Rice-Husk-Ash-Based Silica as a Filler for Embedding Composites in Electronic Devices

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ABSTRACT: We carried out a feasibility study of the use of black rice husk ash (RHA) as a filler in epoxy resin for embedding material in electrical and electronic applications. We made a comparison by mixing RHA and two commercial fillers, fused and crystalline silica, with epoxy resin at weight fractions ranging from 20–60%. RHA-filled epoxy resin had higher mixing viscosity, coefficient of thermal expansion, and water absorption percentage than commercial-silica-filled epoxy composite. However, the impact strength of all composites was comparable, but the tensile strength and elongation at break of silica-filled epoxy were slightly superior. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3013–3020, 2002

Key words: composites; silicas; fillers

INTRODUCTION

Rice husk is a by-product from the rice mill and accounts for approximately 20 wt % of the rice.[1] Thus, the amount of this waste can be high and can cause an environmental problem of disposal in rice-growing countries. In many studies, researchers have attempted to utilize the rice husk to avoid the accumulation of this waste. One such methods is to use it as a biomass fuel for energy generation.[2,3] However, although the organic part is burnt out during the combustion process, the ash, which is mainly inorganic, is still left for disposal. The majority of the substance in rice husk ash (RHA) is silica in the hydrated amorphous form together with a limited amount of residual carbon and metal oxide. This silica-based RHA also has been on trial to be used as an alternative for silica powder in many applications, for example, in the production of whiteware, cast iron, concrete blocks, and filler in rubber and polymers.[4–7]

Embedment is a technique for the protection of a device or assembly in electrical and electronic applications from moisture, temperature, electrical flashover, current leakage, solvents, chemicals, mechanical shock, and vibration. This protection is vitally important to electronic circuitry, which houses delicate thin wires, transistors, capacitors, resistors, and semiconductors. Silica-powder-filled epoxy resin is one of the most popular choices for embedding material. Epoxy resin is used as an organic matrix because it has excellent heat, moisture, and chemical resistance and good adhesion to many substrates. It is mostly applied in the field of coatings, adhesives, casting, potting, composites, laminates, and the encapsulation of semiconductor devices. However, epoxy resins, due to their low mechanical properties and high coefficient of thermal expansion (CTE) value compared with inorganic materials, do not meet the requirements for electrical applications. Thus, silica particles are commonly used for the reinforcement of the epoxy matrix, to lower shrinkage on curing, to decrease CTE, to improve the thermal conductivity, and to decrease moisture absorption.[8,9] Our objective in this study was; thus, to examine RHA for use as a filler in embedding material for electrical and electronic devices. The physical and mechanical properties of RHA-filled epoxy resin was studied and compared to the composite of epoxy and commercial silica, which is generally used in this type of applications.

EXPERIMENTAL

Materials

The matrix material used in this study was an epoxy resin based on Bisphenol A epichlorohydrin-grade DER 331 from Dow Chemical Co., Ltd. (Bangkok), in the form of a liquid. The hardener used to cure the resin was triethylenetetramine (TETA) and modified cycloaliphatic polyamine adduct (MCPA). The filler used was crystalline-silica-powder-grade Megasil CS-

115, fused-silica-powder-grade Megasil FS-112, and RHA. Silica powder was commercially available and supplied by Korea Semiconductor Materials (Chungnum, South Korea). Rice husk ash was obtained from a rice mill in the form of black powder. The ash was then ball milled for 2 h, heated at 100°C, and passed through a 400-mesh sieve.

Sample preparation

Epoxy resin was heated and stirred at 55°C to decrease the viscosity of the mixing before the filler was added. The mixture was de-aired in a vacuum oven for 1 h, and then the hardener was added. The mixture was then poured into a mold made of Teflon according the shape required and was postcured at 100°C for 3 h. The ratio of the DER331 to MCPA to TETA was kept constant for all formulations at 1:0.57:0.03 for the resin part. The quantity of filler was varied to produce composites with 20, 40, and 60 wt % filler.

Filler characterization

Surface area determination

Surface area of the filler was measured with the Brunauer–Emmelt–Teller (BET) technique (Autosorb-1, Quantachrome, Boynton Beach, FL), which measures the quantity of gas absorbed on the surface of the filler. The as-received filler powder was pressed in the mold to make a 10-mm^3 tablet for measurement. Nitrogen gas was used, and the initial pressure was 450 mmHg.

Particle size analysis

The particle size of the filler was determined with a Mastersizer (Malvern, Worcestershire, UK). The filler was dispersed in a 1M solution of sodium hexametaphosphate and deionized water before it was fed into the instrument.

Moisture content and absorption

This test was carried out according to ASTM D 280. In the case of moisture content, the powder was initially weighed, then heated at 110°C for 2 h, and cooled in the dessicator. The percentage of moisture content in the filler was calculated by the following equation:

Moisture content (%)

$$= \frac{\text{Initial weight} - \text{Dried weight}}{\text{Initial weight}} \times 100 \quad (1)$$

The dried powder was then stored at 23°C and 55% relative humidity for 24 h. The weight after 24 h was

determined, and the moisture absorption was calculated as

Moisture absorption (%)

$$= \frac{\text{Weight after 24 h} - \text{Dried weight}}{\text{Dried weight}} \times 100 \quad (2)$$

Composite characterization

Viscosity of mixing

The mixture between the epoxy resin and filler without the addition of hardener was prepared and tested with a Brookfield viscometer (RV SC4-21, Brookfield, Middleboro, MA) according to ASTM D 2393 with a spindle speed of 120 rpm.

Water absorption

We performed this test according to ASTM D 570 by conditioning the cured specimens at 50°C for 24 h before immersing them in distilled water at 23°C for 24 h. The absorption percentage was calculated similarly to eq. (2).

Determination of the CTE

This test was carried out with a dynamic mechanical analyzer (PerkinElmer DMA 7, Wellesley, MA). A rectangular sample was heated from −50 to 50°C at a rate of 5°C/min, and the slope of the change in the height of the specimen and the increase in temperature was determined as the expansion coefficient.

Tensile test

Tensile tests were performed on a universal testing machine (Instron 4502, Canton, MA) equipped with a 10 kN load cell. All the tests were carried out according to ISO 527 at 23°C and 55% relative humidity. The measurements were carried out at a constant crosshead speed of 5 mm/min. Five replicates were run for each condition. The reported data are the average values. We converted the load–elongation curves into engineering stress–strain plots by dividing the measured load by the initial cross-sectional area and the elongation by the original gauge length.

Impact test

A Charpy impact test was performed on an instrumented impact tester (Radmana ITR-2000, McVan Instruments, Victoria, Australia) with a v-notched specimen following ISO 180 and with an average impact velocity of 4.7 m/s.

TABLE I
Comparison of Surface Areas and Particle Sizes of Fillers

Properties	Fused silica (FS-112)	Crystalline silica (CS-115)	RHA
BET surface area (mm^2/g)	17.34	5.94	4.45
Average particle size (D50) (μ)	21.68	21.44	14.01

RESULTS

Comparison of filler

All the types of fillers were irregular in shape due to the size reduction process by crushing or ball milling. Table I shows the comparison of surface area and particle size among the different types of filler. After it was ball milled and sieved through 400 mesh, the particles of RHA were slightly smaller than the commercial silica. With regard to surface area, RHA had comparable values to the crystalline silica but had lower values than fused silica. Figure 1 shows the moisture content and moisture absorption of all fillers. Fused and crystalline silica absorbed limited amounts of moisture, whereas RHA absorbed a much larger amount.

Mixing characteristic

Figure 2 shows the effect of increasing filler content on the viscosity of the mixture for three different types of fillers. Increasing filler content increased the viscosity of the mixture because the filler particle would act as an obstacle for the flow of the resin. However, the viscosity of the mixtures containing two commercial silica powders was much less affected by filler incor-

poration than was the RHA. The viscosity of the RHA mixture increased exponentially with increasing filler content, whereas the mixture containing silica powder increased the mixture viscosity fairly linearly with filler content. At the same level of filler content, RHA mixture showed greater viscosity at all levels of filler content, whereas the two commercial silica mixtures were comparable. Table II shows the magnitude of viscosity increase of the filled epoxy when compared to the unfilled one. RHA increased the viscosity of the mixture up to 10-fold, whereas only a 3–4-fold increase was observed for silica at the maximum filler content in this study.

Properties of composites

Figure 3 shows a comparison of the tensile strengths of the composites with different types of fillers and filler content. Tensile strength did not change much with increasing filler content for fused-silica-filled and crystalline-silica-filled epoxy, but it decreased slightly with increasing filler content for the RHA-filled composite. In the case of elongation at break and impact strength, all composites showed a decreasing trend with increasing filler content. Elongation at break of the fused silica/epoxy composite was slightly higher than crystalline-silica-filled and RHA-filled epoxy, but impact strength did not differ among the different types of filler (Figs. 4 and 5).

Figure 6 shows the reduction in the water absorption of the composites with increasing filler content. Both type of silica-filled composites absorbed water less than the RHA composite did in all formulations. Moreover, the water absorption of the RHA-filled
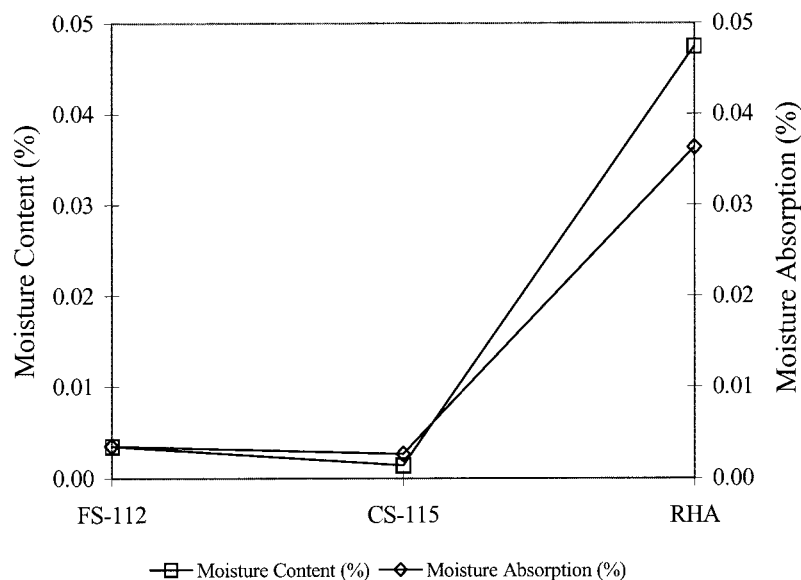

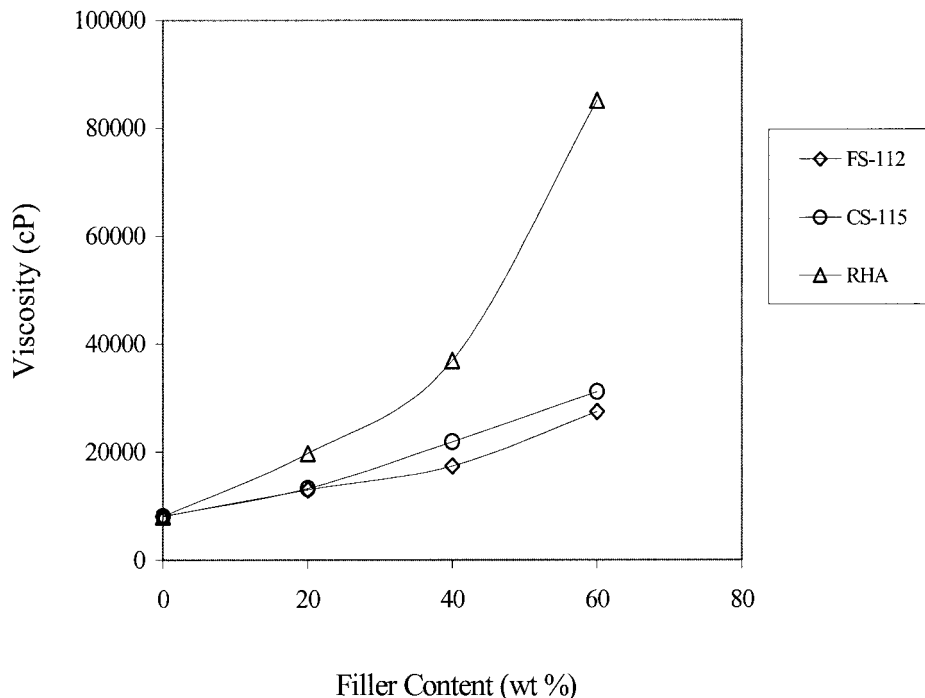**Figure 1** Comparison of moisture content and absorption of fillers.

Figure 2 Influence of filler type on mixing viscosity at various weight percentages.

epoxy at the highest filler weight percentage (60 wt %) increased again back to a level similar to the unfilled epoxy resin. In the case of the CTE (Fig. 7), the addition of rigid fillers obviously decreased the thermal expansion of the composites. Increasing filler content resulted in a slight decrease in thermal expansion. The fused silica/epoxy composite had the lowest thermal expansion, whereas crystalline silica and RHA composites showed comparable values but had higher values than the fused silica composite.

DISCUSSION

From the experiment, we found that fused silica had a higher surface area than crystalline silica and RHA, but both types of silica exhibited comparably low moisture absorption. Therefore, the surface area value determined by the BET technique was not the only controlled factor for greater moisture absorption of

TABLE II
Degree of Increase in Viscosity of Epoxy Filled with Different Types of Fillers Compared to Unfilled Epoxy Resins

	Filler wt %		
Filler	20	40	60
Fused silica (FS-112)	1.60	2.14	3.37
Crystalline silica (CS-115)	1.63	2.69	3.83
RHA	2.43	4.55	10.47

RHA. Generally, RHA-based silica powder particles are porous aggregates of nanosized ultimate particles in nature.[10,11] It is possible that the small pores presented in RHA particles, which are not detectable by BET surface analysis, may increase the surface area of the RHA and, thus, influence the moisture absorption percentage. Another factor for consideration is the presence of carbon and metal oxide in the RHA, which can alter the moisture absorption behavior of the ash.

Viscosity of the mixture is one of the important parameters for the use of encapsulant. Too high a viscosity makes it difficult for the embedding materials to flow through small gaps around the devices; thus leaving an unprotected area. In this study, mixing RHA with epoxy resin increased viscosity much more than the use of two commercial silica as fillers at the similar filler content. Thus, the RHA mixture would be more difficult to use in the manufacturing process. In general, the viscosity of the mixture between rigid filler and polymer liquid depends on the wetting ability of polymer onto the filler surface. Poor wetting will result in a high mixture viscosity.[12] Therefore, it is possible that the wetting ability of the epoxy resin onto RHA particles is not as good as onto silica particles. Therefore, the use of RHA as a filler in embedment has to be considered on the way to control or reduce the viscosity of the mixture. This can be done with a low-viscosity epoxy resin as a matrix or by the treatment of the RHA surface to increase the wetting ability because wetting depends on the surface chem-
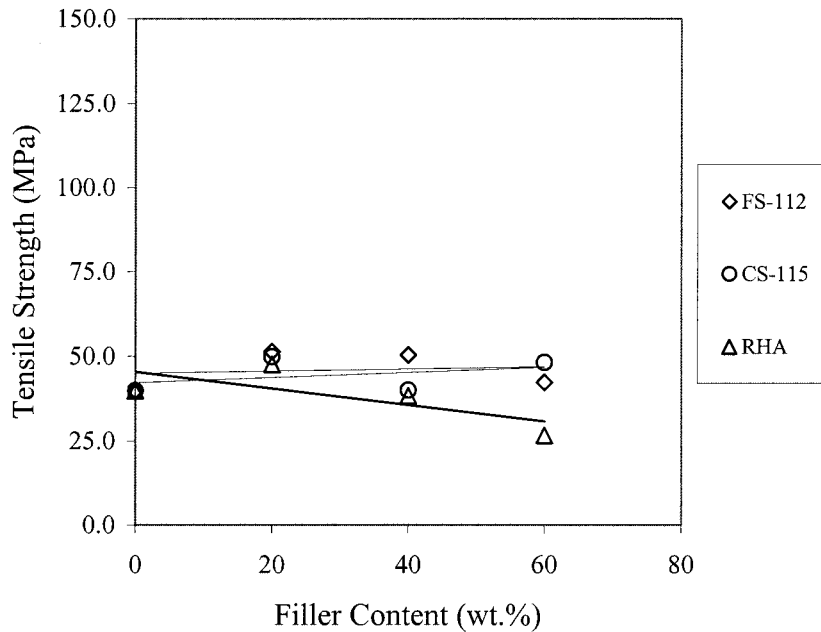
Figure 3 Influence of filler type on tensile strength at various weight percentages.

istry, contamination of filler surface, and surface area.[13]

In the case of mechanical properties, the addition of rigid fillers to the polymer matrix normally results in a decrease in elongation at break and impact strength, but two responses of tensile strength on the basis of degree of adhesion between fillers and matrix can be observed.[14] Tensile strength can either decrease with increasing filler content if the filler/matrix adhesion is weak or increase or be constant with increasing filler content if strong interfacial bonding is presented. When the interface is under stress, debondings of a weak interface can act as crack-initiation sites, which leads to the failure of the composite. Therefore, the higher the filler content is, the greater is the possibility of weak locations in the materials. Strong interfacial adhesion helps to maintain or increase the tensile strength because the stress can be transferred through the interface effectively. Strong interfacial bonding depends on the inherent wetting ability of a polymer
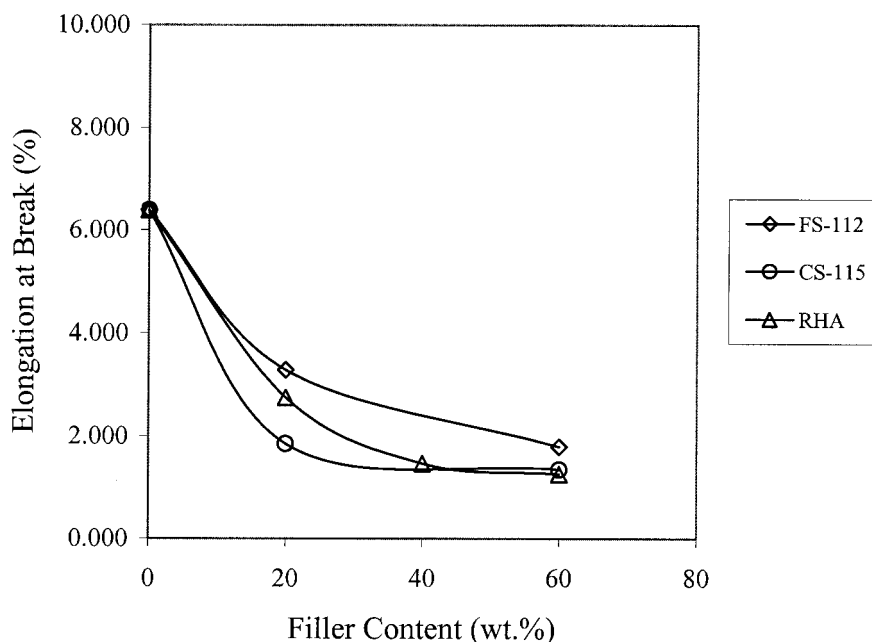

Figure 4 Influence of filler type on elongation at break at various weight percentages.
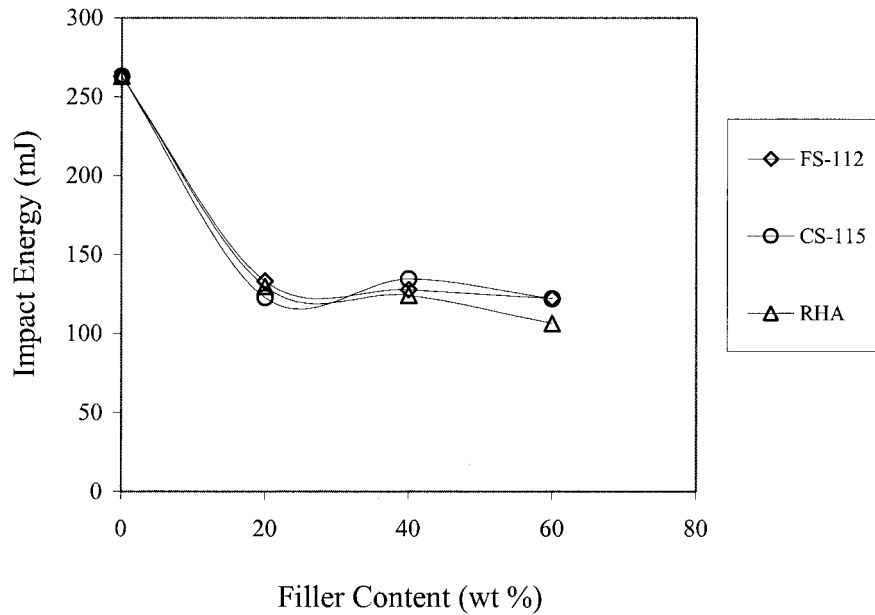
Figure 5 Influence of filler type on impact strength at various weight percentages.

onto the surface of fillers.[15] The main assumptions for good wetting are related to similar polarities of both phases and to low surface tension and low viscosity of the matrix polymer. Therefore, it can be assumed that the adhesion between RHA particles and the epoxy matrix was not as good as silica/epoxy bonding. This was possible due to the lower wetting ability of epoxy resin on to RHA particles as observed in the high increase in mixing viscosity of the RHA mixture as

discussed previously. In addition, the morphology of the ash should be also taken into account. The porous structure of RHA particles is obviously weaker than solid structure of silica. When stress is applied, the possibility of particle fracture leading to weak locations in the RHA composite is greater, which can decrease the tensile strength of the composite.

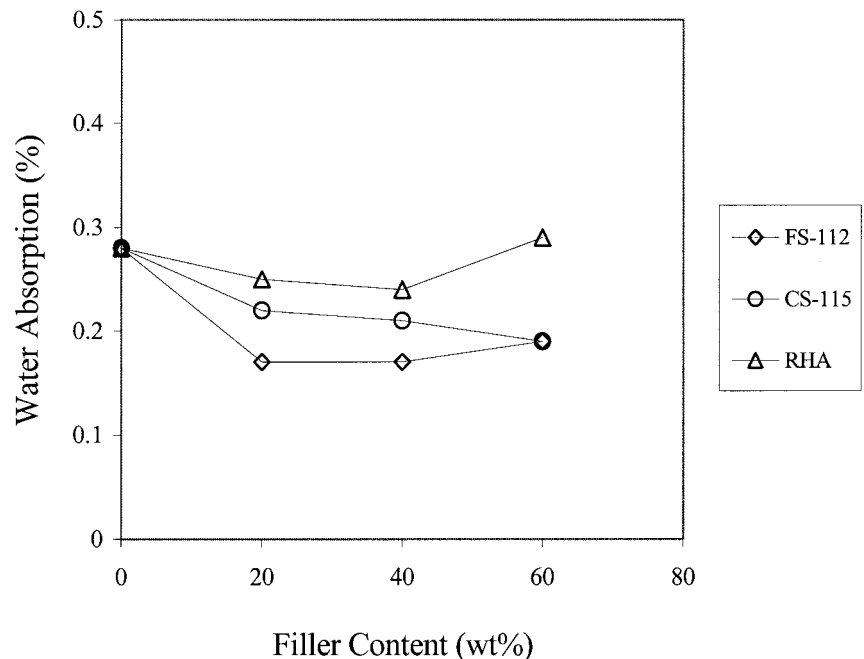One of the main purposes of incorporating ceramic fillers into the polymer matrix for embedment is to

Figure 6 Influence of filler type on water absorption at various weight percentages.
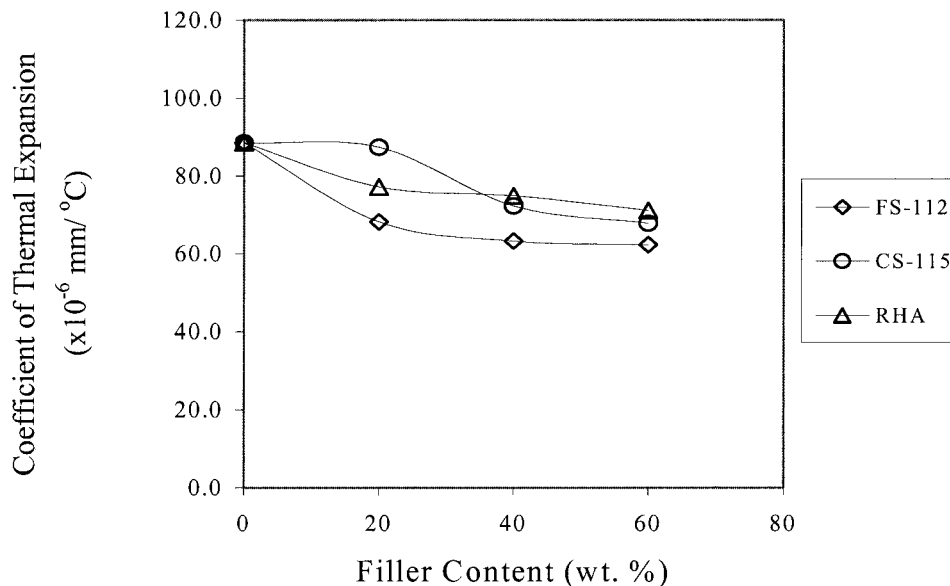
Figure 7 Influence of filler type on the CTE at various weight percentages.

decrease the overall thermal expansion of the material and, hence, reduce the thermal expansion mismatch between the embedding materials and the parts.[16,17] The risk of thermal-stress-induced premature failure of wire bonds, chips, and packages can be reduced. From the experimental results, we found that the fused-silica-filled epoxy produced composites with the lowest CTE. This was due to the fact that fused silica has the lowest CTE, 0.5 ppm/°C, whereas crystalline silica has higher value, 15 ppm/°C.[18] Although RHA is composed of mainly amorphous silica, which should have a lower CTE than crystalline silica, it decreased the thermal expansion of the epoxy resin to a similar level as the crystalline silica. This was possibly due to the presence of residual carbon in the ash and the porous structure, which caused the reduction in effectiveness of the RHA-based silica to reduce thermal expansion of the composite. Other purpose for adding filler to the polymer matrix, which usually absorbs greater amount of moisture, is to decrease the overall moisture or water absorption of the embedding material. Silica-filled composites absorbed lower amounts of water than rice-husk-filled composites. Generally, the absorption of water into a particulated composite can occur through four main locations, the polymer matrix, filler, interface, and defected area. However, the greatest amount of water penetration will occur at the polymer matrix. Because the polymer matrix in this study was similar for all types of composites, the controlled factors of the water absorption of the composites was left to the type of filler and interface. From the previous experiment (Fig. 1), we found that RHA absorbed higher amounts of moisture, whereas the mixing viscosity and tensile strength

results suggested that the interface adhesion of the RHA/epoxy was poorer (Figs. 2 and 3). Hence, the RHA-filled epoxy composite should have had a greater water absorption percentage, which agreed well with the experimental results.

CONCLUSIONS

Although the mechanical properties of the epoxy composites filled with RHA were found to be comparable to those of silica-filled epoxy composites, except tensile strength, which was slightly lower; the mixing viscosity, water absorption, and CTE of RHA composites were greater than those of commercial-silica-filled composites, which could affect the utilization of RHA as a filler in such applications. However, the possibility of using RHA as an alternative for silica in encapsulant for some electronic applications should not be discarded. Control of the combustion to decrease the carbon content and treatment of the surface to increase the wetting ability of the ash could be ways to improve the mismatched properties.

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