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Fabrication of epoxy-montmorillonite hybrid composites used for printed circuit boards via *in-situ* polymerization

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Abstract—Montmorillonite (MMT)-filled brominated epoxy hybrid composites used for printed circuit boards (PCBs) are successfully prepared by *in-situ* polymerization by a careful choice of fabrication process. The characteristics of the composite are assessed by Inductance Capacitance Resistance meter (LCR), Transmission Electron Microscopy (TEM), Differential Scanning Calorimetry (DSC), Thermal Gravimetric Analysis (TGA), Thermal Mechanical Analysis (TMA) and a universal tester. The dielectric study reveals that the incorporation of MMT filler into epoxy significantly reduces (i.e. by up to 36%) the dissipation factor, with a marginal reduction in the dielectric constant. The hybrid composites also exhibit better thermo-mechanical properties. With regard to thermal stability, the introduction of a small amount of MMT leads to an improvement in the glass transition temperature (T_g), a marked decrease in the coefficient of thermal expansion (CTE) at different temperature ranges, particularly above T_g, and a slight improvement in the mechanical properties such as Young's modulus and tensile strength. We observe a negligible trend but good resistance for moisture absorption compared with unmodified epoxy resin systems.

Keywords: Montmorillonite; epoxy; hybrid composite; PCB.

1. INTRODUCTION

Polymer/clay hybrid composites are currently under intense study as next generation materials because they offer the potential to realize novel properties and to tailor these properties extensively. Recent and ongoing research on polymer–inorganic hybrid composites has shown dramatic enhancements in stiffness, strength and thermal properties over those of unreinforced polymers, without compromising on brittleness and processibility [1–5].

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Epoxy is widely used as interlayer dielectrics for printed circuit boards (PCBs) and as a packaging material in the fabrication of microelectronic devices because of its good thermoxidative stability, high mechanical and excellent electrical properties, and superior chemical resistance [6–8]. In microelectronic devices, large differences in the coefficients of thermal expansion (CTE) between epoxy and aluminum, copper, or silicon dioxide can cause devices to crack, peel, and bend, and high moisture absorption can short-circuit and damage the devices. Also, the microelectronic technology trend is towards high-speed, high-frequency electronic devices [9, 10], which require that the interlayer materials possess even lower dielectric constants (D_k) and dissipation factors (D_f). Hence, the requirement of low CTE and low moisture absorption by materials is quite stringent in the PCB industry.

The most promising candidate of the layered silicates is montmorillonite owing to its natural abundance and high aspect ratio. Natural montmorillonite (MMT) is composed of silicate sheets of about 1 nm thickness and a diameter of 100 nm to several micrometers with adsorbed exchangeable alkali or alkaline earth cations such as Na^+, K^+ or Ca^{2+}. MMT can be broken down into submicrometer size disc-like particles of approximately 10:1 aspect ratio consisting of a stack of nanometer-thick layers of very high stiffness and strength [1, 3, 11]. Before the preparation of polymer/MMT hybrid composites, modification is generally required through ion exchange reaction between organic and inorganic cations to render hydrophilic MMT more organophilic and to increase interlayer spacing of MMT. The weak van der Waals bonding between layers once polymerization is complete allows the polymer chain to intercalate. The exfoliated layer structure has higher phase homogeneity than the intercalated counterparts; thus it is more desirable for enhancement of the properties of the composites, although it is rare to achieve complete exfoliation of clays [12, 13].

Introducing MMT layers into the PCB used laminating epoxy resin has great potential as an attempt to improve composite dielectric, thermal and mechanical properties while still retaining its industry processibility. In this paper we describe a process for fabrication of epoxy/MMT hybrid composites, microscopic assessment of their structure and properties characterization.

2. EXPERIMENTAL

2.1. Materials

Source clay montmorillonite (MMT) was purchased from Aldrich, the average particle size being 20–50 µm. Araldite laminating resin brominated difunctional epoxy EP8008 and tetrafunctional epoxy EP1031 were obtained from Huntsman. The chemical structures of brominated epoxy resin, which is made from diglycidyl ether of bisphenol A (DGEBA) and tetrabromobisphenol-A (TBBA), are shown in Fig. 1. The hardener, dicyandiamide (DICY, purity $> 99.5\%$), and the accelerator,

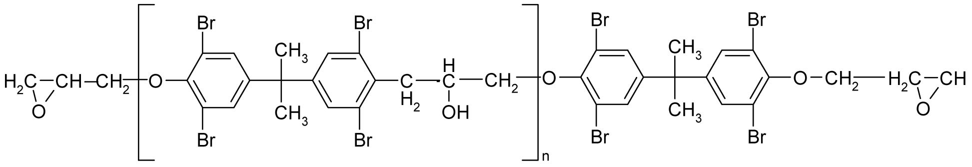


Figure 1. Schematic drawing of the chemical structure of brominated epoxy.

2-methylimidazole (2-MI, purity > 99.0%), were obtained from Neuto Products and Tokyo Kasei Kogyo respectively. The couple agent was Shin-Etsu KBM-403, 3-glycidoxypropyltrimethoxysilane, and the organic modifier was 4,4′-oxydianiline (ODA).

2.2. Preparation of organically modified MMT

In order to create a good epoxy–clay hybrid structure which leads to better dielectric properties for PCBs applications, the key is to load the clay gallery with hydrophobic onium ions and then expand the gallery region by appropriate diffusion in the epoxide and curing agent solution: 4,4’-oxydianiline (ODA) was commonly used as an organic modifier [13–16]. ODA was dissolved in 0.01 N HCl solution, and the montmorillonite was then gradually added in stoichiometric proportions and vigorously stirred for 3 h at 60°C. After the treatment, the montmorillonite suspension was repeatedly washed with deionized water. (The filtrate was titrated with 0.1 N $AgNO_3$ until there were no AgCl precipitates, ensuring a complete removal of chloride ions.) The filter cake was placed in a vacuum oven at 80°C for 12 h. The deep blue color powder obtained was termed organoclay [14].

It is widely accepted [17–20] that the polar cationic head group of the modifier molecule preferentially resides at the polar layer surface and the nonpolar aliphatic tail radiates away from the surface of the clay layers. An ion exchange reaction occurs between ammonium salts and inorganic cations in the galleries of MMT to lead to a more hydrophobic MMT. The swelling agent ODA also increases the MMT layer-to-layer spacing. The result of these two changes facilitates the intercalation of epoxy or monomer molecules into MMT interlayers.

2.3. Dispersion of MMT in epoxy matrix

In order to promote the compatibility between organic/inorganic components and improve the homogeneous dispersion of the MMT filler into the epoxy matrix, the organically modified MMT should be further treated with a certain coupling agent. Therefore, the organoclay was thoroughly pre-dispersed in 1% of KBM-403 acetone solution for 30 min. It was then mixed with epoxy resin using a high-shear laboratory homogenizer to achieve homogenized clay particle dispersion. After that, we added stoichiometric 50% dicyandiamide N,N-dimethylformamide (DMF) solution with stirring for another 12 h at a mild shear rate. A highly viscous epoxy/MMT solution was eventually obtained.

2.4. Preparation of epoxy/MMT hybrid composites

The epoxy/MMT hybrid composites were prepared by an *in-situ* cast polymerization approach, in which polymerization takes place after mixing monomer or oligomer with organically modified montmorillonite. The advantage of *in-situ* polymerization is the tethering effect, which enables the clay's surface organic chemical to link with polymer chains during polymerization. The tethering effect not only renders the montmorillonite layer compatible with epoxy, but also delivers more stabilized linkage to epoxy matrix. This is illustrated by its high mechanical properties. The procedure of polymerization is to place the prepared epoxy/MMT solution in a vacuum oven at 60°C for 30 min to de-aerate, then thermally treated consecutively at 80°C for 1 h, and 120°C for 2 h to completely eliminate the acetone and DMF. Finally, the temperature was raised to 180°C and maintained for 3 h to achieve full curing. The MMT filler was incorporated into the epoxy system with variety ratios of 0.01, 0.1, 0.2, 1 and 2% by weight.

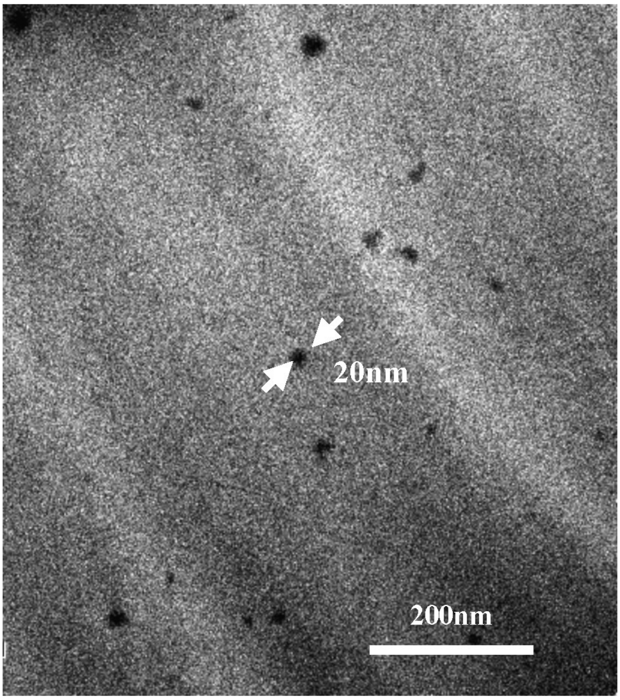
2.5. Characterizations

The dielectric properties of the composite material were investigated using a HP 4284A precision LCR Meter, with 1 MHz frequency and 1 V output voltage. Silver paint was used to ensure good electrical contacts on samples of typical dimensions. Thin sections of 15 nm thick samples were obtained using a RMC MT-XL ultra microtome. TEM studies were performed on a JEOL JEM-2010 microscope operating at an acceleration voltage of 120 kV. The intensity of electron beam should be minimized in order to prevent degradation of the sample. The differential scanning calorimetric (DSC) curves were recorded on a Perkin-Elmer DSC7 under the protection of N_2 with a heating rate of 20°C/min. The thermal gravimetric curves were measured on a Netzch TGA/DSC under N_2 flow. The temperature range was 50–700°C with a heating rate of 10°C/min. The coefficient of thermal expansion (CTE) and T_g were measured with a Perkin-Elmer thermal mechanical analyzer (TMA-7). The temperature range used was from 30 to 200°C and the heating rate was 10°C/min. Before being measured, the samples were pretreated to 200°C for 20 min to eliminate residual stress. The stress–strain curves of the epoxy/MMT composite films were recorded on an MTS 812 universal tester at room temperature, at a drawing rate of 0.7 mm/min. Moisture absorption measurements of the epoxy/MMT composites were carried out in a humidity chamber, entirely immersed in distilled water for 24 hours at 25 ± 1.1°C and 85% relative humidity.

3. RESULTS AND DISCUSSION

3.1. Result of dispersion of MMT in the epoxy matrix

The status of clay partial dispersion in the epoxy matrix and composite structure can be characterised and verified by transmission electron microscopy. Figures 2(a)



(a)

Figure 2. TEM micrograph the ultrathin-section of fully cured epoxy/MMT composite film containing: (a) 0.1 wt%, (b) 1 wt% MMT.

and 2(b) are TEM micrographs of the ultrathin-section of epoxy/MMT composite consisting of 0.1 wt% and 1 wt% MMT. The dark shape represents the MMT particles while the grey background represents the epoxy matrix. The TEM micrograph indicated that MMT filler dispersed in the epoxy matrix homogeneously in morphology with an average size around 20 nm. Figure 2(b) shows the presence of a few black agglomerates at higher clay loading. However, it is still within the acceptable micro-domains level.

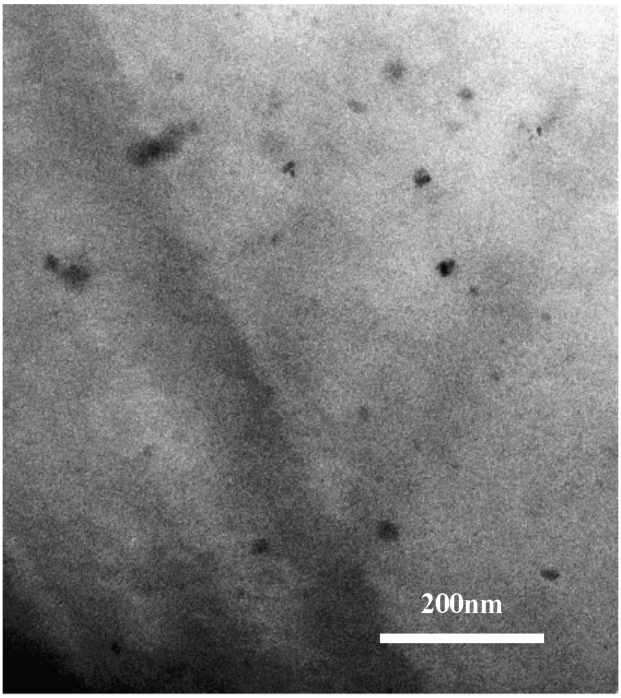
3.2. Dielectric properties of epoxy/MMT composites

The dielectric constant can be determined by equation (1):

$$D_k = \frac{Ct}{0.225A}, \tag{1}$$

where D_k is the dielectric constant, C is the dielectric capacitance, a function of frequency, A is the area of a 1-inch disc, and t is the effective thickness of the specimens.

The dielectrical study reveals that the incorporation of MMT filler into epoxy significantly reduces (i.e. by up to 36%) the dissipation factor (D_f), with a marginal



(b)

Figure 2. (Continued).

reduction in the dielectric constant (D_k), as shown in Fig. 3. When the MMT content approached 0.2 wt%, the lowest D_k (5.0338) and D_f (0.0163) values for composite were obtained. When the MMT content was below 0.2%, the decrease of both D_f and D_k with each increase of the filler concentration might have been caused by the formation of a more uniform electronic environment surrounding the composites. At relatively lower filler concentrations, MMT layer-rich domains may act as electrical conductivity barriers, hindering chemical shifts with the layer charge. However, at higher filler contents (above 0.2 wt%), the morphology of the system plays a major role, and epoxy-rich domains are larger as a result of the aggregation of MMT when the filler content was high. The electrical conductivity effect of these domains might thus be higher, affecting the dielectric constant and dissipation factors. Therefore, D_f and D_k may exhibit a tendency to increase. In the filler content range we studied, D_f and D_k only leveled off or increased slightly.

3.3. Mechanical properties of epoxy/MMT composites

One of the primary reasons for adding fillers to a polymer is to improve its mechanical performance. Unfortunately, in traditional composites, this often comes at the cost of a substantial reduction in ductility, and sometimes in impact

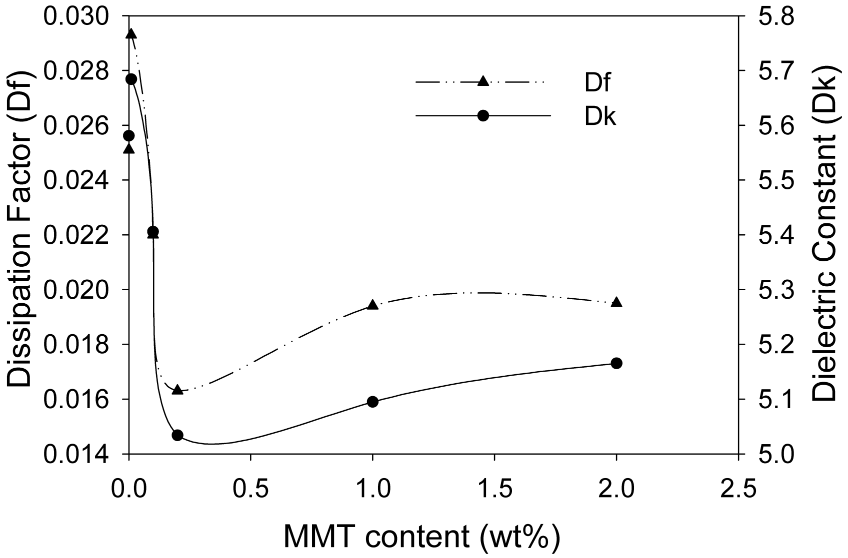
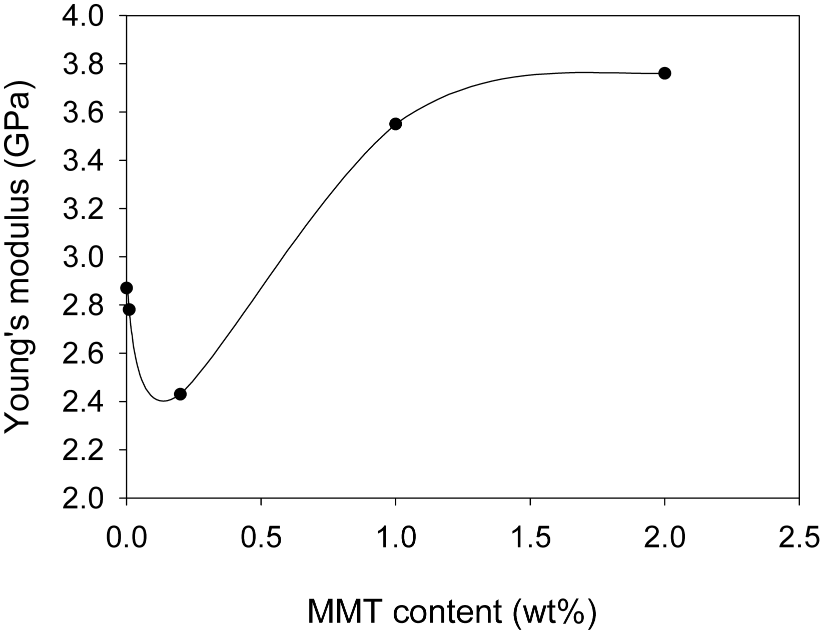


Figure 3. Relationship between the MMT content and the dielectric constant (D_k) and dissipation factor (D_f) of the epoxy/MMT composites.

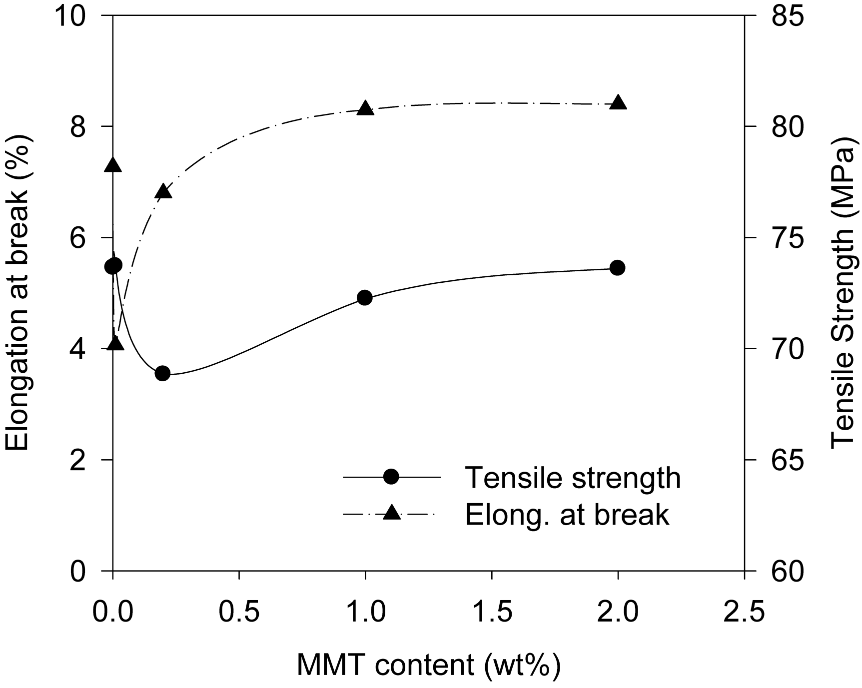
strength, because of stress concentrations caused by the fillers. Well-dispersed MMT fillers, on the other hand, can improve the modulus and strength without sacrificing too much ductility, because the hybrid structure does not create large stress concentrations [14, 21]. However, uniform distribution of the MMT layers is the key to allowing the yielding process to take place throughout the matrix [12].

With the introduction of a small amount of MMT, which has a higher modulus than epoxy matrix, the Young's modulus and tensile strength increase with filler content above 0.2 wt% as expected (Fig. 4). However, both of them decrease slightly with increasing clay concentration below 0.2 wt%. This phenomenon can be explained by the mechanism of mechanical properties of the epoxy/MMT being controlled by two competing factors. The first factor is interaction between MMT and the epoxy, which limited the cooperative motions of the epoxy chain segments. Young's modulus and tensile strength will be increased by increasing the amount of MMT content. The second factor is that the dispersed MMT particles may generate a crack or cracks resulting from the fracture of the composite, which causes a stress concentration effect resulting in lower tensile strength. Therefore, these two competing effects contributed to a minimum point for Young's modulus and tensile strength, although these are still within the acceptable range for PCB application [22].

By contrast, no obvious change is observed in the elongation at break, even when a slight decrease is measured in the full filler content range when compared with the unfilled system. Since montmorillonite clay is rigid, almost all of the elongation comes from the polymer matrix, and the measured elongation of the composites is lower than the actual elongation of the pure epoxy. It can be concluded that the effect



(a)



(b)

Figure 4. Relationship between the MMT content and composite mechanical properties: (a) Young's modulus (b) Elongation at break and Tensile strength.

of MMT is in general more dominant in the elongation at break behaviour. On the other hand, the reduced segmental movement of epoxy matrix with the introduction of MMT and the expected extent of intercalation of polymer chain into the MMT layer would also lead to an increase in glass transition temperature, T_g. This result was consistent with the TMA measurement for the epoxy/MMT composite in Fig. 5.

Weaker interfacial interaction will occur at higher filler content due to agglomeration of the clay particles. The expectation is that the strength would increase up to a certain clay concentration and start decreasing thereafter. An objective of future research is to determine the optimum reinforcement MMT concentration that results in maximized hybrid composite stiffness and strength.

3.4. Thermal properties of epoxy/MMT composites

The interaction of the polymer with MMT particles significantly changes the polymer mobility and relaxation dynamics; for instance, polymer chain may intercalate into the MMT layer. Without the help of confinement, the T_g can be increased if the polymer is tightly bound to the filler. On the other hand, the T_g can decrease if the interaction between the filler and the matrix is weak. Figure 5 shows that an increase in the filler content will increase the glass transition temperature by up to 20°C compared to the unfilled epoxy. Therefore, we expect that modifying the MMT surface and making it compatible with the matrix will help to further increase the composite glass transition temperature.

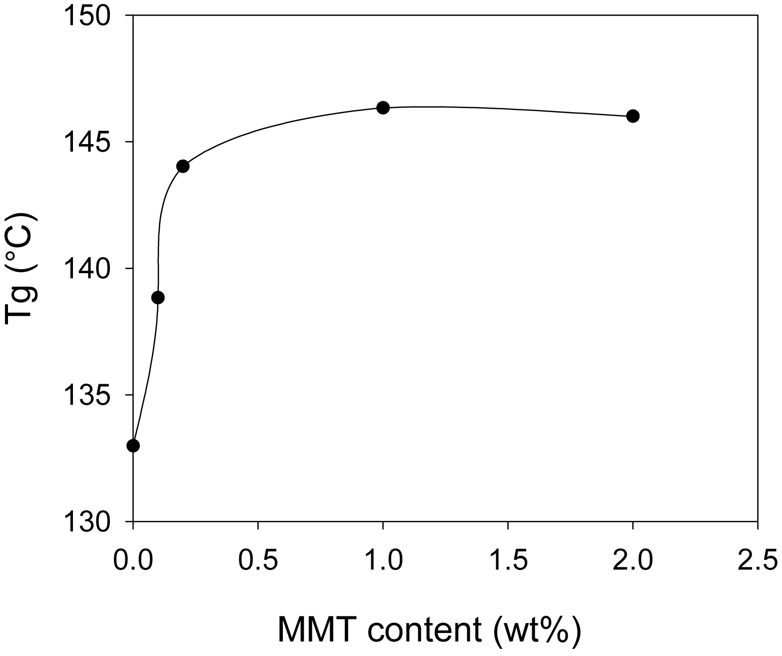
MMT clay is a low thermal-expansion silicate, and significantly influences the CTE of epoxy/MMT composites. From the TMA measurement results, the overall trend for CTE decreases significantly with increases in the filler content, as expected. However, the filler content has a greater impact on composite rubber status (above T_g) than on glass status (below T_g), which decrease up to 39% and 14%, respectively. This may be caused by the MMT layer structure, which exhibits a greater barrier effect in rubber status than in glass status to hinder the movement of the epoxy chain, leading to a more stable polymer matrix. The onset decomposition point for the composite shift to higher temperatures obtained from thermal gravimetric analysis (TGA) tests further confirms that layer structure hinders the evaporation of the small molecules generated in the thermal decomposition (Fig. 6). Enhancements in thermal stability (or size-stability) with MMT filler are desirable for PCB and microelectronic applications.

3.5. Water resistance of epoxy/MMT composites

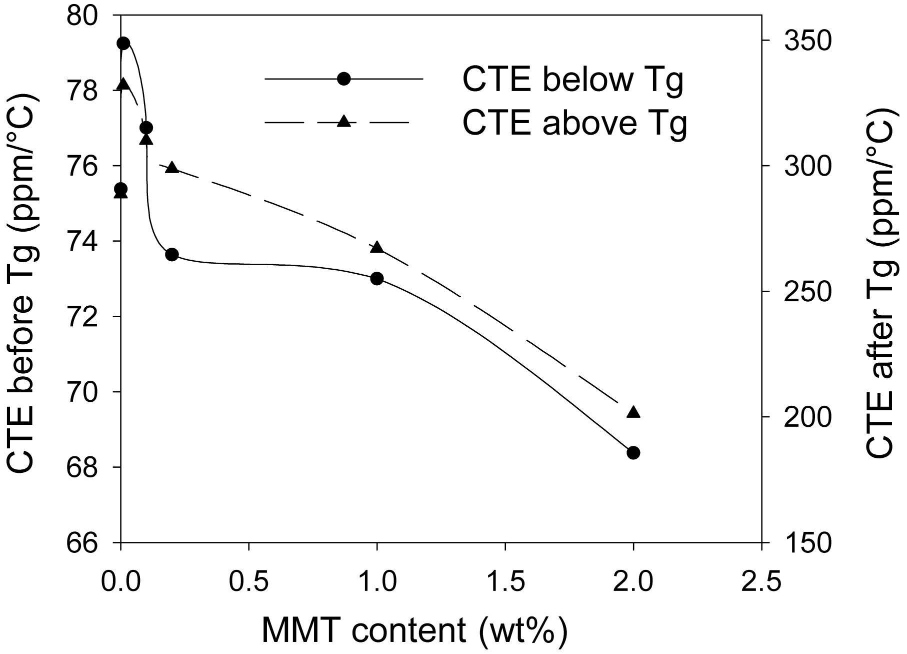
The percentage of moisture absorption was calculated based on equation (2):

$$\text{Moisture absorption } (\%) = \frac{W_\mathrm{m} - W_\mathrm{d}}{W_\mathrm{d}} \times 100\%, \tag{2}$$

where W_m and W_d represent the moisture-absorption weight and the dried weight of the epoxy/MMT composite, respectively.



(a)



(b)

Figure 5. Relationship between the MMT content and (a) T_g, (b) CTE of the epoxy/MMT composites.

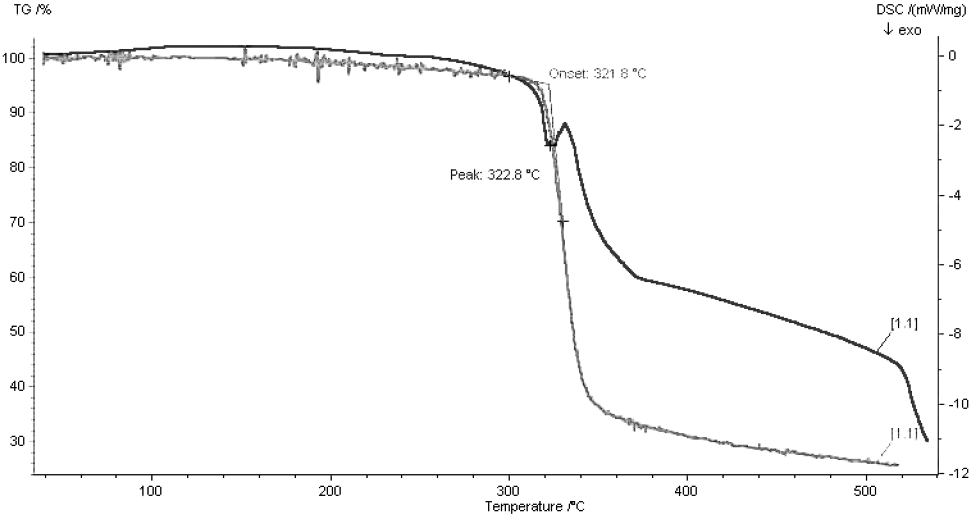


Figure 6. Typical high temperature DSC and TG curves for epoxy/MMT composites (0.01 wt%).

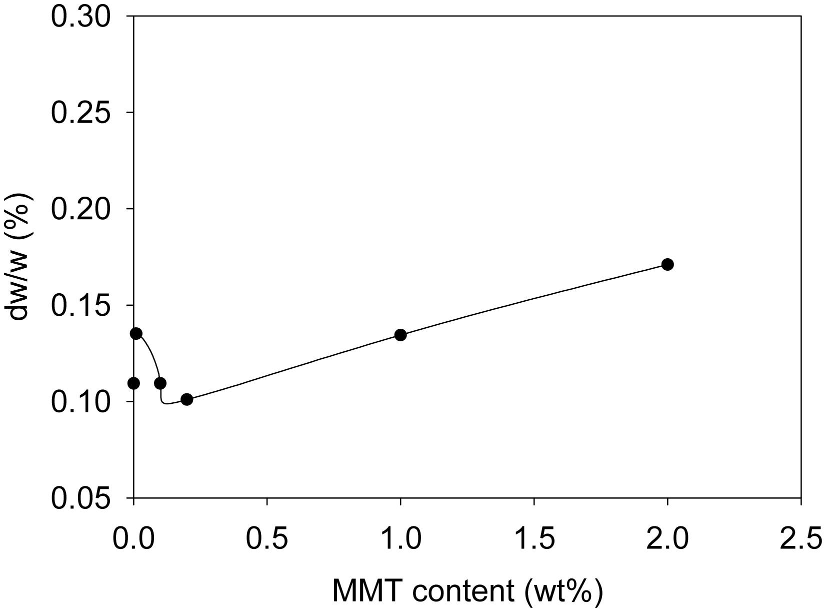


Figure 7. Comparison of moisture absorption with a variety of MMT contents.

From Fig. 7, the introduction of MMT led to a slight decrease in the water uptake when the filler content was below 0.2%. However, the unfilled epoxy also gained quite low moisture absorption (0.109%) compared with the minimum point (0.101%) achieved in the filler content range we studied. This could arise for the following reasons. First, a fortunate aspect of the *in-situ* polymerization method is the potential to graft the polymer onto the particle surface, which may lead to a chain orientation to create a strong interaction domain [6, 16]. A polymer chain in close proximity to the MMT filler might have caused the formation of a "bound polymer", which was either physisorbed or chemisorbed and therefore restricted the water uptake. Second, the possible optimized aspect ratio of the MMT layers possessed excellent barrier properties, and in particular the intercalated structure of the MMT layers might have maximized the available surface area of the reinforcing phase. However, when the filler concentration further increases above 0.2 wt%, the "bound polymer" structure may lead to filler particle aggregation occurring.

3.6. Comparison with PCB raw materials

The mechanical properties, water adsorption, and dielectric strength of the epoxy-MMT composites show the optimum properties at 0.2 wt% MMT. This achieved best water resistant and dielectric properties, while still maintaining acceptable mechanical properties for PCB applications. However, further modelling study is needed to reveal the structure–properties relationship at molecular level, which would enable development and optimization of the epoxy/MMT system.

Table 1 compares the MMT-filled epoxy properties with the PCB raw materials pure epoxy and glass fiber.

Filling with MMT obviously improves the thermal and mechanical properties of PCB-based epoxy resin, such as glass transition temperature, coefficient of thermal expansion and Young's modulus, when these are compared with unfilled systems. It also achieves quite a low dissipation factor, which may be beneficial for high-frequency PCB applications. As glass fiber possesses extremely low D_k, D_f and CTE, we expect that it is possible to further improve those properties once epoxy/MMT is blended with glass fiber in the industrial application of PCBs.

4. CONCLUSIONS

- MMT-filled brominated epoxy hybrid composites have been successfully prepared by *in-situ* polymerization by a careful choice of fabrication process. The dielectrical study reveals that the incorporation of MMT filler into epoxy signif-

Table 1.
Comparison of the various properties with PCB raw materials

Materials	Dielectric constant D_k (1 MHz)	Dissipation factor D_f (1 MHz)	T_g (°C)	Coefficient of thermal expansion (ppm/°C)		Water absorption (%)	Young's modulus (GPa)
				($<T_g$)	($>T_g$)		
Epoxy/MMT	5.03∼5.58	0.016∼0.019	130∼146	68∼79	200∼300	0.10∼0.17	2.78∼3.76
Pure epoxy	5.58	0.025	133	75.3	288.7	0.11	2.87
Glass fiber	3.56∼5.80	0.001∼0.005	–	1.7∼2.8		–	51.6∼72.3

icantly reduces (i.e. by up to 36%) the dissipation factor (D_f), with a marginal reduction in the dielectric constant (D_k). When the MMT content approached 0.2 wt%, minimum low D_k (5.0338) and D_f (0.0163) composites were obtained.

- Epoxy/MMT composites exhibit better thermo-mechanical properties. In this condition of good thermal stability, the introduction of a small amount MMT also led to improvements in the glass transition temperature, a marked decrease in the coefficient of thermal expansion at different temperature ranges, particularly below T_g, and a slight improvement in mechanical properties such as Young's modulus. We also observed a negligible tendency but good resistance to moisture absorption compared with unmodified epoxy resin systems.
- From the point of view of PCB base materials application, further development and optimization of the epoxy/MMT system requires the development and application of models for the prediction of core properties of interest in industrial applications, such as D_k, D_f, T_g, and CTE. Micromechanics modelling of matrix–filler interaction behaviour are needed in future work, which will help to provide a deeper understanding of the mechanism of clay dispersion.

Acknowledgement

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