Rheology and Processability of Diglycidylether of bisphenol-A (DGEBA) and Polyurethane (PU) based Isotropic Conductive Adhesives Filled with Different Size-distributed Silver Flakes and Silver Particles

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Abstract — **The study investigates the rheological behaviour of Diglycidylether of bisphenol-A (DGEBA) and Polyurethane (PU) based isotropic conductive adhesives (ICAs). Each of the systems were formulated with the following fillers: a) silver flakes, b) silver powder and c) mixture of silver flakes and silver powder. A volume fraction ranging from 0.2 to 0.8 silver fillers were added to the epoxy systems. Oscillatory stress sweep test was performed to evaluate the G' and G" of the DGEBA and PU based isotropic conductive adhesive pastes. The results show that the structural breakdown of DGEBA and PU pastes could be used to understand the processability and stability of the formulated system. The solid and liquid characteristics of the PU based ICAs were lower when compared to the isotropic conductive adhesives formulated with DGEBA epoxy resin.**

Index Terms—**Rheology; Silver Flakes; Polyurethane (PU); Isotropic Conductive Adhesives; Oscillatory test; Reometer; fillers**

I. INTRODUCTION

THE electronics industry has been striving to find a suitable replacement for lead-based, Sn-Pb solder paste after introduction of legislation to ban the use of lead in electronic products. Due to the toxicity of lead in electronic products, legislation has been proposed to reduce the use of and even ban lead from electronics.

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Lead-free solders (Pb-free solders) and isotropic conductive adhesives (ICAs) have been considered as the most promising alternatives of lead-based solder [1-2].

ICAs offer numerous advantages over conventional solder, such as environmental friendliness, low temperature processing conditions, fewer processing steps, low stress on the substrates, and fine pitch interconnect capability. Therefore, ICAs have been used in liquid crystal display (LCD), UHF RFID tag antennas, smart card applications, flip–chip assembly and ball grid array (BGA) applications as a replacement to solder [3].

The ICAs materials consist of two components; a polymer matrix and electrically conductive fillers. Traditionally bisphenol-A based epoxies has been used widely used in the electronic packing industry due to their excellent reliability, good thermal stability and high Young's modulus [4]. As thecurrent trend for miniturisation is set to continue towards flexible electronic components with the aim of integrating into sensors or biocompatible electronic components, bisphenol-A is not suitable for this application due to high Young's modulus, hardness and brittleness. Polyurethane (PU) is seen as promising replacement for bisphenol-A based isotropic conductive adhesives due to well-known mechanical properties and can exhibit greater flexibility [4].

Rheological characterisation of pastes materials is the key to understanding the fundamental nature of the ICA suspensions; for example the effect of particle size distributions of silver flakes or powders on the flow and deformation behavior of the pastes. Paste materials are dense suspensions, which exhibit complex flow behavior under the influence of stress. The formulation of new materials such as Polyurethane (PU) based ICAs will require an extensive understanding of the rheological behavior, which is significant for the assembly of flexible electronic devices. A number of studies have reported the rheological behavior of the Diglycidylether of bisphenol-A (DGEBA) based isotropic conductive adhesives with silver flakes as the conventional filler materials [5-7]. But the rheological studies on PU based conductive adhesives are limited.

The aim of this study is to investigate the rheological

behaviour of concentrated PU and DGEBA based isotropic conductive adhesives. The rheological responses under oscillatory shear stress were examined as a function linear visco-elastic region (LVER), volume fraction and particles size (silver flakes; silver powder; mixture of silver flakes and silver powder).

II. INTRODUCTION TO OSCILLATORY SHEAR TESTING

The oscillatory stress sweep is typically used to characterise the visco-elastic effect of emulsions, dispersions, gels, pastes and slurries. Furthermore oscillatory experiments can be designed to measure the linear or the non-linear visco-elastic properties of dense suspensions such as solder pastes. A sinusoidal stress as a function of the angular velocity (ω) and the stress amplitude (σ_o) is applied on the samples. The applied stress and the resultant strain are expressed as:

$$\sigma = \sigma_o \sin(\omega.t) \tag{1}$$

$$\gamma = \gamma_o \sin(\omega.t + \delta) \tag{2}$$

where δ is the phase shift, $\omega = 2\pi f$ where f is the frequency, and t is the time. The ratio of the applied shear stress to the maximum strain is called the "complex modulus" (G^*) and is a measure of a material's resistance to deformation:

$$G^* = \frac{\tau_0}{\gamma_0} \tag{3}$$

The complex modulus can be divided into elastic and viscous portion representing the magnitude of the strain in-phase and out-of-phase with the applied stress, respectively. The elastic component is called the "storage modulus" and defined as:

$$G' = \left(\frac{\tau_0}{\gamma_0}\right)\cos(\delta) = G^* \cos(\delta) \tag{4}$$

The viscous component or "loss modulus" is defined as:

$$G'' = \left(\frac{\tau_0}{\gamma_0}\right)\sin(\delta) = G^* \sin(\delta) \tag{5}$$

The complex modulus and phase angle can be expressed as functions of the storage and loss modulus:

$$G^* = G' + iG'' \tag{6}$$

In this study the rheological parameters; storage modulus (G') and loss modulus (G") is correlated to the solid and liquid characteristic of the DGEBA and PU based isotropic conductive adhesives.

III. EXPERIMENTAL

A. Equipment

The rheological curve test measurements were carried out with the Physica MCR 301 controlled stress rheometer.

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 parallel 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).

B. Formulation of ICA pastes

In this study, viscosities of formulated isotropic conductive adhesives (ICAs) at different volume fraction of filler with different particles size are investigated. Table 1 show the chemicals used in the formulation of ICAs, which was purchased from Sigma-Aldrich. The epoxy and silver powder/flakes were mixed according to the ratios shown in Table 2. The ICAs materials were formulated into volume fraction (ϕ) of 0.2, 0.4, 0.6 and 0.8. Usually, the filler contents are determined by weight percentage. For example, for the formulation volume fraction of 0.2, 20% of metal filler (silver powder) is mixed with 80% Diglycidylether of bisphenol-A. The summary of all the systems investigated in this study is presented in Table 3. The silver flakes/powder size were measured under scanning electronic microscope (SEM) and found that the flake/particle size is approximately 10 μm and 250 μm, as shown in Fig. 1 and Fig. 2. An X-ray diffraction test was carried out on the silver flakes and powder; the phases in Fig. 3 show the existence of Ag only, which confirms that the material is pure silver.

TABLE I
CHEMICALS USED IN THE PREPARATION OF ISOTROPIC CONDUCTIVE ADHESIVES (ICAs)

Components	Chemicals	Manufacturer
Resins	Diglycidylether of bisphenol-A (DGEBA) Polyurethane (PU)	Sigma Aldrich
Curing Agent	Ethylene diamine	Merck and Co
Fillers	Silver flakes and silver powder	Sigma Aldrich

TABLE 2
SIZE AND VOLUME FRACTION OF FILLERS INVESTIGATED

Filler size (μm)		
Silver Flakes	Silver Powder	Volume Fraction of Filler
10	250	0.2
		0.4
		0.6
		0.8

TABLE 3
SUMMARY OF THE SYSTEMS INVESTIGATED IN THIS STUDY

| Components	Formulation
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
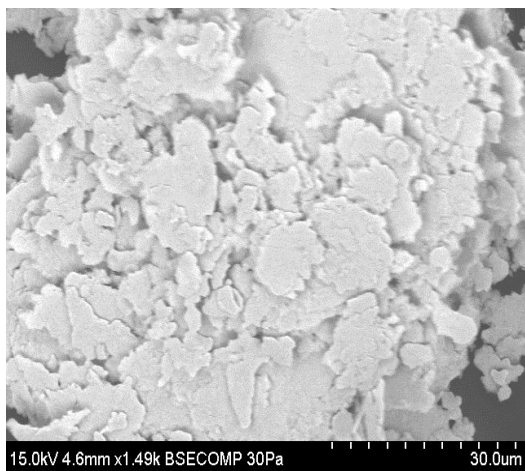
Fig. 1. Scanning Electron Microscope (SEM) microstructure of silver flakes
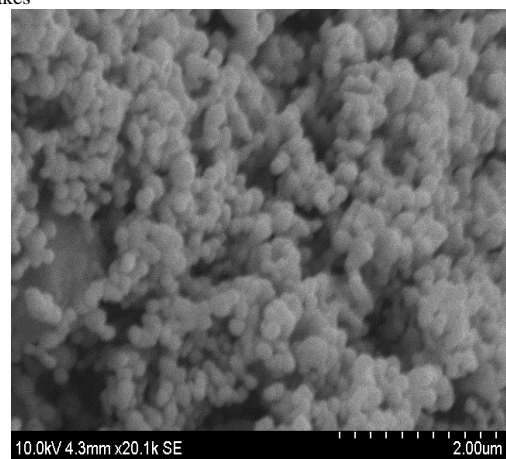

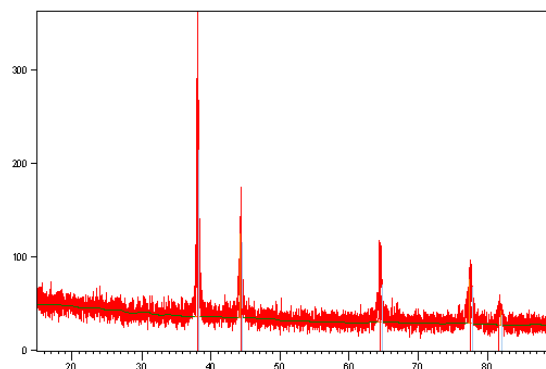Fig. 2. Scanning Electron Microscope (SEM) microstructure of silver powder

Fig. 3. XRD Data for Silver (Ag)

C. Oscillatory Stress Sweep Test

In the oscillatory stress sweep experiment, initially a large stress sweep range of 0.0001-1000 Pa is applied to all the pastes samples. The oscillatory stress results showed that there are inconsistency in the measured parameters; storage modulus (G') and loss modulus (G") at low shear stress. At higher volume fractions, the rheometer had difficulty in taking consistent measurement at shear stresses of 0.001 Pa as opposed to lower volume fractions. This is the reason why some of the rheological data is presented at different shear stresses. This indicates the development of inherent structural strength as a result of the transition the paste undergoes from Newtonian to Non-newtonian, due to the addition of filler materials.

The linear visco-elastic region is defined as the maximum deformation can be applied to the sample without destroying its structure. It should be noted here that the linear data is not particularly relevant for real application processing but can be useful in looking for particle-particle interactions [8]. The length of the LVE region of the elastic modulus (G') with respect to the applied shear stress can be used as a measurement of the stability of a sample's structure, since structural properties are best related to elasticity prior to structural breakdown. In the LVE 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.

IV. RESULTS AND DISCUSSION

DGEBA based isotropic conductive adhesives

For the DGEBA epoxy formulation with silver flakes at $\phi = 0.2$, the loss modulus (G") was greater than the storage modulus (G'), as shown in Fig. 4. The G' showed a LVE region up to 0.5 Pa after which the G' values dropped showing a structural breakdown in the paste. The loss modulus, G" value is constant with increasing shear stress as it gives the response which is exactly out of phase with the imposed perturbation, and this is related to the viscosity of the material.

A similar trend was observed at $\phi = 0.4$, but with a higher LVE region up to 1 Pa followed by structural breakdown, shown in Fig. 4. At $\phi = 0.6$ and $\phi = 0.8$, the measured storage modulus (G') is greater than loss modulus (G") with

increasing shear stress. In addition, as the volume fraction is increased from $\phi = 0.2$ to 0.8, the measured LVE region increases from 0.5 Pa, 1 Pa, 10 Pa and 100 Pa, respectively prior to structural breakdown. The shift of LVE region to higher stress range could be due to the strong interaction between different layers of flakes within the system.

Fig. 5 represents the DGEBA epoxy formulated with silver powder with a particle size of 250 µm. At $\phi = 0.2$ and $\phi = 0.4$, the G" was greater than G', which indicates the liquid-like behaviour of the paste is predominant, as shown in Fig. 5. For the volume fraction of $\phi = 0.6$ and $\phi = 0.8$, the storage modulus (G') was greater than loss modulus (G"). At lower volume fraction $\phi = 0.2$ and $\phi = 0.4$, the addition of silver particles did not affect the Newtonian continuous phase of the epoxy resin. Hence the paste did not show any structural breakdown as observed for silver flakes. The measured LVE region for $\phi = 0.6$ and $\phi = 0.8$ was up to 0.8 Pa and 1 Pa, which is lower when compared to the DGEBA formulated silver flakes. Beyond the LVE region, the flocculation of silver powder in the DGEBA system is easily broken down over narrow range of shear stress as illustrated by Fig. 5. The results show that a larger particle size has lower contact surface area and has poor dispersion ability.

A bimodal distribution was formulated with a mixture of silver flakes and silver powder, as shown in Fig. 6. As with previous systems, at $\phi = 0.2$ and 0.4, the G" is greater than G' due to lower concentration of the silver flakes and powder in the systems. However, at $\phi = 0.2$ and 0.4, G' value increases with the applied shear stress and gradually begins to drops after 0.2 Pa. At $\phi = 0.6$ and $\phi = 0.8$, the LVE region has increased up to 10 Pa and 50 Pa. These values are higher than DGEBA/silver powder system but lower than DEGBA/silver flakes systems. Previous study by Walberger and Mchugh [9] concluded that there will be always an increase in G' and G" due to the addition of filler but where the increase in both functions with addition of filler is not the same, the effect on G' is considerably greater within the linear visco-elastic region. Beyond the LVE region, the paste sample showed a gradual structural breakdown as opposed to silver flakes and powder systems. The results seem to indicate that the flake in the system restricts the movement of the particles, which delays the structural breakdown.
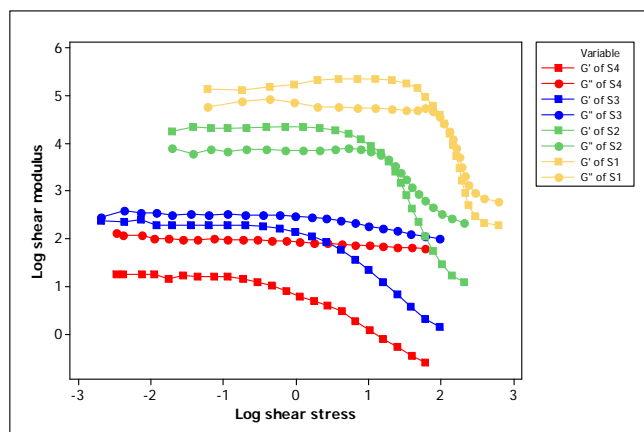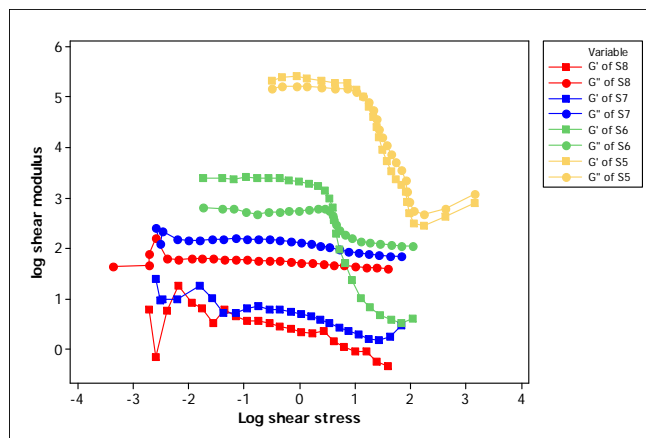

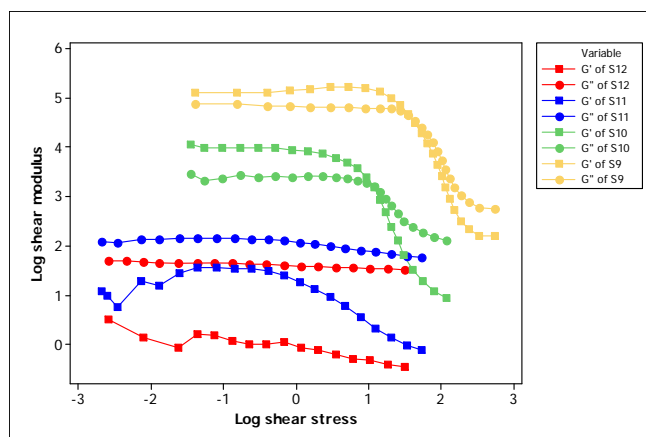Fig. 5. Silver powder and DGEBA epoxy resin

Fig. 6. Silver flakes and powder with DGEBA epoxy resin

PU based isotropic conductive adhesives

The PU systems with silver flakes as the filler material showed that the constant G" at $\phi = 0.2$ and 0.4, while the G' decreased after 0.01 Pa, as shown in Fig. 7. The LVE region of the PU at $\phi = 0.2$ and 0.4 was approximately 0.01 Pa meanwhile $\phi = 0.6$ and 0.8 was approximately 5 Pa and 10 Pa, respectively. Beyond the LVR region, a gradual structural breakdown was observed for sample at $\phi = 0.6$ and 0.8 as opposed to DGEBA/silver flakes system. But the overall measured solid (G') and liquid (G") characteristic of PU based ICAs were lower compared to DGEBA based ICAs, which could prove to be attractive for the assembly of flexible electronic devices.

At lower volume fractions $\phi = 0.2$ and 0.4, the G' did not change significantly with increasing shear stress, as shown in Fig. 8. The observed trend was similar to the DGEBA/silver powder system. When the volume fraction was increased to $\phi = 0.6$ and 0.8, the samples showed a LVE range of up to 9 Pa and 20 Pa, respectively. The linear region measured for PU/silver powder was considerably higher than DGEBA/silver flakes systems. Despite the difference in LVE region, both these systems (PU/silver powder and DGEBA/silver flakes) showed a rapid structural breakdown. When the volume fraction ϕ exceeds 0.50 under equilibrium condition with no imposed flow, the silver powder system which is a monodispersed hard sphere suspension begins to order into a macrocrystalline structure of face centered cubic (fcc) or hexagonal close packing (hcp). With increasing applied stress, the drop in G' and G"

Fig. 4. Silver flakes with DGEBA epoxy resin

arises forced flow of three dimensionally ordered structures of fcc or hcp. At volume fraction of $\phi = 0.8$, an increase in G' and G" was observed after 200 Pa and similar result was observed for DGEBA/silver powder formulation. At high volume fraction above 50 % by volume for hard sphere suspensions, the increase in G' and G" could be attributed to development of lubrication stress as a result of close network formed between particles. This causes a strong hydrodynamic force; considerable amount of solvent is trapped interior to the particle cluster. The trapping of the solvent apparently decreases the mobile solvent volume fraction, or in effect, increase the particle volume fraction [10].

A bimodal distribution system with silver flakes and silver powder was formulated with PU. In this system, the G' is greater than G" for all volume fractions and the measured LVE region up to 0.1 Pa for $\phi = 0.2, 0.4, 0.6$ and 0.01 Pa for $\phi = 0.8$, as shown in Fig. 9. This system showed the lowest LVE region when compared to all the other systems. This could be due to the orientation of crystal in the direction of closest packing of the spheres is aligned to flow velocity, while the planes containing the closest packing are parallel to the shearing surfaces. Beyond the linear region, the sample showed a gradual breakdown in the paste structure as opposed to silver powder system. Beyond the linear region, the hydrodynamic force prevents them from sustaining their ordered state by forming a three-dimensional network or clustering, which results in the structural breakdown.
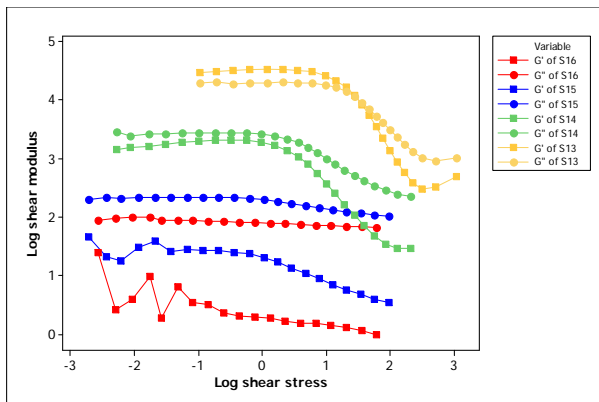

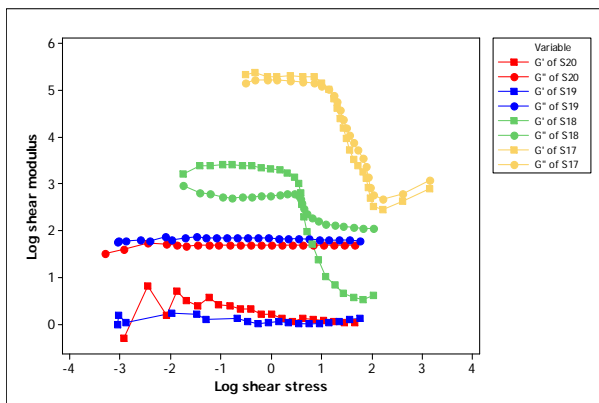Fig. 7. Silver flakes and Polyurethane (PU) resin
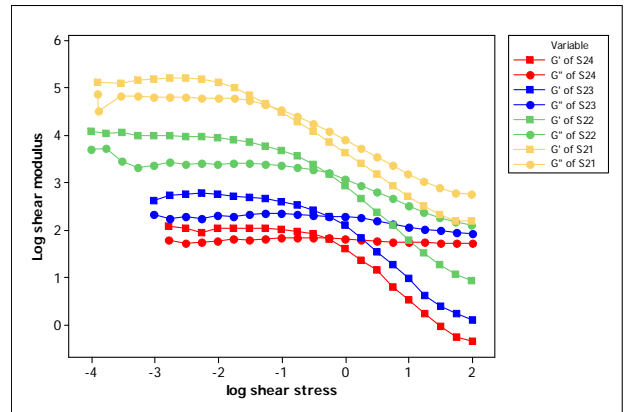

Fig. 8. Silver powder and Polyurethane (PU) resin

Fig. 9. Silver flakes and powder with Polyurethane (PU)

V. CONCLUSION

From the oscillatory test on PU and DGEBA it is clear that G' and G" could be used diagnostically to assess the state of the dispersion, since the linear visco-elastic region varies from one system to another. The study found that the volume fraction of the filler materials is shown to affect the G' and G" values. In addition, the particle size of the fillers is found to also influence the flow behaviour of the systems. The study showed that the processability of the systems is related to the solid (G') and liquid (G") characteristic of the material beyond the linear visco-elastic region. The extent of the structural breakdown could be used to determine the stability of the formulated systems. The silver powder based PU and DGEBA experience a rapid structural breakdown and increased in G' and G" values at higher shear stress. For the PU system, the mixture of silver powder and flakes produced a much stable system with a gradual structural breakdown as opposed to DGEBA systems. In addition, the solid (G') and liquid (G') characteristic of PU were lower compared to DGEBA could be a drop in replacement for DGEBA based isotropic conductive adhesives.

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