

CENTRIFUGAL PREPARATION OF HIGH FILLER CONTENT EPOXY–CALCITE/TALC–NANOSILICA HYBRID COMPOSITES

N. Daud^{1,2*} and R. A. Shanks¹

¹*School of Applied Sciences, RMIT University, Box 2476 GPO, Melbourne, VIC 3001, Australia*

²*Chemistry Department, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, Tanjung Malim, Perak, Malaysia*

**norlinda.daud@student.rmit.edu.au*

Keywords: nano-material, biomimetic, sedimentation, epoxy resin.

Abstract

High-filler content composites are difficult to prepare in synthetic systems because of the high viscosity of the resin-filler dispersion, need to compact irregular filler particles into minimum volume and entrapment of air that gives voids in the cured composite. The aim of this investigation was to employ planetary–centrifugal dispersion to mix, disperse and degas high filler content of calcite/talc-nanosilica epoxy suspensions. The combination of nano- and micro-particles allowed more complete space filling within the composite. The high calcite-nanosilica epoxy composite was uniformly dispersed with relatively few minute voids. In contrast, talc platelets were randomly oriented and resisted compaction leading to decline in glass transition temperature at higher filler loading. The high-density composites were dimensionally stable with enhanced modulus, flexural strength and thermal stability.

1 Introduction

Natural composites, such as nacre, demonstrate a remarkably high hardness and strength given its composition of about 95 %·w/w of brittle, inorganic CaCO₃ tablets and ~5 %·w/w of biopolymers [1]. The excellent mechanical properties of nacre originate from its unique layered microstructure in which the organic layers and aragonite tablets form an ordered brick-and-mortar structure. In synthetic systems, fabrication of high volume fraction mineral composites usually results in a non-uniform reinforcement distribution and porosity in the matrix. Typically, compound with a high content of filler are difficult to process due to the high viscosity of the resin-filler suspension and entrapment of air often creates voids in the cured composite [2].

In this work, planetary-centrifugal dispersion was employed in the preparation of hybrid high filler composite to overcome the high viscosity of the resin-filler suspension during processing. The objective was to develop planetary mixing and centrifugal sedimentation of the fillers to enhance packing efficiency and produce layering of fillers, while producing high modulus and high strength composites. A filler close packing technique is quite important in preparing a high-filler content composite to enhance compaction [2]. Hence, a combination of nano- and micro- sized fillers particles are essential to give efficient space filling. Preliminary dispersion of nano-silica produced a viscous, gel-like resin suspension. The addition of calcite/talc increased the viscosity and was difficult to process under normal processing

conditions. However, under extreme centripetal force caused by rotation at 2000-2200 min⁻¹, the high viscosity resin suspension behaved like a lower viscosity substance and more readily mixed with the micron sized fillers. Flow under high centrifugal force was enhanced so that mixing occurred by rotation of the container. Superimposed upon the centripetal force was an opposed planetary rotation that provides the shear for mixing and dispersion. Degassing was promoted when the planetary motion was minimal at the start and finish of the dispersion program. A non-rotation cycle compacted and degassed the dispersion by centrifugal sedimentation.

2 Experimental

2.1 Materials

The epoxy prepolymer used in this study was diglycidyl ether bisphenol-A (DGEBA) (DER 332) with epoxide equivalent weight of 176 g/eq. A stoichiometric amount of diethylenetriamine (DETA) with amine equivalent weight of 20.6 g/eq was used as a curing agent. Both the epoxy resin and the curing agent were obtained from Sigma-Aldrich. High-surface-area fumed silica (Aerosil 300), SiO₂, with primary particle size of 7 nm and average surface area of 300 m²g⁻¹ was supplied by Degussa. Talc (T63A) with average surface area of 3.2 m²g⁻¹ was supplied by Orica Chemicals. Calcium carbonate, CaCO₃, with average particle size of 1.7 μm was obtained from Omya. CaCO₃ used was in the calcite form, as verified by wide-angle X-ray diffraction pattern. All fillers were dried in an oven prior to use.

2.2 Composite Preparation

The aim of this investigation was to employ planetary-centrifugal dispersion to mix, disperse and degas high-calcite/talc content, nano-silica containing epoxy resin suspensions. Hence, composites with different total amount of fillers were prepared as shown in Table 1. Silica particles were pre-dispersed in epoxy resin with the aid of ultrasonication before addition of calcite/talc. Preliminary dispersion of nano-silica produced a viscous, gel-like resin suspension. Addition of calcite/talc further increased the viscosity and was difficult to process under normal processing condition. However, extreme centripetal force from rotation at 2000-2200 min⁻¹ causes the highly viscous gel-like resin suspension to flow, as would a low viscosity liquid under quasi-quiescent conditions. After 20 min of mixing, dispersing and degassing, a stoichiometric amount of curing agent was added and mixing under centripetal force was continued for another 5 min. Degassing is promoted when the planetary motion was minimal at the start and finish of the dispersion program. The dispersion was left to cure at room temperature for 3 d and post-cure at 100 °C and 150 °C for 3 h.

Composites	Epoxy [%·w/w]	Nano-silica [%·w/w]	CaCO ₃ [%·w/w]	Talc [%·w/w]
100E	100	-	-	-
60E-1S-39C	60	1	39	-
40E-1S-59C	40	1	59	-
20E-1S-79C	20	1	79	-
60E-1S-39T	60	1	-	39
40E-1S-59T	40	1	-	59
20E-1S-79T	20	1	-	79

Table 1. Composite formulation and identification of abbreviation for epoxy composites.

2.3 Characterisation

The composites were characterized by thermogravimetry (TGA), dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM). The thermal decomposition temperature was determined by TGA using Perkin-Elmer Pyris 1 thermogravimetric analyzer.

Samples of about 3.0 mg were heated from 50 to 850 °C at a heating rate of 10 K·min⁻¹. The purging gas (flow rate: 20 mL·min⁻¹) was nitrogen between 50-700 °C, then it was changed to air at 700 °C. The DMA was performed with a Perkin-Elmer DMA8000, using a single cantilever bending mode, at a frequency of 1 Hz and oscillation amplitude of 0.05 mm. The specimens were heated from 30 °C to 200 °C at 2 K·min⁻¹. Surface morphology of the fractured composites were examined under scanning electron microscope (SEM) FEI Nova NanoSEM (2007). The sample was prepared by submerging it in liquid nitrogen for 2 min and breaking it transversely with a rapid impact.

3 Results and Discussion

3.1 Morphology

The morphology of nanosilica-calcite and nanosilica-talc epoxy composites are shown in Figure 1(a) and 1(b) respectively. The SEM micrograph in Figure 1(a) confirms uniform distribution of the nanosilica and calcite particles in the hybrid composite. The surface fracture of the composite showed that the filler was well dispersed and embedded in the epoxy polymer resin. Nanosilica is expected to fill spaces between the micro-size filler particles as illustrated in Figure 2(a). Judging from the surface morphology, ultrasonication and planetary-centrifugal dispersion led to an effective dispersion of fillers in polymer matrix. In contrast, talc platelets were randomly dispersed in the epoxy resin giving voids of various sizes due to bridging of the talc platelets. Bonding strength at interfaces between the filler particles and the epoxy resin seemed to be lower for the talc-nanosilica epoxy composite.

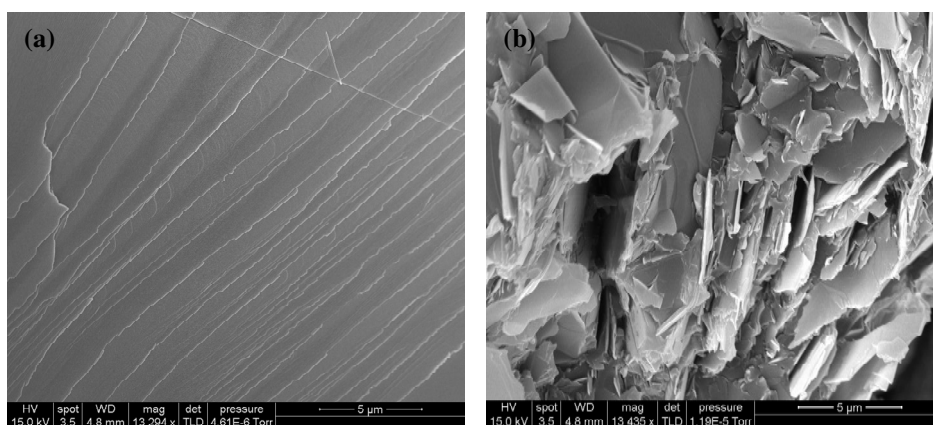


Figure 1. SEM images of the fracture surfaces of (a) 20E-1S-79C; and (b) 20E-1S-79T.

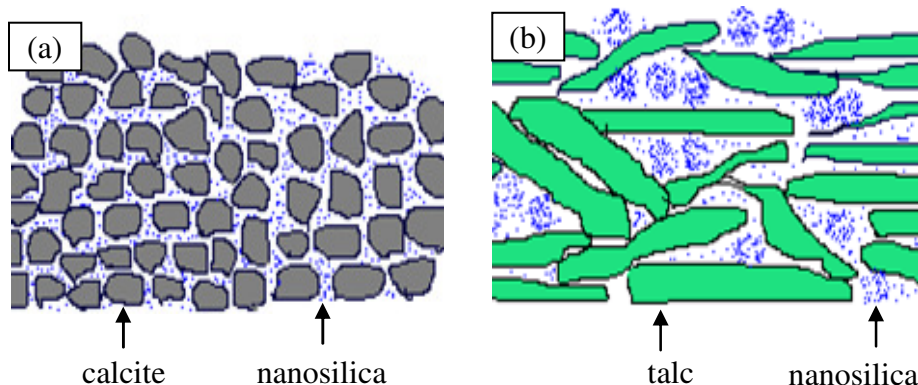


Figure 2. Schematic drawing of dispersion (a) nanosilica-calcite; and (b) nanosilica-talc.

3.2 Thermogravimetry

The thermal stability and final composition of epoxy hybrid composites were measured with TGA, as shown in Figure 3 and the data are summarized in Table 2. Thermal degradation of pure epoxy (100E) in a DGEBA-DETA system under nitrogen atmosphere ($T = 50-700\text{ }^{\circ}\text{C}$) was a one-stage reaction. The major evolved gases of epoxy resin formed during the early thermal degradation were bisphenol-A and higher phenol compounds. The bisphenol-A originated from the scission of the C-O bond of the ether group and it could break into a variety of small molecules such as phenol and isopropyl phenol with increasing the temperature [3]. The degradation process proceeded through reactions of isomerisation, intramolecular cyclisation, chain transfer and other reactions that involve the radicals formed in the initial stages of degradation. At temperature $> 700\text{ }^{\circ}\text{C}$, the carbon residue was burned off as the purge gas flowing over the sample was switched to air. No residue remained at $850\text{ }^{\circ}\text{C}$.

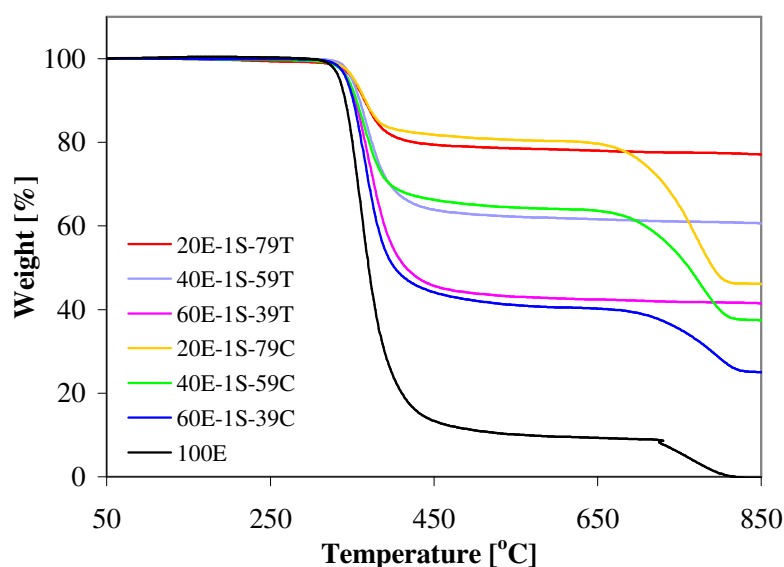


Figure 3. TGA curves of epoxy and its composites.

Sample	Filler content [%·w/w]	Residue [%·w/w]	$T_{a,10\%}$ [$^{\circ}\text{C}$]	Max rate [%/min]
100E	0	0	341	17
60E-1S-39C	36.0	25.0	351	12
40E-1S-59C	61.0	37.4	355	7.2
20E-1S-79C	78.7	46.0	365	4.2
60E-1S-39T	41.4	41.4	352	10
40E-1S-59T	60.5	60.5	359	6.8
20E-1S-79T	77.0	77.0	365	3.5

Table 2. Composition and thermal stability of epoxy composites.

The pattern of the thermogravimetry curves of the epoxy hybrid composites was similar to the pattern of the pure epoxy, since the thermal weight loss of the hybrid composites was coming from the organic epoxy resin component. However, composites containing calcite showed a two-stage reaction, in which the second weight loss at temperature $> 600\text{ }^{\circ}\text{C}$ was due to the loss of CO_2 gas from the CaCO_3 filler. The residue remained at $850\text{ }^{\circ}\text{C}$ in the hybrid composites mainly contained inorganic fillers: silica and talc/CaO. Therefore, the residual

yield was used to determine the composition of filler in the epoxy-talc composite. But for the epoxy-calcite hybrid, the filler composition was calculated based on the first weight loss of the composite and the residual yield of pure epoxy in inert atmosphere. The maximum amount of filler loading in the epoxy-calcite and epoxy-talc nanosilica hybrid composites were 78.7 % and 77.0 % respectively (Table 2).

Thermal stability properties of the pure epoxy and its composites were measured as the decomposition at temperature of 10 % weight loss ($T_{d, 10\%}$) and maximum degradation rate (max rate). All hybrid composites showed enhanced thermal stability relative to the pure epoxy resin (Table 2). $T_{d, 10\%}$ of hybrids was significantly higher than pure epoxy and this temperature increased with the contents of inorganic filler. In addition, the maximum degradation rate decreased considerably with filler loading. For example, the value is reduced by 29 % for 60E-1S-39C and 41 % for 60E-1S-39T. The high thermal stability observed for the hybrid composites is considered to be related to the tortuous path of degradation products, which is dependent upon the distribution of fillers particles in the resin and the interaction between fillers and polymer matrix. The fillers were considered to be acting as a thermal barrier, thereby protecting the polymer from degradation.

3.2 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical behaviour of pure epoxy and its hybrid composites were studied by DMA. The temperature dependence of storage modulus (E'), loss modulus (E'') and $\tan \delta$ are shown in Figures 4-6 and the data are summarized in Table 3. Results showed that the storage modulus of the polymer and its hybrid composites decreased gradually before it declined rapidly as it was heated through the glass transition region (Figure 4). As expected, the storage modulus of the polymer increased significantly with filler loading. Fillers introduce a rigid phase in the polymer, and the bulk modulus of the composite is a function of the filler volume fraction. Hence, the storage modulus of the composites was increased as the amount of filler increased.

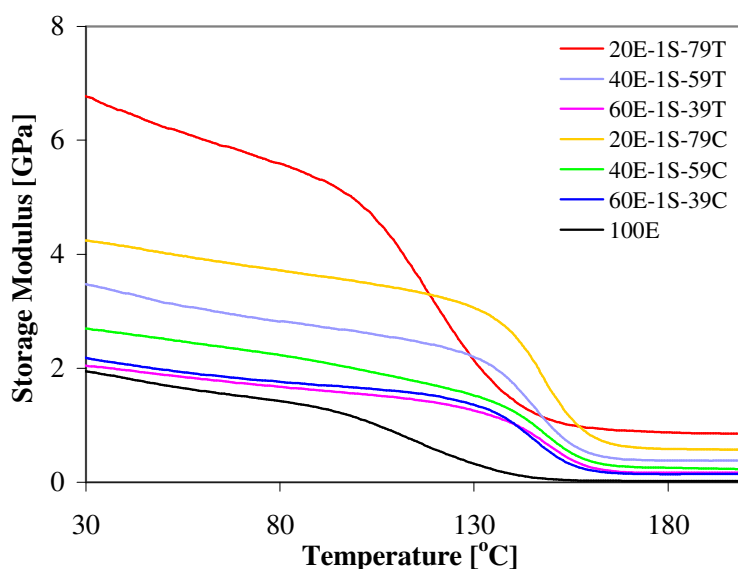


Figure 4. Storage modulus (E') of pure epoxy and its composites.

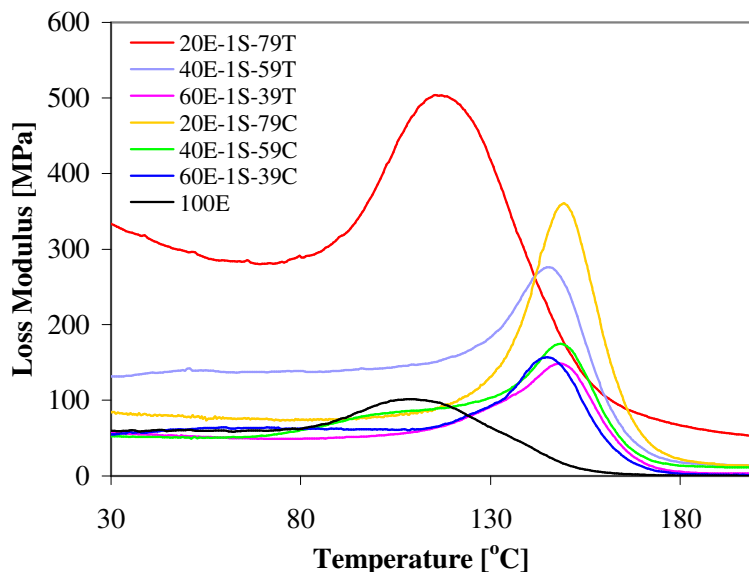


Figure 5. Loss modulus (E'') of pure epoxy and its composites.

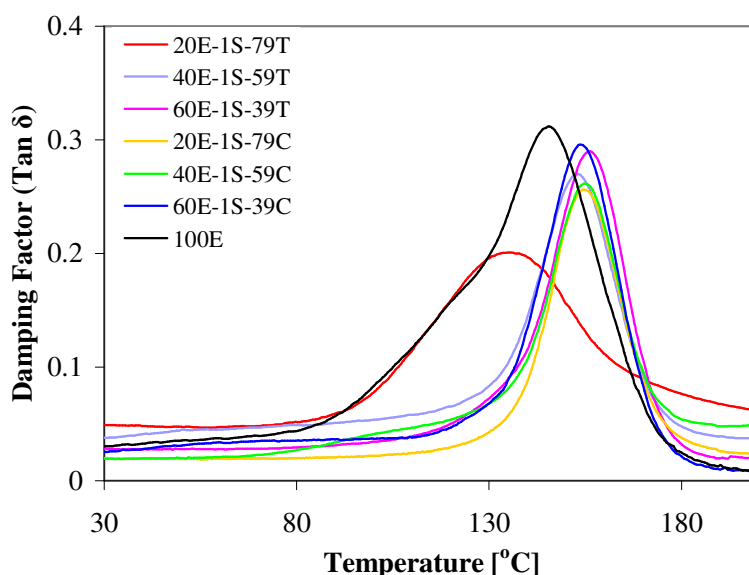


Figure 6. $\tan \delta$ of pure epoxy and its composites.

For DMA study, glass-transition temperature (T_g) can be measured using three parameters, which are E' onset (occurs at the lowest temperature and relates to mechanical failure), E'' peak and $\tan \delta$ peak. The most commonly used parameter is T_g taken from the peak of $\tan \delta$ versus T plot. This is a good measure of the ‘leather-like’ midpoint between glassy and rubbery states of a polymer. Alternatively, T_g from the peak temperature in the E'' versus T plot is more closely related to the physical property changes attributed to the glass transition in plastics. It reflects molecular processes and agrees with the concept of T_g as the temperature at the onset of segmental motion [4]. In Table 3, T_g ($\tan \delta$) is the temperature corresponding to the peak of the $\tan \delta$ versus T curve and T_g (E'') is the glass-transition temperature at the maximum of E'' versus T plot. T_g measured at the E'' curve is always lower than those corresponding to the $\tan \delta$ peak. Generally, in composite system, the addition of rigid fillers in matrix made it difficult to move the polymer chain and therefore damping

decreased and T_g shifted to higher temperature. Interestingly, in this study, the effect of filler loading on T_g of the hybrid composites showed two different patterns depending on the type of fillers. Addition of calcite significantly enhanced T_g of the epoxy composite and T_g gradually increased with filler loading. The decrease in damping and the increase in T_g with filler loading imply that the epoxy chain mobility was restricted due to interaction of epoxy and filler particles.

Sample	E' [GPa]	$T_g (E'')$ [°C]	$T_g (\tan \delta)$ [°C]
100E	1.94	109.8	145.6
60E-1S-39C	2.18	145.1	153.6
40E-1S-59C	2.69	148.5	154.6
20E-1S-79C	4.24	149.3	154.7
60E-1S-39T	2.05	148.3	156.2
40E-1S-59T	3.47	145.6	152.9
20E-1S-79T	6.77	115.3	135.0

Table 3. E' and T_g derived from E'' and $\tan \delta$ of pure epoxy and its hybrid composites.

In contrast, the effect of filler loading in the talc-epoxy system demonstrated a different T_g trend. Addition of 40 % filler (60E-1S-39T) increased T_g tremendously, but T_g declined significantly at higher talc loading. T_g value for 60E-1S-39T composite was 148.3 °C, which is similar to the 60 % filler content in calcite-epoxy nanocomposite (40E-1S-59C). The initial increase in T_g followed by a decline in T_g with a higher filler content, as observed in epoxy-nanosilica-talc composite, has been reported for other nanofiller-epoxy composites [5,6]. The depression in T_g at higher nanofiller loading is directly related to the increased in the interfacial area between the fillers and the polymer matrix. If the interaction between the polymer matrix and the nanofiller is strong, the mobility of the chain can be effectively restricted, therefore T_g increases. However, at higher nanofiller loadings, it is difficult to disperse the nanofiller and thus, agglomeration of the nanofiller easily occurs, which results in a weak interaction between the nanofiller and the polymer [5].

In this study, however, the amount of nanosilica was the same for all calcite and talc epoxy composites. Therefore, we expect the different trend in T_g to be mainly due to the different dimensions of the filler particles, which affect the arrangement of filler in compacted hybrid composites. Calcite particles have a granular shape, which allow them to arrange closely together in compacted epoxy composites. Nanosilica is expected to fill the empty space between the micro-size calcite particles, as illustrated in Figure 2(a). As a result, the epoxy chain mobility was restricted due to optimum cohesion in the compacted composite hence the glass transition is completed at a higher temperature. Conversely, due to the flake-like shape of the talc particles, it was difficult to arrange or stack the filler in a hybrid composite especially at higher filler loading. A random orientation of talc platelets in the epoxy composite is illustrated in Figure 2(b) and this distribution was verified by SEM image (Figure 1b). The random arrangement of the talc platelets gave voids and consequently bonding strength at interfaces between the talc particles and the epoxy was poor (Figure 1b). The poor bonding strength implies that more free volume exists at the filler-polymer interface, thus, it cannot effectively confine the mobility of the epoxy chain. As a result, the polymer chains show a relatively high mobility at high talc loading, leading to the decline in T_g .

The results showed that the storage modulus of the composites was directly increased with filler loading (Figure 4). This contradicts with the previous explanation regarding the T_g pattern in the talc-epoxy hybrid composite, because the greater damping would correspond to the lower filler content resulting from a greater elasticity. However, this could be justified based on the fact that, when a material is under a sinusoidal stress, the probability of finding a filled zone inside a composite increases with content of filler, thus causing an increase in storage modulus and the material would become less deformable [7].

4 Conclusion

High-calcite/talc-nanosilica epoxy composites have been prepared by a planetary-centrifugal dispersion process and the combination of nano- and micro- fillers allowed more efficient space filling within the composite. High density gave a ceramic like texture to the composites and they were dimensionally stable with enhanced modulus, flexural strength and thermal stability. The high-calcite epoxy nanocomposites were uniformly dispersed with relatively few minute voids, resulting from the high centripetal shear force. However, due to the flake-like shape of the talc particles, the distribution of talc was random, leaving relatively large voids in the composite.

References

- [1] Meyers M.A., Chen P.Y., Lin A.Y., Seki Y. Biological materials: structure and mechanical properties. *Progress in Materials Science*, **53**, pp. 1–206 (2008).
- [2] Kozako M., Okazaki Y., Hikita M. *Preparation and evaluation of epoxy composite insulating materials toward high thermal conductivity* in Proceeding of 2010 International Conference on Solid Dielectrics, Potsdam, Germany, (2010).
- [3] Deng B.L., Chiu W.Y., Lin K.F., Fuh M.R. Thermal degradation behavior of epoxy resin blended with propyl ester phosphazene. *Journal of Applied Polymer Science*, **81**, pp. 1161-1174 (2001).
- [4] Turi, E.A. *Thermal Characterization of Polymeric Materials*. Academic Press, New York, **1**, pp. 980 (1997).
- [5] Yung K.C., Zhu B.L., Yue T.M., Xie C.S. Effect of the Filler Size and Content on the Thermomechanical Properties of Particulate Aluminium Nitride Filled Epoxy Composites. *Journal of Applied Polymer Science*, **116**, pp. 225–236 (2010).
- [6] Sun Y., Zhang Z., Moon K.S., Wong C.P. Glass transition and relaxation behavior of epoxy nanocomposites. *Journal of Polymer Science Part B: Polymer Physics*, **42**, pp. 3849–3858 (2004).
- [7] Nunez L., Nunez M.R, Villanueva M., Castro A., Rial B. Study of the epoxy system BADGE (n=0)/1,2-DCH/CaCO₃ Filler by DMA and DSC. *Journal of Applied Polymer Science*, **85**, pp. 366–370 (2002).