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EFFECTS OF RUBBER-MODIFIED ON THERMAL AND MECHANICAL PROPERTIES OF EPOXY MOLD COMPOUND

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ABSTRACT

In a semiconductor packaging, the thermal stress greatly influenced the package cracking, passivation layer cracking and aluminium pattern deformation. The effects of thermal stress that resulted from the use of plastic encapsulants will contribute to shrinkage of the plastic upon curing and thermal mismatch between the resin and the device. Therefore, an innovative low stress epoxy molding compounds (EMC) were formulated by utilization of rubber modification technology. The characteristics can be achieved a lower Young's modulus and coefficient of thermal expansion (CTE). The EMCs are generally prepared from a blend of an epoxy resin, hardener, fillers, catalyts, low stress agent, and colorants. This article reports the effects of the modified EMC by liquid poly (methyl methacrylate) grafted natural rubber copolymer on the thermal and mechanical properties of EMCs as a function low stress agent. The addition of rubber significantly decreased the flexural strength and elastic modulus the EMCs without lowering the T_g. Therefore, this properties of EMCs found considerably used in semiconductor packaging. Various characterization have been done on the EMC such as thermal expansion using thermo mechanical analyzer (TMA), storage modulus and tan δ using dynamic mechanical analyzer (DMA) and flexural properties using Universal Testing Machine. Morphological observations were done using the scanning electron microscopy (SEM).

INTRODUCTION

Epoxy molding compounds (EMCs) for semiconductor packaging have been and will continue to be the main stay of encapsulation material in view of the low cost and productivity advantages. On the other hand, as chip sizes become larger due to increase integration of devices, compacter package are in demand to realize the higher integration and are designed to be smaller and thinner in outer dimension. These trend increased thermal stress in the device package system which often causes package cracking during thermal shock testing under accelerating ambient .The prevailing surface mount technology (SMT) also causes thermal stress to devices. Therefore, it is necessary to design the device package so as to reduce the thermal stress and to increase the strength and toughness of the cured EMCs for high reliability semiconductor devices [4].

The coefficient of thermal expansion and elastic modulus of EMC are major factors of the thermal stress, because the CTE of EMC is higher than chip and substrate. The chip and substrate relatively have consistent material constants during the fabrication,

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molding, testing and working process, while the properties of EMC depends on the time and temperature. Varius additives of EMC such as hardener, catalyst, filler, coupling agent, flame retardant, stress relief agent, colorant and mold release agent, etc., could chage the properties of EMC with influencing the reliability of package including many variations due to the change of material constants by mixing above additives. Among the additives, fillers such as silica (SiO_2) particle decrease the CTE, thermal shingkage, cost and moisture absorotion of package and increase the thermal conductivity and viscosity in porportion to the amount of filler used [8].

Increasing the amount of silica filler used in an encapsulant has effectively lowered the CTE however this approach not only increased the viscosity of the resin composition, resulting in poor moldability [5]. The viscosity can be reduce by use of spherical shaped fillers and optimization of particle size distribution of fillers. In order to prevent the package cracks, lowering of the elastic modulus of the EMC by modification with a low stress agent is the one method should be useful for reducing thermal stress in the package.

Therefore, it has already been study by many researcher in modification with a rubber to developed the low stress EMC. According to Anjoh et al 1998 [2], modification of encapsulation compounds with siloxane polymers is carried out to decrease not only the elastic modulus but also the thermal expansion. Siloxane dispersed as particle into the resin matrix, forming a two phase structure (sea island stucture).The phase seperation structure allows the elastic modulus and the thermal expansion to be lowered without lowering the T_g. Lowering T_g, usually causes other trade offs, one which is poor moisture resistance. From the past experiences lowering of thermal expansion and elastic modulus without lowering the T_g is a difficult task [6].

In this studies, liquid poly (methyl methacrylate) grafted natural rubber copolymer (PMMA-grafted NR) has been used to study the effect on the thermal and mechanical properties of EMCs in different composition of rubber. Various characterization have been done on the EMC such as thermal expansion using thermo mechanical analyzer (TMA), storage modulus and tan δ using dynamic mechanical analyzer (DMA) and flexural properties using Universal Testing Machine at room temperature. Morphological observations were done using the scanning electron microscopy (SEM).

MATERIAL AND METHODS

Materials

Epoxy resin (EPIKOTE resin 828K) used in this study was a commercial product from Hexion Specialty Chemical, Korea. Polyether amine D230, the epoxy-curing agent, was supplied by Texaco Chemical Company and triphenylphosphine (TPP) was used as the catalyst. The liquid PMMA-grafted NR was bought from Green HPSP (M) Sdn Bhd. The fused spherical silica was supplied by Denki Kagaku Kogyo Kabuishiki Kaisha, Japan and having a mean particle diameter of 30 µm. A pigment colour and carnauba wax were used as additives. The basic formulation is shown in Table 1.

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Table 1: Basic formulation of epoxy molding compound

Materials	wt%
Bisphenol A diglycidyl ether resin	16
Amine hardener (Jeffamine D230)	5.3
Low stress agent (PMMA-grafted NR)	5-15
Fused silica (spherical)	75
Catalyst (TPP)	max 0.6
Mold release agent (carnauba wax)	max 0.6
Carbon black	max 0.5

Sample preparation
Epoxy resins (EPON 828) were added in 32% by weight of curing agent (polyetheramine D230). The mixtures were fully mixed with the fillers 75 wt% and stirred by a mechanical stirer at 100 rpm for 10 min. The mixture were poured into the twin screw extruder at 95 °C for approximately 10 min. Then, the melt-mixed EMC was cooled and crushed into a powder. The EMC was molded at 175 °C for 5 min using compression molder and fully cured at 175 °C for 2h in a convention oven.

Dynamic Mechanical Analysis
Glass transition temperature and dynamic flexural modulus were measured by Perkin-Elmer DMA at a frequency of 1 Hz and temperature range -70 to 200 °C at scan rate of 2 °C/min under three point bending mode.

Coefficient of thermal expansion
CTE measurements of the EMC were performed on a Thermal Mechanical Analyzer (TMA) (Perkin Elmer, model TMA-7). These samples had a dimension 4.56 x 7.70 x 3.73 mm. The samples were mounted on the TMA and heated from 28 to 200 °C at heating rate of 10 °C/min. The static force used for this samples are 50 mV. The coefficient of thermal expansion was determined from the slope of the plot between the thermal expansion and temperature.

Flexural properties
Flexural measurements were carried out using Universal Testing Machine at ambient temperature, according to ASTM D790 using 3-point bending configuration at 5 mm/min deformation rate.

Morphology
Flexural surface morphology studies of selected EMC were analyzed using scanning electron microscopy (SEM, model SUPPRA 55VP) at magnification 50K X and

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electron heat transfer (EHT) used is 3 kV .The flexural surface was gold coated to avoid electrostatic charging during inspection.

RESULTS AND DISCUSSION

A molded encapsulant should have sufficient mechanical strength to protect a chip from physical and thermal damage. Also, the crack resistance of an encapsulant against thermal stresses in IC integrated was increased by decreasing the elastic modulus of the materials. The flexural strength and elastic modulus of EMC as a function of the composition of the PMMA-grafted NR in epoxy composite are shown in Figure 1 respectively. The result shows that flexural strength of EMC was decreased due to composition of the PMMA-grafted NR was increased the agglomeration between filler and matrix. Another possible reason to explain the low strength of EMC is weak interaction between the silica interface of spherical fused silica and matrix when added more the liquid PMMA-grafted NR in the system. Agglomeration will cause defect to the composite because of the presence of void between the particles [1]. On the other hand, PMMA-grafted NR and fused silica are polar and hydrophilic material, which fused silica tend to stick the PMMA-grafted NR blend area in the epoxy composite and resulting in inhomogeneous distribution. In Figure 1, the flexural modulus of EMC was decreased with increasing the volume fraction of liquid PMMA-grafted NR since PMMA-grafted NR has lower modulus.

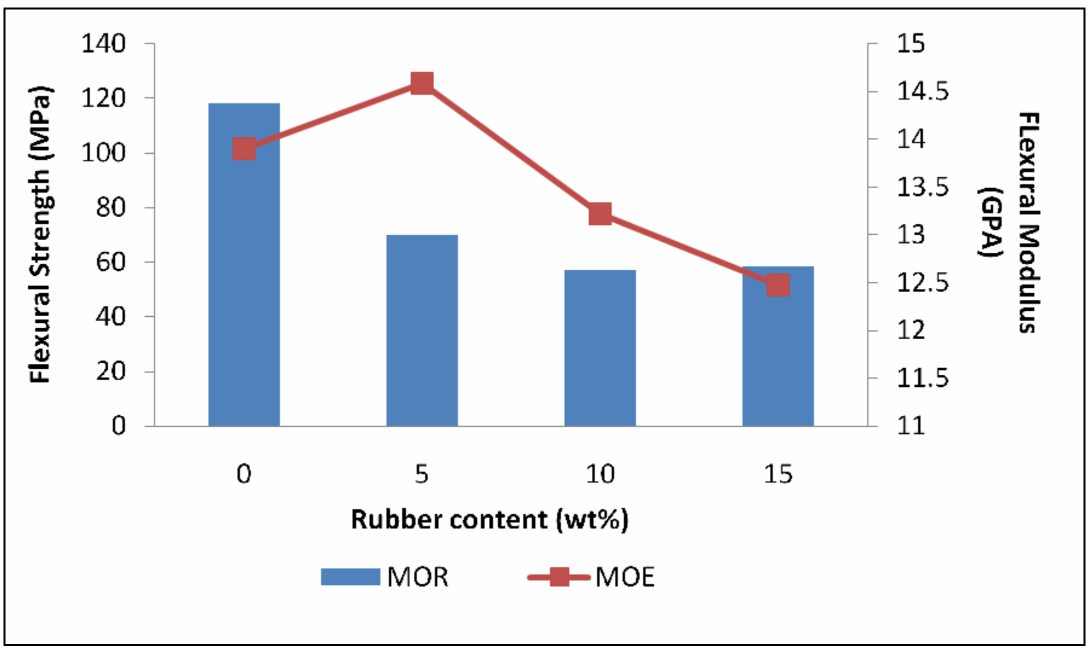

Figure 1: Effect of PMMA-grafted NR loading on flexural strength and modulus of EMC filled spherical fused silica

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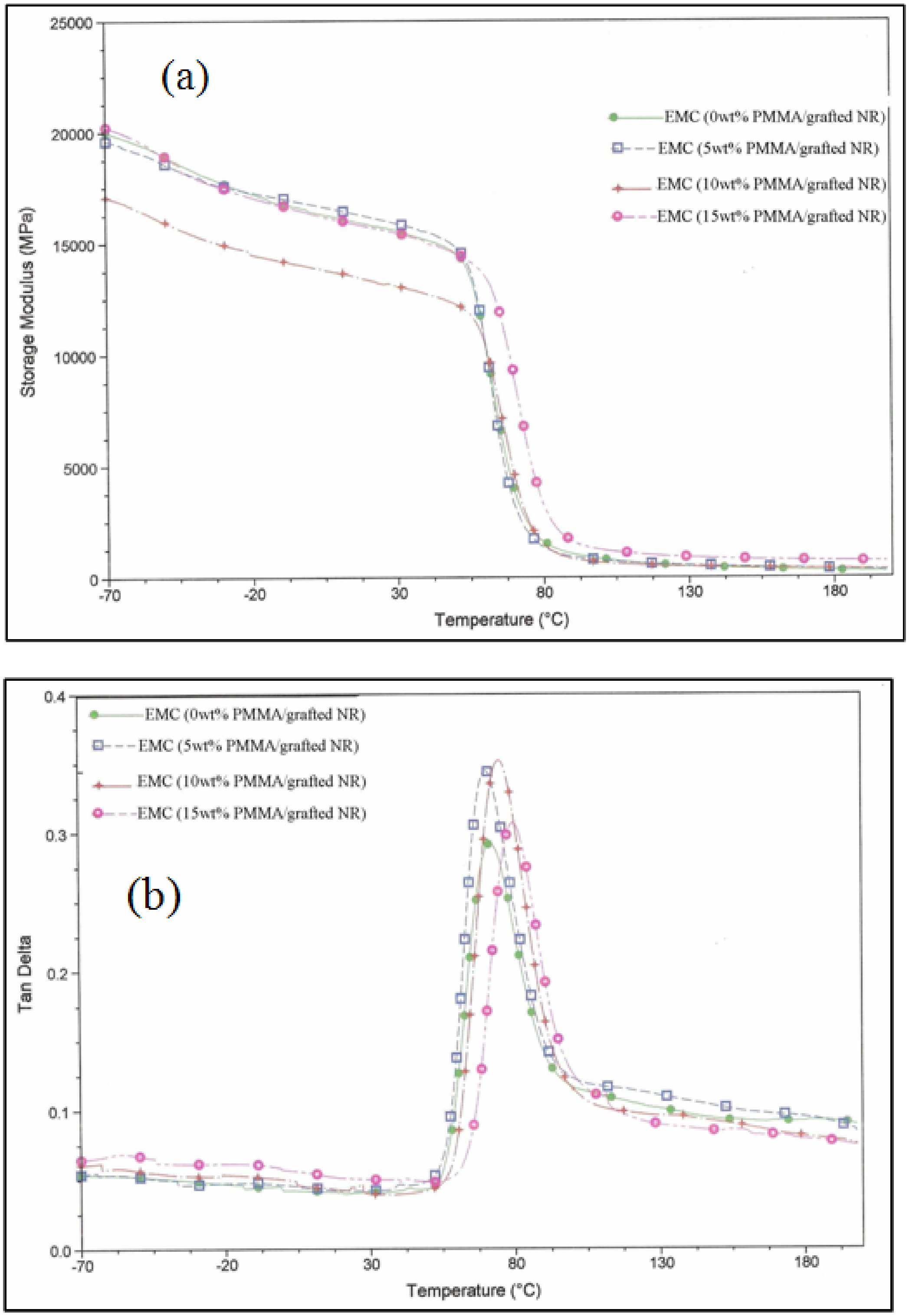

Figure 2: (a) *E´* and (b) tan δ of EMC modified with PMMA-grafted NR and control EMC

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Dynamic mechanical analysis plays an important role in understanding the dynamic behavior of the materials under a wide range of temperature. Figure 2(a) and 2(b) show the temperature dependence of storage modulus and tan δ for EMC without rubber modified and EMC with rubber modified respectively, at 75 wt% of filler content. The EMC without PMMA-grafted NR showed the higher storage modulus over the whole temperature range studied, due to the stiffening/strengthening effect of rigid particles of high content and EMC with different composition of rubber modified shows the low storage modulus which contains micrometer scale rubber particles in the EMC [7]. The presence of rubber particle in epoxy composite reduces rigidity of the encapsulant as reflected in the lower flexural storage modulus [3]. While adding 15wt% of PMMA-grafted NR in EMC give the highest storage modulus due to the increasing motion of the polymer chains. From Figure 2 (b) it can be seen that the T_g of EMC shifted toward the high temperature, followed by EMC modified with 5wt%, 10wt% and 15wt% of PMMA-grafted NR. The glass transition temperatures of the EMCs are shown in Table 2. All the EMCs system has T_g above 70 °C. Peak value of tan δ occurs at the T_g. The sharp peak of the tan δ shows the mobility of the molecular sample. The mobility of the molecular samples was increased by modification of the PMMA-grafted NR. The T_g of EMC is slightly increased at higher rubber content. According Schina 2000 [9], the increase in the T_g observed as a function of curing represents the increase in the molecular weight of the resin system.

Table 2: Glass transition temperature of EMC modified with different rubber content

	0wt%	5wt%	10wt%	15wt%
T_g (°C)	71.98	70.62	74.71	79.81

Figure 3 shows the CTE properties of spherical fused silica filled epoxy composites at 75wt% silica loading. From the results, the CTE values are very low; it is due to the very low CTE of fused silica contained in EMC (0.5 ppm/°C). In the literature CTE value for neat epoxy is ~80 ppm/°C (below T_g) and ~ 130 ppm/°C (above T_g) [7]. From Figure 3, it can be observed that the CTE below T_g is slightly changes when adding more rubber because the rubber at this temperature is rigid and the mobility of rubber particle is low. The CTE value at above T_g is decreased with increasing rubber content in EMC and lower than EMC without rubber modified except EMC filled spherical fused silica modified with 15wt% of rubber (52.4 ppm/°C). In this case, by adding more rubber in epoxy composite causes the increasing mobility of rubber at above T_g and the rubber chain has the space for internal movement at higher temperature. By adding the rubber in composite material, the rubbers binds the filler and matrix then prevent it from expanding as much as it would on its own.

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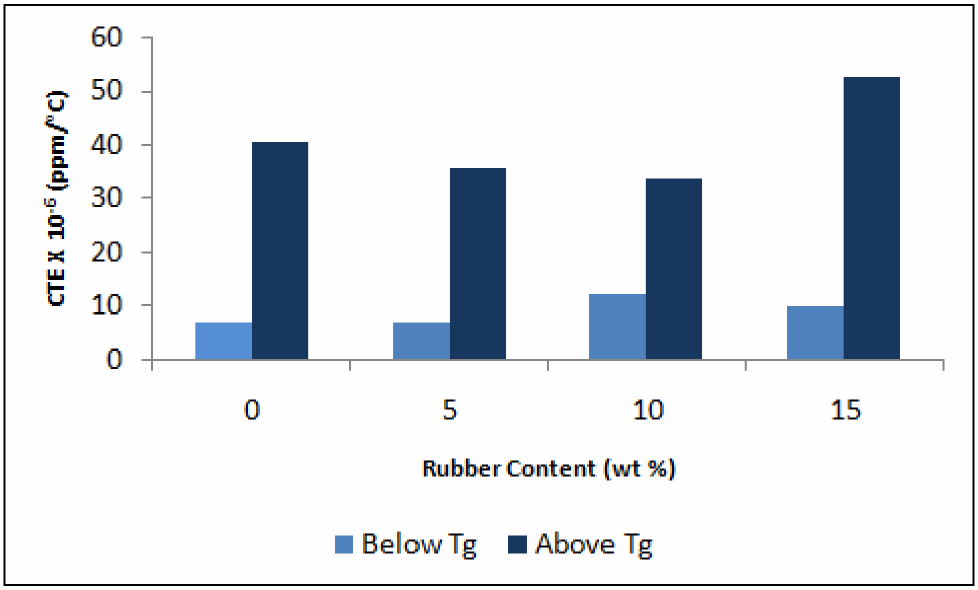
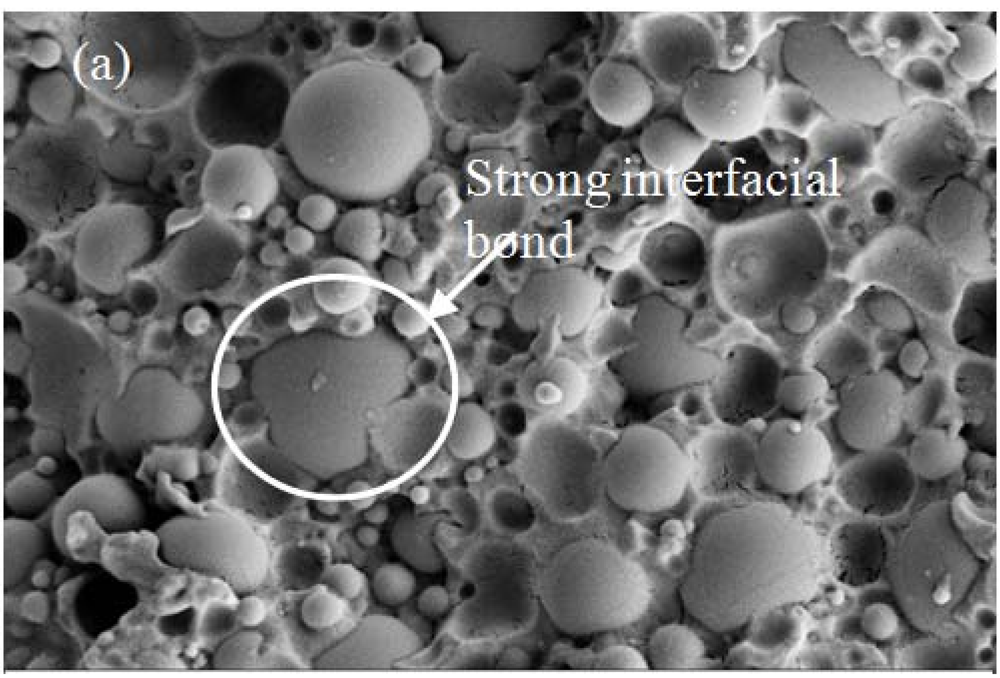


Figure 3: CTE of EMCs with different rubber content

Figure 4 shows the micrograph of (a) EMC without rubber modified and (b) EMC with 5% wt rubber modified after flexural test. Spherical filler shape having higher particle surface results in more contact area between the filler and matrix. From the micrograph, the interphase of EMC 0%wt PMMA-grafted NR is better judging from the adhesion between the contact of matrix and fused silica than interphase of EMC modified with PMMA-grafted NR having weak interfacial bond between matrix and fused silica.



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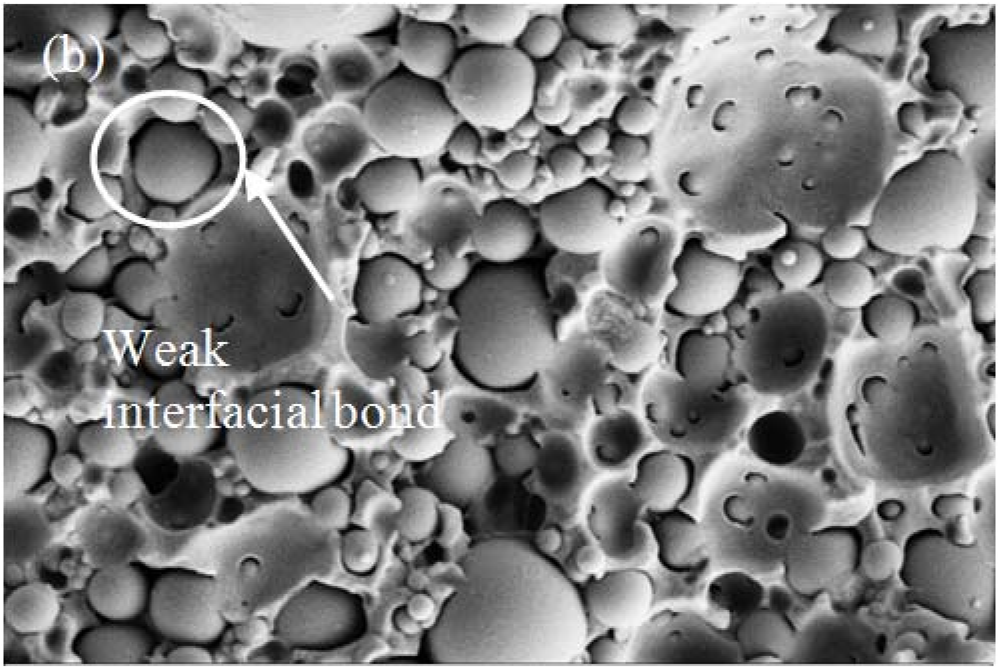

Figure 4: SEM micrographs of flexural surface of (a) EMC control and (b) EMC modified with 5wt% loading of PMMA-grafted NR

CONCLUSION

Dispersed rubbers were used to reduce the stress of epoxy composite cured for electronic encapsulation application and of the results rubber modified was greatly affected decreasing the flexural modulus and CTE without lowering the T_g. Increasing the rubber contents give the higher thermal expansion value of the EMC. Small amount of rubber is resulted in low coefficients of thermal expansion to minimize thermal stresses. SEM micrographs show that rubber modified epoxy resin exhibited lowest flexural properties, which is mainly attributed to the poor filler-matrix interfacial adhesion.

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REFERENCES

[1]. Ahmad. F. N., Jaafar. M., Palaniandy. S. & Azizli. K. A. M. (2008). *Composite science and technology*. **68**, 346-353.

[2]. Anjoh. I., Nishimura. A., & Eguchi. S. (1998). *IEEE transactions on electron devices*. **3**, 743-752.

Corresponding Author: ras@pkrisc.cc.ukm.my

[3]. Chew. S. & Tan. A. C. (2003). *IEEE transactions on electronics packaging manufacturing*. **26**, 211-215.
[4]. Ho. T.H & Wang. C.S. (2001). *European polymer journal*. **37**, 267-274.
[5]. Ho. T.H. & Wang. C.S. (1994). *Journal of polymer research.* **1**, 103-108.
[6]. Kuwata. K., Iko. K. & Tabata. H. (1985). *IEEE transactions on components, hybrids, and manufacturing technology*. **4**, 486-489.
[7]. Sham. M. L. & Kim. J. K. (2004). *Composites: Part A.* **35**, 537-546.
[8]. Shin. D. K. & Lee. J. J. (1998). *IEEE transactions on components, packaging, and manufacturing technology*. **4,** 413-421.
[9]. Teh. P. L. Jaafar. M., Akil. H. M., Seetharamu. K. N., Wagiman. A. N. R., & Beh. K. S. (2008). *Polymers for advanced technologies*. **19**, 308-315.

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