

Properties of Epoxy/Silica Thin Film Composite for Electronic Application

Mariatti, M.^{1*}, Foo, Y.L.¹, Azizan, A.¹, and Sim, L.C.²

¹ School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia

² Intel Technology (M) Sdn. Bhd., Pulau Pinang, Malaysia

* School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia, mariatti@eng.usm.my

ABSTRACT

In line with the miniaturization trends of the product designs in electronic industry, conventional packaging technology has been replaced. A polymer resin needs to suit to certain polymer processing methods in order to achieve substantial performance in terms of mechanical, thermal, optical, electrical and so forth. An epoxy based composite thin film is successfully fabricated by using spin coating method. Comparing this with the conventional method, spin coating allows controllable-uniform thickness ranging from micron to nano-size. Parameters such as spin rate and viscosity need to be controlled in order to produce a uniform composite thin film. Silica fillers are incorporated into the epoxy resins in order to improve the thermal and mechanical properties as well as its dimensional stability. The two types of silica studied in this research are the micron and nano-sized silica. It is observed that the properties of thin film produced are governed by the size of the particulates. It is expected that lower loading of the nano-sized silica is required to achieve the same desirable properties relative to high loading of micron sized silica.

KEYWORDS: Thin film, spin coating, epoxy, and silica filler.

1. INTRODUCTION

Thin film is the size reduction of bulk materials in one dimension. According to ASTM D 882-02, a material is known as thin film when the thickness is less than 0.25mm. Thin films of polymers are getting acceptance for technological applications ranging from multicolor photographic printing to paints, adhesives, index-matched optical coatings, photoresists and low dielectric electronic packaging [1]. In comparison to bulk properties, much less is known about the properties of polymers when they are processed into thin films. Typically, the polymer-substrate and polymer-air interfacial energies or kinetic barriers play important roles in determining the morphology and dynamics in thin films.

In the polymer thin film fabrication, conventional methods such as dip coating, solution casting and hot press are widely used. Although these methods involved lower cost and simpler processing method, the lack of uniformity and uncontrollable thickness of the film become an issue for precision fabrication. In line with

the packaging development, spin coating method which is commonly used in the photoresist application in semiconductor industry had replaced the conventional method in thin film fabrication. In comparison with the conventional methods as shown in Table 1, spin coating method is more prominent in producing high uniformity film with specific thickness. The film with the range from micron to nanometers thickness can be easily produced with the control of parameters such as spin rate and viscosity.

Table 1. Comparison of thin film fabrication methods [2-5].

	Spin coating	Dip coating	Solution casting	Hot press
Fabrication control	complex (3 stages)	Complex (due to concentration control and dipping rate)	Simple	Simple
Thickness control	good control with spin rate (with spin coat calculation model)	poor, concentration control with few trial needed to get proper concentration	poor, thickness according to depth of dish and shrinkage	Good control
Thickness of product	nano to micron	nano to micron	micron	micron
Substrate / shape	any flat substrate	irregular shape, glass substrate is preferable	only flat substrate	only flat substrate
Uniformity of film	good	poor	poor	good
Production rate	Fast	Slow (few trial to obtain required thickness)	fast	slower than spin coating (resin need to be coagulated before hot press)
cost	expensive	less expensive	cheapest	expensive
Commercialize	easy due to controlled thickness and production rate	difficult due to variability in thickness uniformity	Difficult due to difficulty in thickness control	Difficult due to slow production rate

In order to achieve optimal performance in terms of mechanical, thermal, optical, electrical and so forth, a polymer resin needs to suit certain polymer processing methods. Being polymers that fit in that category, epoxy resins are usually the primary choice selected. Pure epoxy resins exhibit good adhesion to glass and metals, excellent chemical resistance and electrical insulating properties. However, there were researches that show the blending of inorganic fillers with epoxy resins will improve the thermal, mechanical, electrical properties as well as its dimensional stability [6-9].

Together with the advances in nano-science and nano-technology, there is an increasing interest in polymer nano-composites both in scientific research and engineering applications. For example, epoxy/silica nano-composites have been used as the electronics and optical packaging materials. Nanoparticles are of great interest due to their extremely small size and large surface to volume ratio, which lead to difference in their

properties compared to bulk of the same chemical composition [10]. Hence, the effect of micron and nano-sized silica filler on the tensile properties of thin film was investigated in this research.

2. EXPERIMENTAL

The spherical silica powder grade SS-0020 with mean particles size of $4.83\mu\text{m}$ from KOSEM and the fumed nanosilica grade S5130 with mean particles size of 7nm from Sigma Aldrich were treated in the oven under 110°C to remove moisture content. The dried silica powder were then mix with polyetheramine based curing agent, EC 301 from BASF by using Hielscher UP200S Ultrasonic Stirrer at amplitude 60 and cycle 0.5 for 10 minutes. The loading of the micron-sized silica was varied from 5wt% to 30wt% while the nano-sized silica was varied from 0.5wt% to 2wt%. EPON 8281 from Hexion was then added into the curing agent mixture and ultrasonicated for 5minutes to homogenize the mixture. Before the epoxy system was spin coated, vacuum oven was used to remove all the entrapped bubbles formed during the ultrasonic stirring. Any entrapped bubbles in the epoxy system will cause defect such as pin holes on the epoxy thin film. For the spin coating process, a transparency was used as a substrate for the film and the epoxy system was deposited on the stationary substrate. Constant spin-up rate was used for all the epoxy system with the spin rate at 1000rpm for 30 seconds and continue with second spin-up rate at 1500rpm for 60 seconds. The film was then left in rest for 3minutes on the stationary substrate before the curing under 80°C for 2 hours.

3.0 RESULTS AND DISCUSSION

Figure 1 shows the stress-strain curve for the epoxy/silica thin film composite with minimum and maximum loading using micron and nano-sized silica filler. It can be seen that all the thin film samples failed in the brittle mode with no plastic deformation except for the thin film with 30wt% micron-sized and 2wt% of nano-sized silica filler. For a material to be characterized as brittle, the value for tensile strength (*TS*) will be the same with the value for break strength [11]. For the thin film with 30wt% micron and 2wt% nano-sized silica filler, the break strength obtained is slightly different from the *TS* value.

As indicated in the stress-strain curve, the elongation at break (*EB*) obtained for the maximum loading of micron-sized silica filler in the epoxy film (30wt%) is almost the same with the *EB* of the neat epoxy film. No significant changes of the *EB* were seen even when the maximum loading of micron-sized silica filler was added into the epoxy thin film. On the other hand, loading of 2wt% nano-sized silica filler shows a significant increase in the *EB*. Brittleness of the film was effectively reduced with incorporation of nano-sized silica filler. This small toughening mechanism by nano-sized silica filler makes the film able to stretch further compared with the neat

epoxy and micron-sized silica filled epoxy thin film. This shows the agreement with the results obtained by Battistella et al. (2008) where they demonstrated the capability of the nano-sized silica filler to increase the toughness of the epoxy nanocomposites at low volume fraction.

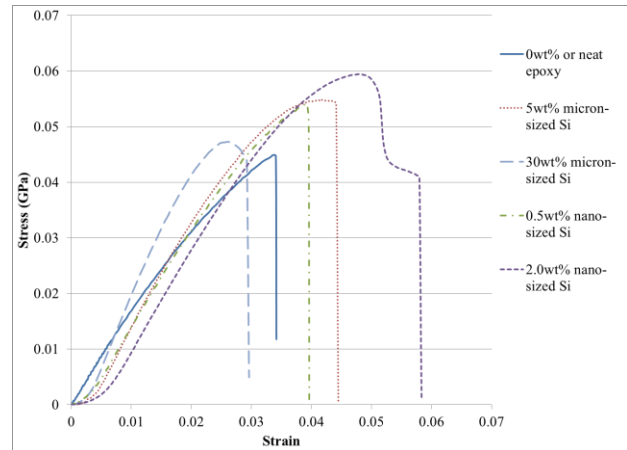


Figure 1. Stress-strain curve for epoxy thin film composite with minimum and maximum loading of micron and nano-sized silica.

The *TS* of the epoxy thin film composite for different loading of micron and nano-sized silica was shown in Figure 2. As expected, it was found that the *TS* for the epoxy/silica thin film composite increased with the increase of both micron and nano-sized silica loading. Besides, the *TS* for thin film obtained by 15wt% micron-sized silica are equivalent to the *TS* obtained by just 2wt% of nano-sized silica. The higher surface area to volume ratio of the nano-sized filler tends to have better reinforcing efficiency than larger sized filler even at a very low loading [13]. Hence, only small amounts of nano-sized fillers are needed in order to achieve the equivalent tensile properties using micron-sized fillers.

However, when the micron-sized silica loading is more than 15wt%, the *TS* value for the micron-sized epoxy/silica thin film seems to be fluctuated. The fluctuating of the *TS* value might be due to the significant variation of the film thickness produce under a constant spin rate as the viscosity is increased with the increase of micron-sized silica loading. The higher viscosity yield a thicker film produced under the same constant spin rate, as shown in Figure 3. Hence, there might be a “virtual” effect of the micron-sized silica filled epoxy film thickness on the value of the *TS*. Unlike particles with micron level dimension, nano-fillers are capable to increase the mechanical properties of the composite without significantly increasing the viscosity of the epoxy system [13-14].

The large dropped of *TS* value for thin film with 30wt% micron-sized silica is due to the high aggregates density caused by the poor dispersion of the silica filler. This can be supported by SEM image of tensile fracture surface for thin film in Figure 4. The absence of dispersing agent

in the epoxy composite caused the poor silica filler dispersion irrespectively to the size filler. However, the agglomeration effect tends to be more significant on the tensile properties when the loading is high. Therefore, during the present of tensile stress, the aggregates acted as foreign body and initiated the cracks in the composite.

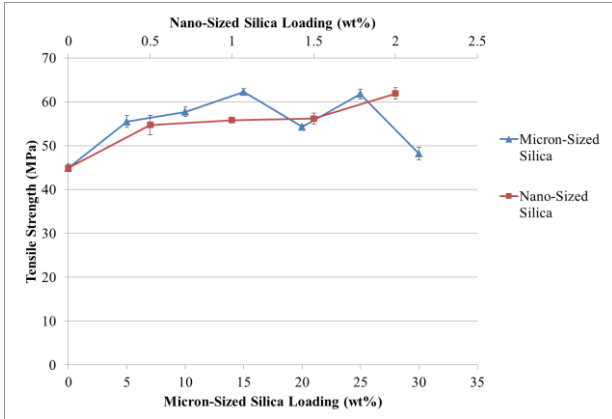


Figure 2. Tensile strength for epoxy thin film composite with different loading of micron and nano-sized silica.

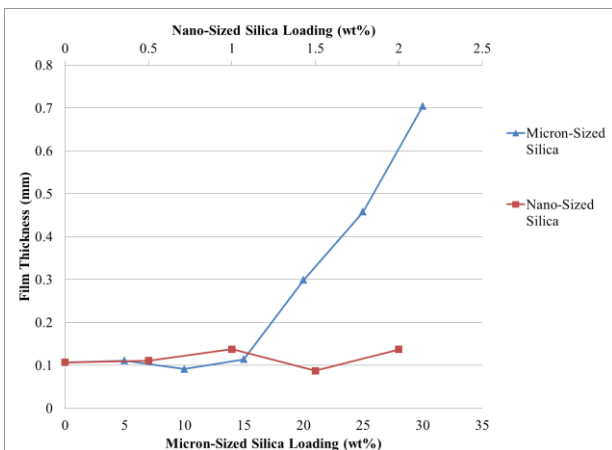
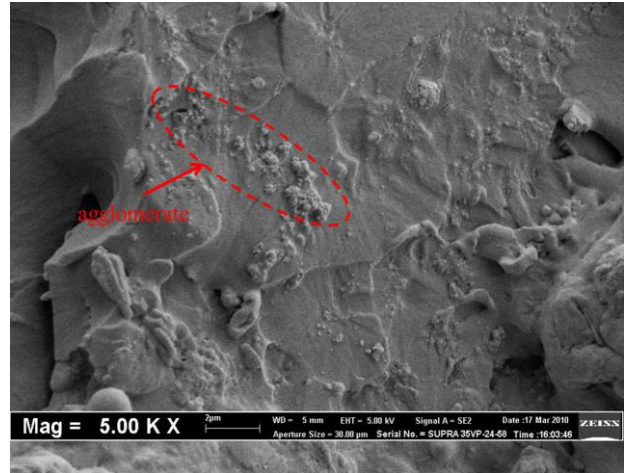


Figure 3. Thickness of the micron-sized silica/epoxy thin film with different silica loading.

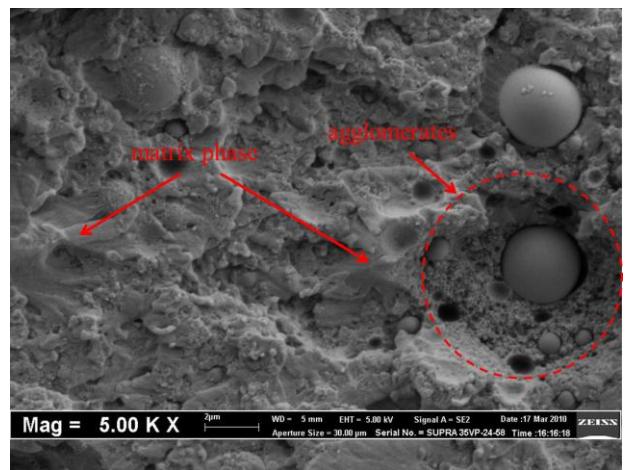
Besides, obvious phase separation was observed for both of the samples. Fillers were not fully encapsulated in the matrix during the tensile pull out. This indicates the poor miscibility of the silica filler and epoxy matrix which causes the drop of *TS* value for the thin film with maximum loading of micron-sized silica.

From the TGA thermogram shown in Figure 5, the TGA curve for micron and nano-sized silica/epoxy thin film have similar pattern with the neat epoxy thin film. This shows that the thermal weight loss of the epoxy/silica thin film came from the epoxy resin. Small amount of weight loss is observed at temperature around 100°C to 125°C indicates the moisture content in the epoxy/silica thin film composite. The moisture content in the 0wt% or neat epoxy film was higher compared with the silica/epoxy thin film. This is because in the epoxy matrices, the hydrophilic functional group, amine in the curing agent couple strongly with the water molecules by

forming hydrogen bonding with these hydrophilic groups [15]. However, with the incorporation of heat treated silica filler into the epoxy system, the amount of the hydroscopic epoxy matrix is reduced. Hence, less moisture content was observed in the silica/epoxy thin film composites.



(a)



(b)

Figure 4. SEM image of tensile fracture surface for epoxy thin film composite under 5000x magnification with (a) 10wt% micron-sized silica loading, (b) 30wt% micron-sized silica loading

The initial decomposition temperature (*IDT*) is characterized as temperature at which the sample achieves a 5% of weight loss. It was found that the T_{max} and *IDT* tend to shift to the higher temperature region with the increase of the silica loading. The slight increase in the thermal stability of the composite with the addition of fillers is due to the higher thermal stability of the silica particles [16]. It was also observed that film with 2wt% of nano-sized filler achieve the same thermal stability with the 30wt% micron-sized silica. This shows that the thermal stability can be enhanced by low weight fraction of nano-sized filler instead of high weight fraction of micron-sized filler. However, film with 1wt% nano-sized silica shows the lowest value of *IDT* and T_{max} .

This might be due to too low silica content in the system to protect the epoxy resin from heat [17].

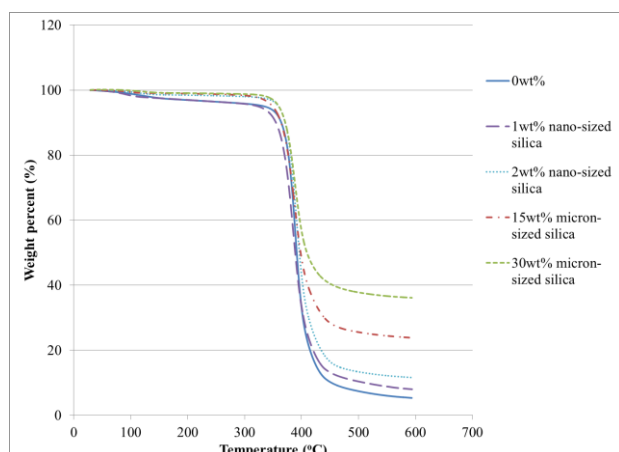


Figure 5. TGA thermogram for different loading of micron and nano-sized silica in epoxy thin film composites.

4.0 CONCLUSIONS

Silica/epoxy thin film composites were successfully fabricated by using spin coating method. With the higher loading of both micron and nano-sized filler content, tensile properties and thermal stability of the thin film were improved. Meanwhile for the effect of particles size, nano-sized silica filler shows a more stable and significant increase in the tensile compared to the micron-sized silica filler. The *TS* of the thin film obtained by 2wt% nano-sized silica filler is equivalent to the 15wt% micron-sized silica. Besides, the thermal stability of thin film with 2wt% nano-sized filler is also equivalent to the 30wt% of micron-sized filler. This shows the capabilities of the filler with nano level dimension to achieve good tensile properties and thermal stability of thin film composite at lower weight fraction in compared to the micron-sized silica filler.

Acknowledgement

The authors are very grateful to Intel Technology (M) Bhd. and University Sains Malaysia for awarding us with the research grants that made this study possible. We would like thank Intel Technology (M) Bhd. for the student fellowship granted to the second author.

References

[1] Ade, H., Winesett, D.A., Smith, A.P., Anders, S., Stammler, A., Heske, C., Slep, D., Rafailovich, M.H., Sokolov, J., & Stohr, J. Bulk and Surface Characterization of a Dewetting Thin film Polymer Bilayer, *Applied Physics Letters* 1998; 73:3775

[2] Seema, A., Dayas, K.R. & Varghese, J.M. PVDF-PZT-5H Composites Prepared by Hot Press and Tape Casting Techniques, *Journal of Applied Polymer Science* 2007; DOI 10.1002/app.26673.

[3] Nan, G. Pellicles and Films Making from Polymer

Solution, *Buletinul Universiti Petrol* 2006; 2:99

[4] O'Reilly, J. Epoxy/Single-Walled Carbon Nanotube Nanocomposites and Thin Films, *Biomedical Science* 2008

[5] Yimsiri, P. & Mackley, M.R. Spin and Dip Coating of Light-Emitting Polymer Solutions: Matching Experiment with Modelling, *Chemical Engineering Science* 2006; 61(11):3496

[6] Alapati, S. & Thomas, M.J. Electrical Treeing in Polymer Nanocomposites, *Fifteenth National Power Systems Conference (NPSC), IIT Bombay* 2008 December.

[7] Cheng, L.H., Zheng, L.Y., Li, G.R., Yao, Z. & Yin, Q.R. Manufacture of Epoxy-Silica Nanoparticle Composites and Characterization of Their Dielectric Behavior, *International Journal of Nanoparticles* 2008; 1(1):3

[8] Liu, Y.L., Wei, W.L., Hse, K.Y. & Ho, W.H. Thermal Stability of Epoxy-Silica Hybrid Materials by Thermogravimetric Analysis, *Thermochimica Acta* 2004; 412:139

[9] Teh, P.L., Mariatti, M., Wagiman, A.N.R. & Beh, K.S. Effect of Curing Agent on the Properties of Mineral Silica Filled Epoxy Composites, *Polymer Composite* 2008; 29(1):27

[10] Sun, Y., Zhang, Z. & Wong, C.P. Influence of interphase and moisture on the dielectric spectroscopy of epoxy/silica composites, *Polymer* 2005; 46(7):2297

[11] Askeland, D.R. & Fulay, P.P. *Essentials of Materials Science and Engineering*, 2nd Edition, Cengage Learning, Canada 2008

[12] Battistella, M., Cascione, M., Fiedler, B., Wichmann, M.H.G., Quaresimin, M. & Schulte, K. Fracture Behaviour of Fumed Silica/Epoxy Nanocomposites, *Composites: Part A* 2008; 39:1851

[13] Konsta-Gdoutos, M.S., Daniel, I.M., Metaxa, Z. & Cho, J. Thermo-Mechanical Characterization of Epoxy/Silica Nanocomposites, *Proceedings of the 13th International conference on Experimental Mechanics*, July 1-6, Alexandroupolis, Greece 2007

[14] Johnsen, B.B., Kinloch, A.J., Mohammed, R.D., Taylor, A.C. & Sprenger, S. Toughening Mechanisms of Nanoparticle-Modified Epoxy Polymers, *Polymer* 2007; 48:530

[15] Chow, W.S. Water Absorption of Epoxy/Glass Fiber/Organo-montmorillonite Nanocomposites 2007; 1(2):104

[16] Li, Y., Fu, S., Li, Y., Pan, Q., Xu, G., & Yue, C. Improvements In Transmittance, Mechanical Properties and thermal Stability of Silica-Polyimide Composite Films by A Novel Sol-Gel Route, *Composites Science and Technology* 2007; 67:2408

[17] He, L., Liu, P. & Ding, H. Microstructures and Thermal Properties of Polycaprolactone/Epoxy Resin/SiO₂ Hybrids, *Journal of Adhesion and Interface* 2006; 7(4):32