, 2009). This resulting in poor recovery of the solder paste after the paste being force out from the stencil aperture and solder paste would slump easily. As stated earlier, the paste rheology dictates it's flow behavior during the printing process, and there have been numerous attempts to correlate paste rhelogical properties to the stencil printing performance. Therefore in this study, the thixotropic test method is used to evaluate the pastes thixotropic behavior with respect to its printability.

2.3 Previous studies on rheology of pastes (solder paste and ICAs)

The shear rheology of solder paste and ICAs has been characterized by several authors. In the study by Batchelor (1970) reported a comprehensive overview of the rheological behavior of solder paste and ICAs. They identified factors such as particle distribution and shape, volume fraction of fillers, and resins material as those that affect the rheology of the pastes. Another study by Glaessgen and Mackay (1981) reviewed the role of the filler materials, filer size, shape and distribution and their effect on paste performance.

In a study by McGrath *et al.* (2008), a combination of dynamic shear rheology, thermo-mechanical analysis (TMA), scanning electron microscopy (SEM), and fracture toughness testing was utilized to characterize the thermal, mechanical, chemical, and fracture properties of solder paste as a function of average filler size, size distribution, particle shape, loading, and paste crosslink density. Small changes in particle size, shape, and size distribution had little impact on the final properties. The shear storage modulus-temperature profile exhibited a subtle broadening in the glass transition, T_g region and at the temperature slighty above the T_g with increased filler loading. The broadening was more pronounced in the lower crosslink density, the author concluded that this effect is likely due to particle-particle contacts that increase with increasing filler loading. This study reviewed the role of the filler size, shape of particle, loading, paste crosslink density and their effects on paste performance.

In a study by Kim *et al.* (2004), in a solder paste printing process, one of the most important parameters is the viscosity of the solder paste. The solder particle content can have a profound effect on the viscosity and rheological properties of the solder paste. Solder particle content is usually specified by weight percent. Using weight percent is convenient for certain purposes, but it is the volume occupied by the powder that determines the ultimate viscosity. In general, the viscosity of a disperse system increase as the volume fraction of the suspended solder particles increases. The viscosity increases totally with increasing solder particle content. This study emphasized the importance of viscosity in stencil printing process as the viscosity of solder paste must be low enough to force out from the squeegee yet high enough to reshape. The interaction between the particles and the flux vehicle system has a direct effect on the flow behaviour of the solder pastes. Therefore, oscillatory test is needed to study the liquid and solid (G' and G") characteristics of solder paste beyond the linear visco-elastic region.

Melvis *et al*. (2009) review the concept of thixotropy with a focus on particulate suspensions. It is most often the result of relatively weak attractive forces between the particles. They will cause the formation of flocs, which normally evolve into a space-filling particulate network. The interparticle bonds are, however, weak enough to be broken by the mechanical stresses that occur during flow. The result is that during flow the network breaks down in separate flocs, which decrease further in size when the strain rate is increased. Reducing the shear rate can cause a growth of the flocs; arresting the flow will allow the particulate network to

rebuild. The stresses in the suspension depend on the microstructure and will vary accordingly during or after flow. When the structural changes require a finite amount of time, the same will apply to the stresses, resulting in thixotropic behavior. This resulting in poor recovery of the solder paste after the paste being force out from the stencil aperture and solder paste would slump easily.

Another study by Shahzada *et al.* (2006) showed that storage modulus, G' and loss modulus, G'' increase with additives loading. The solder paste behave as more viscous and more elastic. However, the viscosity decrease dramatically with increasing shear rate, this implies that the network structures are compromised of weak physical bonds which can be disturbed by shear. The solder paste shows thixotropy behaviour because shear forces from mixing are able to break the interaggregate Hydrogen bonding. At very high shear rates, no thixotropy behaviour because the three-dimensional network structure get completely ruptured inelastically. These findouts was well agreed with the study by Malucelli *et al.* (2007). The implication of these finding is that solder paste will exhibit fluid like behaviour at higher stresses, which can facilitate the aperture filling process during stencil printing.

The creep-recovery test is a technique used to assess time-dependency behaviour of a printing process. A sample under the test is exposed to a constant value of stress in shear direction and the strain is monitored with time. After the strain is stable, the stress is removed while strain is still monitored. Typically time

dependent behaviour called thixotropy is revealed. This test can be useful for some pastes for characterizing the tendency of a paste to slump with the slump propensity correlated with the relaxation in strain after the stress is removed. Bao *et al.* (1998) and Nguty *et al.* (2000) used the creep-recovery test to predict slump tendency in different pastes. These early reports on work on the viscoelastic behaviour of pastes identified the need for more information on the solid and liquid characteristics of the pastes especially on linear visco-elastic region of pastes.

In one study by Durairaj *et al.* (2008), the rheological properties and the printing performance of lead-free solder pastes was evaluated. This study investigates the rheological behaviour of the pastes (solder paste and isotropic conductive adhesives) used for flip-chip assembly. Oscillatory stress sweep test are performed to evaluate solid characteristic and cohesiveness of the lead-free solder pastes and isotropic conductive adhesive paste materials. The results show that the G' (storage modulus) is higher than G" (loss modulus) for the pastes material indicating a solid like behaviour. It result shows that the linear visco-elastic region for the pastes lies in a very small stress range, below 10 Pa. In addition, the stress at which the value of storage modulus is equal to that of loss modulus can be used as an indicator of the paste cohesiveness. The measured cross-over stress at G'=G" shows that the solder paste has higher stress at G'=G" compared to conductive adhesives. Creep-recovery test method is used to study the slump

behaviour in the paste materials. The conductive adhesive paste shows a good recovery when compared to the solder pastes.

Four basic print defects occur during stencil printing:

- Skipping: low volume of solder paste
- Slump: print deposits lose height and spread at the base
- Bridging: particles and flux merge from adjacent prints to form a continuous deposit

2.4 Previous studies on the Stencil Printing Process

Surface mount technology (SMT) is an important method used in the electronic assembly industry to produce modern electronic products. Various electronic products increasingly require higher density, enhanced performance, smaller size, and lighter weight, driving the advanced development of new packages, new manufacturing technologies, and sophisticated equipment. A typical surface mount assembly (SMA) line comprises a stencil printer, high-speed chip shooter, multi-purpose chip shooter, and reflow furnace for populating PCBs (Printed Circuit Boards) using reflow soldering. The populated PCBs are transferred across the assembly line using an automatic conveyor system. During the first step of SMA, solder paste is deposited onto the PCB pads via stencil printing. Air pressure then is applied to a squeegee, forcing the solder paste roll to the front of

the squeegee blade. In na study by Tshung (2008), the high pressure squeezes the solder paste into the stencil aperture, and the squeegee travels across the surface of the stencil, after which leaving paste on the PCB pads, after the release of the stencil. Next, the surface mount components (SMCs) are picked and placed on the pasted pads using chip shooters. Finally, the solder paste is reflowed and solder joints are established through reflow furnace.

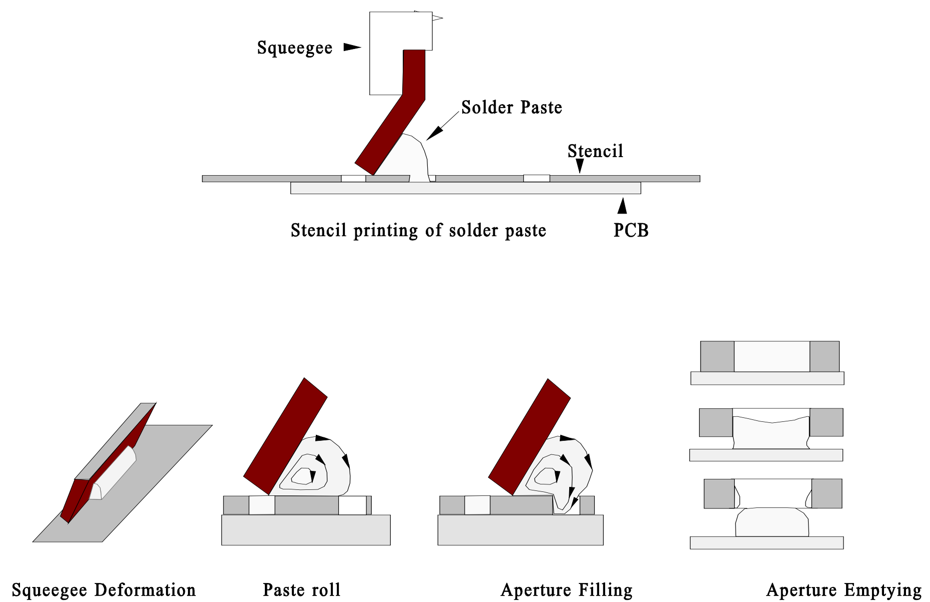


Figure 2.4 : Sub-processes in solder paste printing (Durairaj *et al*., 2009)

According to a study by Durairaj *et al.* (2008), the paste printing process is known to be controlled by a number of process parameters, which can be divided into four groups: printer, stencil, environmental, and paste parameters. Some of these parameters are fixed (e.g. stencil) while the paste properties such as viscosity are constantly changing during the print cycle. The key physical sub-processes include: (i) paste pre-print treatment, (ii) squeegee deformation (iii) paste roll, (iv) aperture filling, (v) aperture emptying and (vi) paste slump. These sub-processes are linked together by the properties of the pastes such as its flow history and its rheology. The pressure in the paste during and after aperture filling helps determine whether the paste will adhere onto the substrate, stencil or squeegee after aperture emptying. As stated earlier, the paste rheology dictates the paste's behaviour during the printing process; and there have been numerous attempts to correlate paste rheological properties the stencil printing performance.

Lead-free solder paste printing process accounts for majority of the assembly defects in the electronic manufacturing industry. Most defects such as poor release, slumping and bridging originate from poor understanding of the flow properties and processing of solder pastes. Durairaj *et al.* (2009) conducted an investigation on rheological behaviour and stencil printing performance of the lead-free solder pastes Sn/Ag/Cu. From this study, it was found that the solid characteristics, G' is higher than the liquid characteristics, G'' for the paste material. This indicated that the solder paste has a higher cohesiveness resulting in poor withdrawal of the paste during the stencil printing process.

Tshung (2008) reported that averages of 60% of soldering defects are attributed to solder pastes stencil printing process. The desired paste deposit volume and the occurrence of printing defects (such as bridge, slump, and scoop) determine stencil printing performance, which is influenced by numerous variables including stencil design, stencil printer, solder paste selection, product configuration, and parameter settings. The rheology of [illegible] paste can be attributed to particle size, particle distribution, and changing of viscosity during the print stage. The correct choice of solder paste type and its ingredient can improve printability, solderability and solder joint reliability. The rheological property of solder pastes influences printing pattern consistency, tack and slump performance. The author observed a strong relationship between snap-off height and paste deposit volume.

2.5 Materials of ICAs

ICAs offer several advantages over solder. They are environmentally friendly, eliminating the lead (Pb) and flux associated with normal soldering processes, and their associated cleaning/disposal problems, reducing coefficient of thermal expansion (CTE) mismatch design limitations, and offering lower temperature processing and less complicated assembly processes. However, a better understanding of the design, reliability, material, and manufacturing characteristics of various conductive adhesive technologies must be achieved before an assessment of their leverages as a component attachment replacement

can be made. The processing parameters, such as temperature, pressure, cure time, and materials and shelf life are critical to the success of making reliable electrical and mechanical interconnections at time zero and during the life cycle. At this stage, they are not ready to replace solder throughout the electronics industry due to questions that remain concerning the electrical and mechanical reliability of the adhesive joints. Their implementations are currently limited to low cost applications and specialty applications where solder cannot be used. Research and development in the past has evaluated both the electrical and mechanical reliability of these materials for specific electronic packaging processes (Liu and Rorgren, 1993).

2.5.1. Conductive Filler

Several factors influence the use of metal fillers. Silver is the most conductive of the frequently used metals, although it is also expensive. Some researchers have explored the use of copper or other low-cost materials instead of silver, but their results have largely proved unsatisfactory. One problem is that oxides and other films on the particles' surface are non-conductors and therefore dramatically change the electrical properties of the composites. This effect is most significant with the smallest particles. Therefore, only metals with high corrosion resistance, such as silver or gold, can be used. Nickel is also of interest because of its low rate of oxidation. According to Kusy (1977), silver coated plastics or glass

particles can be used as a metal filler, but the mixing processes have been known to fragment the fragile silver coating, reducing metal-to-metal contacts. Electrical properties of the composites made from the coated particles are very sensitive to processing conditions. Very thin silver coated layers are unsuitable.

Liu (1999) suggested that silver is the most commonly used conductive filler for isotropic conductive adhesives because of its high electrical conductivity, chemical stability, and lower cost compared to gold. Unlike many other metals such as copper, that become non-conductive after being oxidized due to exposure to heat and humidity, silver oxides also show high conductivity.

In another study by Shimada et al. (2000), the other important attribute is that silver can be easily precipitated into a wide range of controllable sizes and shapes. The silver fillers are typically fabricated into flakes and pretreated with organic lubricants to ensure the proper rheology of the ICAs.

Wong et al. (2000) investigated the organic lubricant on the surface of silver flakes and found that it can greatly affect the performance of ICAs, including the dispersity of the Ag flakes in the ICA, rheology, and electrical conductivity of the ICA.

Phuapradit et al. (2002) presented a review of mixture of silver flakes and particles with broad size distribution associated with rheology and electrical properties. Flakes can provide improved conductivity by allowing the flake-like

particles to overlap one another. On the other hand, the voids caused by the overlapping can be filled with the small particles. Other silver systems were also developed to improve the performances of silver-based conductive adhesives.

Researchers used highly porous Ag power as filler material for ICAs (Kottaus, et al., 1997). They illustrated that the thermo-mechanical properties of the adhesives using porous Ag were improved because of the infiltration of the resin into the pores. The electrical performance of these systems, however, needs further improvement. Researchers utilized a mixture of silver flakes and low-melting-point alloy fillers (LMPA) as the conductive filler (Lu and Wong, 2000). During the curing of the adhesive, the LMPA filler melts and forms metallurgical interconnections between the Ag flakes and the metallisations of the substrates.

2.5.2 Resins: Thermoplastics and Thermosets

Lyons (1991) investigated the effect of resin materials on the properties of ICAs. Two types of polymers can be used as the adhesive resins: thermosets and thermoplastics. Lyons summarised that thermoset materials do not flow at high temperatures due to the interlocked cross-linked structure after cure. They are materials that are initially monomers, which polymerise during curing (hardening) process. Three-dimensional cross-linked molecular structures are formed after curing as a result of the physical links or branch points that tie the polymer chains together. The relative number of branch points is called the cross-link density, and

materials with high cross-link densities tend to be stiffer but more brittle. The degree of chemical conversion at which the cross-link structure first forms is called the gel point and the phenomenon is know as gelation.

The material cannot flow as a true liquid after gelation. Viscosity depends upon molecular weight and increases during the polymerisation reaction, and effectively goes to infinity at the gel point. Thermoplastic materials consist of long polymer chains that have few side branches, and the chains are not physically linked. They can flow at a high temperature since they do not process the cross-link network structures that prevent flow of thermoset polymers. The properties of these materials depend on the structure of the backbone chain. High temperature engineering thermoplastics have been introduced that rival the performance of thermoset. They can withstand the temperatures of soldering operations without physical deformation and flow because they possess exceptionally rigid chain high molecular weight structures that resist large scale molecular motion until very high temperatures. They are amorphous glasses, such as polyetherimide and polyethersulfone.

Thermoset epoxy resins are the most common polymer matrices used for conductive adhesives. The epoxies based on the diglycidyl ether of bisphenol-A (DGEBA), which is synthesized by reacting bisphenol A and epichlorohydrin, are the common materials for liquid adhesives. DGEBA epoxy has an epoxide functionality of 2 for its average molecular weight of 380. Modification to the

base resin usually consists of varying the epoxy equivalent weight or increasing the viscosity. The main ingredients of an epoxy system consist of the resin and the hardener. Sometimes an accelerator is added to facilitate curing, leading to the desired reaction products at desired temperatures. Notice the bisphenol A resin contains active three-member rings. Ring opening reactions with hardeners produce highly cross-linked structures in a curing process. Several of hardeners have been found effective, resulting in different rates of curing, different reaction products and product properties. They can be grouped into three major categories: catalytic (Lewis acids and bases), amines (aliphatic and aromatic), and anhydrides. In the case of anhydrides, tertiary amine accelerators, or catalysts, are added to promote curing.

Klosterman et al. (1995) reported that aliphatic amines generally cure rapidly and can react at low temperatures. Elevated temperature cures are often required of aromatic amines, as the functional groups are tied to more rigid moieties. Epoxy curing involves sequential opening of the three-member rings. Each can form two chemical bonds with hardeners. Therefore, the original DGEBA molecule theoretically serves as a cross-linking point, connecting four branches. The viscosity of the resin first decreases as temperature increases. Meanwhile, as the extent of cure reaction increases, the polymeric structure becomes cross-linked. At the gel point, the increased cross-linking causes the material viscosity to rise greatly and further flow is prohibited. As a consequence, the system cures and stiffens, and the material is no longer process able.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

This chapter presents a description of the chemicals used, experimental equipment, and parameters used for different parts of the study. In this study, the variation of rheology and volume fraction of ICAs with three types of fillers (silver flakes, silver powder and mixture of silver flakes and silver powder) are investigated. The investigation are divided into four parts. The relationship between viscosities and volume fractions of material paste can be described by some empirical models namely Krieger-Dougherty model, Quemada model and Eilers model (Agote et al., 2001). The results and discussion of this study will be presents in chapter 4. The study of linear-viscoelasticity based on oscillatory stress and frequency sweep experiments is presents in chapter 5, Chapter 6 presents an investigation of thixoptropic behaviour of the pastes. The study which is presents in chapter 7 is to study on the thermal properties of the pastes. The results obtained is benchmark against the commercial solder paste and ICAs.

3.2 Methodology

1) 0.8 by volume fraction of epoxy resins and 0.2 by volume fraction of fillers were weighed and mixed.
2) 10% by weight of curing agents was weighed and mixed with the mixture.
3) Mixture was sonicated for 30 minutes.
4) Rheological and thermal properties characterizations.

3.3 Sample preparation

In this study, viscosities of formulated isotropic conductive adhesives (ICAs) at different volume fraction of filler were being benchmark against commercial available conductive pastes (lead-free solder pastes and ICAs). In order to minimize separation and prolong shelf life, manufacturers prescribed specific storage conditions was followed in this study, for example the ICAs and solder pastes used in this study are stored in a fridge unit at -20˚C and -4˚C, respectively. As it is important to carry out the experiments on the paste samples at room temperature, the procedure used in the study is to bring out the ICA and solder paste from the fridge prior to the rheological tests, and to allow these pastes to attain room temperature.

Table 3.1 shown the chemicals used in the formulation of ICAs. As shown in table 3.2 and table 3.3, the parameters being investigated in these studies were size of filler and volume fraction of filler. Constituent of commercial solder paste and ICA's investigated is shown in table 3.4.

Table 3.1: Chemicals used in the preparation of ICAs.

Chemical Functions	Chemicals	Manufacturer
Resin	Diglycidylether of bisphenol-A (DGEBA)	Sigma Aldrich
	Polyurethane (PU)	
Curing agents	Ethylene diamine	Merck & Co.
Fillers	Silver flakes and silver powder	Sigma Aldrich

Table 3.2: Size and volume fraction of filler investigated.

Filler size (μm)		Volume fraction of filler
Silver flakes	**Silver powder**	
10	250	0.2
		0.4
		0.6
		0.8

Table 3.3: Samples investigated.

System	Parameter
S1	0.8-silver flakes/0.2-DGEBA
S2	0.6-silver flakes/0.4-DGEBA
S3	0.4-silver flakes/0.6-DGEBA
S4	0.2-silver flakes/0.8-DGEBA
S5	0.8-silver powder/0.2-DGEBA
S6	0.6-silver powder/0.4-DGEBA
S7	0.4-silver powder/0.6-DGEBA
S8	0.2-silver powder/0.8-DGEBA
S9	0.8-silver flakes+powder/0.2-DGEBA
S10	0.6-silver flakes+powder/0.4-DGEBA
S11	0.4-silver flakes+powder/0.6-DGEBA
S12	0.2-silver flakes+powder/0.8-DGEBA
S13	0.8-silver flakes/0.2-PU
S14	0.6-silver flakes/0.4-PU
S15	0.4-silver flakes/0.6-PU
S16	0.2-silver flakes/0.8-PU
S17	0.8-silver powder/0.2-PU
S18	0.6-silver powder/0.4-PU
S19	0.4-silver powder/0.6-PU
S20	0.2-silver powder/0.8-PU
S21	0.8-silver flakes+powder/0.2-PU
S22	0.6-silver flakes+powder/0.4-PU
S23	0.4-silver flakes+powder/0.6-PU
S24	0.2-silver flakes+powder/0.8-PU

Table 3.4: Constituent of commercial lead-free solder paste and ICA's investigated

Paste samples	Particle size distribution (µm)	Particle shape	Flux Medium/Binder	Solder alloys/materials (percentage by weight)
P1	20-45	Spherical	Flux Vehicle System	Tin95.5%/Copper0.7%/ Silver3.8%
P2	20-45	Spherical	Flux Vehicle System	Tin96.5%/Silver3.5%
P3	8-10	Flakes	Epoxy resin	Silver88%

3.4 Rheometry

All the flow curve test measurements were carried out with the Physica MCR 301 controlled stress rheometer. The rheometer setup was shown in Figure 3.1. In order to avoid the formation of wall slip at the interface between the plate and conductive paste, a parallel plate geometry was chosen with a diameter of 25 mm. A gap height of 0.5 mm was used between the upper and lower plate, as shown in Figure 3.2. Prior to loading the sample onto the rheometer, the conductive paste was stirred for about 1-2 min to ensure that the paste structure is consistent with the particles being re-distributed into the paste. A sample was loaded on the peltier plate and the geometry plate was then lowered to the gap of 0.5 mm. The excess paste at the plate edges was carefully trimmed using a plastic spatula. Then the sample was allowed to rest for about 1 min in order to reach the equilibrium state before starting the test. All tests were conducted at 25˚C with the temperature controlled by the Peltier-Plate system. Each test was repeated for three times for stabilisation (with fresh samples used for each test). Table 3.5 shown the experimental parameters set for the flow curve test. Flow curves are basic rheology characteristics showing static properties of flowing materials. They express a relation between shear rate or shear stress applied to the viscosity of a material, which flows. Table 3.6 and table 3.7 shown the experimental parameters set for the oscillatory and frequency sweep tests which study the visco-elastic properties of the pastes. Table 3.8 and 3.9 presents the experimental parameters set for steady shear rate thixotropic and hysteresis loop tests.

Figure 3.1: Rheometer setup

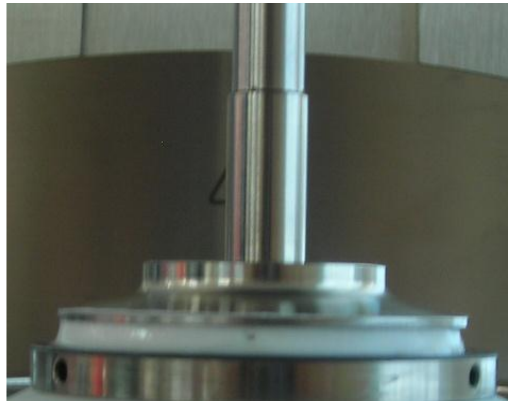


Figure 3.2: Parallel plate rheometry

Table 3.5: Experimental parameters for flow curve test

Experimental values				
Initial shear rate (s^{-1})	**Final shear rate (s^{-1})**	**Number of measuring point**	**Interval between measuring point (s)**	**Overall Duration (s)**
0.001	100	31	3	100

Table 3.6: Experimental parameters for the oscillatory stress sweep test

Experimental values				
Strain (%)	**Angular frequency (s^{-1})**	**Number of measuring point**	**Interval between measuring point (s)**	**Overall Duration (s)**
0.001-100	10	25	5	125

Table 3.7: Experimental parameters for the frequency sweep test

Experimental values				
Strain (%)	**Angular frequency (s^{-1})**	**Number of measuring point**	**Interval between measuring point (s)**	**Overall Duration (s)**
0.001	1-100	26	5	130

Table 3.8: Experimental parameters for the steady shear rate test

Experimental values					
Initial shear rate (s^{-1})	**High shear rate (s^{-1})**	**Number of measuring point**			**Overall duration (s)**
		Interval 1	**Interval 2**	**Interval 3**	
0.001	100	20	20	20	240

Table 3.9: Experimental parameters for the hysteresis loop test

Experimental values				
Initial shear rate (s^{-1})	**High shear rate (s^{-1})**	**Number of measuring point**		**Overall duration (s)**
		Up curve	**Down curve**	
0.001	100	20	20	240

3.5 Instrumental (DSC)

Differential scanning calorimetry (DSC) tests measurements were carried out with a Mettler Toledo DSC 823e calorimetry. The image of DSC was shown in Figure 3.3. Dynamic analysis at 10˚C/min heating rate in the temperature range from 25 to 300˚C under nitrogen purge gas (50 ml/min) were performed. The experiments were conducted under a nitrogen atmosphere in order to eliminate oxide formation during the process. The temperature is divided into three cycles: 25 to 300˚C; 300 to 25˚C; and 25 to 300˚C respectively. Small sample quantities were used (<5 mg). The samples were loaded in aluminium pans.

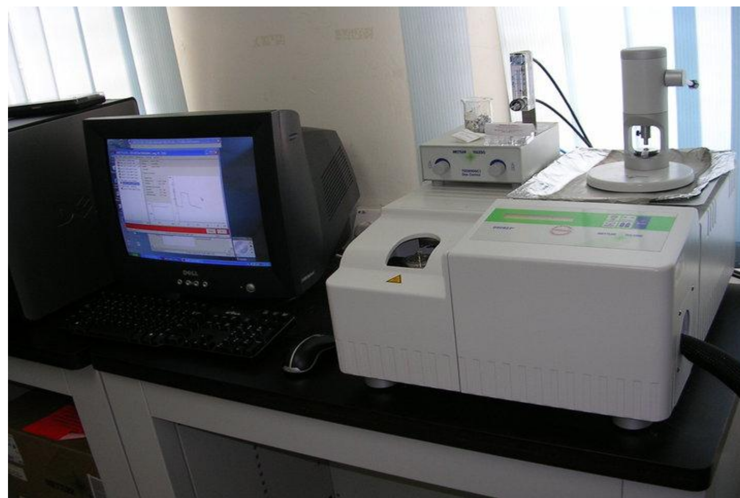


Figure 3.3: Differential Scanning Calorimetry (DSC) setup

Differential scanning calorimetry (DSC) has been widely used for characterizing polymeric materials and determining the thermal behaviour of alloys. Generally, DSC can be used to provide direct information on the following thermally driven reaction dynamics of materials (Kuck, 1986; Abys et al., 1995):

1. Endo- and exo-thermic chemical reactions;
2. Melting point (T_m), phase change transition and glass transition temperatures (T_g);
3. Latent heat of fusion and solidifications;
4. Specific heat capacity and thermal cycling effects.

Additionally, the DSC can provide secondary information such as indications of supercooling. The fundamental principle of using DSC as a thermo-analytical tool is the requirement to measure, as a function of temperature, the difference in heat that is required to increase the temperature of a sample with respect to a reference material. In general, both the sample and reference are maintained at approximately the same temperature throughout the experiment and a temperature programme is established so that the temperature of the sample increases linearly with time. Thus, if the sample undergoes a physical transformation during heating, such as a phase transition, precipitation or recrystallisation, a heat flow or local heat input is established to maintain both the sample and the reference material at the same, or nearly the same, temperature.

DSC measurement of heat flow is based on the measurement of the energy required for a transition within a sample occur. The energy consumed by the sample is determined by measuring the difference in energy absorbed in heating the sample to the energy required to heat an empty reference pan. During DSC measurement, all reactions absorbing or emitting thermal energy are recorded. These are indicated by peaks and troughs on the DSC scan trace. For example, in soldering processes, the endo-thermic troughs indicate solvent evaporation and melting, whilst the exo-thermic peaks may indicate other phenomenon such as oxide formation (Sherman and Mackay, 1990).

It is to be noted that the term “peak” refers to the maximum temperature of either the endo-thermic or the exo-thermic reactions where appropriate. In reality, the profile of the endo-thermic reaction is a downward trough and the exo-thermic reaction is an upward peak.

In this study, the curing reaction of isotropic conductive adhesives (ICAs) was examined with a DSC. Tests were conducted to investigate the effect of size and volume fraction of conductive fillers; and different types of polymeric resins on the thermal properties of the ICAs. The results obtained were compared with the commercial solder pastes and ICA.

CHAPTER 4

VISCOSITY CHARACTERISATION AND EMPIRICAL MODELLING

4.1 Introduction

This chapter presents the effects of size and volume fraction of fillers on the viscosity of ICAs. With regard to paste material, the volume fraction and the maximum volume fraction can also influence the viscosity of the paste. The relationship between viscosities and volume fractions of material paste can be described by some empirical models namely Krieger-Dougherty model, Quemada model and Eilers model (Einstein, 1906; Agote et al., 2001; Loebecke et al., 2009). Therefore, in this study, the variation of viscosity and volume fraction of ICAs with three types of fillers (silver flakes, silver powder and mixture of silver flakes and silver powder) are investigated. The results obtained is benchmark against the commercial available solder paste and ICAs. Finally, the relationship between viscosities and volume fraction of ICAs is described by empirical models mentioned above.

4.2 Results and Discussion

4.2.1 Effect of size of the filler particles on viscosity of ICA pastes

Figure 4.1 showed the flow curves of commercial solder pastes and ICA while Figure 4.2 (a), (b) and (c) showed the flow curves of formulated ICAs. As expected, as the shear rate is increased, all the pastes showed a decrease in the viscosity. The drop in viscosity clearly indicates the pastes are shear thinning in nature and the structure of the pastes was undergoing changes due to destruction of flocculations in the suspensions (Bao et al., 1998). Maintaining a constant volume fraction of filler while reducing the particle size of filler leads to an increase in the viscosity of ICAs. The effect of this change on the viscosity of the system is shown in Figure 4.3. This data indicates that a higher number of smaller particles results in more particle-particle interactions and an increased resistance to flow. Clearly as shear rate increases, this effect becomes less marked, suggesting that any particle-particle interactions are relatively weak and broken down at high shear rate. The smaller filler particles have larger specific surface area. This is considered a possible reason for particle-to-particle contact in the ICAs and, consequently, the viscosity of ICAs with smaller filler particles will be higher than that with larger filler particles.

In this study, comparison was made based on two filler of different particle size; silver flakes of 10 μm and silver powder of 250 μm. The effect of filler particle size on the viscosity has been reported for ICAs with 0.8 volume fraction of filler

load. It is noted that at zero shear rate, the viscosity of ICAs with silver flakes filler has the highest viscosity, 79300 Pa.s followed by 55900 Pa.s for mixture of silver flakes and silver powder filler and 53800 Pa.s for silver powder filler. As the particle size (10 µm for silver flakes and 250 µm for silver powder) of filler decreases, the viscosity increases. A smaller particle size filler tends to have higher contact surface area and hence disperse better in the flux system. In addition, the filler particles tend to agglomerate into larger flocs in the system and this lead to increase of resistance of flow of the ICAs and viscosity is higher.

On the other hand, a larger particle size filler has lower contact surface area and has poor dispersion ability, therefore, viscosity is lower. Figure 4.4 (a), (b) and (c) presents the viscosities for the formulated samples with different silver and polyurethane as resin. The similarities with the samples formulated with DGEBA resin, 0.8 volume fraction of silver filler/0.2 polyurethane samples give the highest viscosity and the viscosities is decreasing when shear is applied. However, the viscosity of the samples which formulated with DGEBA are more consistent compared with the samples formulated with PU. Hence, DGEBA is a better resin than polyurethane.

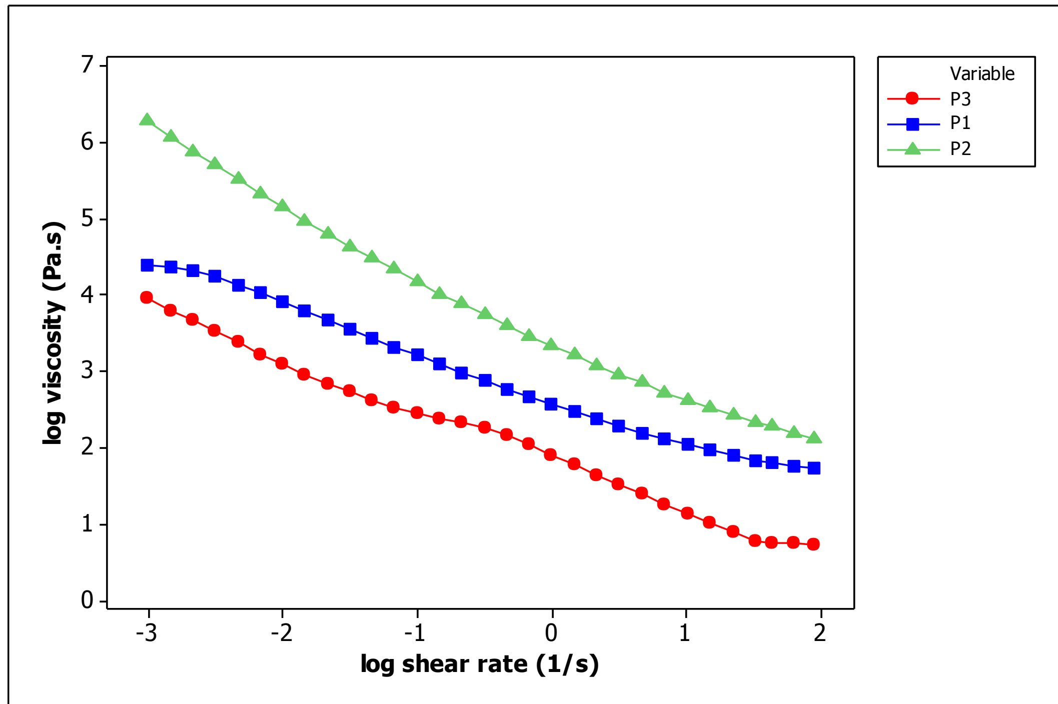
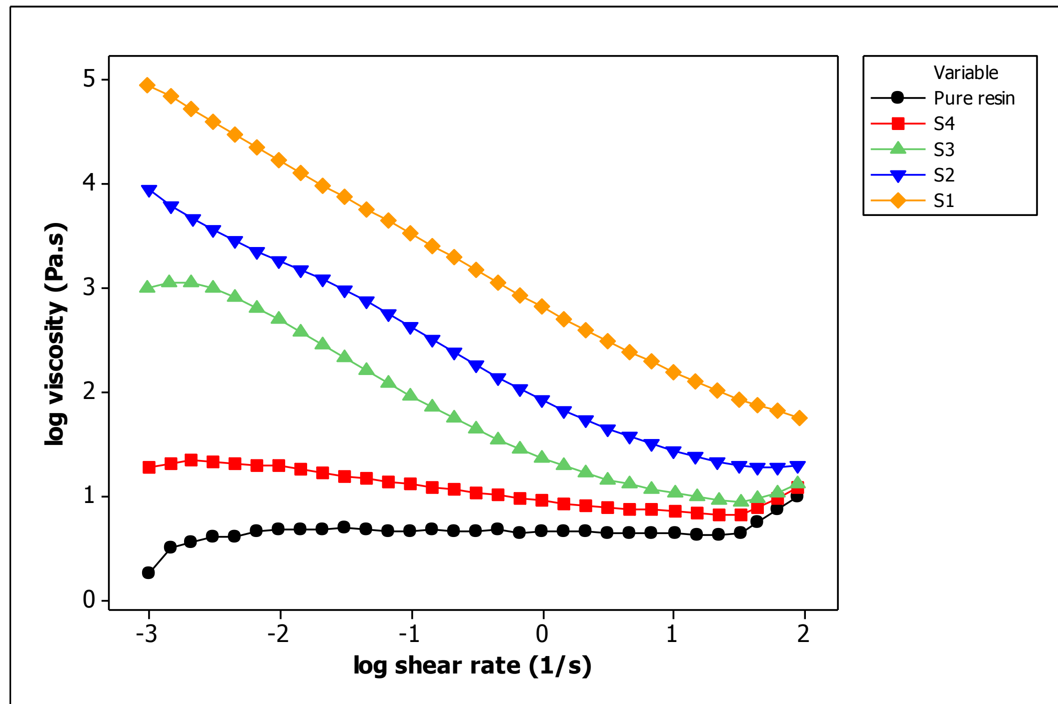
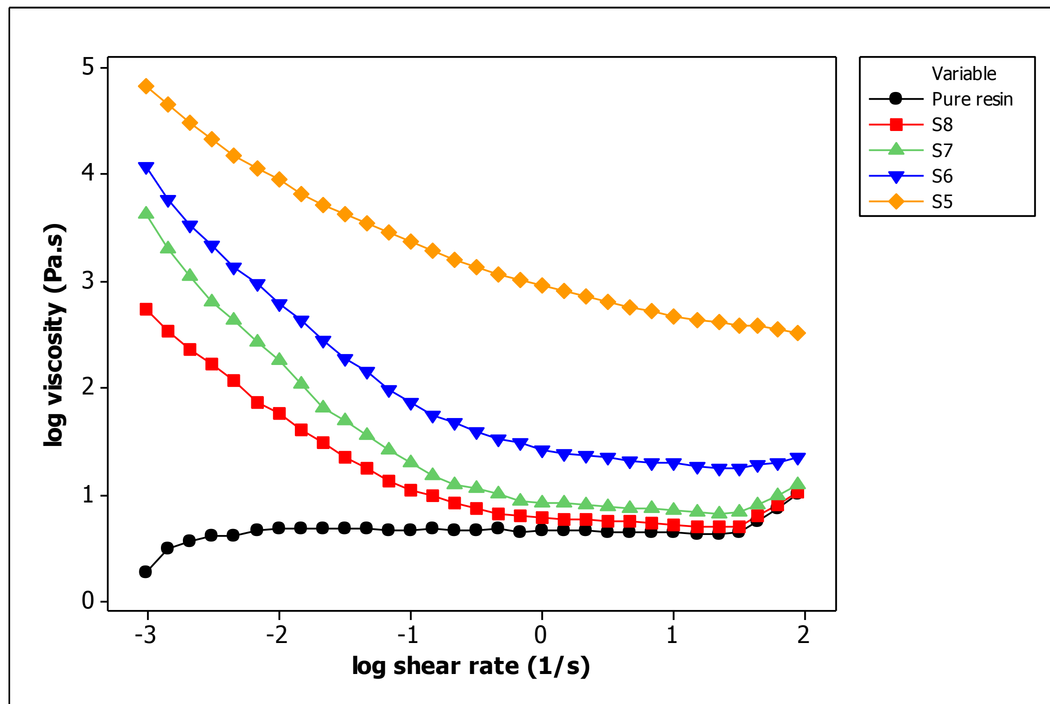


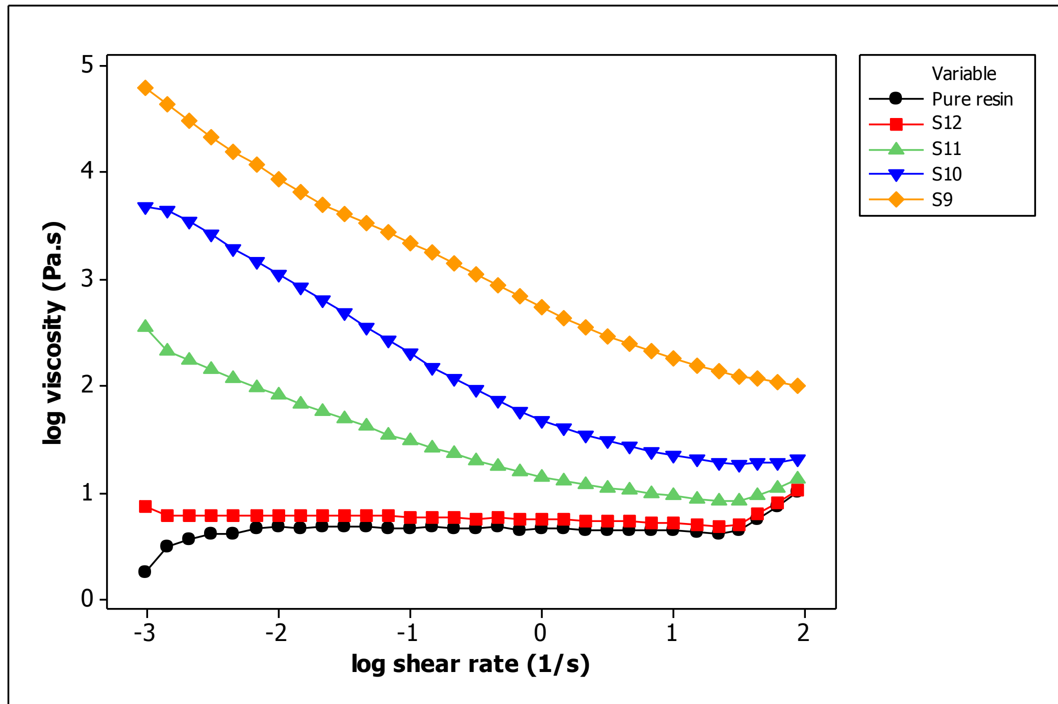
Figure 4.1: Flow curve of commercial solder paste and ICAs



(a) silver flakes/ DGEBA



(b) silver powder/ DGEBA



(c) mixture of silver flakes and silver powder volume fraction/ DGEBA

Figure 4.2: Flow curve of formulated samples (a) silver flakes/DGEBA, (b) silver powder/DGEBA and (c) silver flakes and powder/DGEBA

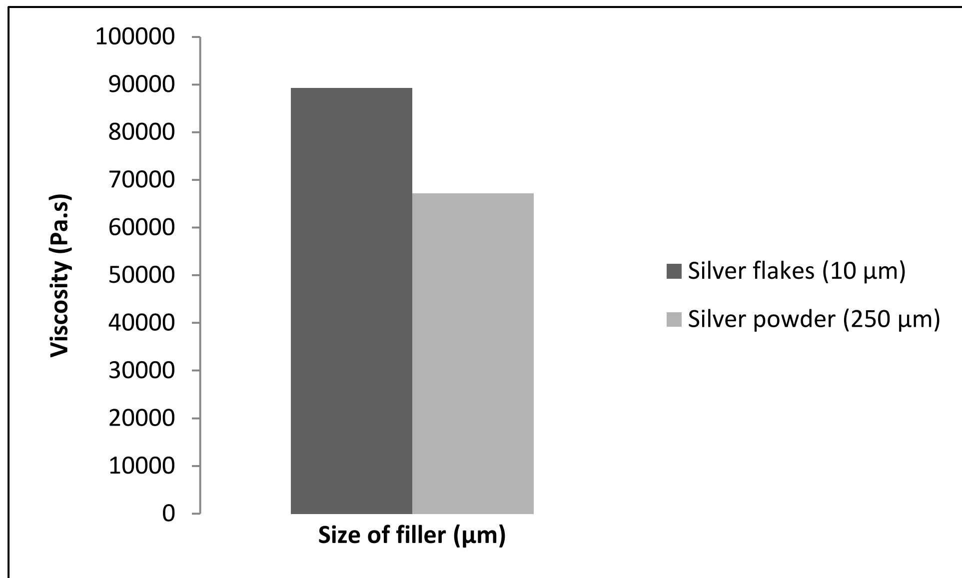
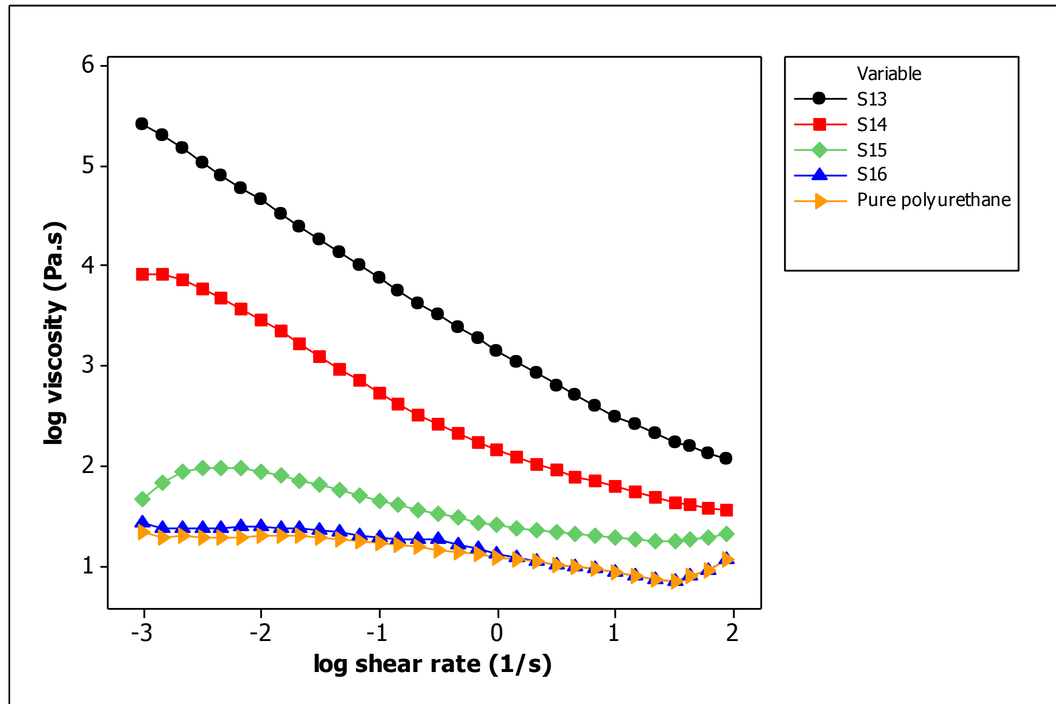
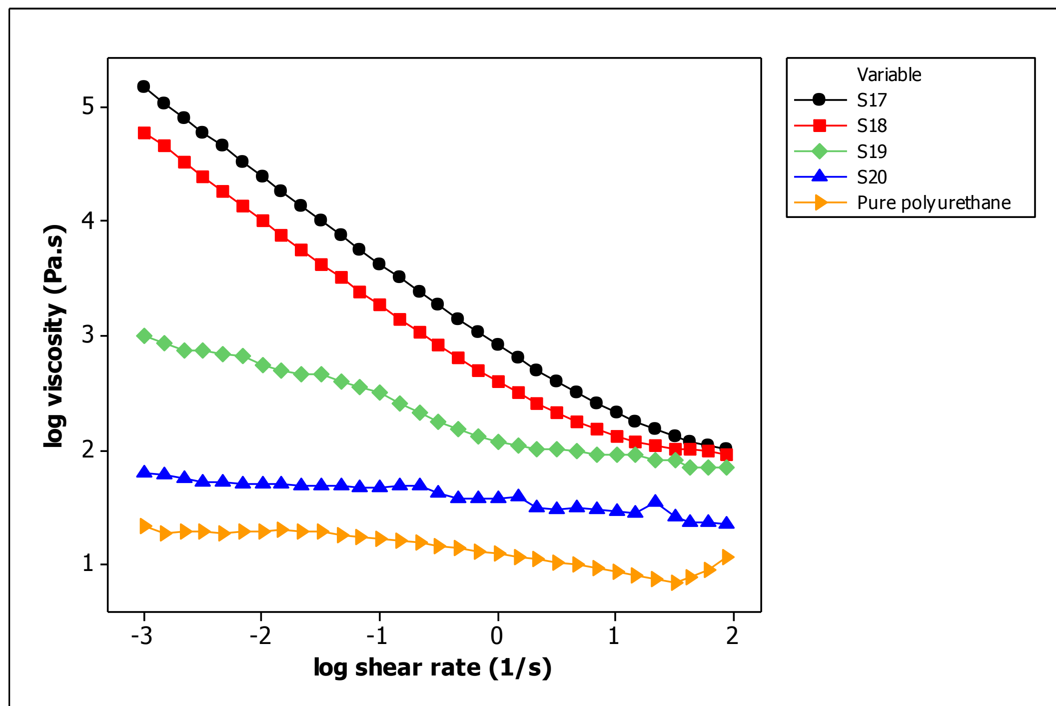


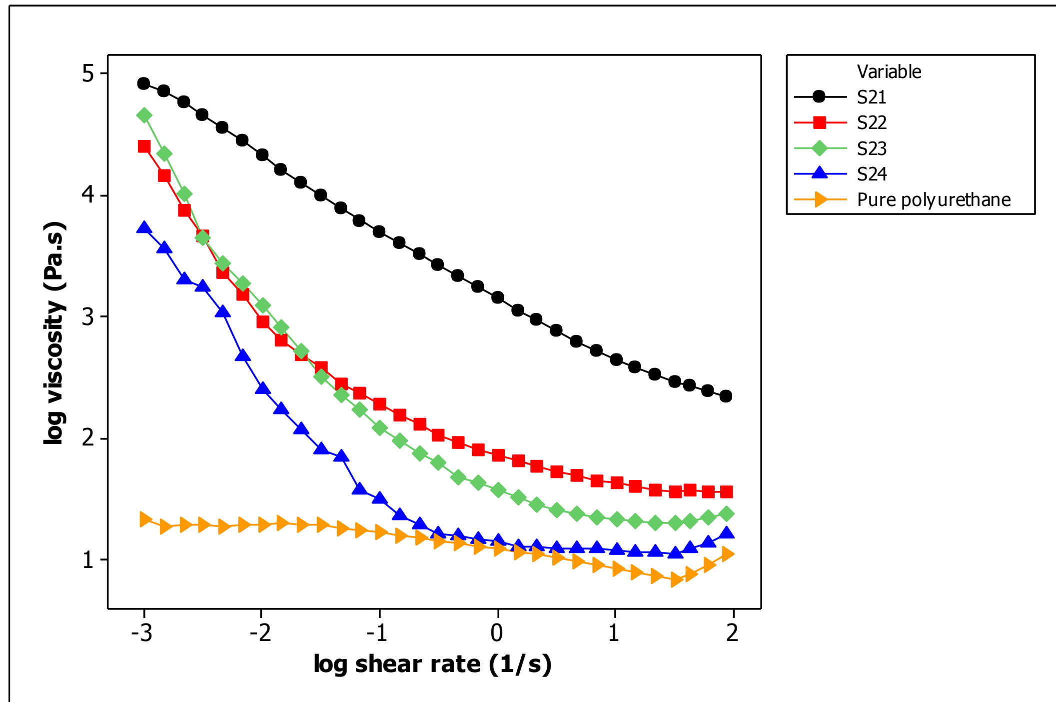
Figure 4.3: Viscosity of ICA increase as size of filler decrease (constant volume fraction at zero shear rate)



(a) silver flakes/polyurethane



(b) silver powder/ polyurethane



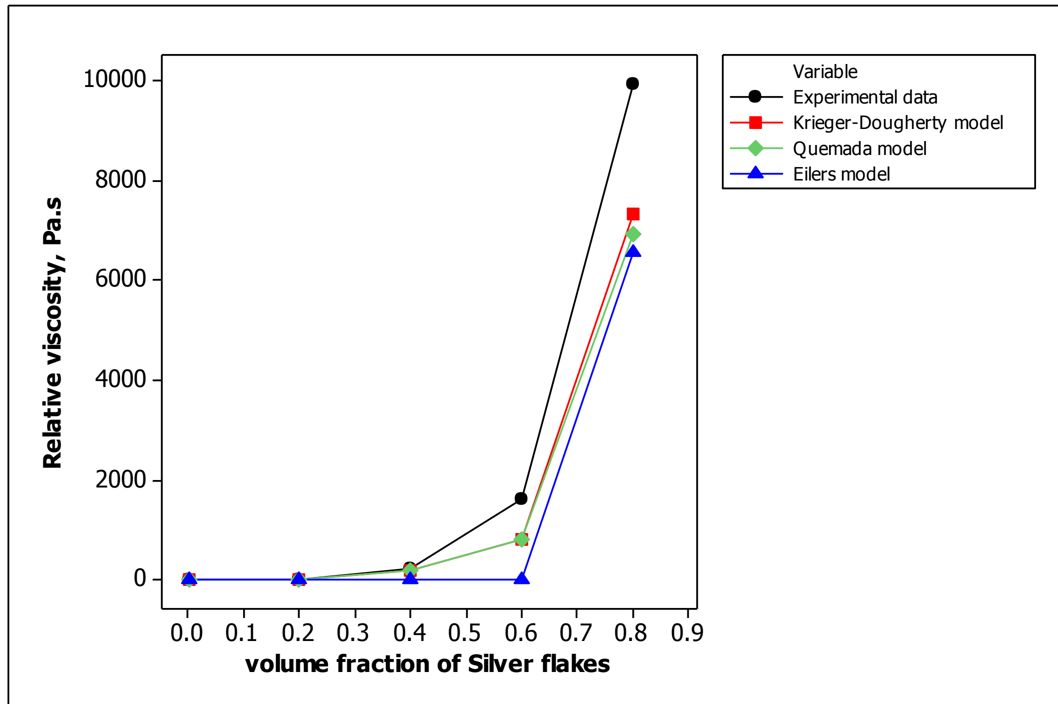
(c) mixture of silver flakes and powder/ polyurethane

Figure 4.4: Flow curve of formulated samples (a) silver flakes/PU, (b) silver powder/PU and (c) silver flakes and powder/PU

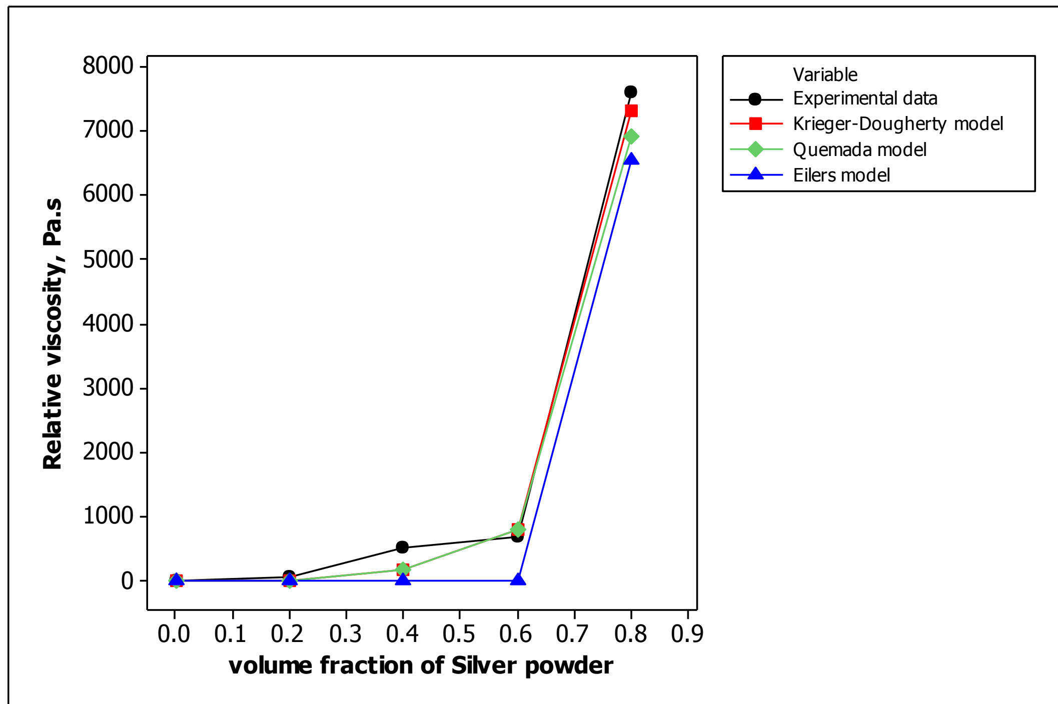
4.2.2 Effect of volume fraction of filler on viscosity of ICA pastes

The filler content can have a profound effect on the viscosity and rheological properties of ICAs. Filler content is usually specified by weight percent. Using weight percent is convenient for certain purposes, but it is the volume occupied by the filler that determines the ultimate viscosity (Bullard et al., 2009). In general, the viscosity of a disperse system increase as the volume fraction of the suspended filler increases. Figure 4.5 (a), (b) and (c) show the effect of increasing

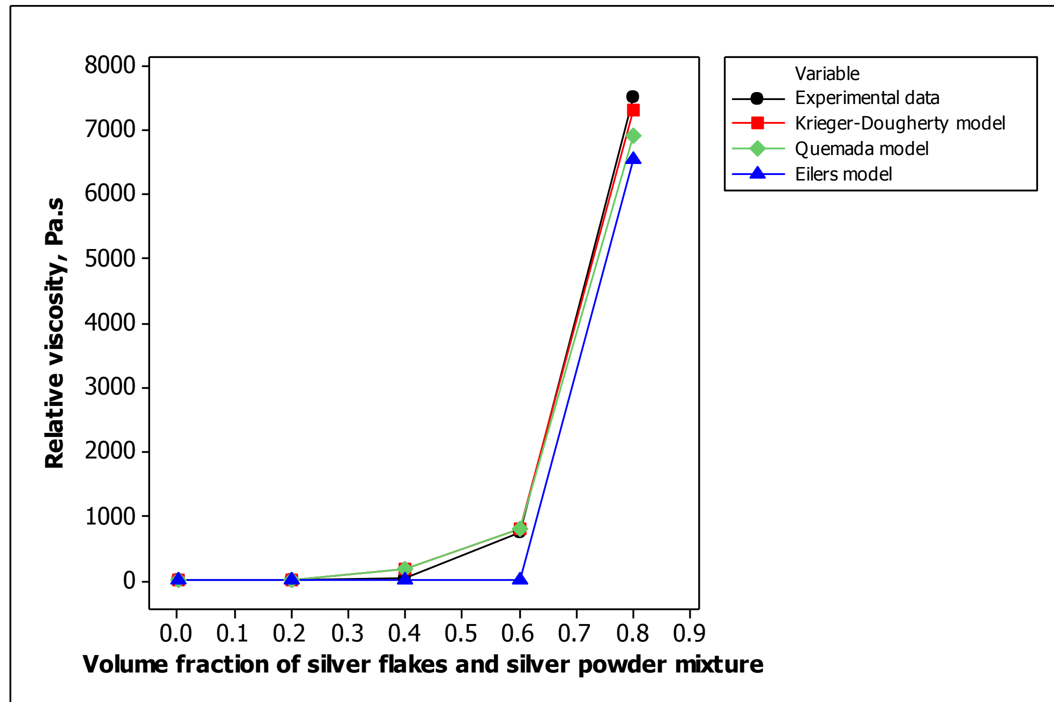
the suspended filler content on relative viscosities of the ICAs with different types of filler (silver flakes, silver powder and mixture of silver flakes and silver powder) with DGEBA resin. The viscosities increase totally with increasing filler content. Although the fillers load increase in the range of 0.2 to 0.6 volume fraction, there is not much change in the viscosity of the ICAs. In this range, the viscosity was nearly unaffected by filler concentration. The viscosities show a sharp increase at a fillers content of 0.8 volume fraction. With increasing concentration of the filler, the inter-particle interactions increase weakly at first and then rather strongly as the concentration becomes higher and higher. The concentration at which particle-particle interactions begin depends on the contact surface area and collision between the filler particles. At volume fraction 0.8, the fillers are sufficient enough to have close contact, resulting in a higher degree of fillers agglomeration (Irfan and Kumar, 2008). This network is essentially a continuous linkage between fillers and epoxy system. This give a clear indication that the perfect filler network occurred 0.8 of fillers volume fraction.



(a) silver flakes



(b) silver powder



(c) silver flakes and powder mixture

Figure 4.5: Relative viscosity versus volume fraction of (a) silver flakes (b) silver powder and (c) silver flakes and powder mixture

4.2.3 Rheological comparison of formulated ICAs to the commercial solder pastes and ICAs

From the point of view of desired rheological properties, high viscosity that ensures pastes stability, the most satisfying results were obtained on P2 sample which exhibited the highest viscosity, 1830000 Pa.s among all the samples at zero shear rate. The zero shear rate viscosities of P1 and P3 samples were 90163 Pa.s and 9180 Pa.s respectively. In a stencil printing process, as if the viscosity of the

solder paste was too high, the paste might not wet the surface of the substrate and more energy was needed to force the paste penetrate the aperture (Haslehurst and Ekere, 1996). As shear rate was increased, three of the pastes exhibited shear-thinning behavior. When the pastes was subjected to high shear rate, the structure of the pastes was undergo changes (Barnes et al., 1989). However, these changes should not beyond the visco-elastic boundary of the paste because the paste should regain its viscosity to prevent slump formation (Durairaj et al., 2009). Based on Figure 4.6, the formulated ICAs, S2 (0.6 volume fraction with silver flakes filler) has the zero shear viscosity, 8790 Pa.s which is very close to the zero shear viscosity of commercial ICAs sample, 9180 Pa.s. Commercial lead-free solder paste, P1 shows zero shear viscosity of 90163 Pa.s which is the closest viscosity to the formulated ICAs of S1 (0.8 volume fraction with silver flakes filler), 89300 Pa.s. The results seem to suggest that the formulated ICAs (0.6 and 0.8 volume fraction of silver flakes) are correlated well to the commercial solder pastes and ICA.

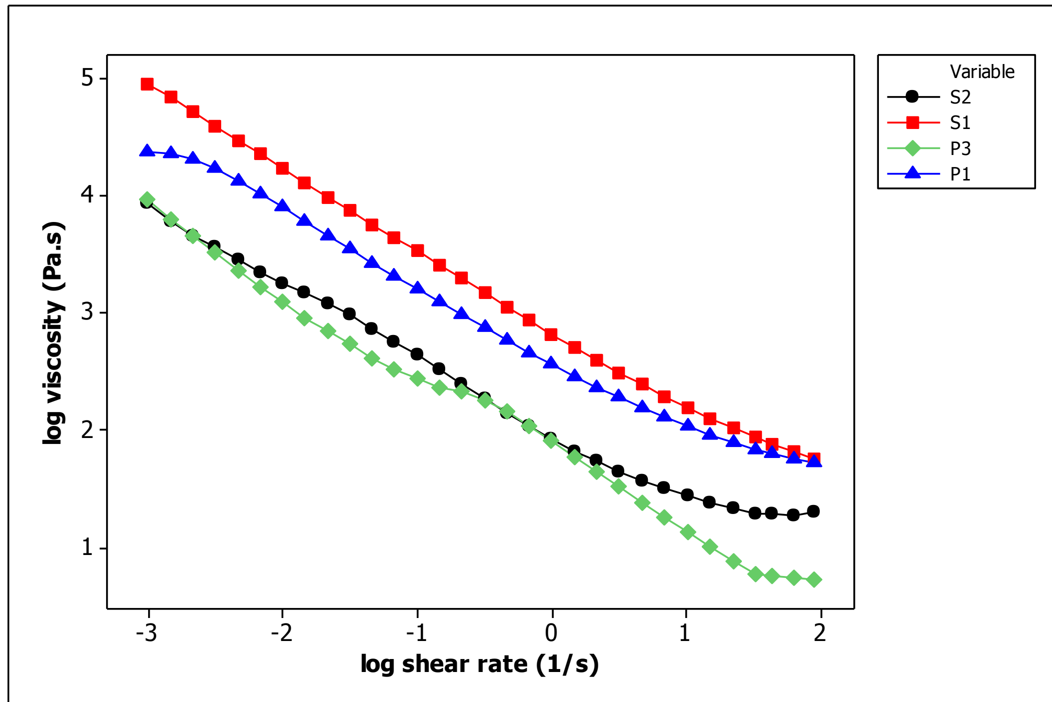


Figure 4.6: Comparison of formulated ICAs to commercial solder pastes and ICA

4.2.4 Determination of maximum packing factor

The functional dependence of relative viscosity on volume fraction of fillers and particle size was determined. Three empirical models have been studied to estimate the maximum packing factor, $\phi_{m.}$ Figure 4.5 (a), (b) and (c) show the data of relative viscosities versus volume fraction for each epoxy-filler system. Fitting are based on three different empirical models namely Krieger-Dougherty, Quemada and Eilers models. The viscosities show a sharp increase at a fillers content of 0.8 volume fraction for all epoxy-filler system. Therefore, the

experimental maximum packing factor, ϕ_m is 0.8. In Table 4.1, the determined parameter of the epoxy-filler systems of all fitted models are summarised in comparison to the experimental maximum packing factor, ϕ_m. The Krieger-Dougherty model well characterises the experimental data with the highest correlation coefficients, R^2 among all three empirical models for all epoxy-filler system.

Viscosity is sensitive to small variation in particle properties such as surface roughness, size and shape polydispersity. The intrinsic viscosity, $[\eta]$ represents the effective shape factor of the suspended filler particles for their movement in the shear field imposed (Loebbecke et al., 2009). Although ϕ_m and $[\eta]$ in the empirical models are both significant parameters affected by the degree of agglomeration, in particular, $[\eta]$ can be related to the hydrodynamic volume of the filler particles. For spheres, $[\eta]$ is expected to be 2.5 (Einstein, 1906). As shown in Table 4.1, system 1 (silver flakes-epoxy system) shows the lowest R^2 values while system 3 (mixture of silver flakes and silver powder) shows the highest R^2 values. This might be due to the non-uniform shape of silver flakes. In addition, silver flakes are not perfectly in sphere shape.

Particle size distribution influences particle packing. A polydisperse population with a broad size distribution packs more closely than a monodisperse sample. For polydisperse sample, smaller particles fill the gaps between larger ones and the ϕ_m is greater (Larson, 1999). Therefore, for polydisperse system (mixture of

silver flakes and silver powder), the calculated ϕ_m is greater. As the volume fraction of fillers in the epoxy-filler system goes up, the particles become more closely packed together and it becomes more difficult for them to move freely. Therefore, particle-particle interactions increase and resistance to flow (viscosity) rises. As the volume fraction nears maximum for the sample, viscosity rises very steeply (Loebbecke et al., 2009). This is evident with rheological data obtained in Figure 4.5 (a). (b) and (c) as there are significant changes in viscosity from volume fraction of 0.6 and 0.8 of fillers.

Table 4.1: Fitting of three different empirical models.

Empirical model	**Parameter**						
	Intrinsic viscosity, [η]	**System 1 Silver flakes**		**System 2 Silver powder**		**System 3 Silver flakes + silver powder**	
		Maximum packing factor, ϕ_m	**Regression model, R^2**	**Maximum packing factor, ϕ_m**	**Regression model, R^2**	**Maximum packing factor, ϕ_m**	**Regression model, R^2**
Krieger-Dougherty	2.5	0.705	0.8636	0.782	0.996	0.788	0.998
Quemada		0.690	0.8021	0.780	0.989	0.788	0.996
Eilers		0.637	0.6780	0.775	0.969	0.780	0.975

CHAPTER 5

VISCO-ELASTIC STUDIES

5.1 Introduction

This chapter presents the study on the visco-elastic behaviour of commercial paste (solder paste and ICAs) and formulated ICAs. The chapter consists of three parts: the first part describes the visco-elastic behaviour of paste. The second part presents the results of oscillatory stress and frequency sweep experiments. The final part presents the summary of the experimental study.

5.2 Results and Discussion

5.2.1 Study of paste structures within the linear visco-elastic region (LVER)

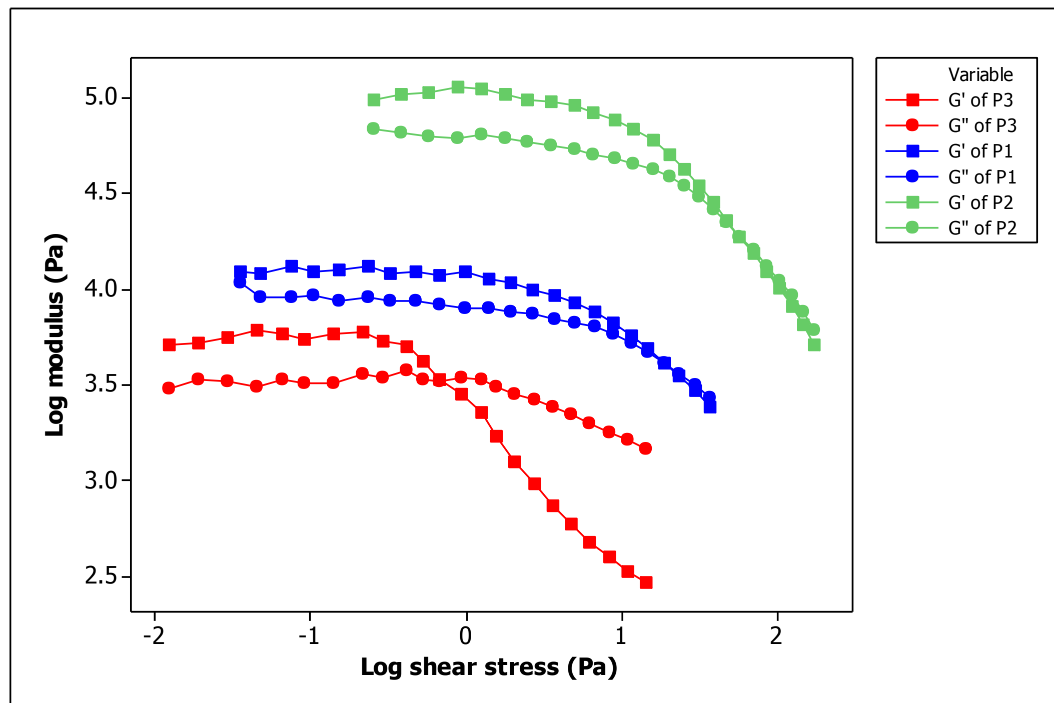
The linear visco-elastic region is defined as the maximum deformation can be applied to the sample without destroying its structure. In this region, the particles stay in close contact with each other and recover elastically to any applied stress or strain. As a result, the sample acts as a solid and the structure remains intact. Beyond this region, the structure is gradually destroyed with increasing stress or strain. In this region, the storage modulus, G' and loss modulus, G", which represents the solid and liquid characteristics can provide an insight into the paste behaviour prior to structural breakdown. In this study, volume fraction of filler

content was analysed with the size range of 10 µm (silver flakes) and 250 µm (silver powder); and the results were benchmark against commercial pastes.

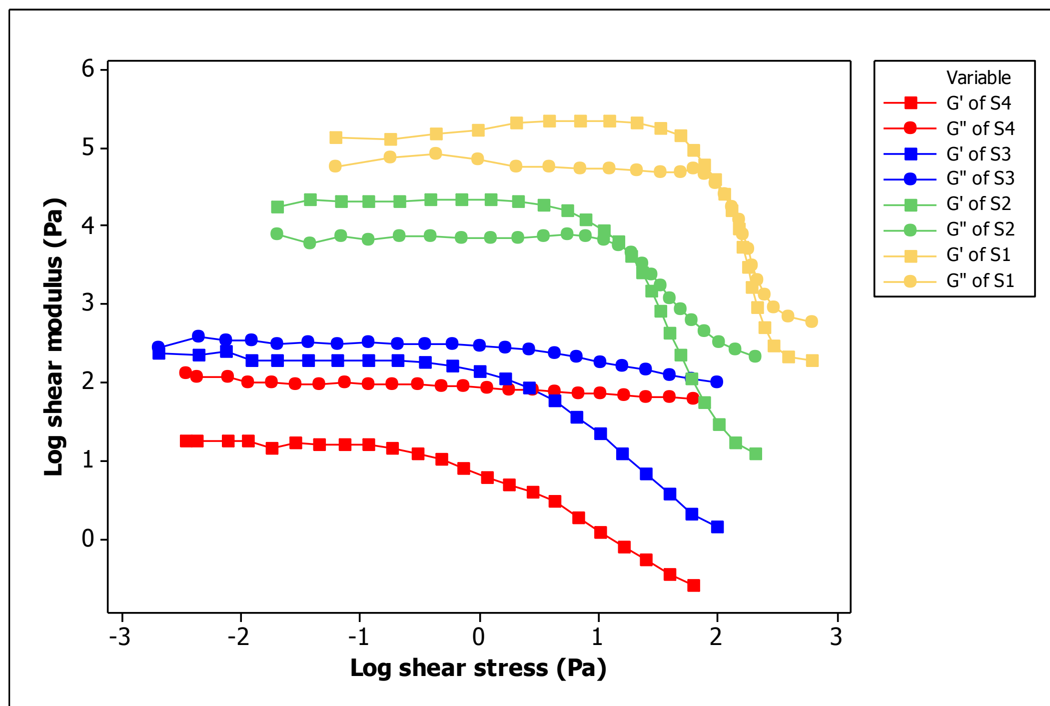
Before making detailed dynamic measurements to probe the sample's microstructure, the linear visco-elastic region (LVER) must first be defined. This is determined by performing the amplitude stress sweep and a frequency sweep tests. As discussed previously, the LVER can also be used to determine the stability of a suspension. The length of the LVER of the elastic modulus (G') can be used as a measurement of the stability of a sample's structure, since structural properties are best related to elasticity. A sample that has a long LVER is indicative of a well-dispersed and stable system. Both oscillatory stress sweep and frequency sweep results showed that the linear visco-elastic region (LVER) for commercial lead-free solder paste and all 0.8 volume fraction of formulated ICAs were below 100 Pa meanwhile the lead-based solder paste and all 0.6 volume fraction of formulated ICAs were below 10 Pa. This means that the LVER for 0.8 volume fraction of ICAs lies within wide stress range and on the other hand, ICAs of 0.6 volume fraction lies within small stress range. In addition, at low shear stresses, the pastes showed a dominant elastic behaviour (G'>G"). This is true for 0.6 and 0.8 volume fraction of all types of fillers as shown in Table 5.1.

Figure 5.1 showed the results for oscillatory stress sweep tests for all the samples. Based on Figures 5.1 (b) to (g), 0.2 and 0.4 volume fraction of all epoxy-filler systems which represented as sample S3, S4, S7, S8, S11, S12, S15, S16, S19 and S20, the viscous behaviour was dominant (G">G') except for S23 and S24 which

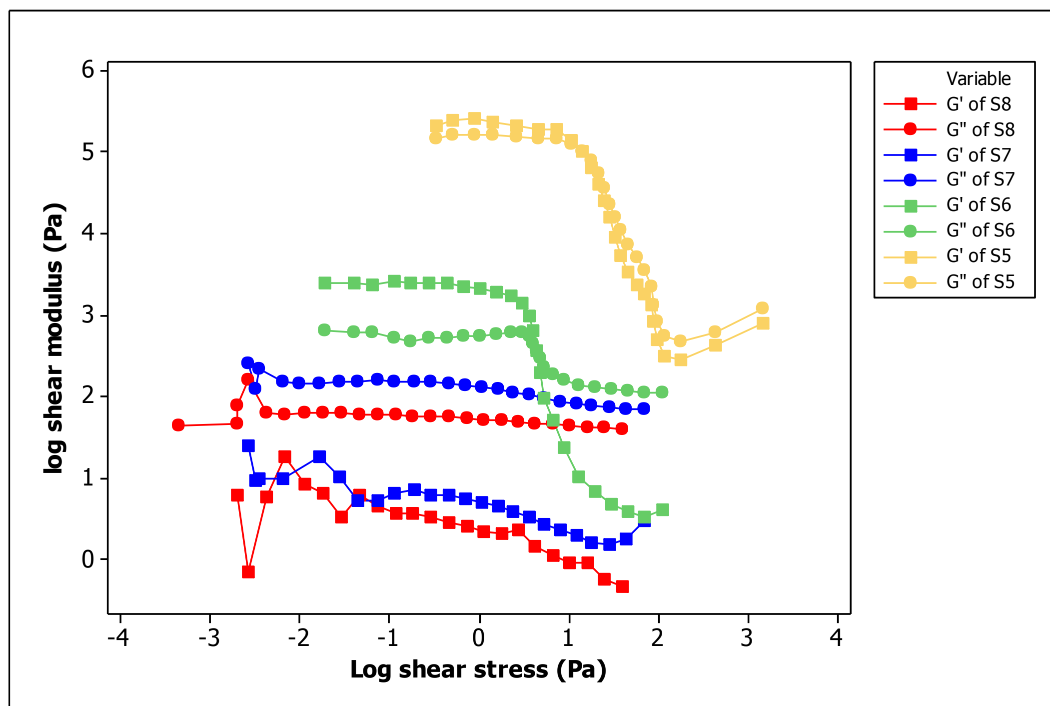
are the combination of silver flakes+powder-polyurethane. The elastic properties, G' increase totally with increasing filler content (Rajinder 2005). The concentration at which particle-particle interactions begin depends on the contact surface area and collision between the filler particles. At volume fraction 0.8 (S1, S5, S9, S13, S17, and S21), the fillers are sufficient enough to have close contact, resulting in a higher degree of fillers agglomeration (Irfan and Kumar, 2008). This network is essentially a continuous linkage between fillers and flux system.



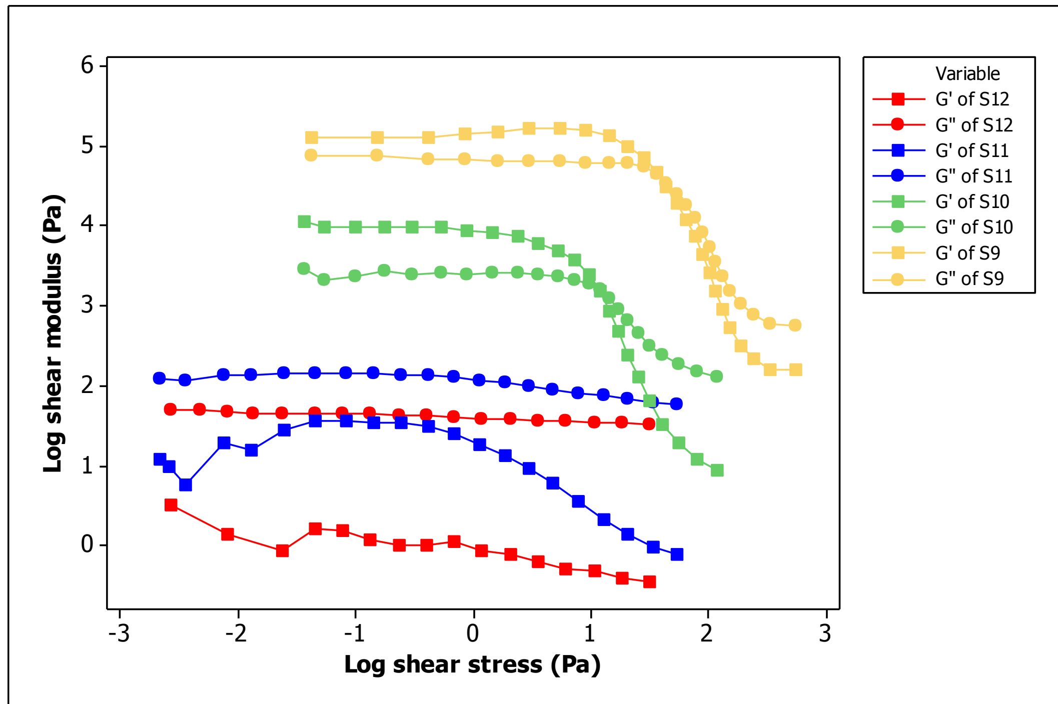
(a) Commercial samples



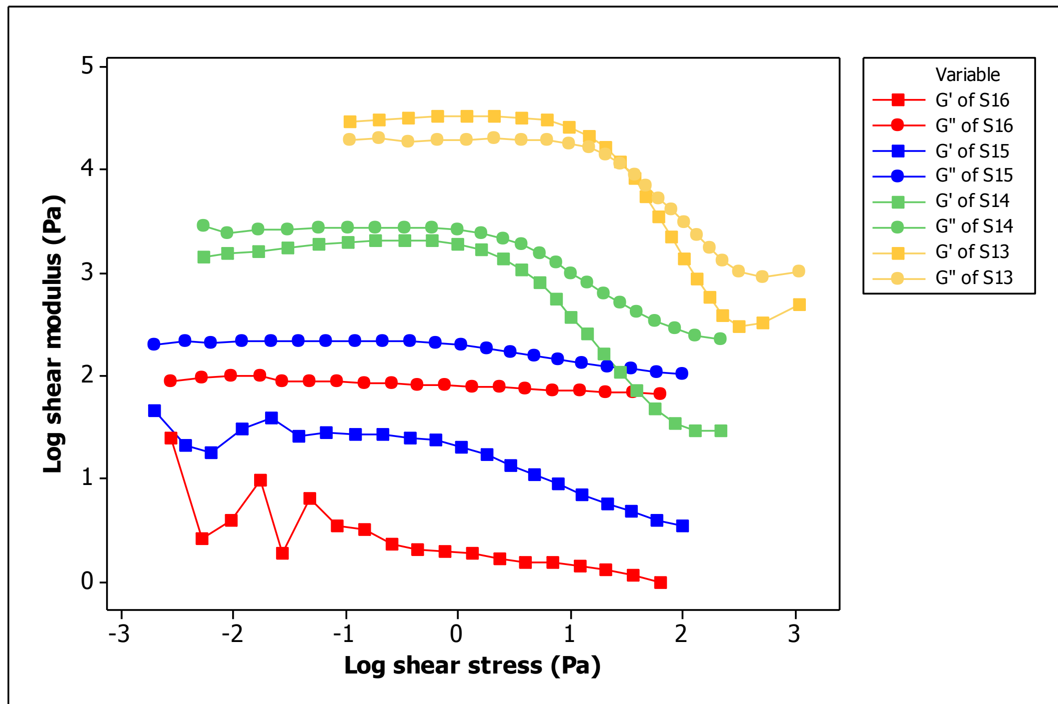
(b) silver flakes/DGEBA



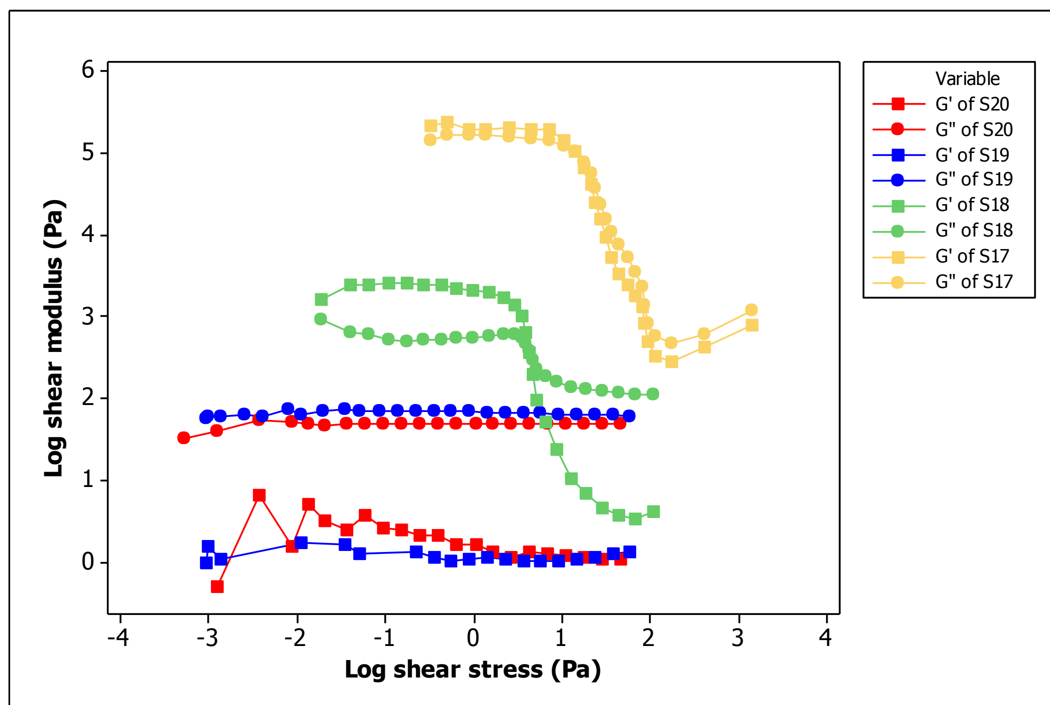
(c) silver powder/DGEBA



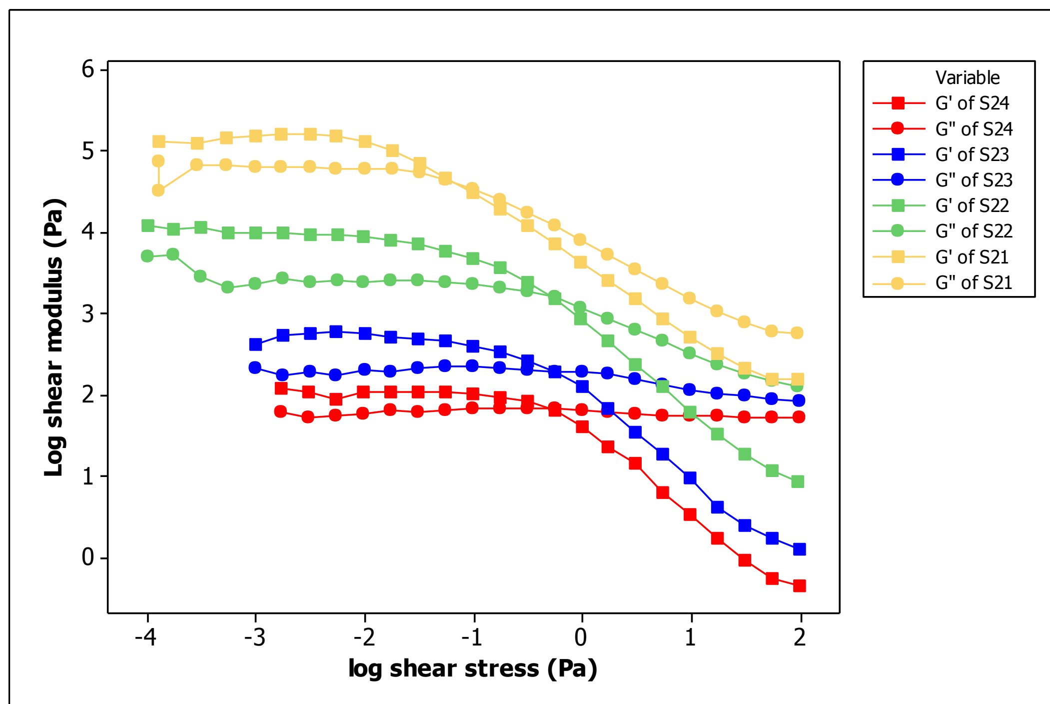
(d) silver flakes and powder/DGEBA



(e) silver flakes /PU



(f) silver powder /PU



(g) silver flakes and powder /PU

Figure 5.1: Oscillatory stress sweep for (a) commercial paste, (b) silver flakes/DGEBA, (c) silver powder/DGEBA, (d) silver flakes and powder/DGEBA, (e) silver flakes/PU, (f) silver powder/PU and (g) silver flakes and powder/PU

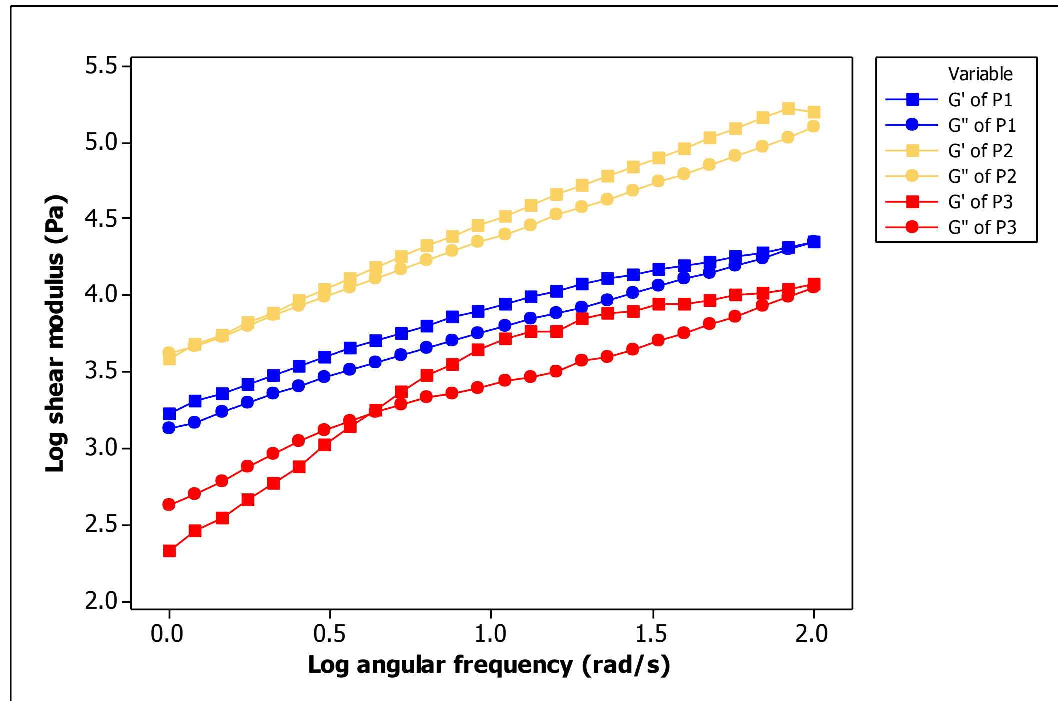
Based on the frequency sweep tests which can be seen in Figure 5.2 (a) to (g), all three commercial samples are classified as well-structured systems. This is because G' is greater than the G", particles are strongly associated and sedimentation is unlikely to occur. Same applied to the formulated ICAs with 0.6 and 0.8 volume fraction of filler contents (S1, S2, S5, S6, S9, S10, S13, S17, S18, S21 and S22), G' is dominate and both G' and G" are almost independent of frequency except for S14 which is 0.6-silver flakes-PU system. This might be due

to the shear-rate dependent of polyurethane, PU. As could seen from the flow curve in Figure 5.3, viscosity of polyurethane, PU decreases with increasing shear rate. Same as applied to oscillatory test, when shear is increase, viscosity of PU is decreasing and the system is gradually change from solid-like behaviour to liquid-like behaviour. Hence G" is dominate over G' in sample S14. Unlike diglycidyl ether bisphenol A, DGEBA, its viscosity is almost independent of shear rate, hence G' is dominate in S2 which is 0.6-silver flakes-DGEBA system. While for 0.2 and 0.4 volume fraction of filler contents (S3, S4, S7, S8, S11, S12, S15, S16, S19, S20, S23 and S24), G" is dominate over G', systems are classified as weakly-structure (Irfan and Kumar, 2008). In these system sedimentation may occur. The viscous modulus, G" for sample formulated with 0.2 volume fraction of silver powder fluctuates throughout the experimental process than that of sample formulated with silver flakes. The fluctuation in the G" could be due to the settling of the filler resulting in two distinct phases within the paste. A visual observation of the paste showed separation of the flux from the filler, as shown in Figure 5.4. However, this separation was not observed for samples formulated with silver flakes, as shown in Figure 5.5.

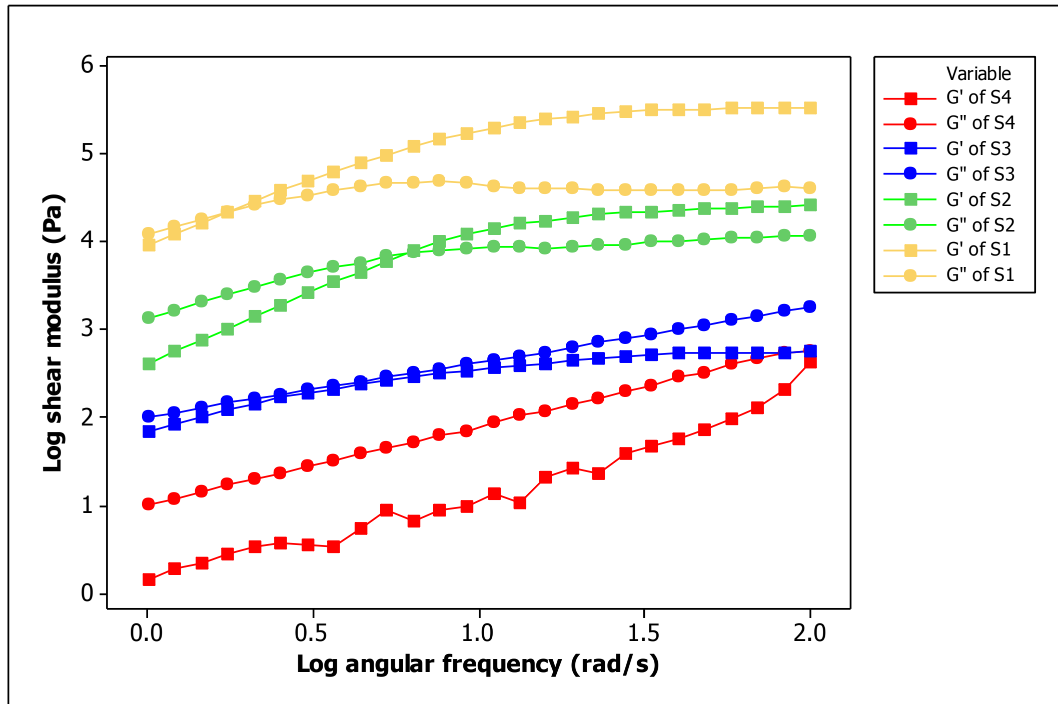
Further analysis of the elastic behavior of paste was carried by calculating the ratio of viscous properties to elastic properties (G"/G') within the LVER, as seen in Table 5.1. The ratio G"/G' gives an indication of the strength of interaction within the internal structure of a suspension. A lower G"/G' ratio indicates that the material is elastic in nature (Durairaj et al., 2008). From the results in Table 5.1,

among all three commercial sample pastes, lead-free solder paste has the lowest value for G''/G' of 0.80 followed by ICA and lead-based solder paste with a value of 0.95 and 0.96 respectively. From the ratios, lead-free solder paste is more elastic. The lower ratio could indicate that the paste is very cohesive or tacky, which could result in poor paste withdrawal during the aperture emptying process. The high solid characteristic or cohesive nature of the paste in the lead-free solder paste could be influenced by a number of factors such as particle size and the epoxy-filler chemistry. In Table 5.1, all the formulated ICAs of 0.6 and 0.8 volume fractions have the G''/G' value in the range of 0.71 to 0.93. The lowest G''/G' value, 0.71 goes to S5 which is 0.8-silver powder-0.2-DGEBA system. From this lowest ratio, the paste is said to be more elastic. This lowest G''/G' value might be due to the high filler concentration. Meanwhile the highest G''/G' value, 0.93 is S13, 0.8-silver flakes-0.2-PU system. For, S10, 0.6-silver flakes+powder-0.4-DGEBA system has the G''/G' value of 0.8 which is same as the G''/G' value of commercial lead-free solder paste. This means that both of these pastes share the same visco-elastic properties. In addition, as shown in Table 7, the G' for silver powder-epoxy systems are higher than the silver flakes-epoxy system. This might be due to larger size of silver powder, 250 µm agglomerates into larger flocs and the paste formed is more dense, therefore, the paste is more in solid-like behaviour. As for silver flakes+powder-epoxy system, the G' is higher than that of silver flakes. The smaller silver flakes filler particles (10 µm) tend to fill in the space between the larger silver powder (250 µm) particles-

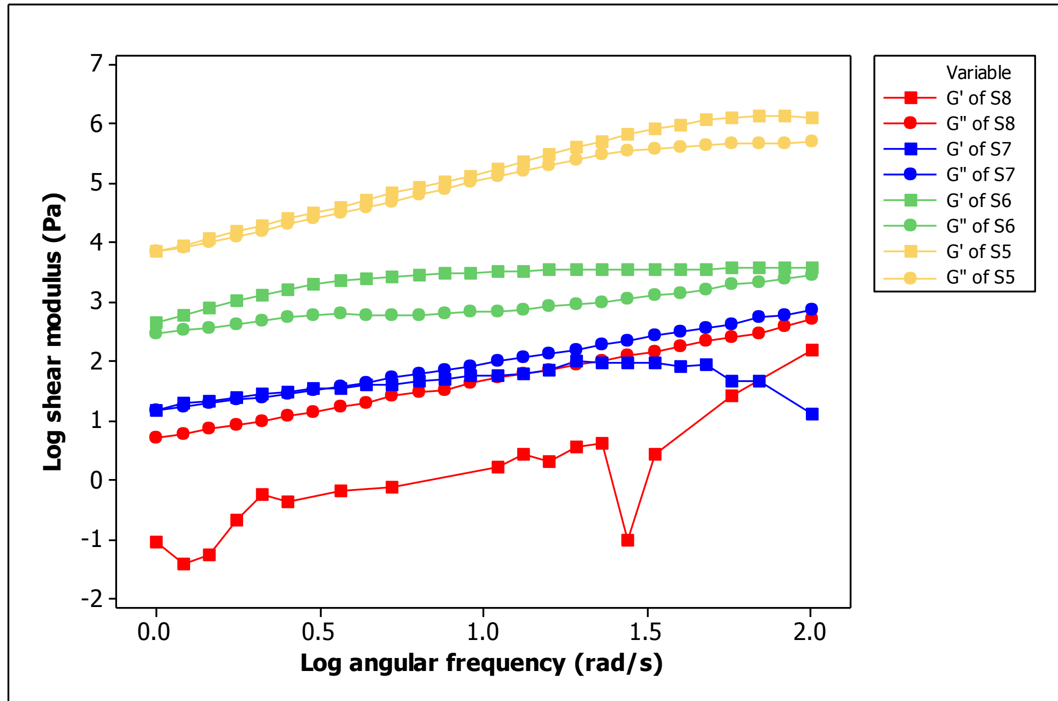
particles interaction and this lead to closer contact between particles and the elastic properties of the paste is increasing eventually.



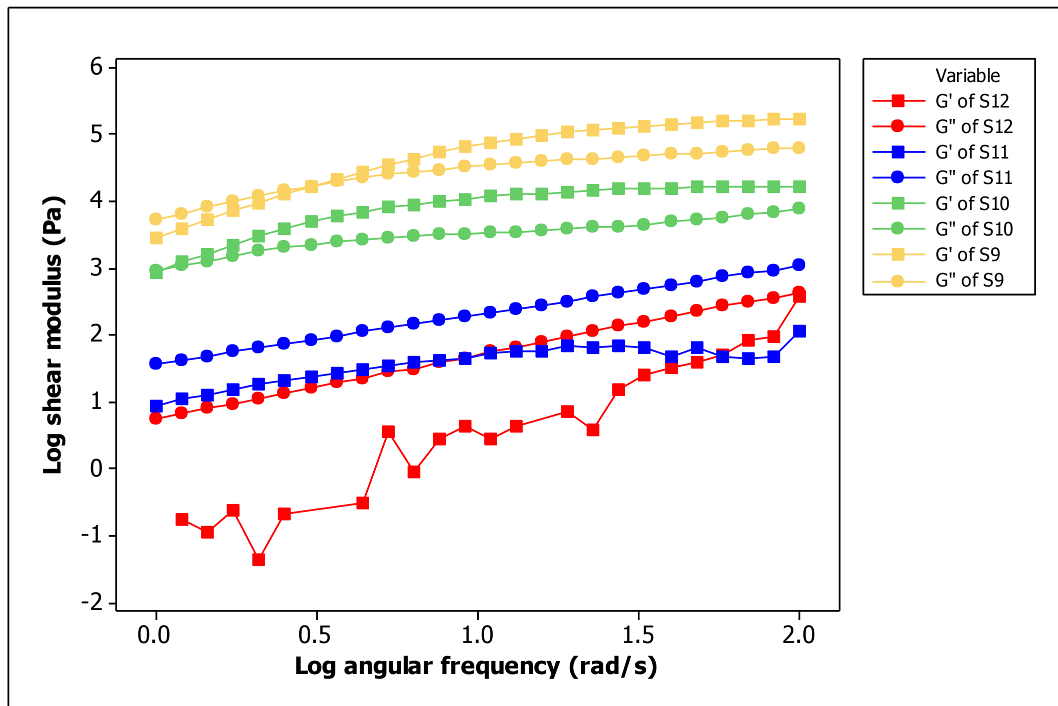
(a) Commercial samples



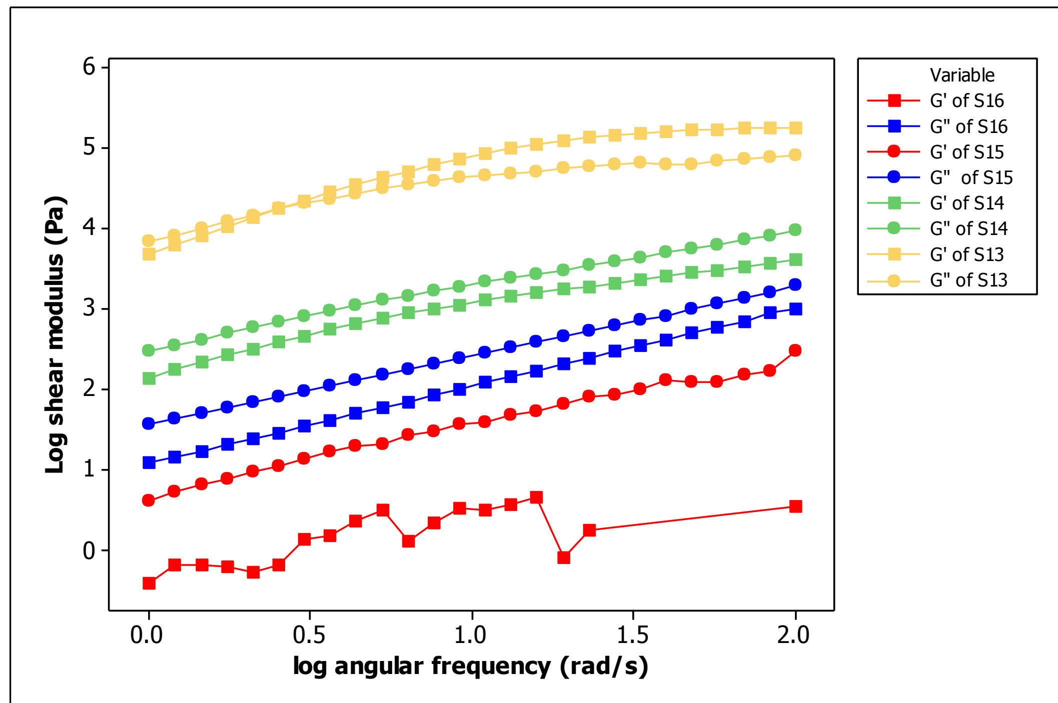
(b) silver flakes/DGEBA



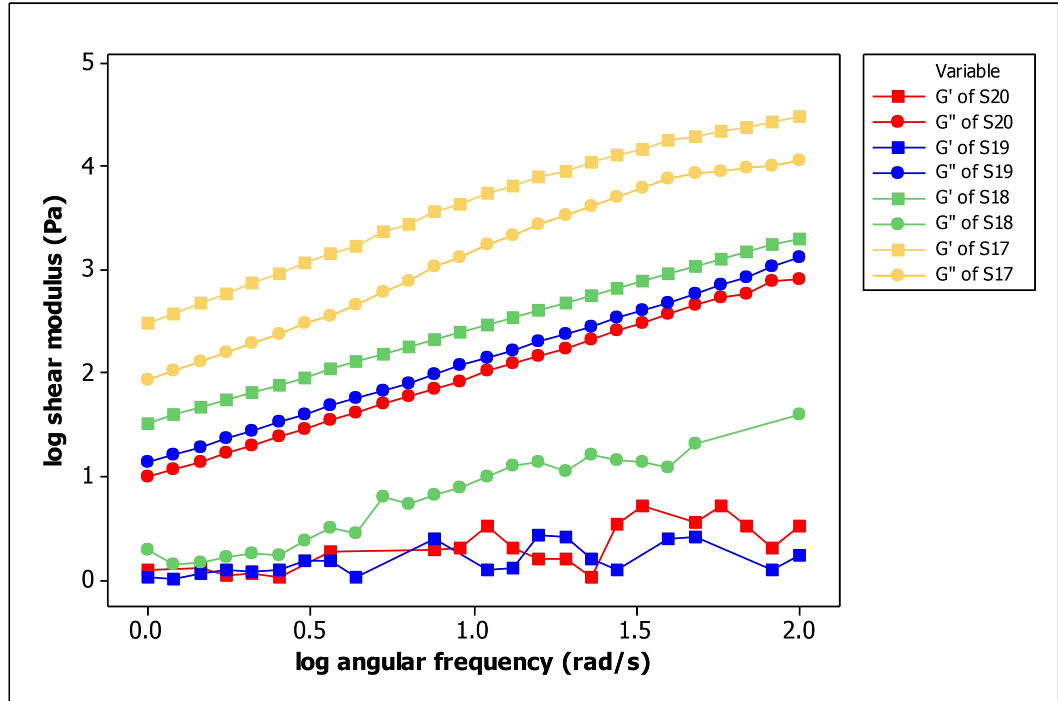
(c) silver powder/DGEBA



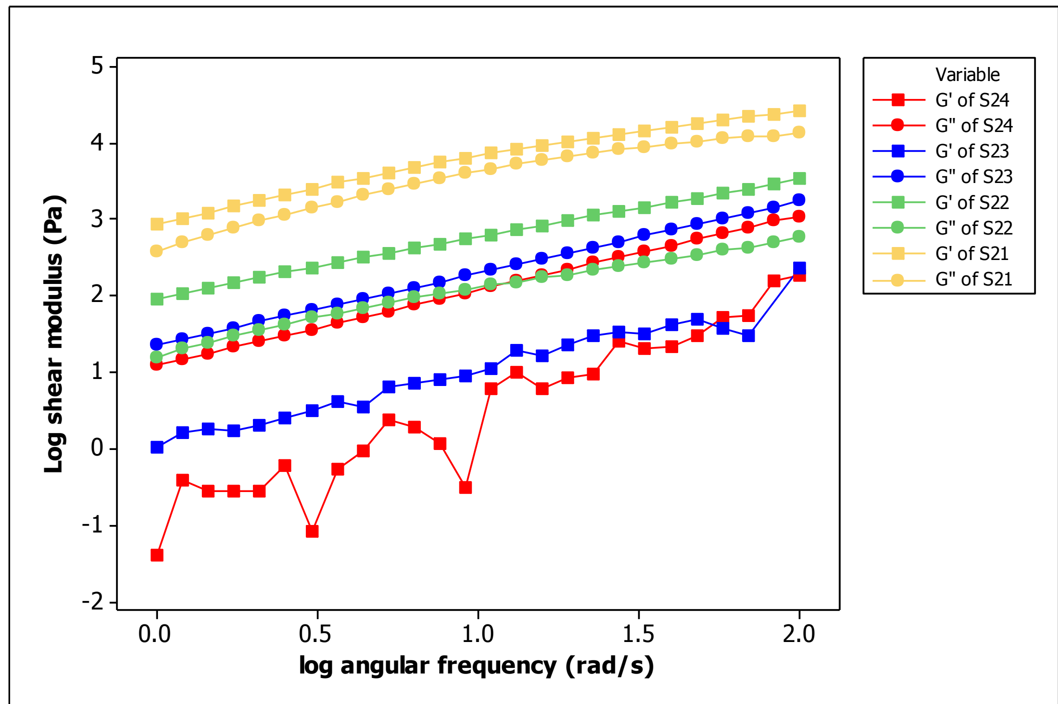
(d) silver flakes and powder/DGEBA



(e) silver flakes/PU



(f) silver powder/PU



(g) silver flakes and powder/PU

Figure 5.2: Frequency sweeps for (a) commercial paste, (b) silver flakes/DGEBA, (c) silver powder/DGEBA, (d) silver flakes and powder/DGEBA, (e) silver flakes/PU, (f) silver powder/PU and (g) silver flakes and powder/PU

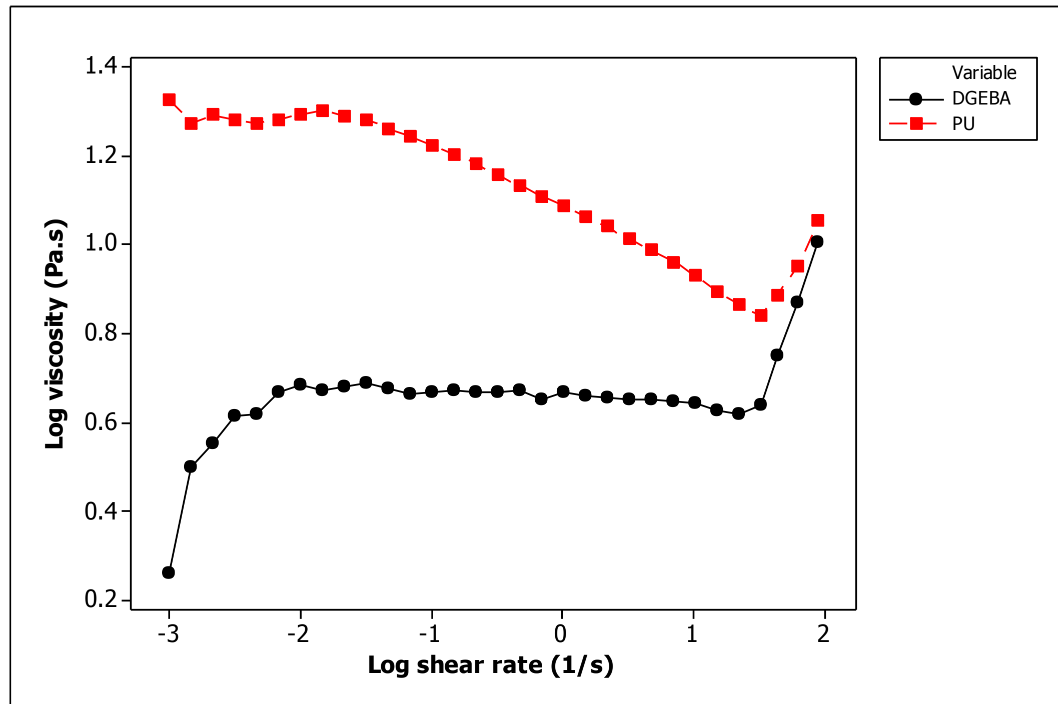


Figure 5.3: Flow curve for pure resins.

Figure 5.4: Separation of flux medium from the filler in sample S8 (0.2-silver powder/0.8-DGEBA flux system).

Figure 5.5: No separation of flux medium from the filler in sample S4 (0.2-silver flakes/0.8-DGEBA flux system).

5.2.2 Correlation of stress at G'= G'' to the paste cohesiveness

The yield point, G'= G'' is the highest shear stress value in an oscillatory stress sweep curve at which the solder paste still does not flow. It is the point where the external forces (gravity, squeegee) applied are greater than the internal forces of the rheological network in the solder paste (Lapasin et al., 1997). Below the yield point the behavior of the solder paste is elastic. It behaves more like a solid substance. It does not deform. In a stencil printing process, it does not separate nor does it slump. After the yield point, the paste behavior crosses over from solid-like to liquid-like behaviour (Durairaj et al., 2009). Figure 5.6 showed the measured yield point for 0.8 volume fraction of epoxy-filler system. Results showed that silver powder-DGEBA system has the highest yield point, 52.12 Pa while mixture of silver flakes and silver powder-PU system has the lowest yield point, 5.83 Pa. Yield point could be use as an indicator for accessing the cohesiveness of the paste. This is an important characteristic because the increase in the liquid behaviour will contribute to the paste flow ability from the stencil aperture. A large value of yield point will indicate that the paste require a significant amount stress to change from solid to liquid state. At the same time it also indicate that the stronger the rheological network and the lower the tendency for sedimentation of solder particles. Hence, silver powder-DGEBA system show the most cohesive and tacky behaviour and sedimentation is less likely to occur. However, this high cohesiveness could affect the flow of the paste into the

apertures, subsequently poor paste release from apertures in a stencil printing process.

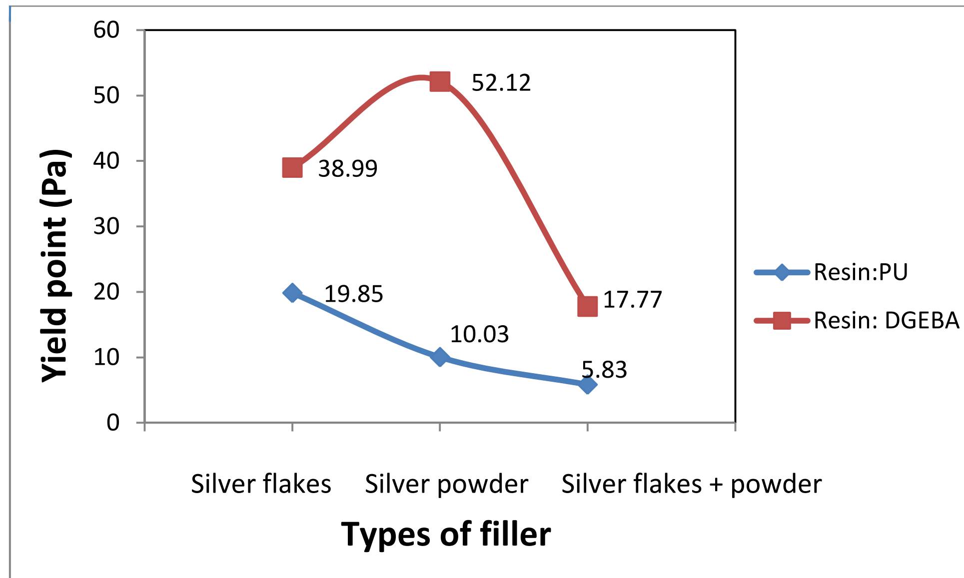


Figure 5.6: Plot of yield point for 0.8 volume fraction of different fillers and resins flux system.

5.2.3 Correlation of phase angle to quality of pastes formulation

A phase angle (δ) of closer to 0˚ indicates an elastic (solid) behaviour and an angle closer to 90˚ indicates a viscous (liquid) behaviour (Ferguson and Kemblowski, 1991). Visco-elastic behaviour will result in the phase angles between 0˚ and 90˚ (Bao et al., 1998 and Lapasin et al., 1997). The phase angle could provide a swift way of assessing the transition from solid- to liquid-like behaviour of the paste material, for example, a low phase angle may indicate the

paste is very tacky or in contrast, a high phase angle may indicate a paste that could slump easily.

The value of phase angle for commercial samples and formulated 0.2, 0.4, 0.6 and 0.8 volume fraction of filler content samples are presented in Table 5.1. As expected, all samples lie between 0˚ and 90˚. The oscillatory results confirm that the pastes are visco-elastic in nature, which in agreement with previous studies (Bao et al., 1998; Durairaj et al., 2008 and Lapasin et al., 1997). Of all three commercial samples, P2 showed the lowest phase angle, 38.6˚ and this indicates that this paste is very cohesive. In formulated sample, S5 which is 0.8-silver powder/0.2-DGEBA system showed the lowest phase angle, 35.4˚ and the paste is said to be high cohesive or tacky. This might be due to the high volume fraction of filler content and lead to strong particle-particle interactions (Rajinder 2005). The larger filler size of silver powder, 250 µm over silver flakes, 10 µm make the epoxy-filler system with silver powder tends to agglomerate into larger flocs and resist the flow ability of the system (Irfan and Kamar, 2008). Henceforth, the phase angle could be used by scientist and engineers to design a paste which has minimal separation during and after the printing process. In addition, the formulators can use the phase angle as a tool to check the overall quality of dispersion from one batch of paste to another.

Table 5.1: Summary of the oscillatory stress sweep parameter within the LVER for commercial pastes and formulated ICAs of 0.2, 0.4, 0.6 and 0.8 volume fraction of fillers.

Sample	G' (Pa)	G'' (Pa)	G''/G'	Phase angle, δ
P1(commercial lead-free solder paste)	4910	4696	0.96	43.8
P2 (commercial lead-free solder paste)	25058	20046	0.80	38.6
P3 (commercial ICAs)	4227	4015	0.95	43.5
S1 (0.8-silver flakes/0.2-DGEBA)	69673	54473	0.78	37.9
S2 (0.6-silver flakes/0.4-DGEBA)	8788	6871	0.78	37.9
S3 (0.4-silver flakes/0.6-DGEBA)	180	306	1.70	59.5
S4 (0.2-silver flakes/0.8-DGEBA)	15	95	6.30	81.0
S5 (0.8-silver powder/0.2-DGEBA)	410401	290937	0.71	35.4
S6 (0.6-silver powder/0.4-DGEBA)	642	461	0.72	35.8
S7 (0.4-silver powder/0.6-DGEBA)	3.6	62	17.2	86.6
S8 (0.2-silver powder/0.8-DGEBA)	2	49	24.5	87.7
S9 (0.8-silver flakes+powder/0.2-DGEBA)	71602	55272	0.77	37.6
S10 (0.6-silver flakes+powder/0.4-DGEBA)	2492	1993	0.80	38.6
S11 (0.4-silver flakes+powder/0.6-DGEBA)	35	142	4.06	76.1
S12 (0.2-silver flakes+powder/0.8-DGEBA)	2	44	22.0	87.4
S13 (0.8-silver flakes/0.2-PU)	16383	14108	0.86	40.7
S14 (0.6-silver flakes/0.4-PU)	114	107	0.93	42.9
S15 (0.4-silver flakes/0.6-PU)	26	217	8.34	83.2
S16 (0.2-silver flakes/0.8-PU)	10	86	8.60	83.3
S17 (0.8-silver powder/0.2-PU)	51684	45617	0.88	41.3
S18 (0.6-silver powder/0.4-PU)	929	857	0.92	42.6
S19 (0.4-silver powder/0.6-PU)	19	91	4.70	78.2
S20 (0.2-silver powder/0.8-PU)	2	79	39.5	88.5
S21 (0.8-silver flakes+powder/0.2-PU)	21422	16440	0.76	37.2
S22 (0.6-silver flakes+powder/0.4-PU)	2174	1903	0.87	41.0
S23 (0.4-silver flakes+powder/0.6-PU)	394	234	0.59	30.7
S24 (0.2-silver flakes+powder/0.8-PU)	2	94	47.0	88.8

CHAPTER 6

THIXOTROPIC STUDIES

6.1 Introduction

This chapter presents the thixotropic studies of the paste (solder paste and ICAs). The chapter consists of five main parts: the first part presents the basic on newtonian and non-newtonian of fluid while part two is on visco-elasticity. Part three describes the introduction to thixotropic and the significance of thixotropic tests. Part four presents the experimental results. The final part presents the summary of the experimental study.

6.2 Results and discussion

6.2.1 Thixotropic properties of commercial paste

Figure 6.1 shows the hysteresis loop for all paste samples. The samples were constantly subjected to high shear rate, 100 sec^{-1} with time and recover to their initial shear rate, 0.001 sec^{-1}. The overall time interval was 240 s. Effect of increasing shear rate on the viscosity for the paste samples was being investigated. The drop in viscosities for the samples clearly indicates the pastes are shear thinning in nature and the structure of the pastes was undergoing changes due to destruction of flocculations in the suspensions (Durairaj et al., 2009). All three samples show a hysteresis area, for which an area between the up- and down-

curve is observed. The region between the up curve and down curve in hysteresis curve is an indication of the thixotropic behaviour of the pastes. Therefore, all three samples studied are thixotropic suspensions. The enclosed area within the curves indicates the extent of the structural breakdown in the sample for the applied shear (Durairaj et al., 2009).

As expected, the viscosity of the pastes drops with increasing shear rate, which indicates shear thinning behaviour of the pastes. The area between the down curve and up curve indicate that the paste is thixotropic in nature, which have been confirmed in previous studies on solder pastes (Bao et al., 1998; Durairaj et al., 2009). P2 paste shows the highest degree of thixotropy because of the high hysteresis area among all three pastes. The large area within the hysteresis loop in the P1 paste indicates that the sample undergone a large structural breakdown. P1 paste is said to have the weakest structural bonding which easily being broken down by increasing shear rate. The stronger attraction between the particles in P2 paste lead to good recovery after shear rate is removed and P2 is said to have a strong thixotropic behaviour. While for P3 paste, the particle size is range from 8-10 µm which is smaller than P1 and P2 pastes which the particle size is around 20-45 µm. These smaller particles of P2 paste tend to fill up the spaces in between the flocs and form stronger bond. Therefore, P2 paste which consisted of smaller particle size is said to be strongly thixotropic. The viscosity of P2 and P3 pastes drop with increasing shear rates, which is consistent with that of the P1 paste and show that the pastes exhibits shear thinning behaviour. For P2 paste, the

downward curve crosses the ascending curve, the cross over point being situated at 0.01 s^{-1}. On this downward path, the viscosity increase at low shear rate indicates that a network structure is able to be rebuilt when the shear rate goes under a critical value (Bauer and Collins, 1967). The smaller hysteresis loop area (P2 paste) corresponds to a thixotropic state for which the inter-particle bonds would be strong enough to favour a quick rearrangement of the structure. P3 paste shows superposed upward and downward curves at high shear rate. This could just as well correspond to an extremely thixotropic material, capable of rebuilding its structure almost instantaneously (Bauer and Collins, 1967). To support this justification, a steady shear rate test was carried out.

Figure 6.2 shows the steady shear rate plot for all three paste samples. Viscosities of all three pastes are gradually increase after the shear is removed. P3 paste shows a very good recovery after the removal of shear. In addition, the recovery (%) between the shear interval (breakdown) and recovery interval (build-up) in a steady shear rate curve is measured using the equation (2); the calculated recovery are 22.15%, 43.72% and 96.69% for sample P1, P2 and P3 respectively, as shown in Figure 6.3. From the results, it is clear that P3 showed a good recovery compared to P1 and P2. This might be attributed to the smaller particle size in the P3 epoxy resin and this leads to strong interaction between the resins and filler which gives the paste highly elastic behaviour as opposed to the P1 and P2.

$$\text{Recovery}\,(\%) = 100\% - \left[\frac{\text{Viscosity (rest)} - \text{Viscosity (recovery)}}{\text{Viscosity (rest)}} \times 100\%\right]$$

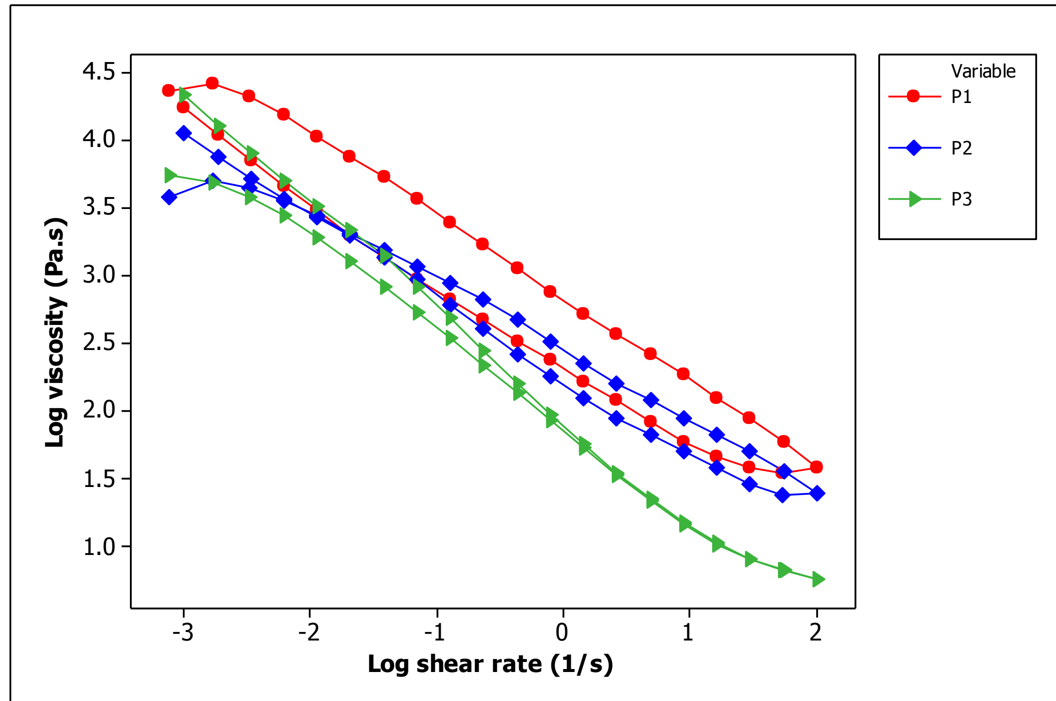


Figure 6.1: Hysteresis loop of commercial pastes

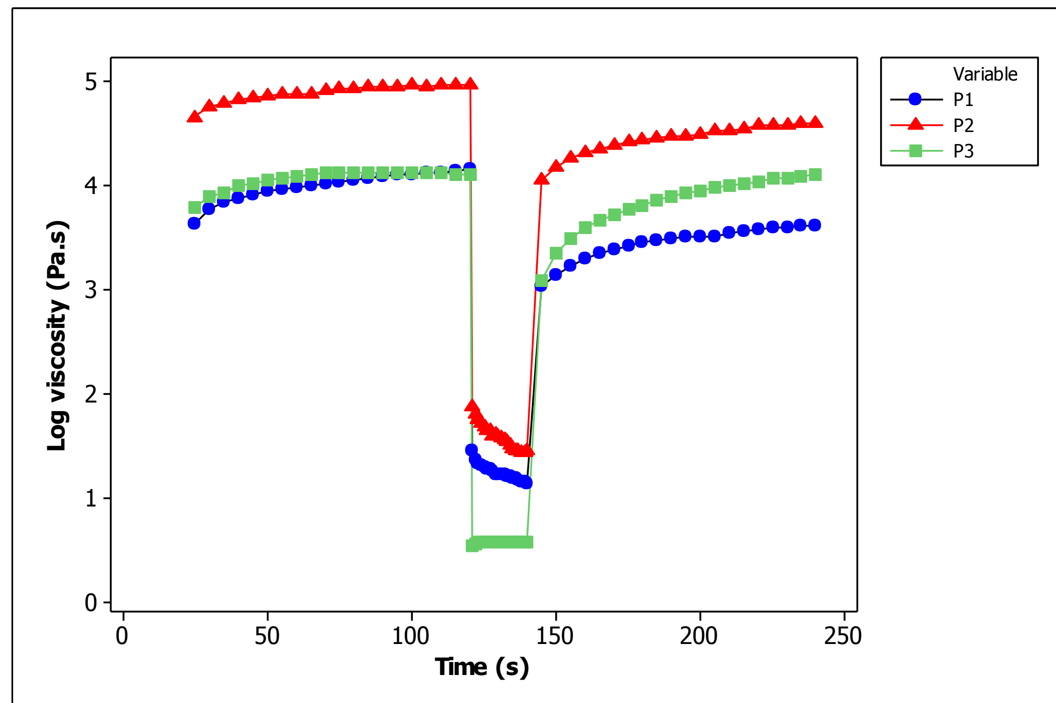


Figure 6.2 : Steady shear rate test of commercial pastes

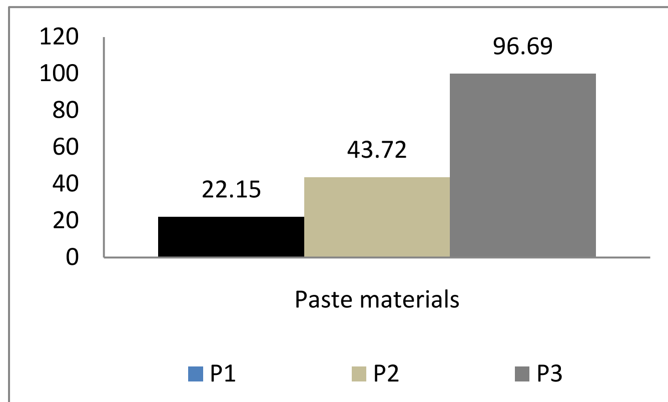


Figure 6.3: Percentage of commercial pastes recovery after removal of shear

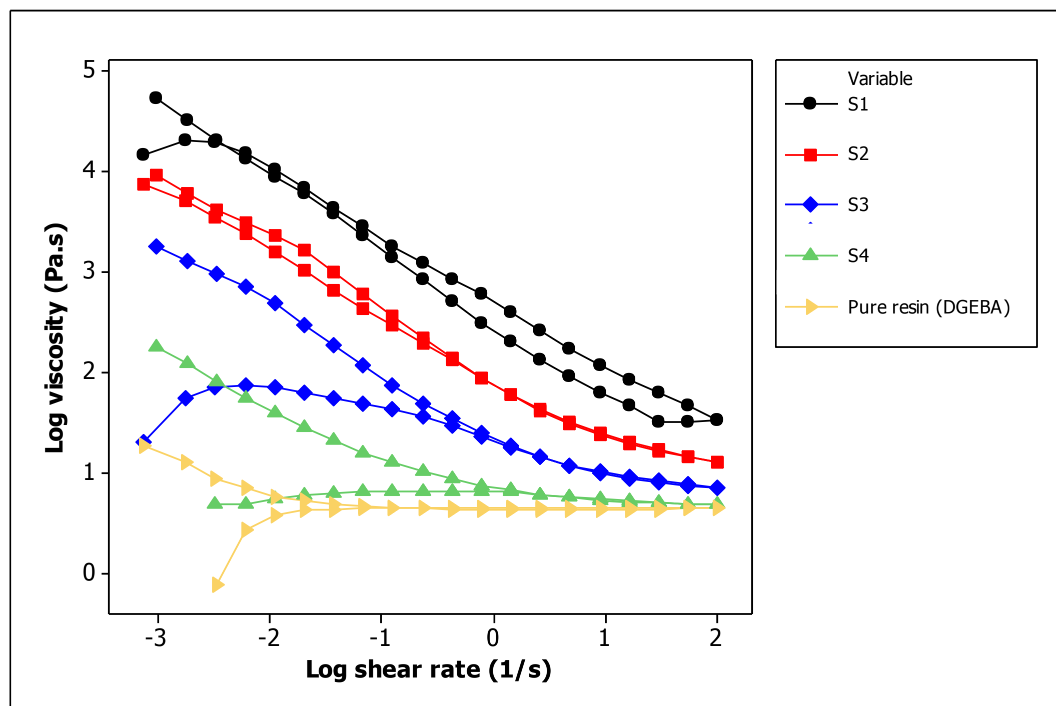
6.2.2 Thixotropic properties of formulated ICA pastes

The hysteresis loop curves for ICA pastes formulated with both diglycidyl ether bisphenol A (DGEBA) and polyurethane (PU) resins are showed in Figure 6.4 and 6.5. The filler content can have a profound effect on the viscosity and rheological properties of ICAs (Bullard et al., 2009). In general, the viscosity of a disperse system increase as the volume fraction of the suspended filler increases. The viscosities increase totally with increasing filler content. With increasing concentration of the filler, the inter-particle interactions increase weakly at first and then rather strongly as the concentration becomes higher and higher. The concentration at which particle-particle interactions begin depends on the contact surface area and collision between the filler particles. At volume fraction 0.8, the

fillers are sufficient enough to have close contact, resulting in a higher degree of fillers agglomeration (Irfan and Kumar, 2008). This network is essentially a continuous linkage between fillers and epoxy system.

Figure 6.4 (a), (b) and (c); and Figure 6.5 (a), (b) and (c) show the effect of increasing the suspended filler content on relative viscosities of the ICAs with different types of filler (silver flakes, silver powder and mixture of silver flakes and silver powder). All the formulated samples, S1 to S24 pastes showed shear thinning behaviour. As shown in Figure 6.4 and 6.5, the viscosities of pure resins (DGEBA and PU) are almost independent of shear rate. As stated earlier, the region between the up curve and down curve in hysteresis curve is an indication of the thixotropic behaviour of the pastes while the enclosed area within the curves indicates the extent of the structural breakdown in the paste for the applied shear (Durairaj et al., 2009). S17 paste shows the highest degree of thixotropy because of the high hysteresis area among all the pastes. The large area within the hysteresis loop in the S5 paste indicates that the sample undergone a large structural breakdown. S5 paste which consists of 0.8-silver powder and 0.2-DGEBA is said to have the weakest structural bonding which easily being broken down by increasing shear rate. In this study, comparison was made based on two filler of different particle size; silver flakes of 10 μm and silver powder of 250 μm. A larger particle size filler has lower contact surface area and has poor dispersion ability, therefore, the particle-particle interactions are relatively weak and easily break when shear is applied (Markley et al., 1999). Filler size of silver powder

(250 μm) is larger than silver flakes (10 μm), hence, ICA pastes formulated with silver powder consist of weak attraction bonding. Most of the pastes except of volume fraction 0.8 shows superposed upward and downward curves at high shear rate. This could just as well correspond to an extremely thixotropic material, capable of rebuilding its structure almost instantaneously (Bauer and Collins, 1967). To support this justification, steady shear rate test were carried out.



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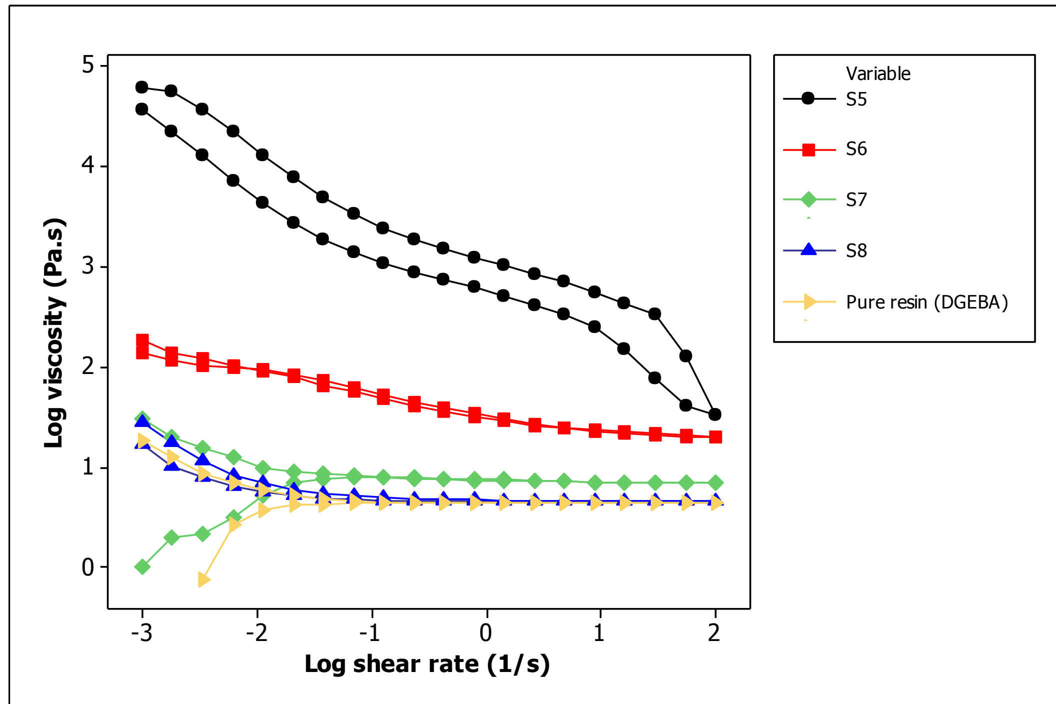

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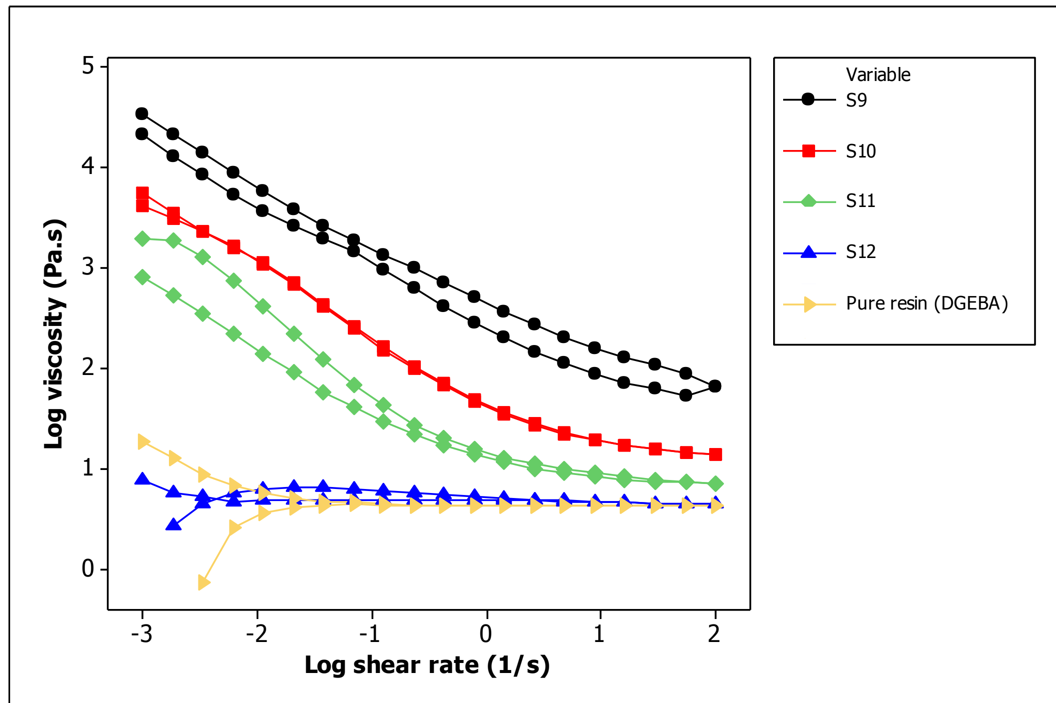

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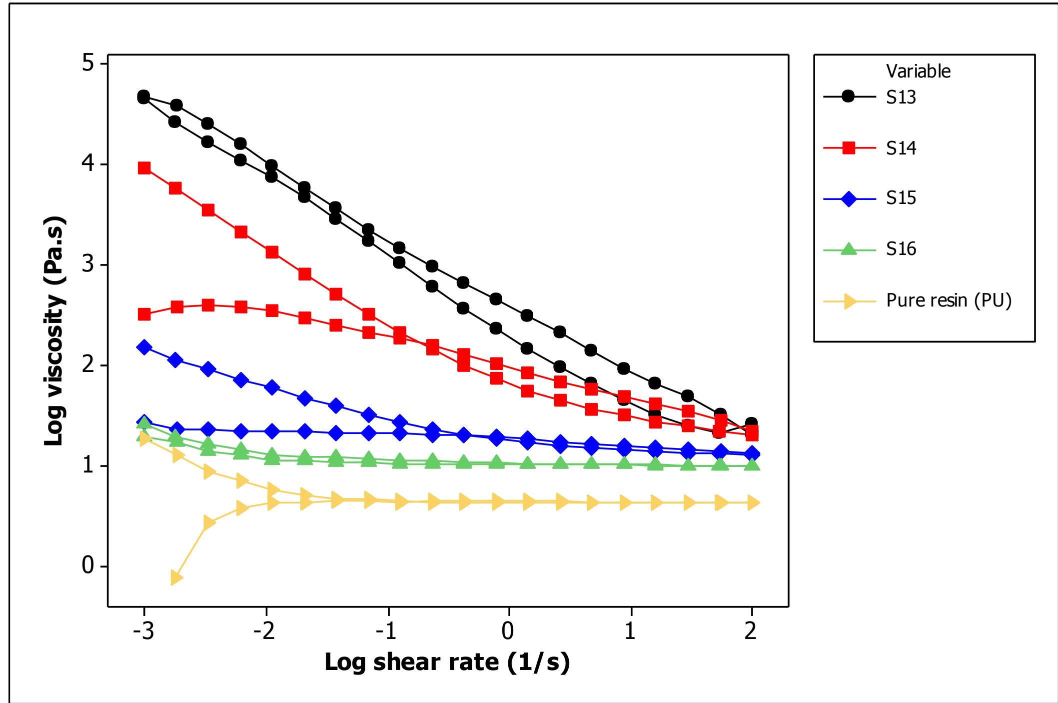
Figure 6.4: Hysteresis loop of ICA paste formulated with DGEBA resins (a) silver flakes (b) silver powder and (c) silver flakes and powder mixture



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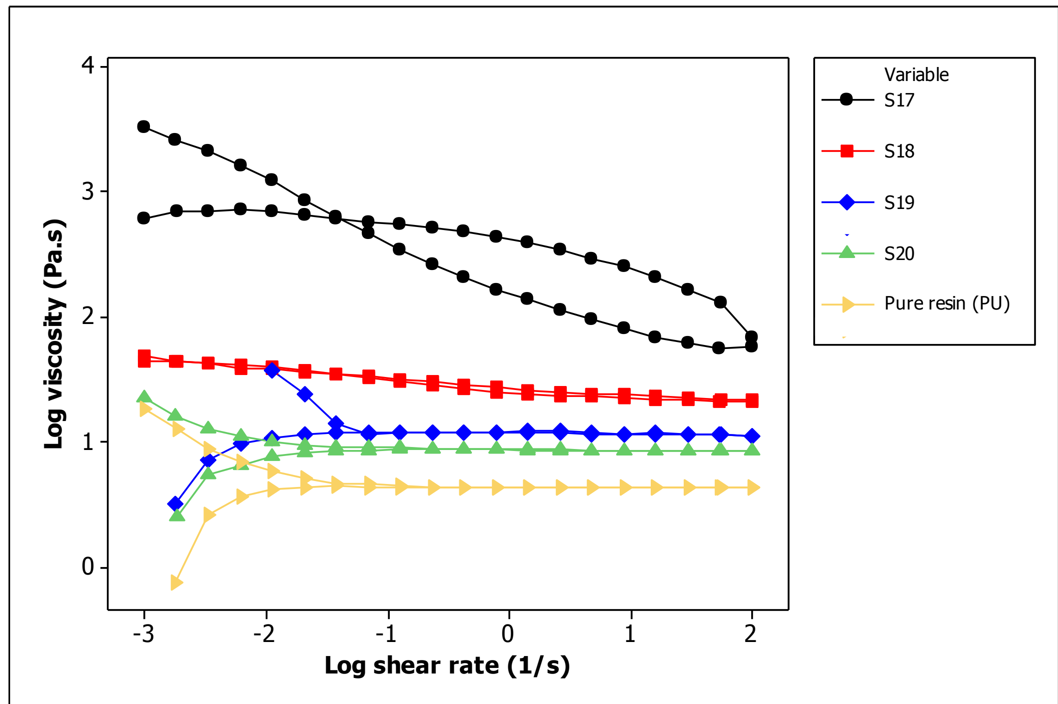

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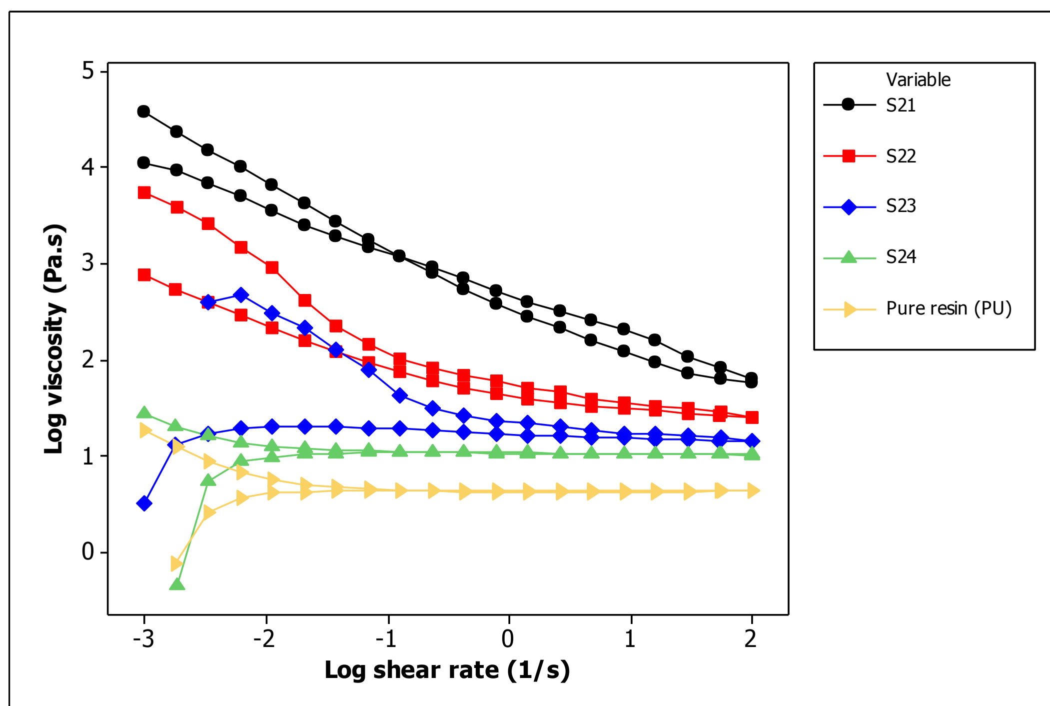


(c)

Figure 6.5: Hysteresis loop of ICA paste formulated with PU resins (a) silver flakes (b) silver powder and (c) silver flakes and powder mixture

Figures 6.6 and 6.7 show the steady shear rate plot for all ICA samples. Viscosities of most paste are gradually increase after the shear is removed (Mewis and Wagner, 2009). ICA pastes with volume fraction 0.6 and 0.8 show a very good recovery after the removal of shear. On the other hand, most of the pastes with volume fraction 0.2 did not show any recovery after the shear is removed. As refer to the hysteresis loop shown in Figure 6.4 and 6.5, pastes with volume fraction 0.2 show superposed upward and downward curves at high shear rate. This could just as well correspond to an extremely thixotropic material, capable of rebuilding its structure almost instantaneously (Bauer and Collins, 1967).

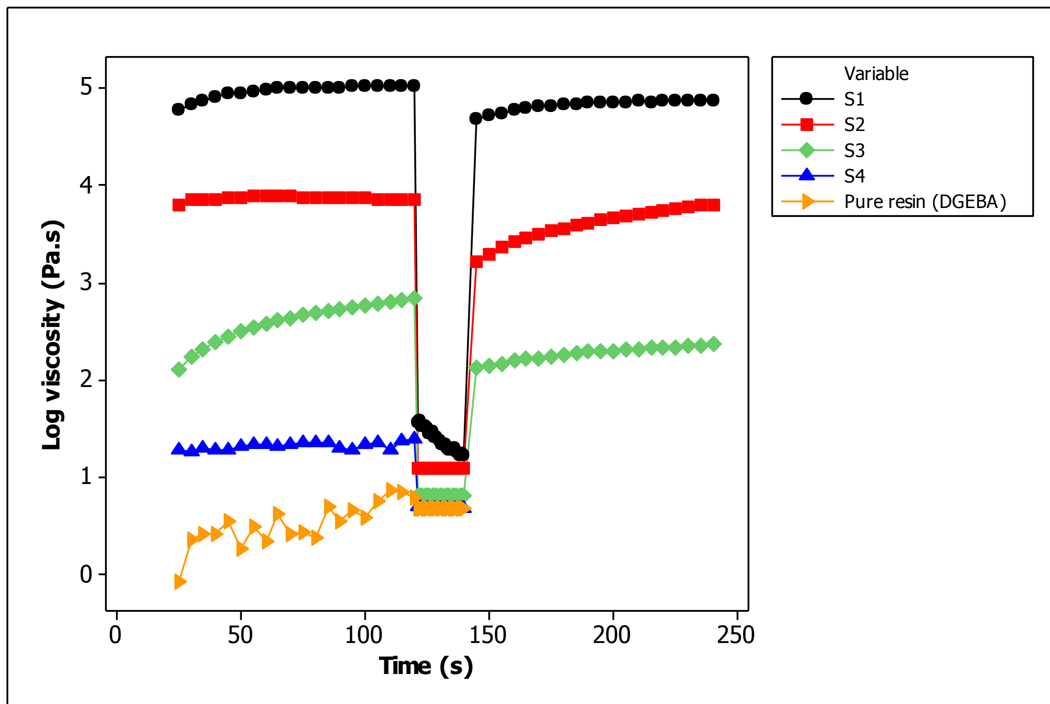
In addition, the pure resins, DGEBA and PU are almost independent of shear rate. This suggested that both DGEBA and PU possess Newtonian behaviour. As stated earlier in chapter 2, Newtonian fluid is independent of the forces acting on it. This means the fluid continues to flow, regardless of the forces applied on it (Larson, 1999; Mewis and Wagner, 2009). Therefore, the structure in DGEBA and PU were not being disturbed when high shear rate is applied and no recovery showed in steady state rate plot. While for pastes with volume fraction 0.2, majority of the composition is resin, hence, properties of the pastes are depend on the resin.

Furthermore the recovery (%) between the shear interval (breakdown) and recovery interval (build-up) in a steady shear rate curve is measured using the equation showed in (9); the paste showed highest percentage of recovery after removal of shear is S9, as shown in Table 6.1. From the results, it is clear that ICA paste formulated with DGEBA resin showed a good recovery compared to that of PU resin. This might be attributed to the lower viscosity of DGEBA which leads to a lower resistance to flow (Bullard et al., 2009). Therefore, ICA pastes formulated with DGEBA are highly elastic behaviour as opposed to those with PU resin. This leads to a good recovery after the removal of shear. As shown in hysteresis loop in Figure 6.4 (b), S5 paste show the largest hysteresis area which indicated a poor recovery. This findings correlated well with the results obtained in steady shear rate test which showed that S5 paste has only 55.87% recovery after the removal of shear which is very low as compared to the other samples. Although the percentage of recovery of S7 paste is 32.20% which is lower than

S5, the curve of recovery as showed in Figure 6.7 (b) is highly scattered. This suggested that S5 paste is not well dispersed and leads to poor stability (Barnes, 1989).

Table 6.1: Percentage of formulated pastes recovery after removal of shear

System	Parameter	Percentage of recovery after removal of shear rate (%)
S1	0.8-silver flakes/0.2-DGEBA	91.04
S2	0.6-silver flakes/0.4-DGEBA	89.55
S3	0.4-silver flakes/0.6-DGEBA	66.52
S4	0.2-silver flakes/0.8-DGEBA	-
S5	0.8-silver powder/0.2-DGEBA	55.87
S6	0.6-silver powder/0.4-DGEBA	58.35
S7	0.4-silver powder/0.6-DGEBA	32.20
S8	0.2-silver powder/0.8-DGEBA	-
S9	0.8-silver flakes+powder/0.2-DGEBA	95.17
S10	0.6-silver flakes+powder/0.4-DGEBA	67.64
S11	0.4-silver flakes+powder/0.6-DGEBA	77.85
S12	0.2-silver flakes+powder/0.8-DGEBA	-
S13	0.8-silver flakes/0.2-PU	81.88
S14	0.6-silver flakes/0.4-PU	85.74
S15	0.4-silver flakes/0.6-PU	-
S16	0.2-silver flakes/0.8-PU	-
S17	0.8-silver powder/0.2-PU	84.53
S18	0.6-silver powder/0.4-PU	58.35
S19	0.4-silver powder/0.6-PU	-
S20	0.2-silver powder/0.8-PU	-
S21	0.8-silver flakes+powder/0.2-PU	56.75
S22	0.6-silver flakes+powder/0.4-PU	63.05
S23	0.4-silver flakes+powder/0.6-PU	-
S24	0.2-silver flakes+powder/0.8-PU	-



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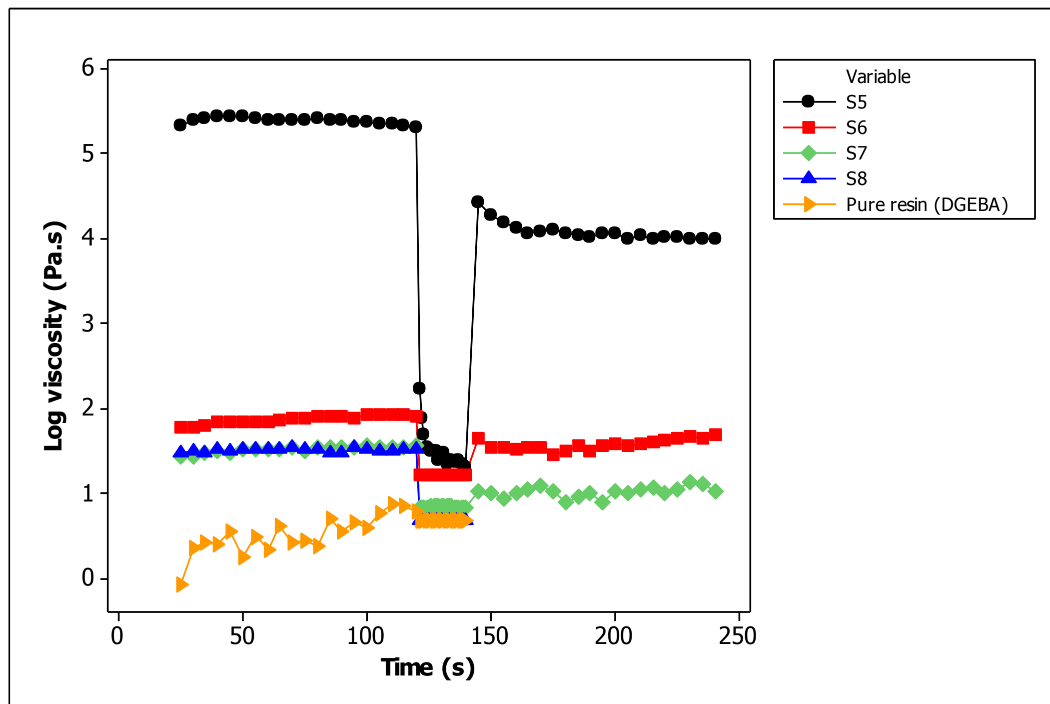

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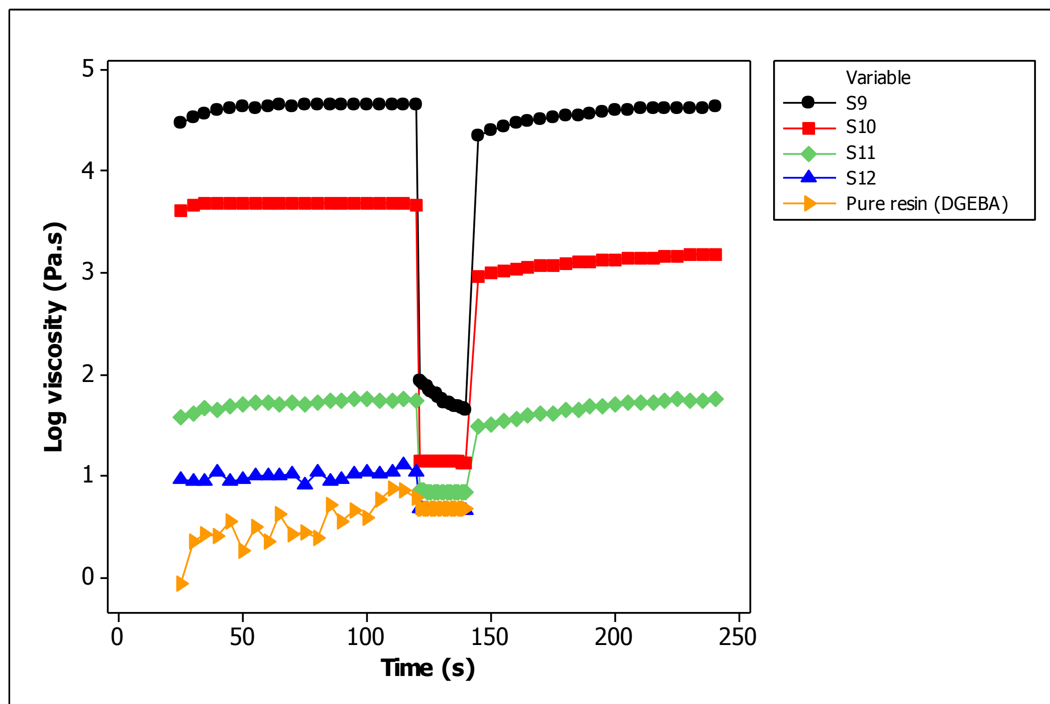

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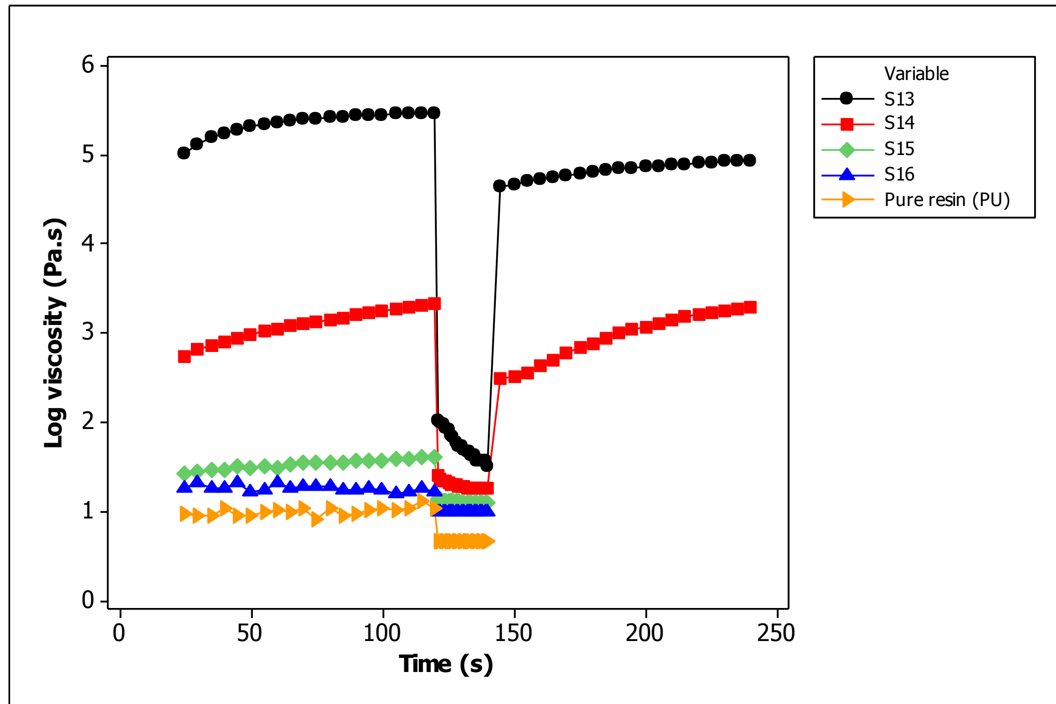
Figure 6.6: Steady shear rate test of ICA paste formulated with DGEBA resins (a) silver flakes (b) silver powder and (c) silver flakes and powder mixture



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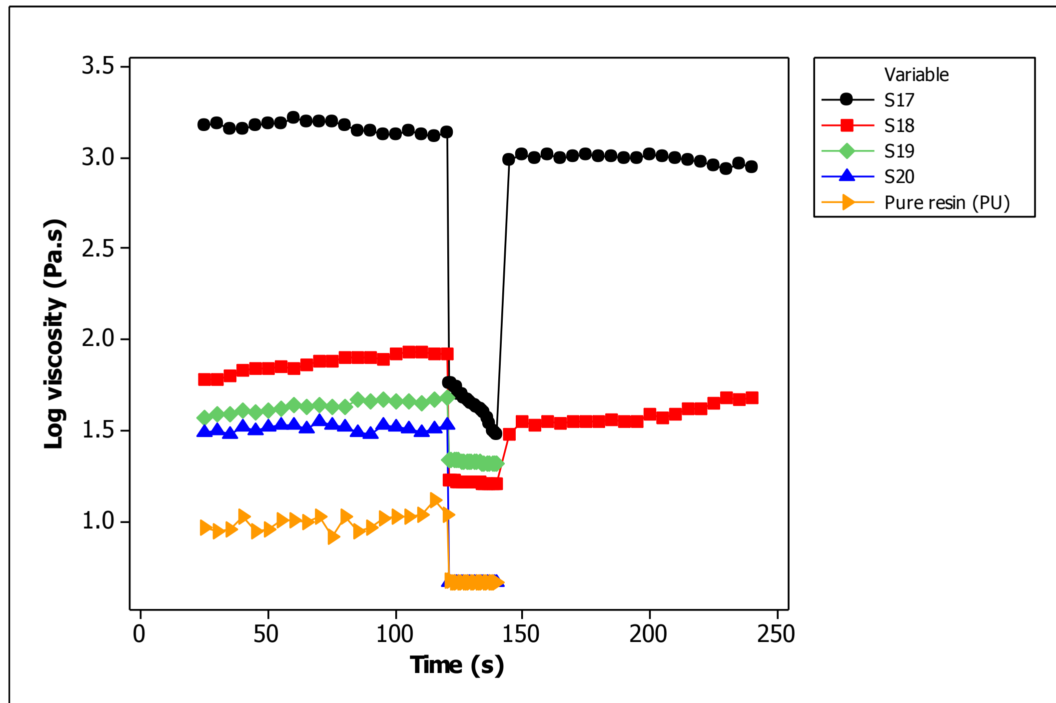

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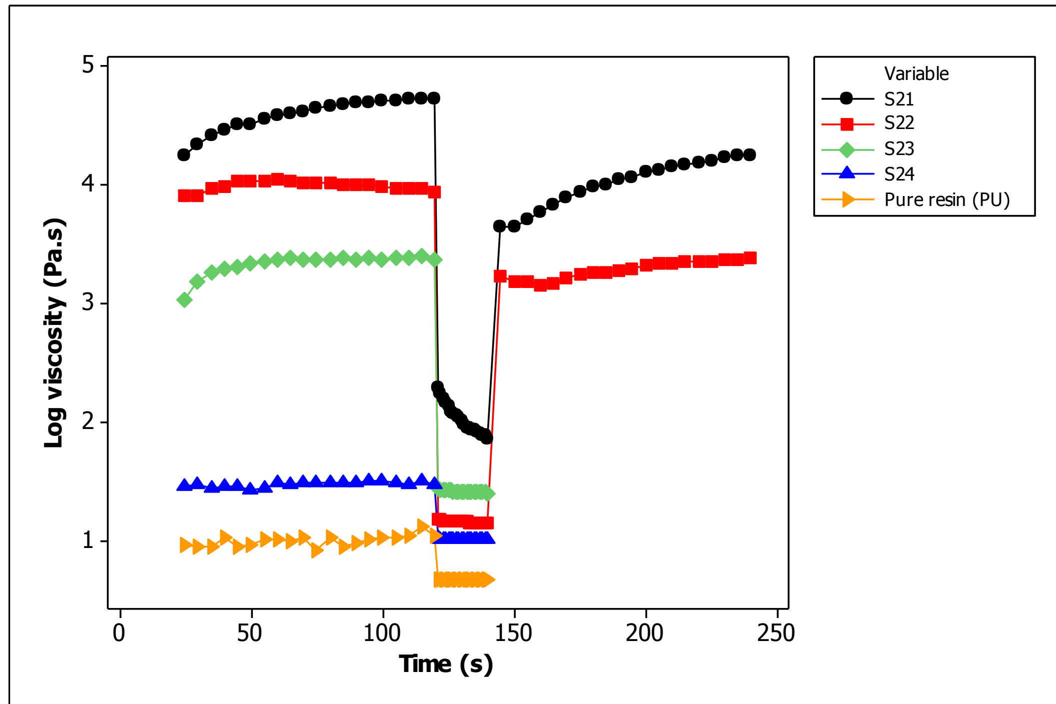

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Figure 6.7: Steady shear rate test of ICA paste formulated with PU resins (a) silver flakes (b) silver powder and (c) silver flakes and powder mixture

CHAPTER 7

THERMAL PROPERTIES OF ICAs

7.1 Introduction

In this study, the curing reaction of isotropic conductive adhesives (ICAs) was examined with a DSC. Tests were conducted to investigate the effect of size and volume fraction of conductive fillers; and different types of polymeric resins on the thermal properties of the ICAs. Samples with desired rheological properties were selected for characterising (P1, P2, P3, S1, S2, S3, S4, S5, S9, S13, S14, S15, S16, S17 and S21).

7.2 Results and Discussion

As mentioned earlier, the significant of this study is to obtain an understanding to the thermal properties of isotropic conductive adhesives (ICAs) and thermal reactions which occur during cure process. The properties of an ICA is depending upon the properties of the individual components and on the interfacial properties (Liu, 1993). Hence in this study, the curing reaction of isotropic conductive adhesives (ICAs) was being examined. Tests were conducted to investigate the effect of size and volume fraction of conductive fillers; and different types of

polymeric resins on the thermal properties of the ICAs. The results obtained were compared with the commercial solder pastes and ICA.

7.2.1 Properties of epoxy resins in the ICAs

Epoxy resin is one of the most important thermosetting polymer materials in an ICA. The cure reaction of epoxy resins involves the formation of a rigid three-dimensional network and it is a complex process, but understanding the mechanisms of the cure reactions are essential for a better knowledge of thermal properties of certain ICAs (Wong and Lu, 2000) . As shown in Figure 7.1, there is an exo-thermic peak observed before an endo-thermic trough. This observation suggested that crystallisation of epoxy, diglycidyl ether bisphenol A (DGEBA) occur. When analyzing crystallisation peaks by DSC, it is important to understand the kinetics of the crystallization process. Crystallization from the melt is a two-step process; nucleation (the rate-limiting step) must first occur then rapid growth proceeds. In addition, most materials will exhibit some supercooling behavior. A supercooled liquid is a compound, which exists in the liquid state below its melting temperature resulting in an inherently unstable phase (Sherman and Mackay, 1990). Unlikely, a crystallisation peak is not seen in epoxy, polyurethane (PU) as shown in Figure 7.2. This results suggested that the phase conversion of PU is more stable than that of DGEBA. Tabulation of melting point, T_m of ICAs is shown in Table 5. The melting point of DGEBA-epoxy system is lower than

that of PU-epoxy system. This might be due to the crystallisation process in the DGEBA epoxy which is a rapid and energetic process which results in a fast return to a steady state (solid) when the crystallisation process is complete. On the other hand, the rate of cure for PU-epoxy is slower. However, it can be seen in Figure 7.1 and 7.2 that the DGEBA-epoxy has a wider endo-thermic trough than PU-epoxy. This might be due to an inconsistency in the epoxy-filler system mixture (Lu and Wong, 2000; Liu, 1999). The width of the peak or trough is used as an industrial measure of the quality of a paste and may indicate the tendency of the paste to have mashy or non-equilibrium behaviour (Liu, 1993; Khoo et al., 1996). In overall, the results suggested that PU-epoxy is a more stable thermosetting polymer material.

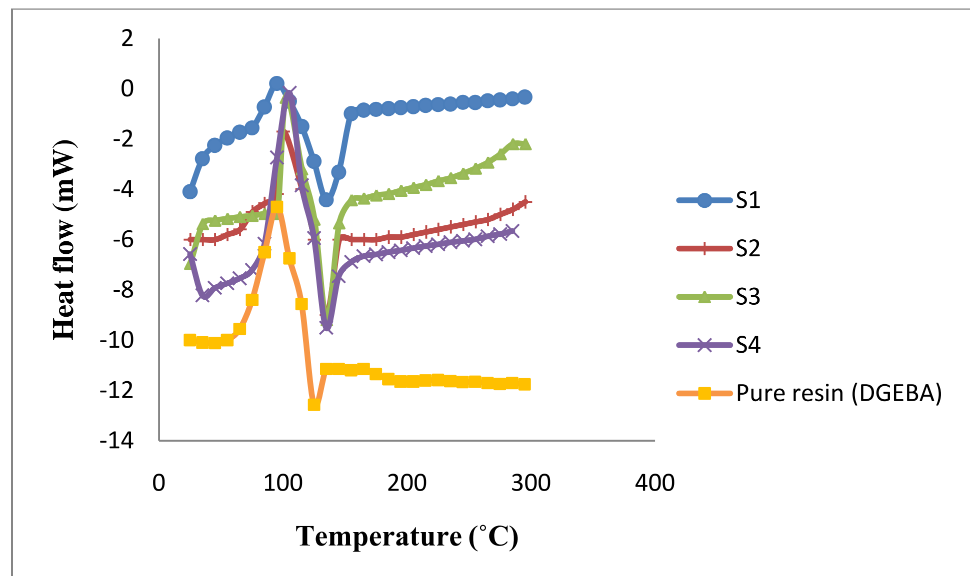


Figure 7.1: DSC curves of silver flakes-DGEBA systems.

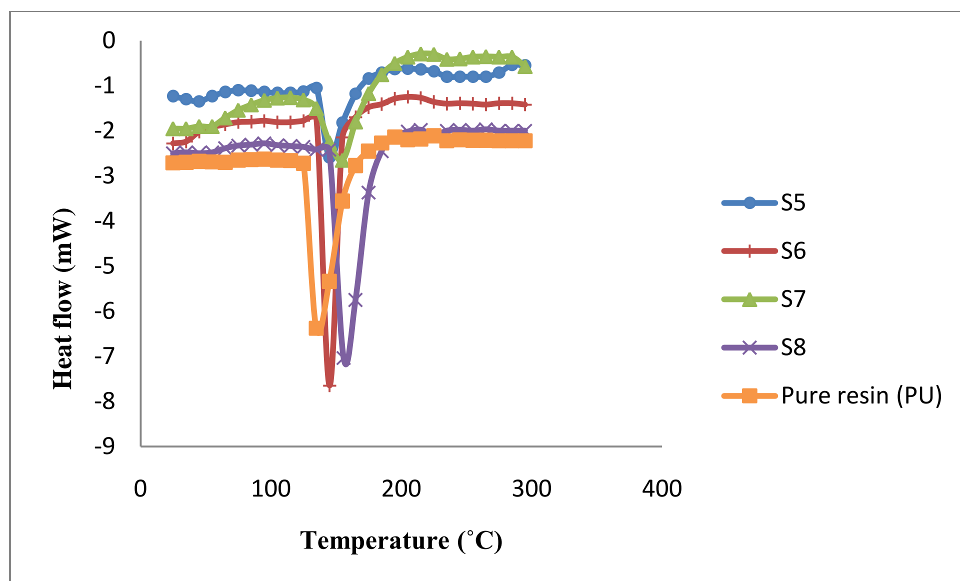


Figure 7.2: DSC curves of silver flakes-PU system.

Table 7.1: Melting points of formulated ICAs

System	Parameter	Melting point (˚C)
S1	0.8-silver flakes/0.2-DGEBA	134.81
S2	0.6-silver flakes/0.4-DGEBA	134.99
S3	0.4-silver flakes/0.6-DGEBA	135.27
S4	0.2-silver flakes/0.8-DGEBA	135.82
S5	0.8-silver powder/0.2-DGEBA	129.86
S9	0.8-silver flakes+powder/0.4-DGEBA	154.87
S13	0.8-silver flakes/0.2-PU	144.89
S14	0.6-silver flakes/0.4-PU	144.99
S15	0.4-silver flakes/0.6-PU	154.88
S16	0.2-silver flakes/0.8-PU	155.75
S17	0.8-silver powder/0.2-PU	134.90
S21	0.8-silver flakes+powder/0.2-PU	136.73

7.2.2 Effect of filler on the thermal properties of ICAs

Silver (Ag) is used as the filler in this study because of its high electrical conductivity, chemical stability, and lower cost compared to gold (Liu, 1999). By comparing the differential scanning calorimetry (DSC) curves of ICAs of all filler's (silver flakes) volume fraction with that of the corresponding unfilled epoxy as shown in Figure 7.3 and 7.4 , it can be seen that the unfilled epoxy has a lower melting point, T_m. Thus the cure reaction of the unfilled epoxy occurs at lower temperature range. This implies that the silver flakes in the conductive adhesives increase the energy barrier of the cure reaction to a certain extent (Markley et al., 1999). In addition, this indicates that the curing agent catalyses the reaction more efficiently in the unfilled epoxy. It could be caused by the fact that the silver flakes in the ICAs diffuse in between the epoxy molecules and the curing agent could not contact with the epoxy as easily as it does in the unfilled epoxy system (Kottaus et al., 1997). As the volume fraction of filler silver flakes increases, the melting point of the filler-epoxy system is decreases. This is mainly due to the reduction of elasticity of the paste due to filler addition and thereby reducing the deformability of the paste. An increase in filler loading reduces the ability of paste to absorb energy. Therefore, as volume fraction of silver flakes increases, the melting point is decrease (Wong and Lu, 2000; Lu et al., 1999; Liu, 1999).

As shown in Table 5 the melting point, T_m of silver flakes-epoxy system is higher than that of silver powder-epoxy system. It is noted that the size of silver flakes (10 μm) is smaller than silver powder (250 μm). Using smaller-size filler in formation of ICAs exhibited high interfacial areas and able to form strong inter-particle bond cause an aggregation in the ICA paste.

Therefore, more heat energy is needed to break this strong attractive force in the inter-particle bond (Markley et al., 1999). This explains the higher melting point, T_m of the silver flakes-epoxy system which has a smaller size of filler. On the other hand, dispersion of smaller size silver flakes into broad size silver powder is seen to have a higher melting point than the monodisperse of broad size silver powder system itself. This might be due to the dispersion of smaller size filler particles filled in the space in between the broad size filler particles causes a stronger attraction force to the epoxy and hence more energy is needed to break the bond (Wong and Lu, 1999) . Therefore, mixture of silver flakes and silver powder epoxy system has a higher melting point than the silver powder epoxy system.

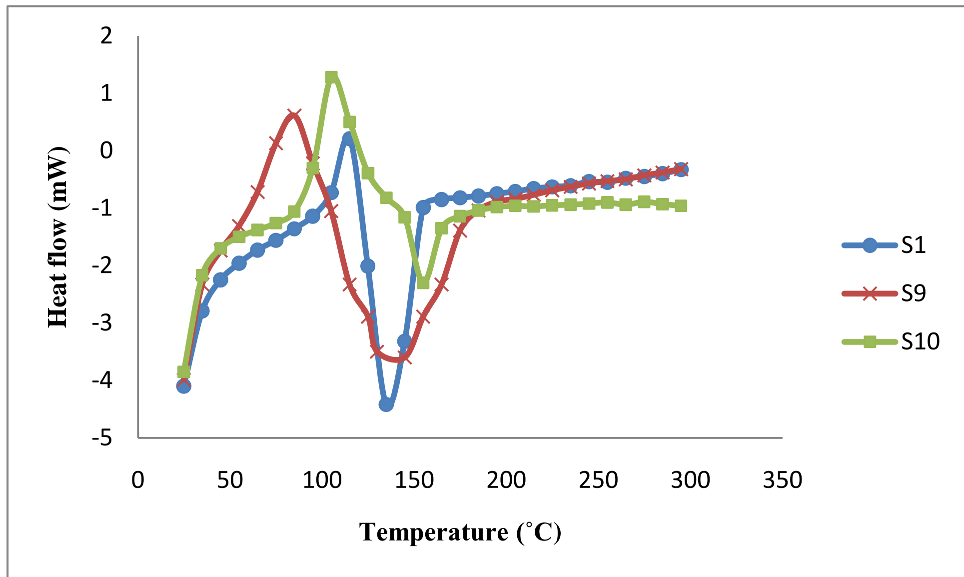


Figure 7.3: Comparison of different filler particle size in DGEBA epoxy systems

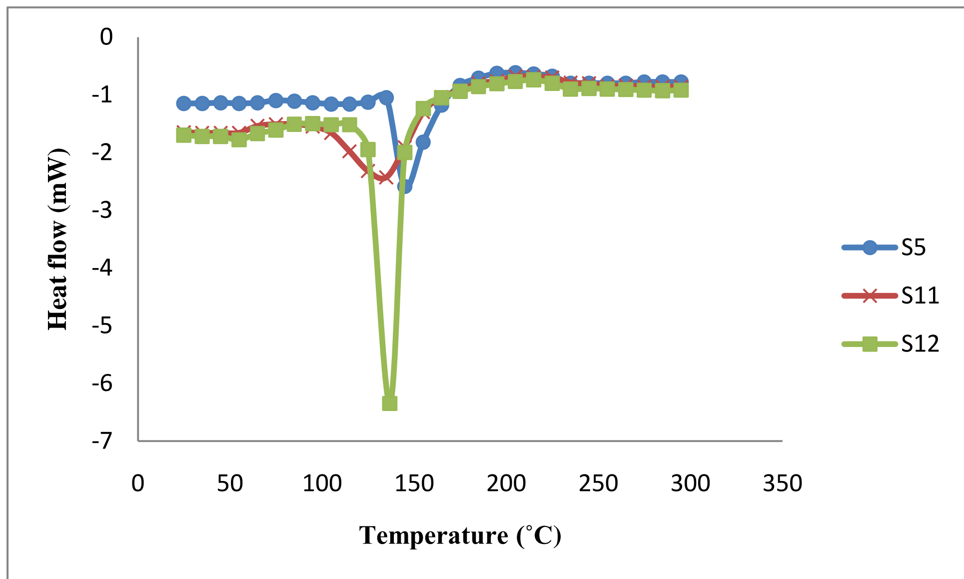


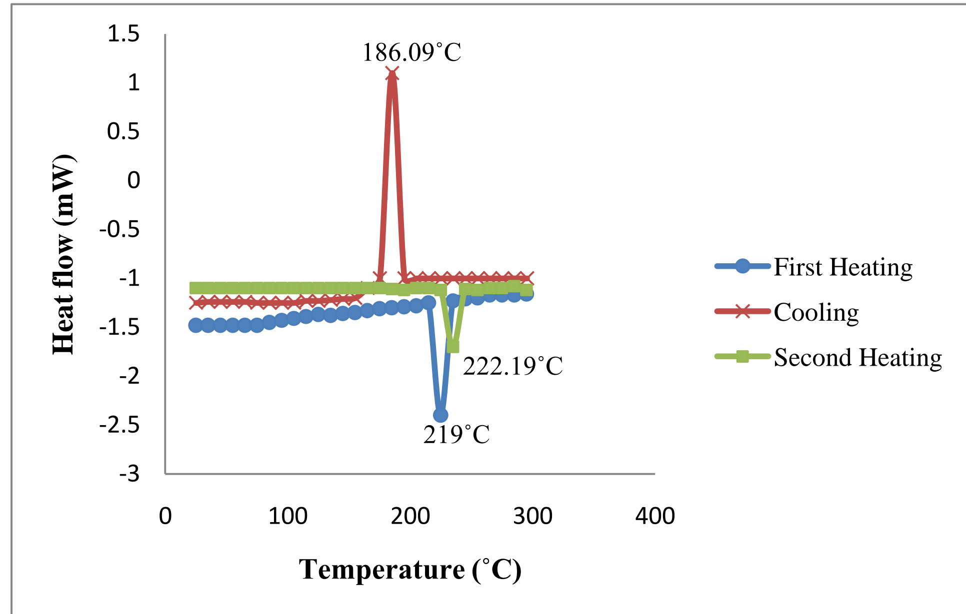
Figure 7.4: Comparison of different filler particle size in PU epoxy systems

7.2.3 Comparison of the formulated ICAs with the commercial pastes

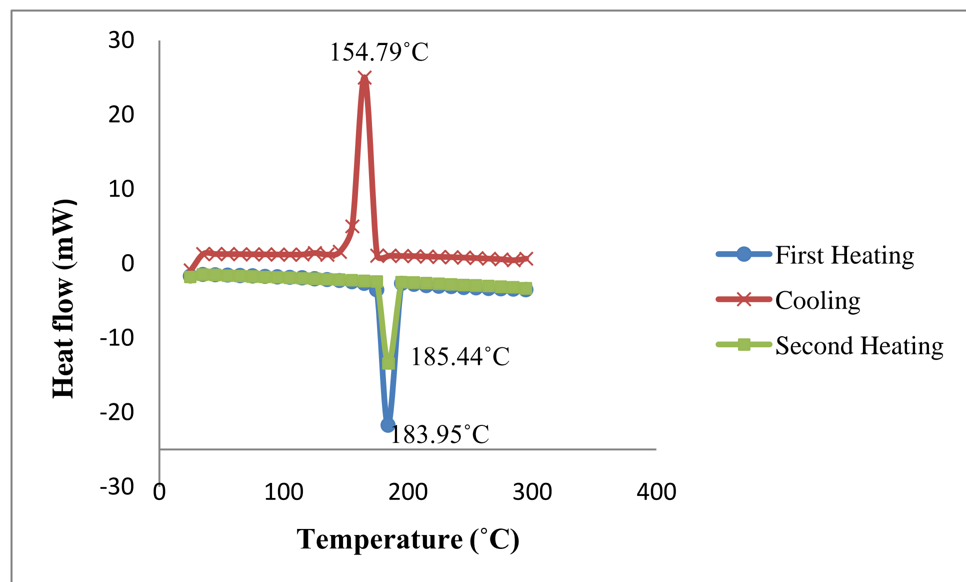
The DSC curve of the commercial Sn-Cu-Ag solder alloy, P1 shown in Figure 7.5 (a), (b) and (c) indicates that the solder alloy melts at 219˚C, Sn-Ag solder alloy, P2 melts at 183.95˚C and the commercial ICA, P3 melts at 154.98˚C. As can be seen at Figure 7.5 (c), the glass transition temperature of P3 paste is at 114.97˚C. At this temperature, ICA start to transform into a glassy-state. In order to get a complete kinetic model for simulating the cure reactions of the pastes, the heating range is divided into three cycles: 25-300˚C; 300-25˚C; and 25-300˚C respectively. The objective to divide the heating range into three cycles is so confirm a complete cure reaction of the paste. Figure 7.5 (a) and (b) showed that phase conversion for P1 and P2 solder paste samples is reversible. This results suggested that P1 and P2 samples are thermoplastic-based solder pastes. Thermoplastics are also referred to as re-meltables and hot melts. This class of materials typically has a long linear molecular structure, which allows these materials to melt and flow when heated to a specific melting point without significantly altering their intrinsic properties (Kuck, 1986).

On the other hand, P3 sample is seen to be irreversible cure. This is due to the thermoset properties in the paste. Thermosets differ from thermoplastic because the cure reaction of thermosets is irreversible and being permanently cure. Therefore, no exo-thermic peak is observed during the cooling process and no endo-thermic trough can be seen during the second heating. This suggested that

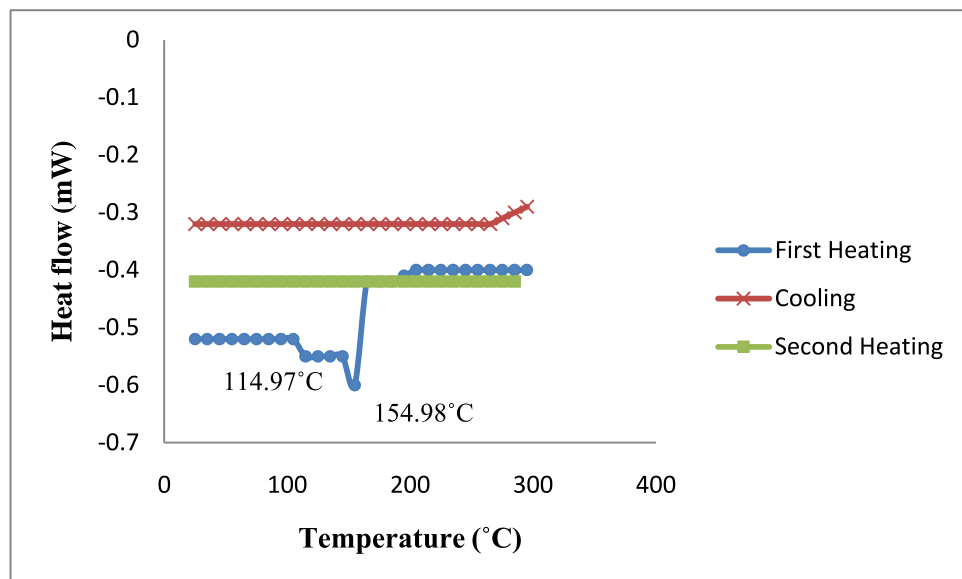
the P3, ICA sample is completely being cured. Same observation is seen in all formulated ICA samples. Based on Table 7, ICAs formulated with polyurethane (PU) epoxy and silver flakes filler showed the most similar melting temperature with the commercial ICA sample, P3.



(a)



(b)



(c)

Figure 7.5: DSC curves of commercial pastes (a) P1 (b) P2 (c) P3

CHAPTER 8

SUMMARY, CONCLUSION AND FURTHER WORK

8.1 Introduction

This chapter presents the summary, conclusions and suggestions for future work for the study carried out on the rheological characterisations of isotropic conductive adhesives (ICAs) for Microsystems Assembly Technology. The key of objectives of the study were as follows:

1) To study the effect of filler size and volume fraction on viscosity measurement of ICA pastes.
2) To study the visco-elastic behaviour of pastes.
3) To study the thixotropic behaviour of pastes.
4) To investigate the thermal properties of ICA pastes.

8.2 Summary

The summary section is divided into four main sections namely; the summary of the findings from the investigation of the of filler size and volume fraction on viscosity measurement of ICA pastes, study of visco-elastic behaviour of pastes, study of thixotropic behaviour of pastes and thermal properties of ICA pastes.

8.2.1 Study of the effect of filler size and volume fraction on viscosity measurement of ICA pastes

The relationship between the filler concentration and viscosity is clarified. With increasing concentration of the filler, the inter-particle interactions increase weakly at first and then tremendously at 0.8 volume fraction. System 1 (silver flakes-epoxy system) shows the highest viscosity due to well dispersion of smaller particle size of filler, 10 µm. The results seem to suggest that the viscosity of formulated ICAs (S1 and S2) are correlated well to the commercial solder pastes and ICA. Since viscosity increase sharply at 0.8 volume fraction for all system, the experimental maximum packing factor, ϕ_m is 0.8. Among all the empirical models, Krieger-Dougherty model fitted best with the experimental data with the highest correlation coefficients value, R^2. The effect of size and volume fraction of filler are important factors that can be used in the development of new formulation of solder pastes and ICAs.

8.2.2 Study of visco-elastic behaviour of pastes

To study the rheological properties of ICAs, the effect of filler size, filler concentration and types of resins on the visco-elastic behaviour of isotropic conductive adhesives (ICAs) were studied in this present investigation. In this study, the results obtained were benchmark against commercial solder pastes and

ICA. As expected, the results for commercial samples showed that the storage modulus, G' is higher than loss modulus, G'' indicating a solid-like behaviour. This is true for formulated 0.6 and 0.8 volume fraction of epoxy-filler system (S5, S6, S9, S10, S13, S17, S18, S21 and S22). However, 0.6 volume fraction of silver flakes-polyurethane system (S14) showed that G'' is dominate over G'. This might be due to the viscosity of polyurethane which dependent on shear. With increasing shear stress, the paste sample gradually change from solid- to liquid-like behaviour. This might be due to the breakdown of particles interaction in the flux system. The poor paste roll and paste withdrawal from stencil during printing process could be related to the solid characteristics (G') and liquid characteristics (G'') of the pastes measured in the oscillatory sweep test. Same as oscillatory sweep test, the frequency sweep test could be used to study the visco-elastic behaviour of the pastes. In addition, frequency sweep test could be used to determine formation of sedimentation in the pastes.

Another parameter investigated is the yield point which is the stress at G'= G'', which is an important indicator of paste cohesiveness. The results shows that a higher value of yield point, the greater the degree of cohesiveness of the pastes, indicate that the paste require a significant amount stress to change from solid to liquid state. The results obtained showed that silver powder-DGEBA system has the highest yield point, 52.12 Pa which means the paste has the strongest particles interaction. Hence, more stress is needed to force this paste release from the stencil aperture during printing process.

The phase angle could provide a swift way of assessing the transition from solid- to liquid-like behaviour of the paste material. A low phase angle may indicate the paste is very tacky or in contrast, a high phase angle may indicate a paste that could slump easily. Of all three commercial samples, lead-free solder paste showed the lowest phase angle, 38.6° and this indicates that this paste is very cohesive. In formulated sample, S5 which is 0.8-silver powder/0.2-DGEBA system showed the lowest phase angle, 35.4° and the paste is said to be high cohesive or tacky. This might be due to the high volume fraction of filler content and lead to strong particle-particle interactions. Monitoring properties such as visco-elastic behaviour is of paramount importance when setting goals for increasing yields because it provides a consistent and reliable performance at all times.

8.2.3 Study of thixotropic behaviour of pastes

In this study, the viscosity of several pastes (solder pastes and isotropic conductive adhesive) are examined to find the effect shear rate on the thixotropic behaviour of the pastes and to correlate paste rhelogical properties to the stencil printing performance. The thixotropic test method is used to evaluate the pastes thixotropic behavior with respect to its printability. Formulated ICAs were benchmark against the commercial pastes. Several parameters were studied in the

formulation of ICAs, i.e.: effect of filler's size, effect of filler's concentration and effect of types of resins.

The presence of an area between the down curve and up curve shows that the paste materials are thixotropic in nature. From the results, S5 paste showed the largest area between the down and up curve indicating the structural breakdown in the paste as results of the shear rate and shows that the paste has poor thixotropic behaviour (poor recovery). The findings from the study show that smaller filler size leads to large surface area and better inter-particle attraction. As the volume fraction of filler increases, the viscosity of the paste increases as well. Resins also play an important role in the ICA formulation because resin with lower viscosity leads to a lower resistance to flow, therefore, higher elastic behaviour and exhibit good recovery after the removal of shear. This study emphasized the importance of thixotropic in stencil printing process as the viscosity of solder paste must be low enough to force out from the squeegee yet high enough to reshape. The structural breakdown and recovery of the pastes is an important parameter that can be used in the development of new formulation of solder pastes and isotropic conductive adhesives.

8.2.4 Investigation of the thermal properties of ICA pastes

From the experimental results it can be concluded that DSC profiles can provide an indication of thermal properties of ICAs during curing reaction. Some epoxy-filler systems exhibit more than one endo-thermic peak or exo-thermic trough. This was seen in DGEBA epoxy system which exhibit crystallisation peak before the melting trough. However, PU is said to be more stable than DGEBA epoxy due to its more stable phase conversion process and a narrower width of trough indicated that well dispersion of PU in the epoxy-filler systems. Silver flakes-epoxy system which has a higher melting point, T_m due to its smaller filler particle size which has a higher surface area and causes a strong inter-particle bond. Hence, more heat energy is needed to break the bond. An increase in filler loading reduces the ability of paste to absorb energy. Therefore, as volume fraction of silver flakes increases, the melting point is decrease. In overall, ICAs formulated with PU epoxy and silver flakes filler showed the most similar melting temperature with the commercial ICA sample.

8.3 Conclusions

A number of conclusions can be made from the results of the work presented in this thesis:

1) Maximum packing factor, ϕ_m of filler is 0.8.
2) ICAs formulated with silver powder (larger filler size) showed more thixotropic (structural breakdown).
3) ICAs with 0.6 and 0.8 volume fraction showed more solid-like behaviour and stable dispersion.
4) Silver flakes-epoxy system (smaller size) has a higher melting point, $T_{m.}$
5) The results seem to suggest that the formulated ICAs of 0.6 volume fraction of silver flakes are correlated well to the commercial solder pastes and ICA.

8.4 Suggestion for Future Work

The rheological characterisation of isotropic conductive adhesives (ICAs) used for Microsystems Assembly has been reported in this thesis. The characterisation of the pastes and its correlation to the formulation materials is a very complex task. Here are some suggestions for possible further work in this area:

1) Rheology is a way to describe the workability of an adhesive. In some situations the rheology can be described by the viscosity of an adhesive, in other situations the thixotropy of an adhesive is used. It is meaningless to talk about viscosity if the adhesive is thixotropic. Thixotropic materials are characterised by the fact that when not stirred they are form stable but when they are mechanically worked, stirred, they become more or less viscous. By optimisation of the amount and the properties of filler particles and by use of different additives it should be possible to achieve a suitable rheology for stencil printing. In this study, effects of size of filler, volume fraction of filler and types of epoxy resins on rheology of ICAs were investigated and the results suggested that size of filler strongly affected the viscosity of ICAs. Further work is recommended, to disperse the filler with high shear technology such as three roll mill method.

2) Curing of the adhesive, both thermosetting and thermoplastic, results in a slight decrease in the weight of the adhesive. This weight loss is caused by the evaporation of solvent, or reactive solvents. In general, the weight loss is highest for thermoplastic adhesives, where the total amount of solvent must evaporate in order for the adhesive to cure. It is desirable to minimise the weight loss both in consideration of technical and environmental aspects. When substances evaporate from the joint it becomes porous, which affects both mechanical and electrical properties. In relation to the environment organic solvents or reactive solvents may cause health risk

and/or pollution if present in larger amounts For future research, further investigation is recommended for the effects of these variables on other desired properties such as adhesion strength and ICA's reliability.

It is also necessary to take into account such issues as:

1) Process cost and materials availability
2) World resources (materials)
3) Hazards from substitute materials
4) Process effectiveness and joint reliability, which may be totally uncertain

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