

Hardener's Effect on Glass Transition Temperature, Moisture Absorption, and Densities of Epoxy/Silica Micron and Nanocomposites

Abstract: In the field of electronics packaging, materials such as epoxy silica composites have been used greatly. This research paper tested the curing behaviors, glass transition temperatures, moisture absorption, and density of nano and micron sized silica epoxy composites using amine and anhydride hardeners. Results showed that composites with the amine hardener had generally higher glass transition temperatures, lower moisture absorption, and similar densities to that of the composites with the anhydride hardener. In contrast, the composites with the anhydride hardener showed lower T_g 's and higher moisture absorption..

1. Introduction

Due to their exceptional mechanical and electrical properties along with their economical and simple processing ability, epoxy composites have been used extensively over the past 30 years in the microelectronics industry as electronics packaging materials. Likewise, because of the concomitant advances in nanotechnology and the recent commercial availability of nanoparticles there is an increasing interest polymer nano-composites in research as well as in engineering functions. Because the properties of polymer composites can be altered with the dispersion state, geometric shape, surface properties, particle size, and particle size distribution, it is therefore

consistent that nanocomposites show different properties than their micrometer-sized filler counterparts.

Two of the major protecting functions of IC (integrated circuit) packaging are encapsulation and sealing. Used to protect IC devices from harmful environmental and mechanical effects, encapsulating and sealing utilize a process called epoxy polymerization. The fast, clean, and non-erratic production of epoxy polymerization makes it an excellent agent for encapsulation and sealing of microelectronics. To facilitate these polymer composites, an epoxy resin is blended with the micron or nano size filler particles. So as to convert the epoxy resin to hard, infusible thermoset networks, it is necessary to use hardener, which promotes the cross-linking or curing of epoxy resins. Anhydride and amine hardeners, two of the most common curing agents, were used in the formulation of the micron and nanocomposites of this research.

The anhydride-epoxy system of polymerization gives polyester linkage that can be subject to hydrolysis, the decomposition of a chemical compound by reaction with water. Due to the stoichiometric problem posed by the relatively high vapor pressure of the anhydrides at curing temperatures (~150-175C), encapsulants containing anhydride (underfill, cavity fill, and glob top) must go to a transitional gelling stage at a lower temperature (~125c) before curing at a higher final temperature. Despite the inconvenience, epoxy-anhydride systems are still used for liquid encapsulant operation.

Quite an unfavorable system, the amine-epoxy system is criticized because most efficient amines are in the solid or viscous liquid forms, often requiring a solvent to dissolve them in the formulation. Although, the use of solvents in the encapsulations can cause voids during cure, and may plasticize epoxy structure, thus waning its mechanical strength, teraryamide or amine-adducts are still employed for some underfill inceptions.

The primary motivation for this work is to analytically examine the thermal mechanical property changes of epoxy micron and nano composites with different hardeners in terms of polymer-particle interface properties.

2. Theory

The fundamental scientific concept upon which this work is based is the interaction between the nano sized and micron size silica filler and the epoxy polymer.

3. Approach/ Methodology

3.1 Materials and underfill preparation

Silica nano-particles (average diameter = 100nm; Nippon Chemical) and micrometer-sized silica (average diameter = 3 μ m; Nippon Chemical) were commercially available and used as-received. The epoxy used was diglycidyl ether of bisphenol A (EPON828, Resolution Performance Products). The two hardeners used were hexahydro-4-methylphthalic anhydride (HMPA; Lindau Chemicals) and an amine hardener. A polymer encapsulated imidazole derivative from Shikoku Chemicals was used as an underlying catalyst.

The blank epoxy formulation was prepared through the mixing of epoxy, hardener, and catalyst until a homogeneous mixture was achieved. The blank epoxy was used as the control sample. The micrometer-sized silica was mixed into the resin with a high-speed blender for 5 min. The nano-silica was mixed with a sonicator (Sonicator 3000, Misonix) at a power of 450 W. The filler loading was varied from 0% to 40%wt in increments of ten.

The epoxy-silica composite samples were then cured at a ramp of 5°C/min, to 180°C and left to cool to room temperature in curing oven. Once cooled the samples were then polished with the Buehler ECOMET 6 variable speed grinder-polisher and cut with Buehler ISOMET low speed saw.

3.2 Characterizations

3.2.1 Curing behaviors and T_g : The curing behavior and glass transition temperature of the epoxy composites were characterized by a modulated Differential Scanning Calorimeter (DSC, TA Instruments, Model 2920). A 10mg sample was sealed in hermetic aluminum pan. To obtain curing heat flow diagram of the composite a dynamic scanning experiment was conducted with a ramp of 5°C/min, to 300°C. Left in the DSC cell and cooled to room temperature the cured sample was then reheated to 200°C at 5°C/min to obtain another heat flow diagram. The initial temperature of the heat flow step of the second diagram is defined as the DSC glass transition temperature (DSC T_g)

3.2.2 Density and water absorption: Using the Archimedes approach to measure the density, the sample was weighed in air and then in ethanol. The average measurements of at least 4 specimens were reported for each sample. The cured samples were subjected to temperature/humidity aging at 85°C and 85% relative humidity to test their moisture absorption. The samples were taken out of the aging chamber and the increased weight due to moisture uptake was recorded everyday.

4. Results and Discussion

4.1 Glass-Transition Behavior of the Different Nanocomposites

The effects of the filler size and filler loading on the T_g of the polymer were studied with nano sized silica composites with two different types of hardeners, amine and anhydride. The curing behaviors of the nanocomposites were characterized by DSC dynamic heating experiments.

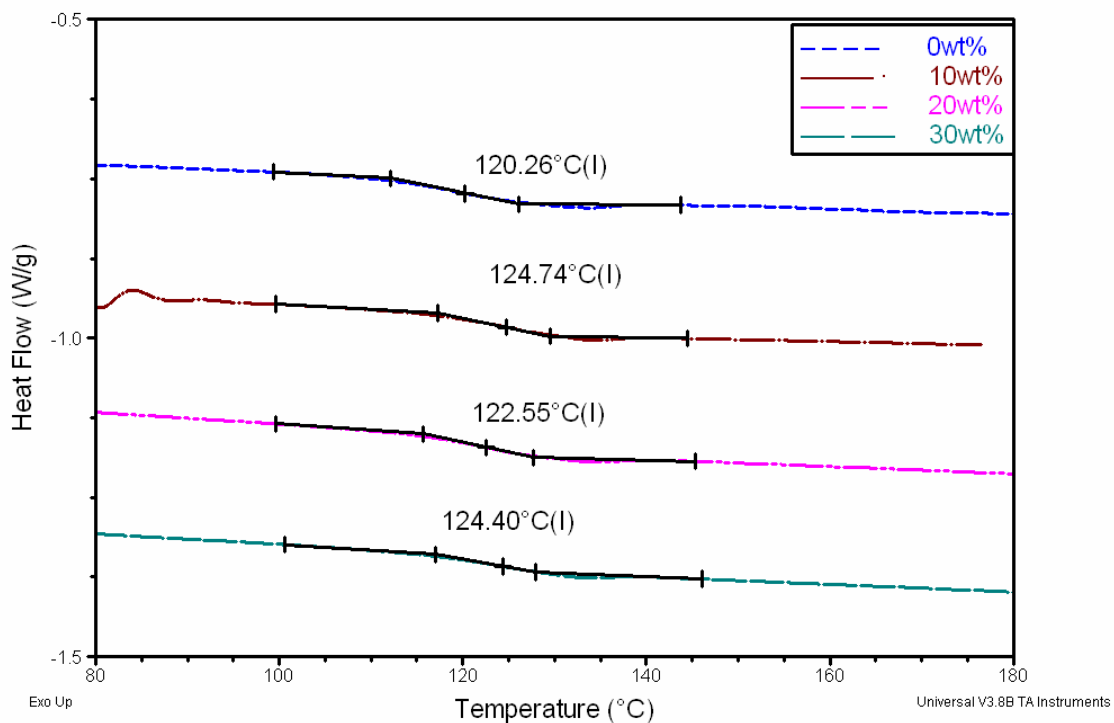


Figure 1: The Glass transition temperature of nanocomposites based on amine hardener

The glass transition temperature of the nanocomposites with amine hardener is shown in Figure 1. While all the glass transition temperatures are in the same range, the 10%wt and 30%wt samples have the closest T_g's, while the pure epoxy and 20%wt sample are further apart.

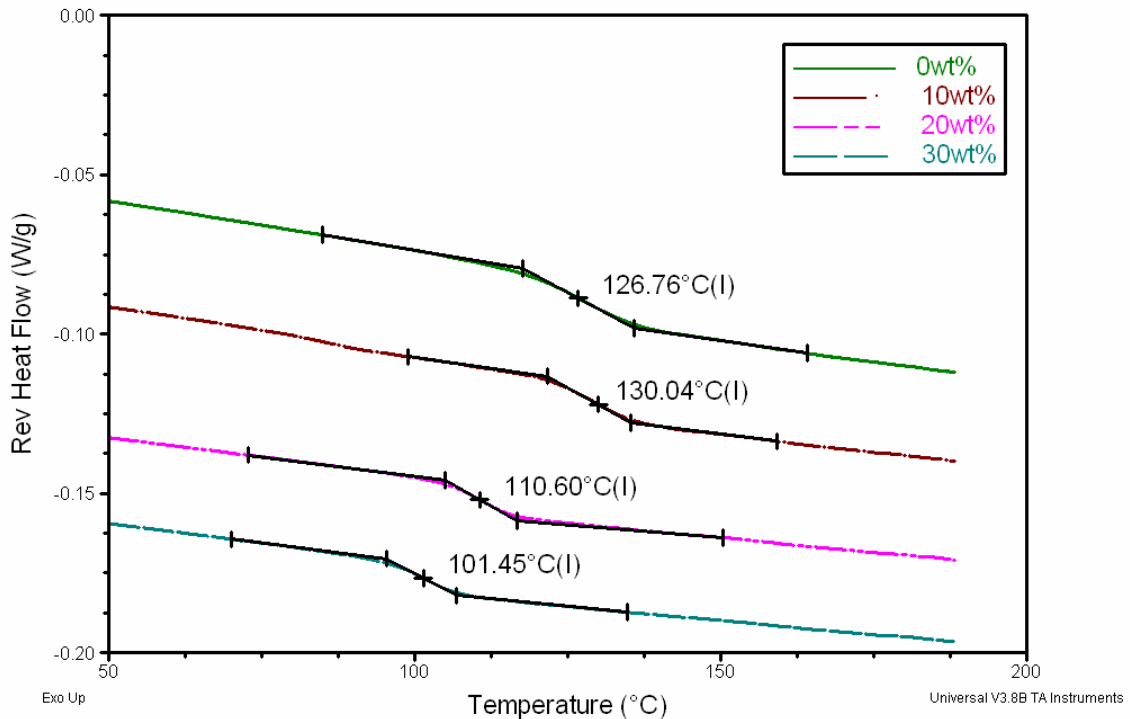


Figure 2: Glass transition temperature of nanocomposites based on anhydride hardener

While all the samples with the amine hardener have the same basic heat flow pattern, the samples with the anhydride hardener (Figure 2) display varying heat flow patterns as well as differing T_g 's. This data shows that samples with anhydride hardener will have a longer cure time than those with amine hardener, in addition to the differing heat flows which could bring a negative effect on the nano-composite sample.

4.2 Moisture absorption of nano and micro silica composites

The nano-silica composites were also characterized in terms of moisture absorption. The cured silica composites were subjected to temperature/humidity aging at 85°C and 85% relative humidity. The samples

were taken out of the aging chamber and the increased weight due to moisture uptake was recorded daily.

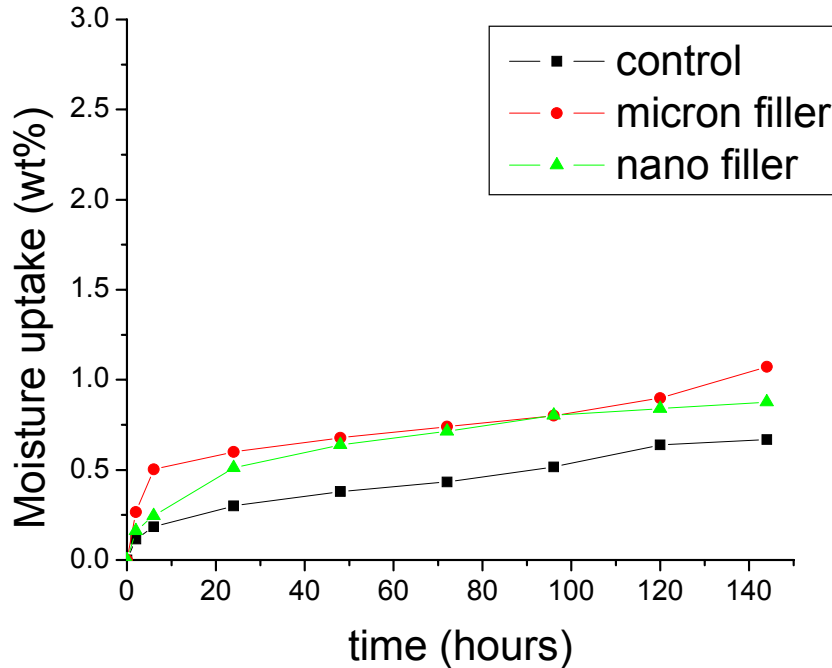


Figure 3: Moisture absorption of composites based on amine hardener with 20wt% nanosilica

Figure 3 shows the moisture absorption of the nanocomposites with anhydride hardener with 20wt% nano-silica. As can be seen from the graph, the micron size filler did not alter the behavior of the moisture absorption of the polymer matrix; however, due to the additional free volume at the interface of the nano sized filler, the moisture absorption was increased significantly. Due to the high moisture absorption in the nanocomposites sample difficulty in reliability during practical applications may occur.

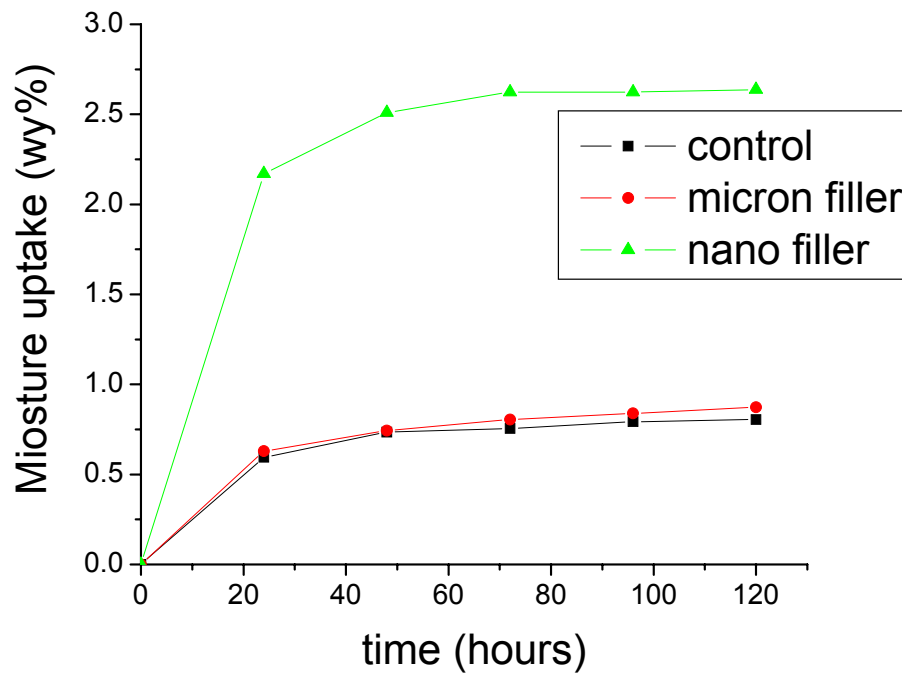


Figure 4: Moisture absorption of composites based on amine hardener with 20wt% nanosilica

The moisture absorption of the nanocomposites with amine hardener with 20%wt nano-silica is shown in Figure 4. As the graph shows, the nano and micron sized fillers, both altered from the control polymer matrix, both varied from the control by roughly the same wt%.

4.3 Density Measurement for nano and micron silica composites

A density measurement using Archimedes approach was conducted for the composite samples, for comparative purposes with the moisture absorption experiments. Figure 5 shows the density of composites with amine hardeners. It can be seen that the density of the micron size filler is slightly higher than that of the nano-size fillers, the difference being at the higher filler loadings.

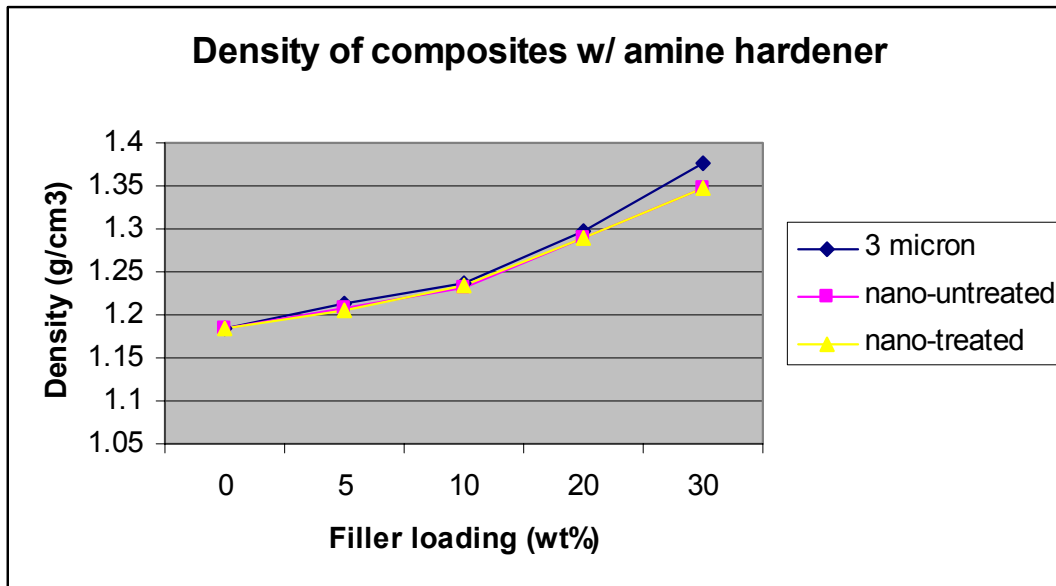


Figure 5: Density measurements of composites with amine hardener

This is consistent with the moisture absorption experiments. Because the nano-size silica can change the free volume of polymer composites, the nanocomposites have a lower density and higher moisture absorption than the micron sized filled composites. The densities of the nano-treated and nano-untreated are the same at all filler loadings. The results of the composites with anhydride hardener, shown in Figure 6, are also consistent with the moisture absorption test. The graph shows that the nano-sized filled composites have a slightly higher density than that of the micron size filled composites, which equates to lower the moisture absorption displayed by the nano size filled composites in comparison to that of the micron size filled composites. By comparison, the composites with the amine hardener had relatively the same densities as that of the composites with the anhydride hardener. Therefore, the use of a different hardener had no effect on the densities of the silica composites.

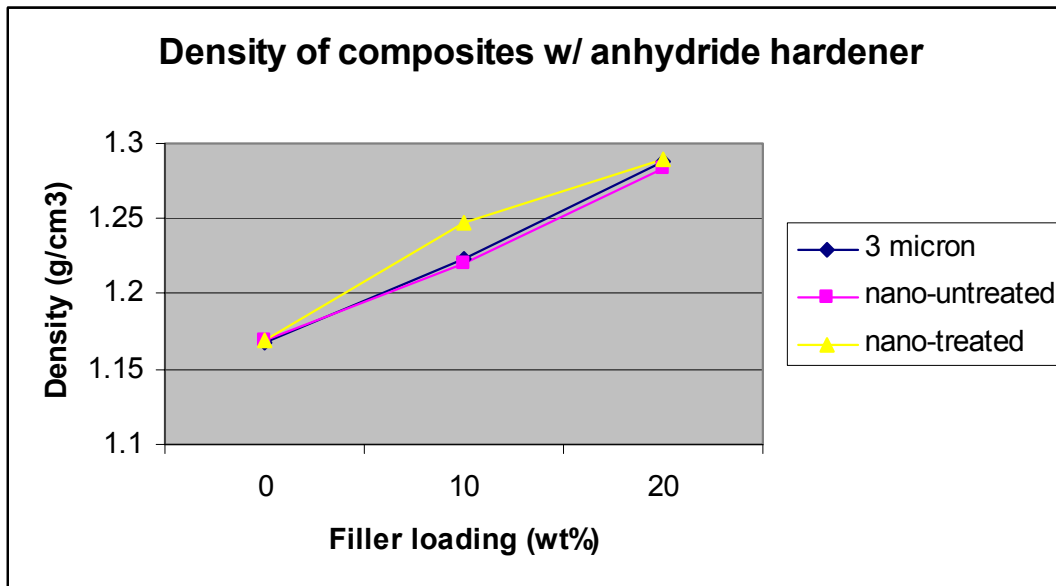


Figure 6: Density measurements of composites with anhydride hardener

5.1 Conclusion

Epoxy micron and nanosilica composites were prepared using different hardeners and characterized for their curing behaviors and thermal mechanical properties. Compared to the composites with the anhydride hardener, those with amine hardener showed generally higher glass transition temperatures and lower moisture absorption. While the composites with the anhydride hardener showed varying T_g 's and higher moisture absorption. However, the use of different hardeners did not affect the densities of either composite significantly.

5.2 What I did and learned this summer

The majority of the composite preparation was done by me. After an orientation to the lab equipment, I was given instruction on what sampled to

prepare and was left to complete the task independently. I recorded the moisture absorption and density measurements, and my mentor completed the DSC tests on the polymer composites. I learned a great deal from my experience this summer, doing research in a lab. However, I don't think that research is the direction I want to go in, although I do admire those that have the fortitude for the job.

6. Acknowledgements

I would like to thank Dr. Leyla Conrad for affording me this great opportunity to learn and grow this summer. I would also like to thank my mentor Yank Yang Sun for all the many things she helped me with, not only in the lab, but in preparing this research paper.

7. References

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