IMPROVEMENT OF PROPERTIES OF SILVER FILLED EPOXY COMPOSITES VIA PROCESSING METHOD

G. Suriati, M. Mariatti*, and A. Azizan

[1]*School of Materials and Mineral Resources Engineering, Engineering Campus, University Sains Malaysia, 14300 Nibong Tebal, Seberang Prai Selatan, Penang, Malaysia*

*(*Corresponding author: mariatti@eng.usm.my;*
Tel. No.: 604 5995262; Fax No.: 604 5941011)

(Received 12 April 2012)

Abstract

Conductive composites consisting of an epoxy matrix and silver flakes were fabricated, and mechanical, thermal and electric properties were investigated as a function of particle concentration and processing techniques. Scanning electron microscope (SEM) was utilized in an attempt to study the effect of the processing method on the distribution of silver flakes in the matrix. As observed by SEM, the use of a homogenizer enhanced the distribution of silver flakes with reducing the particle agglomeration due to the presence of shear force during mixing. The application of shear mixing during the fabrication of conductive polymer composites increased the electric conductivity, flexural modulus, and storage modulus of the silver filled epoxy composite.

Introduction

The demand for advanced materials, such as composite materials with better properties, to meet new requirements or to replace existing materials in a variety of applications, is incessantly increasing [1]. Nowadays, conductive polymer composites have received great attention as an alternative to current lead-solder system. As revealed by numerous researchers [2-5], polymer materials can attain electric conductivity either by synthesis of a polymer of definite chemical structure [6] or by the introduction of electrically conductive filler, such as metal powders, carbon black and graphite [7]. In an electrically conductive adhesive (ECA) which consists of a polymer and a conductive filler, the polymer resin will provide mechanical interconnection, while the conductive filler, which is normally silver flake, provides electric conductivity [8, 9]. For a composite material that consist of two different phases, such as ECA, the distribution of the filler which affects the interface bonding or adhesion between the filler and the matrix has a great influence on the properties of the composite [1]. Furthermore, the distribution of the filler in the polymer matrix depends on particle type and size, specific surface area, volume content of particles, and conditions of mixing [1, 2, 4, 7]. As is known, particle powders tend to agglomerate and stick together due to adhesive forces. Relative to particle mass forces, the adhesive forces increase with decreasing particle size. In order to obtain well dispersed fillers in the matrix, the way of combining the polymer matrix and the filler powder is important in influencing the final composite properties. Various methods, such as ultrasonic, homogenizer, mechanical stirrer and manual mixing, have been used in preparing the conductive composite as reported in previous works [11, 12].

In the present work, a mechanical method using a homogenizer has been compared with manual mixing (by hand) in producing the silver flake filled epoxy composite. The manual mixing method has been used and reported in previous works [9, 13]. Meanwhile, the using of a homogenizer was reported to introduce high shear forces during dispersion. This will break up the filler agglomerates and distribute the individual filler more homogeneously in the polymer [1]. Therefore, the purpose of this work is to examine and compare the effect of two types of different processing techniques on the filler dispersion and composite properties. Electric conductivity and flexural and thermal properties obtained in this study were also related with the morphology of the composites.

1. Experimental

2.1 Materials

The epoxy resin named EPON™ Resin 8281, supplied by Hexion Specialty Chemicals, Inc. was used as a matrix in this research. It is also chemically termed as Bisphenol-A-(epichlorohydrin). The curing agent used in the study is Polyetheramine D230 (PEA D230), supplied by BASF Corporation with a density of 0.946 g/ml at 298 K. Thirty two parts by weight of PEA D230 was added into 100 parts of EPON^{TM} Resin 8281 for curing process. Silver flakes with an average size of 4-8 μm and a density of 10.49 g/cm^3 were used as conductive filler. Filler loadings were varied from 0 vol % to 8 vol %.

2.2 Processing methods

In this study, two different processing techniques were employed to fabricate silver flake/epoxy composite: manual mixing and shear mixing. Manual mixing was carried out according to previous work [9] while for shear mixing, a homogenizer with 20000 rpm was introduced to improve the distribution of the filler in the epoxy matrix. Silver flakes were added into the resin and stirred for about 10 min followed by ultrasonication for 10 min in order to aid the dispersion of the filler in the epoxy. Then, the mixtures were evacuated at 35˚C for about 0.5 h to further remove the microbubbles and macrobubbles. After that, the mixtures were added with a curing agent and were stirred for other 10 min. Finally, the mixture was evacuated at room temperature before curing in an oven at 100°C for 1 h, which was followed by a post-cure at 125°C for 3 h.

2.3 Characterization

For conductivity test, we used an instrument named LCR Meter. The value of volume resistivity is defined as the electric resistance of a cube of material and determined according to (1) and (2):

$$V = IR_v \tag{1}$$

$$\rho_v = \frac{R_v A}{t} \tag{2}$$

where ρ_v is the volume resistivity, R_v is the volume resistance, A is the area of conductor, and t is the thickness of the sample pieces. Three-point bending tests were performed based on the standard test method, ASTM D 790-98. Rectangular cross section specimens with a length of 50

mm and a width of 12 mm were used in the testing. The testing was carried out with an Instron 3366 at room temperature with a crosshead speed of 5 mm/min while the sample's ratio of span length to thickness was maintained at 16 : 1. The fracture surface of the flexural test samples were observed using a Zeiss Supra 35VP Field Emission Scanning Electron Microscope (FESEM). Dynamic Mechanical Analysis was carried out by using a PelkinElmer DMA 8000 in a dual-cantilever mode at a temperature of 30-180°C. The thermal stability and the weight loss profile of silver/epoxy composites were examined using a PerkinElmer TGA 7. All TGA measurements were performed in a nitrogen atmosphere by heating the samples from 30-600°C at a heating rate of 10°C/min. The coefficient of thermal expansion of the composites was measured using a LINSEIS Dilatometer L75/1550. The specimens (20 mm x 4 mm x 1.8 mm) were tested at a temperature that changed from 30°C to 230°C at a heating rate of 3°C/min under an ambient atmosphere.

3. Results and discussion

3.1 Electric conductivity

As the properties of the polymer composite were affected by the dispersion of the filler in the polymer matrix, the use of different mixing techniques was expected to improve the distribution of the filler and hence enhance the electric conductivity of the polymer composite. A better dispersion of filler could result to better surface contacts which increase the current carrier from one particle to another [7]. The theory of percolation threshold indicated that the behavior of a material could change from insulator to conductor at a certain filler loading [3-5]. Figure 1 shows that the electric conductivity of silver flake filled epoxy composites prepared by manual and homogenizer mixing increased with increasing content of silver flakes. Both samples prepared by manual and homogenizer mixing demonstrate a percolation threshold at 6 vol %. The increase in electric conductivity with increasing content of silver flakes could be explained by the following. As the concentration of conducting particles increases, small particle agglomerates are first formed in the systems which then form conducting clusters [4]. As particles contact between these conducting clusters increase, the efficiency of current carrier is improved and furthermore increases the conductivity composites. It also can be seen in Fig. 1 that the conductivity of the samples prepared by shear mixing showed a higher conductivity compared to that of manual mixing. It has been reported that the interfacial resistance between fillers influences the electric conductivity of the composite [14]. Interfacial resistance is the resistance forming at a surface boundary between adjacent regions; in this case, between one particle and another. Our previous work [15] showed that a silver nanoparticle tends to form an aggregate and affects the distribution of the filler throughout the matrix as compared to a micron-sized filler. The poor distribution and agglomeration of silver flakes prepared by manual mixing subsequently increases the surface resistance and reduces the conductivity of the composites.

From the result of electric conductivity, the percolation threshold for both samples prepared by manual and shear mixing were achieved at 6 vol % loading of silver flakes. Below that point, the composite samples remain as insulator. The morphology of the samples observed by SEM (Fig. 2) shows that, at 4 vol % of silver flakes, the matrix content was dominant compared to the filler content. Hence, the metal-to-metal contacts are not sufficient to conduct the current throughout the sample. At a 6 vol % concentration, the conducting bridges, which are referred as to percolation threshold, are created across the single crystal. These bridges may be composed of single particles or of their aggregates. At this moment, the nonconducting system is transformed

into a conducting state. However, above the percolation threshold, which is 6 vol % of filler loading, the conductivity of the samples are remains unchanged, and this result is supported by previous works [5, 9, 16, 17].

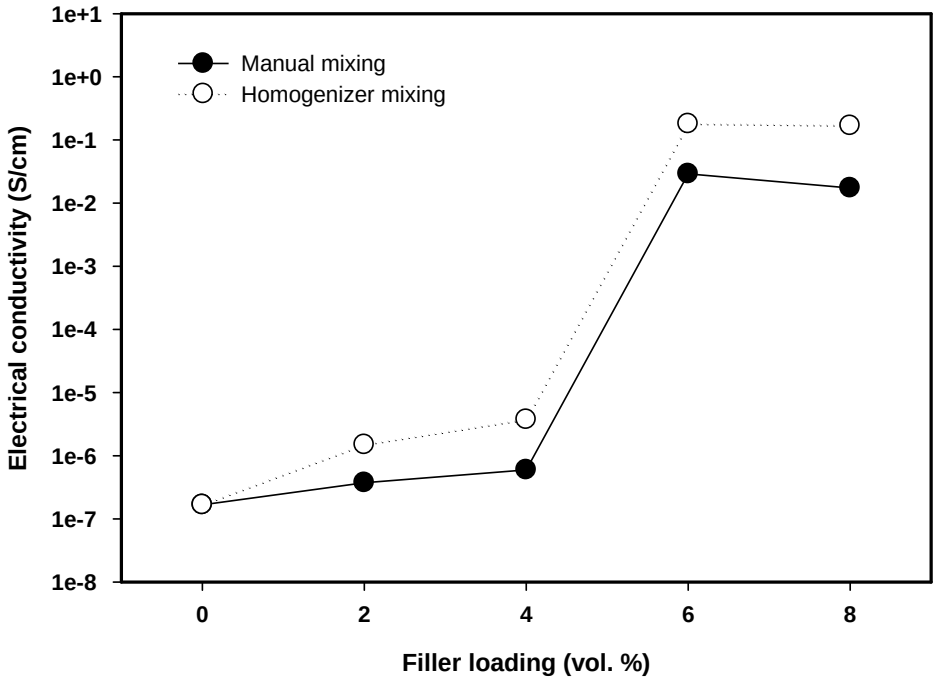
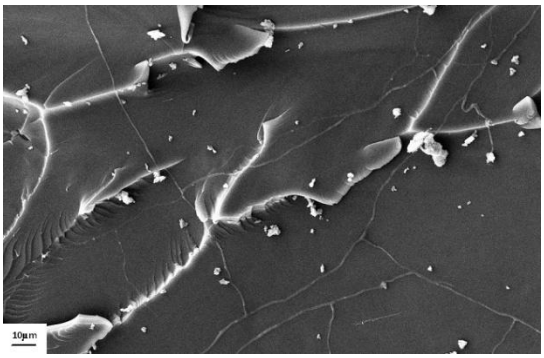
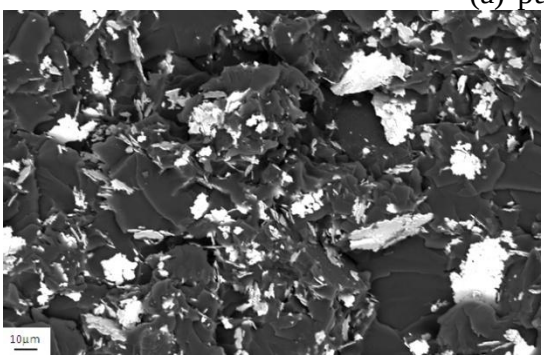


Fig. 1. Electric conductivity of the silver filled epoxy composite prepared by manual and homogenizer mixing.

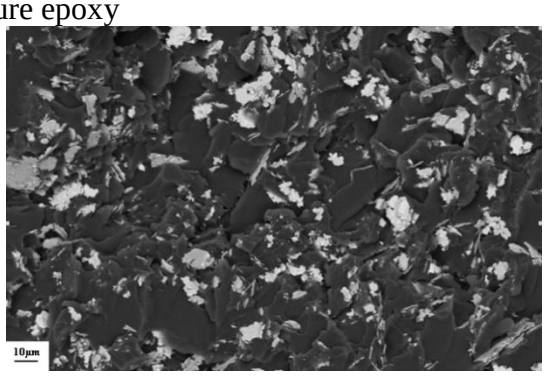
The morphology of the samples depicted in Figs. 2b–2g show that the use of a homogenizer can break up the agglomeration of Ag fillers and subsequently reduced the size of Ag flake particles. At filler loadings of 4, 6, and 8 vol %, it can be seen that the use of a homogenizer gave a better dispersion of the filler (Figs. 2c, 2e, and 2g) compared to the samples prepared by manual mixing (Figs. 2b, 2d, and 2f), respectively. This observation might be due to the introduction of external shear forces generated by the homogenizer which could separate and break up the agglomeration of silver flakes to individual particles followed by better dispersion in epoxy resin compared to manual mixing. The samples prepared by manual mixing, especially at a high filler loading (Fig. 2d) also showed a higher agglomeration compared to the sample mixed with a homogenizer (Fig. 2e), which gave better distribution throughout the epoxy matrix.



(a) pure epoxy

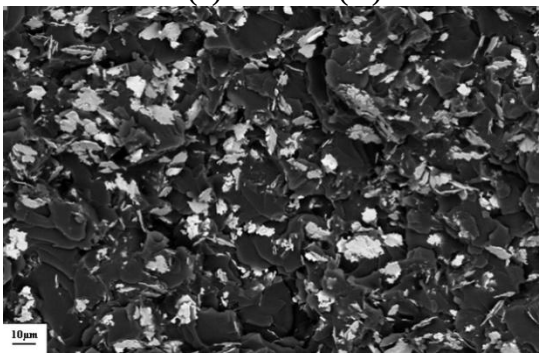


(b) 4 vol % (M)

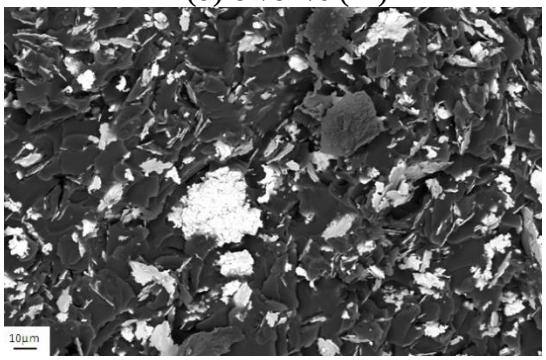


(c) 4 vol % (H)

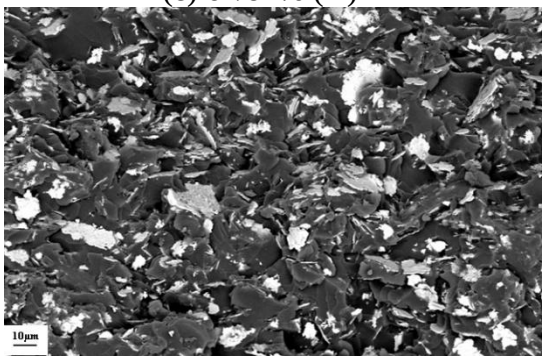
(d) 6 vol % (M)



(e) 6 vol % (H)



(f) 8 vol % (M)



(g) 8 vol % (H)

Fig. 2. Fracture surface of pure epoxy and silver composites at different filler loading. (M) and (H) denote manual mixing and homogenizer mixing, respectively.

3.2 Flexural test

Figure 3 depicts flexural strength and flexural modulus for the silver filled epoxy composites prepared by manual and homogenizer mixing. It is evident from the figure that flexural strength for the composite mixed by a homogenizer at a low filler loading (e.g., 4 vol % and below) does not show any significant improvement and is slightly lower than that of the composite mixed by manual mixing. However, the deterioration in flexural strength at higher filler loading (6 and 8 vol %) for both processing method, which is even lower than unfilled epoxy, could be due to a number of reasons, such as weak interfacial bonding at the silver flakes and matrix interfaces and also a high aggregation of silver flakes with increasing amount of the filler. As the dispersion of the filler throughout the matrix affects the properties of the composite, it can be seen that composite mixed by a homogenizer shows an improvement at a higher filler loading (6 and 8 vol %) compared to those prepared by manual mixing at the same filler loading. From here, it can be seen that high shear forces introduced by the homogenizer were able to break up the particle agglomeration especially at high filler loading where the content of the filler is relatively high. The size distributions of Ag filler in the epoxy matrix (Fig. 4) for samples with 8 vol % of filler prepared by manual and homogenizer mixing were compared. The result clearly showed that silver flakes in the epoxy matrix prepared by manual mixing has a larger distribution which might be caused by agglomerations of the filler compared to the samples which prepared by homogenizer mixing at the same filler loading. The presence of these agglomerations could act as a stress concentrator which led to a decrease in the properties of the composites.

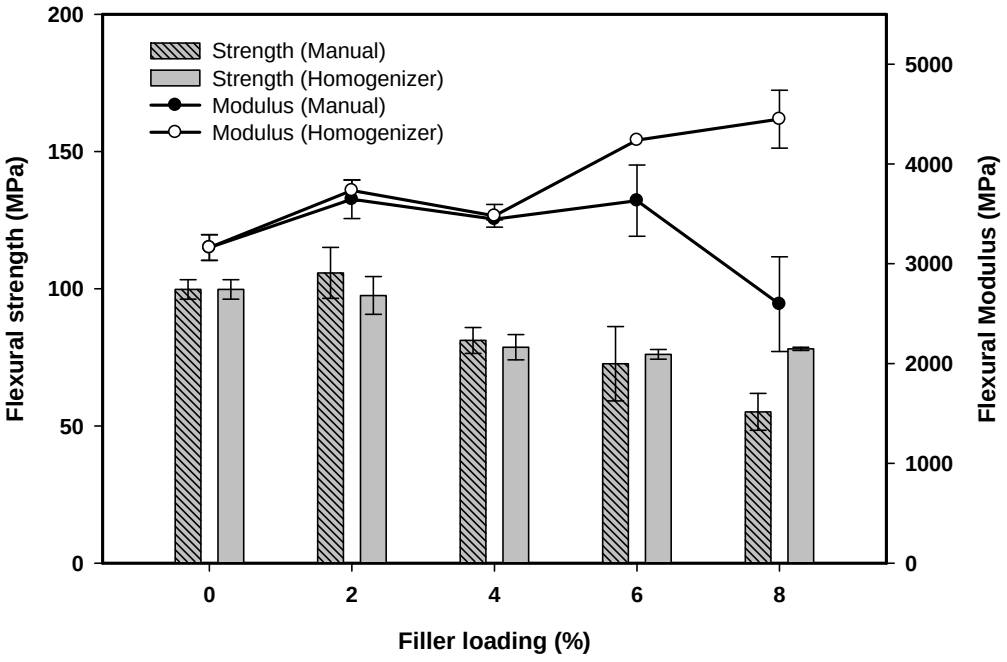


Fig. 3. Flexural strength and modulus at different filler loadings of silver flake filled epoxy composites prepared by different processing methods.

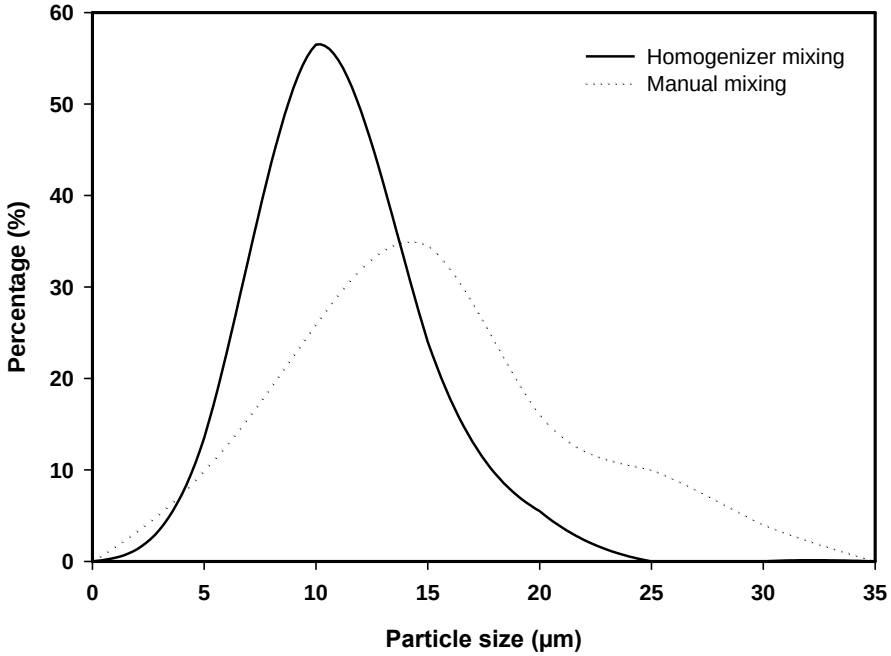


Fig. 4. Size distribution of silver flakes in epoxy matrix (8 vol %) calculated from the SEM image.

According to the rubber elasticity theory, there are four factors affecting the polymer composites elasticity [18]. The modulus of polymer composites could be controlled by the degree of cure, the presence of a solvent, strain induced crystallization, and the effect of fillers. Theoretically, the modulus of a composite material increases with increasing filler loading. The addition of rigid particles to the polymer matrix can easily improve the modulus since the rigidity of an inorganic filler is generally much higher than that of an organic polymer. Hwang [18] reported that the modulus of polymer composite materials increased with an increase in the filler content and a decrease in the filler size. However, despite this factor, it was reported that the size and distribution of filler particles also play an important role. From the result in Fig., we can see that the sample at 8 vol % prepared by manual mixing undergoes a significant decrement of flexural modulus at a higher filler content which is not quite pronounced for the sample prepared by homogenizer mixing. This observation might be due to the filler agglomeration, because at this loading, a high amount of the filler also could increase the viscosity and hence reduce the process ability. The presence of agglomeration subsequently increased the size of filler lumps which then act as a stress concentrator when it is subjected to load. In addition, although most of the composites (except the sample of 8 vol % prepared by manual mixing) exhibit a higher modulus than pure epoxy, they however show final failure at a much lower strain than the pure epoxy.

3.3 Dynamic Mechanical Analysis (DMA)

Figures 5 and 6 depict the storage modulus (*E'*) – and tan delta – temperature profile for unfilled epoxy and silver flake filled epoxy composites prepared by manual and homogenizer mixing, respectively. The curves show a general shape where the storage modulus is much higher

below T_g of the polymer but falls steeply above T_g. In this study, composite samples have a higher storage modulus than the unfilled sample, which proved that the addition of silver particles could reinforce the epoxy matrix. Figure 5 shows that both composites prepared by manual and homogenizer mixing at high filler loading (8 vol %) have a higher value of storage modulus than that at a low filler loading (4 vol %). This observation can be caused by the following. It was believed that an increase in silver filler loading increases the stiffness of the resulted composites and thus increases the storage modulus. Moreover, an increase in storage modulus at a higher filler loading could also be due to the reduction of matrix mobility in the vicinity of the Ag filler as a result of the polymer adsorption onto the filler surfaces. According to Teh et al. [19] and Heimann et al. [20], an increase in storage modulus could also be due to a higher level of crosslink density. It is evident from Fig. 5 that the samples prepared by homogenizer mixing have a higher storage modulus than the samples prepared by manual mixing. However, at a low filler content (4 vol %), the differences in storage modulus between these two mixing techniques are not so apparent compared to the samples prepared at a higher filler content (8 vol %). This observation can be related to the degree of filler agglomeration and filler dispersion in epoxy matrix. It can be suggested that, at a low filler loading, the silver filler could be dispersed well in the epoxy matrix regardless of the mixing technique used. Moreover, at a low filler loading (4 vol %), the agglomeration of the filler is not quite pronounced compared to the composite at a higher filler loading (8 vol %). As the filler content increased, it was believed that the filler-filler interaction is higher than the filler-matrix interaction, which furthermore resulted to the formation of a filler agglomerate in the epoxy matrix. A higher filler-filler interaction furthermore could reduce the crosslink density of the composite and thus result in a decrease in the storage modulus. Therefore, it can be seen that the technique to disperse the filler is very important in order to break up agglomeration and improve the dispersion of the filler.

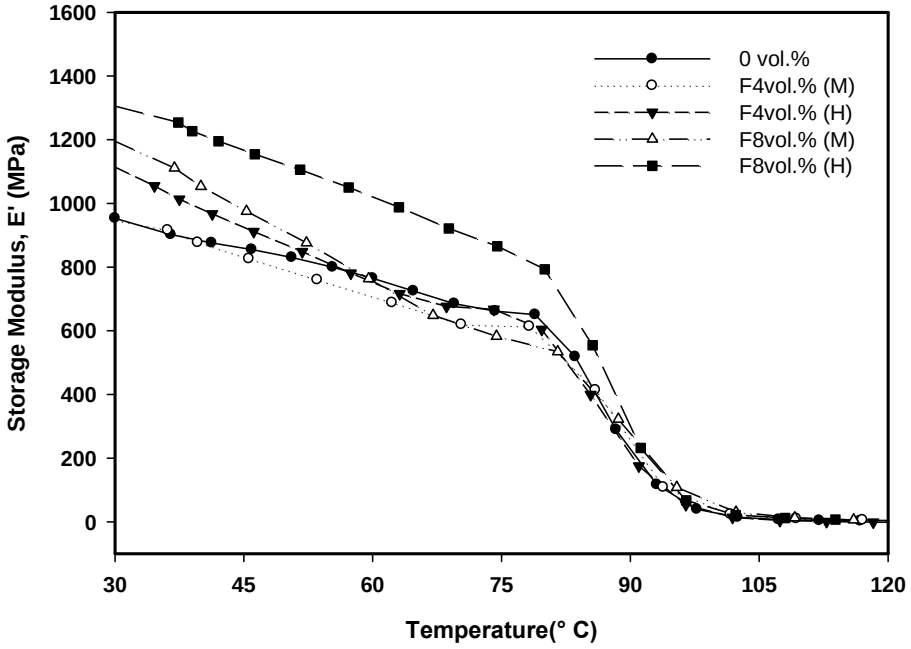


Fig. 5. Storage modulus of the silver flake filled epoxy composite prepared by manual (M) and homogenizer (H) mixings.

Figure 6 shows that tan delta peaks for composite samples are shifted to a higher temperature, which indicates a higher value of T_g compared to the unfilled samples. In general, an increase in T_g is attributed to a good adhesion between the polymer and the reinforced particles; hence, the particles can restrict the segmental motion of cross-links under loading [21]. However, in this study, the T_g value did not show any trend except an increase in the T_g value for the composite sample compared to the unfilled one. A reduction in the T_g value, especially for the samples prepared by manual mixing, are most probably due to the agglomeration of the filler, which leads to imperfect interfacial adhesion. The agglomerated lumps of filler particles would eventually affect the van der Waals interaction between the polymer chains and reduce the crosslinking of the matrix. In addition, a weak filler-matrix interaction could subsequently increase the mobility of the polymer chain when subjected to load and resulted in a decrease in the T_g value of the composites. This observation is supported by Yasmin et al. [13]: the T_g value is also affected by the degree of particle dispersion that includes size, homogeneity, orientation, and spacing between particles.

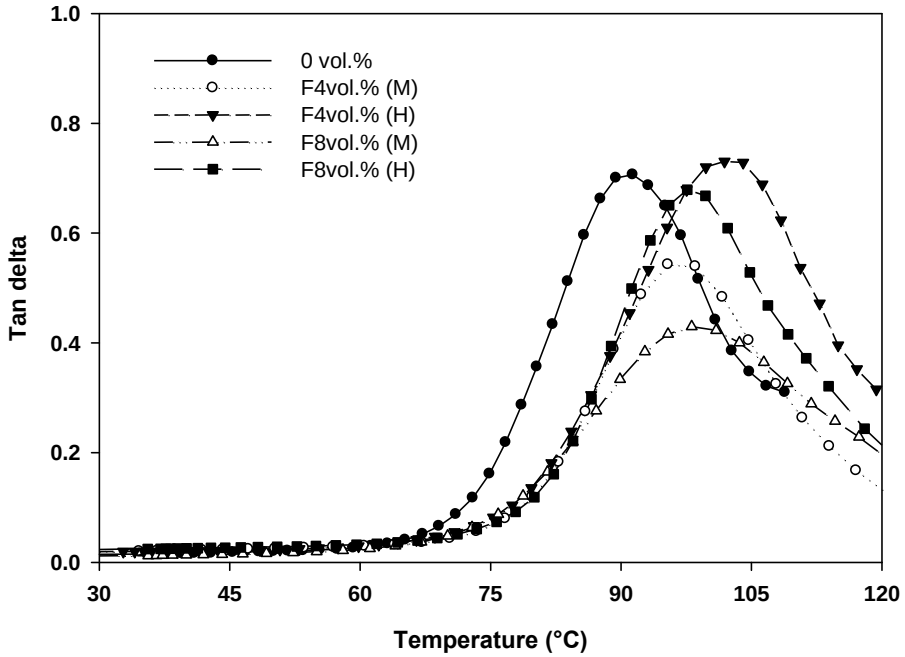


Fig. 6. Tan delta of silver flake filled epoxy composite prepared by manual (M) and homogenizer (H) mixings.

3.4 Coefficient of Thermal Expansion (CTE) Analysis

The differences in CTE between the chip and substrate makes flip chip assemblies vulnerable to thermally induced strains and often result in joint failure. One of effective solutions for this problem is to use a low CTE of the ECA material that mechanically couples the severely mismatched CTE of the chip and the substrate and provides a significant enhancement in assembly reliability [18]. The results of the dilatometer analysis of silver flake filled epoxy composites listed in Table 1 showed that the value of CTE before the glass transition temperature T_g is lower than the value of CTE after T_g. This typical trend is due to an insufficient energy supplied to cause more polymer chains to rotate or mobilize and thus allowing low dimension changes to occur [11]. The reduction in the CTE of the composite sample compared to the

unfilled samples was mainly related to a reduction in the molecular mobility of the macromolecular chains around the silver filler.

Table 1. CTE of the silver flake filled epoxy composite prepared by manual mixing. Values in brackets represent homogenizer mixing

Filler loading (vol %)	CTE before T_g, α_1 (ppm/K)	CTE after T_g, α_2 (ppm/K)
0	84.3	254
4	53.79 (52.45)	177.00 (176.95)
8	45.89 (47.27)	153.57 (167.25)

It is evident from Table 1 that CTE before and after T_g of the sample prepared by manual mixing at 4 vol % has a comparable value with the sample prepared by homogenizer mixing. However, at 8 vol %, the sample prepared by manual mixing shows a much lower value, especially CTE after T_g, than that of the sample prepared by homogenizer mixing. The result obtained could be related to the degree of silver flake dispersion throughout the epoxy matrix. As the dispersion state of the filler in the epoxy matrix influences the thermal properties of the composite behavior, it is necessary to point out that inhomogeneous distribution of the filler particles with considerable agglomerations could be noticed, especially for the sample prepared by manual mixing at a high filler content. For this sample, it can be suggested that the presence of agglomerations of silver flakes obstructs the expansion of the polymer chain, which in turn is lower the CTE value. On the other hand, a better dispersion with a low agglomeration of the filler in the sample prepared by homogenizer mixing could distribute the heat more efficiently compared to the sample that has a higher degree of filler agglomeration.

3.5 Thermogravimetry Analysis (TGA)

Figure 7 illustrated the TGA curves of silver flakes filled epoxy composites. It is observed that the systems seem to be stable up to 300°C, which is suitable to be used for electronic packaging where the application temperature is around 150-200°C. The percentage of weight loss of the samples increased as the temperature increased. The close-up of TGA curves at a temperature of 30°C to 350°C showed that, at a temperature of 320°C, all composite samples experienced ~2-3% weight loss, which can be referred to the volatile component, such as moisture, solvent evaporation, etc. Result shows that, at a low filler content (4 vol %), the sample prepared by homogenizer mixing has a lower value of residue than the sample prepared by manual mixing. However, an anomalous result could be observed for the samples with a higher filler content, which is 8 vol %. The result shows that the sample prepared by manual mixing had a higher residue than the sample prepared by homogenizer mixing. This might be related to the uneven distribution of the filler and the presence of agglomeration or lumps of silver flakes in the composites that furthermore increase the residue content of the samples. Moreover, under close observation (Fig. 7), the samples prepared by homogenizer mixing show a higher thermal stability than the samples prepared by manual mixing at any given filler content. This suggests that the sample prepared by homogenizer mixing provides a better surface interaction between the filler and the matrix and minimum particles to particle interaction. The reason for lowering the thermal stability of the samples prepared by manual mixing can be the perturbation of silver

lumps to the structure of the polymer. The presence of any perturbation could weaken the van der Waals interaction between the polymer chains which reflects the stability of the polymer [10].

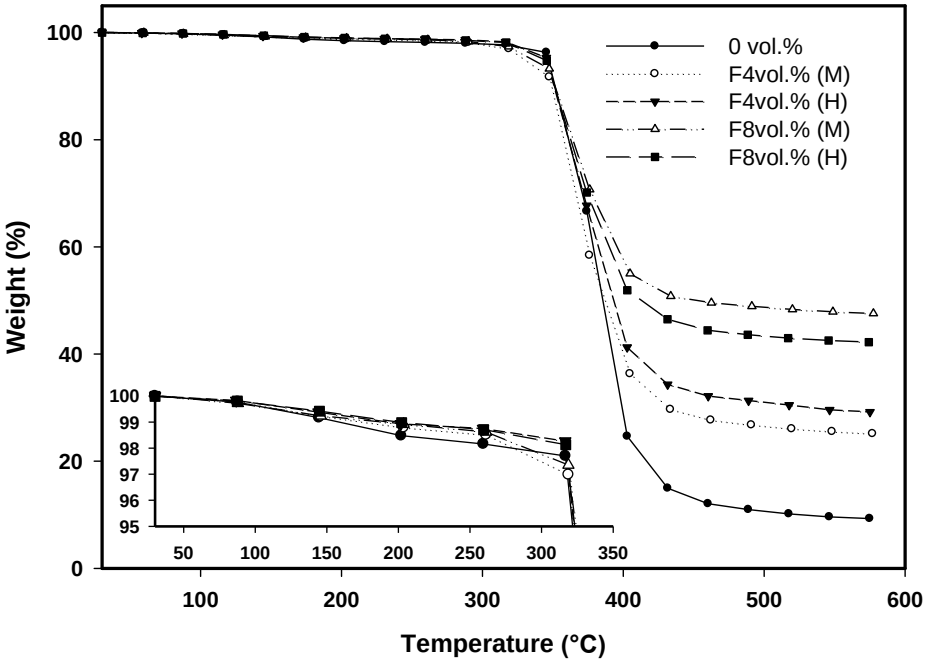


Fig. 7. TGA curve of the silver flake filled epoxy composite prepared by manual (M) and homogenizer (H) mixings.

4. Conclusions

The results of this study indicate that silver filled epoxy composites prepared by the aid of a homogenizer has a higher conductivity compared to the samples prepared by manual mixing. The result was achieved due to a better distribution of the filler throughout the epoxy matrix, which allows better contact and furthermore increases the current carrier in the system. It is also evident that the external shear force generated by the homogenizer subsequently separates and breaks up the silver flake agglomeration and improves the flexural properties of the composite samples. In addition, the thermal properties of the composite prepared by homogenizer mixing show a slightly higher thermal stability, a lower CTE, and a higher T_g compared to the composite prepared by manual mixing.

Acknowledgements

The authors gratefully acknowledge the grant support from the Ministry of Higher Education, Malaysia through FRGS grant and National Science Foundation (NSF). We thank the staff of the School of Materials and Mineral Resources, USM for their help during the experimental measurements and useful discussions.

References

[1] F. Haupert and B. Wetzel, Springer, 45-60, (2005).
[2] D. L. Markley, Q. K. Tong, D. J. Magliocca, and T. D. Hahn in Int. Symp. on Advanced Packaging Materials, (1999).
[3] V. I. Roldughin and V.V. Vysotskii, Prog Org Coat 39, 81-100, (2000).
[4] S. Kumar, T, Rath, R. N. Mahaling, C. S. Reddy, C. K. Das, K. N, Pandey, R. B. Srivastava, and S. B. Yadaw, Mat Sci Eng B 141, 61-70, (2007).
[5] H. P. Wu, X. J. Wu, M. Y. Ge, G. Q. Zhang, Y. W. Wang, and J. Jiang, Compos. Sci. Technol. 67, 1182-1186, (2007).
[6] M. Bouguettaya, N. Vedie, and C. Chevrot, Synthetic Met 102, 1428-1431, (1999).
[7] V. E. Gul, The Netherlands, 1-26, (1996).
[8] Y. Li and C. P. Wong, Mat. Sci. Eng. R 51, 1-35, (2006).
[9] D. I. Tee, M. Mariatti, A. Azizan, C. H. See, and K. F. Chong, Compos. Sci. Technol. 67, 2584-2591, (2007).
[10] N. Chisholm, H. Mahfuz, V. K. Rangari, A. Ashfaq, and S. Jeelani, Compos. Struct. 67, 115-124, (2005).
[11] K. L. Chan, M. Mariatti, Z. Lockman, and L. C. Sim, J. Mater. Sci. Mater. Electron. 21, 772-778, (2010).
[12] S. Khairul Anuar, M. Mariatti, A. Azizan, N. Chee Mang, and W. T. Tham, J. Mater. Sci. Mater. Electron., DOI 10.1007/s10854-010-0207-7, (2010).
[13] A. Yasmin, J. J. Luo, and I. M. Daniel, Compos. Sci. Technol. 66, 1179-1186, (2006).
[14] L. Fan, B. Su, J. Qu, and C. P. Wong, Int. Symp on Advanced Packaging Materials, 193-199, (2004).
[15] G. Suriati, M. Mariatti, and A. Azizan, J. Mater. Sci. Mater. Electron. 22, 56-63, (2011).
[16] Y. P. Mamunya, V. V. Davydenko, P. Pissis, and E. V. Lebedev, Eur. Polym. J. 38, 1887-1897, (2002).
[17] H. Jiang, K. Moon, Y. Li, and C. P. Wong, Electronic Components and Technology Conference, (2006).
[18] J. S. Hwang, Microelectron. Reliab. 48, 645-651, (2008).
[19] P. L. Teh, M. Jaafar, H. M. Akil, K. N. Seetharamu, A. N. R, Wagiman, and K. S. Beh, Polym. Adv. Technol. 19, 308-315, (2008).
[20] M. Heimann, M. Wirts-Ruetters, B. Boehme, and K.-J., Wolter, Electronic Components and Technology Conference, (2008).
[21] S. N. Goyanes, P. G. König, and J. D. Marconi, J. Appl. Polym. Sci. 88, 883-892, (2003).