Thermal Stability and Decomposition Study of Epoxy/Clay Nanocomposites
(Kestabilan Terma dan Kajian Penguraian Epoksi/Lempung Terubah Nano)

S. Dzuhri, N.Y. Yuhana* & M. Khairulazfar

ABSTRACT

This study utilized the incorporation of nanoparticle filler into an epoxy system to study the effect of different nanosized montmorillonite (MMT) fillers on the thermal stability and mechanical properties of epoxy. The sample was prepared using diglycidyl ether of bisphenol A (DGEBA) with different surface treatments of montmorillonite filler by mechanical stirring. The results of thermal stability and mechanical properties of epoxy/clay system obtained from thermal gravimetric analyzer (TGA), universal testing machine (UTM) and scanning electron microscopy (SEM) were discussed. With the same amount of filler introduced into the system, different thermal stability of epoxy composite can be observed. Bentonite, which contained other contaminant components, can downgrade the enhanced properties of the filler.

Keywords: Cloisite; epoxy; montmorillonite; nanocomposite; thermal stability

ABSTRAK

Kajian ini dijalankan bagi mengaplikasikan pengisi bersaiz nano ke dalam sistem epoksi yang memberi kesan terhadap kestabilan terma dan ciri-ciri mekanikalnya. Sampel yang digunakan adalah daripada epoksi diglicidil eter bisfenol A (DGEBA) dengan pengisi montmorilonit yang berbeza olahan permukaan melalui kaedah pengadukan mekanikal. Hasil kestabilan terma dan ciri-ciri mekanikal sistem epoksi/lempung diperoleh daripada alat analisis gravimetri terma (TGA), mesin ujian universal dan mikroskopi elektron imbasan (SEM) dibincangkan dengan teliti. Dengan jumlah pengisi yang sama, hasil kestabilan terma yang berbeza dapat diperoleh. Bentonit yang mengandungi bendasing dapat menurunkan ciri-ciri penambah kekuatan pengisi tersebut.

Kata kunci: Epoksi; kestabilan terma; kloisit; montmorilonit; terubah nano

INTRODUCTION

The incorporation of nanometer-sized fillers in polymer matrices to improve thermal, mechanical, barrier, electrical and optical properties has gained interest recently. The most common types of polymer nanocomposites incorporate silicate, carbon or metal oxide nanoparticles. In polymer nanocomposites, a small amount of silicate nanoparticles (less than 5 wt. %) is commonly used. The types of silicate used include natural silicate (montmorillonite and hectorite) and synthetic silicate (laponite, magadiite and flourohectorite). However, the most commonly used and studied nanoclay is montmorillonite (MMT), a layered aluminosilicate. An interesting feature of the layered silicates is their high aspect ratio. MMT is also available in the market as organically modified clay. This facilitates the dispersion of the layers in a polymer matrix at nanometer scale.

The arrangement of silicate particles in a polymer matrix can be found as microsized agglomerates, as in the case of common fillers, or as intercalated or exfoliated particles (Aijuan & Liang 2002; Becker & Simon 2005; Carrasco & Pagès 2008). Normally, the three structures could be observed in a single polymer/ silicate nanocomposite. Hence, in order to study the polymer nanocomposite morphology, both microstructure and nanostructure must be observed and considered. The most common techniques used are wide angle X-ray diffraction (WAXD), transmission electron microscope (TEM) and scanning electron microscopy (SEM). SEM could also be used to explain the fracture toughness behavior of nanocomposite.

Epoxy/layered silicate nanocomposites exhibit improved thermal, barrier and mechanical properties (Carrasco & Pagès 2008). Table 1 summarizes the research on thermal stability and kinetics of decomposition of epoxy/ clay nanocomposites reported by several researchers.

Based on the Geological Survey Department of Malaysia, there is a bentonite resource in Sabah, Malaysia (Irawan & Samsuri 2007). Bentonite has been commercially used as a flame retardant in plastic material by further purification of the filler content (Cárdenas et al. 2009). Due to the use of bentonite in plastic polymer area, many researchers studied these bentonite properties and tried to maximize the enhancing effect in plastic polymer (Erdemoğlu et al. 2004; Hussin et al. 2011; Ruiz-Hitzky et al. 2011; Sayılkan et al. 2004). Since there is no research regarding nanometer-sized bentonite from Sabah has been reported, hence, the authors has decided to explore its potential as plastic filler in terms of thermal exposure and its morphologies in epoxy. The current research

TABLE 1. Current research of epoxy/clay nanocomposites

Systems	Observations
Epoxy/Cloisite 30B	E_a values are higher for binary system compared to neat epoxy (Yuhana et al. 2012)
DGEBA/MMT	The amount of filler (wt %) influenced the E_a value of the system (Aijuan & Liang 2002; Zhou et al. 2007)
DGEBA/DQPB/MMT	The incorporation of nanofiller into 3,5-diamino-*N*-(4-(quinolin-8-yloxy) phenyl) benzamide (DQPB) resulted in the maintained onset temperature of the system but increased the thermal stability of the system (Isik-Gulsac et al. 2003)
DGEBA/Na$^+$	Increased of natural (Na$^+$) filler content increased the mass loss of the system (Tcherbi-Narteh et al. 2013)

reported results on the effects of commercially available montmorillonite and Sabah bentonite (i.e. montmorillonite) in epoxy on the thermal properties of the binary system. In this paper, the thermal decomposition and morphology study of room temperature cured samples have been reported.

EXPERIMENTAL DETAILS

MATERIALS

Bisphenol A diglycidyl ether (187 epoxy equivalent weight, Epikote 828 obtained from Hexion Specialty Chemical Korea) was used as the polymer matrix. Epikure D230, commonly known as Polyetheramine D230 (PEA), which contain alpha-(2-aminomethylethyl)-omega-(2-aminomethylethoxy)-poly(oxy(methyl-1,2-ethanedyl)) with their amine number, amine value, and water content of 461.7 mg KOH/g, 8.23 meq/g and 0.02 wt %, respectively, was used as a curing agent in the system. Different montmorillonite surface-modified layered silicate clay were used as the filler for the system. These include natural montmorillonite (Cloisite Na), montmorillonite with organically-modified surface (Cloisite 30B) using ammonium bis(hydroxyl ethyl) methyl tallow alkyl salt supplied by Southern Clay Products, USA, as well as a pure solid filler known as Sabah bentonite that contained some amount of montmorillonite, quartz, kaolinite and illite.

SAMPLE PREPARATION BY MECHANICAL STIRRING

Epoxy resin was preheated at 60℃ to lower the viscosity so that it was easier for the added clay to disperse and this step was conducted using HTS 1003 heating plate with heating rate of 2℃/min to ensure that the exothermic peak was not achieved. 2 wt % filler was added into 100 parts of epoxy resin based on the thesis reported by Dat (2013) and mixed by mechanical stirring using LH (VELP Scientifica) stirrer with 3 blades at the speed of 50 rpm for 1 h. This speed assisted the clay to break into small particles and helped to increase the clay/epoxy interfaces. The mixture was then added with 32.8 g of PEA curing agent with continuous stirring for 10 min. The obtained pre-polymer was then poured into a stainless steel mold with the dimensions of $100 \times 100 \times 5$ mm and then cured

at room temperature for 1 week. Later, the samples were characterized using several techniques. Different types of filler used in this study are shown in Table 2.

TABLE 2. Weight % of fillers to 100 parts of resin

Type	Component weight (gram)		
	Cloisite Na$^+$	Cloisite 30B	Sabah Bentonite
DGEBA/PEA	0	0	0
DGEBA/Na$^+$/PEA	2	0	0
DGEBA/30B/PEA	0	2	0
DGEBA/Sabah/PEA	0	0	2

CHARACTERIZATION

Thermalgravimetric Analysis (TGA) Characterization of TGA of the samples used a Netzsch model STA 449 and conducted at different rates of 10, 15, 20 and 30℃/min (Table 3). Some of the parameters examined include onset temperature T_{onset}, temperature at the maximum rate of mass loss T_{max} and residual mass percentage. Then, the kinetic rate for the decomposition of the sample was obtained from the plotted graph using the given formula by Flynn-Wall-Ozawa (Gu & Liang 2003):

$$\ln q = -1.052 \frac{E_a}{RT_{max}} + C,$$

where q is the heating rate (℃/min); C is the Doyle's approximation constant; R is the gas constant (0.008324 kJ/mol K); E_a is the activation energy (kJ/mol); and T_{max} is the temperature at the maximum rate of mass loss (℃).

Kissinger equation was also used for comparison purpose, which is given by the equation:

$$\ln \frac{H_r}{T^2} = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) - \ln\left[\frac{ARn(1-\alpha)^{n-1}}{E_a}\right],$$

where, α is the decompose ratio; n is the reaction order; E_a is the activation energy (J/mol); H_r is the heating rate (℃/min); T is the temperature at the maximum rate of mass loss (K); and R is the gas constant (0.008314 kJ/mol K).

From these two equations, the graphs of ln q vs $1/T_{max}$ from Flynn-Wall-Ozawa and ln (H_r / T^2) vs $1/T$ from the Kissinger equation were plotted and analyzed (Chiang et al. 2006).

Scanning Electron Microscopy (SEM) and Energy Disperse X-Ray Analysis (EDX) SEM analysis was carried out when the sample was totally cured after 1 week using a SEM machine model LEO 1550. The sample was break into a small part and the surface was then coated with gold from 90 to 100 Å before it was sent to the SEM machine to increase the conductivity of electron through the surface of the sample surface. SEM analysis provides an activation voltage that change from 2 to 5 kV. Energy disperse X-ray analysis was also carried out using the same machine as SEM analysis. The main focus of EDX analysis is to determine the amount of atomic number that is possible in the system.

FTIR The FTIR spectra of the organoclays dispersed in the system were recorded with a Nicolet model 6700 spectrophotometer with a scanning range from 4000 to 400 cm^{-1}. The spectra were collected at a resolution of 4 cm^{-1} with over 64 scans. The mixed resin was placed into an optical glass cell according to the attenuated total reflectance (ATR) method.

RESULTS AND DISCUSSION

THERMALGRAVIMETRIC ANALYSIS

Figure 1 shows the TGA curves of the systems used. All the systems studied had undergone a single stage thermal degradation that occurred around 200ºC due to elimination of water from the systems. For the temperature around 365ºC and above, the decomposition of the polymer matrix occurred, which degraded the chemical bonds of the epoxy

TABLE 3. Analyzed data from TGA

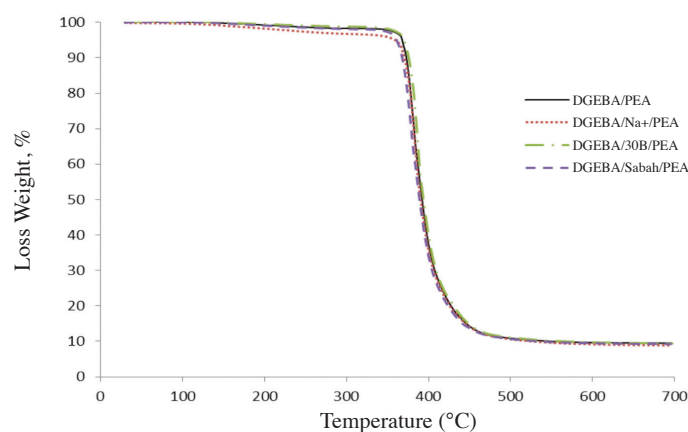| System	Heating rate (ºC/min)	T_{onset} ±0.1ºC	T_{max} ±0.1ºC	Residue (%)
DGEBA/PEA	10	356.4	367.8	10.62
	15	362.7	374.0	8.20
	20	366.7	377.8	7.91
	30	369.9	382.2	9.48
DGEBA/30B/PEA	10	355.9	372.8	8.88
	15	364.5	376.8	5.16
	20	367.4	379.5	6.74
	30	374.7	386.5	9.38
DGEBA/Na$^+$/PEA	10	357.1	374.2	4.97
	15	364.2	375.6	12.44
	20	367.6	379.8	7.78
	30	371.1	383.4	8.79
DGEBA/Sabah/PEA	10	344.6	362.7	9.62
	15	354.2	368.6	8.41
	20	358.3	374.5	8.86
	30	365.4	379.1	9.24

FIGURE 1. TGA curve of the systems

network until the maximum loss was achieved. As shown in Figure 1, the decomposition started to slow down at the temperature around 450ºC due to the blockage of the polymer gallery, which prevented the decomposed material from moving out of the gallery. The relative stability of DGEBA/MMT nanocomposite system was compared according to their initial decomposition temperature as shown in Table 2. DGEBA/PEA was used as the reference. It is already established that the incorporation of filler will increase the thermal stability of the system (Isik-Gulsac et al. 2003). From the result obtained, DGEBA/PEA without filler decomposed polymer matrix at 369.9±0.1ºC at heating rate of 30ºC/min. Meanwhile, DGEBA/30B/PEA decomposed at 374ºC, DGEBA/Na⁺/PEA at 371.9±0.1ºC and DGEBA/Sabah/PEA at 365.4±0.1ºC for heating rate of 30ºC/min. This showed that the incorporation of Sabah bentonite lowered the decomposition temperature of the system due to the presence of other contaminants in the filler. This reason could be proven by the EDX analysis that showed the contents of Sabah bentonite.

The presence of SiO_2, Al_2O_3 and MgO in nanocomposite could enhance thermal stability. Although Sabah bentonite contained material that enhanced thermal stability, however other factors may reduce the decomposition temperature of DGEBA/Sabah/PEA, such as the polymer chain of other components present in Sabah bentonite. Figure 2 shows the derivative (DTGA) graph of the DGEBA/MMT system obtained from TGA. The peak showed in this graph indicated the occurrence of the maximum rate mass loss during the decomposition. In ensuring the stability of the material used, the temperature at this maximum mass loss was required. Once again, the systems that contained Cloisite 30B filler had a higher temperature of the maximum rate of mass loss at 386.5ºC. The incorporation

of chemical organophilic modification on the surface of montmorillonite increased the stability of the composite.

ACTIVATION ENERGY OF EPOXY/CLAY SYSTEM

By using Flynn-Wall-Ozawa method that has been modified by Doyle and Kissinger's method to calculate the kinetic energy of the decomposition process, the graph as shown in Figures 3 and 4 were obtained. The gradient represents the activation energy, E_a. For system with no filler, the activation energy, E_a was 251.05 kJ/mol. Meanwhile, the Ea of 267.69 kJ/mol and 363.11 kJ/mol were obtained for DGEBA/30B/PEA and DGEBA/Na⁺/PEA respectively. In terms of activation energy, Sabah bentonite filler showed the lowest value among other systems (212.03 kJ/mol).

The lowest value obtained for DGEBA/Sabah/PEA was caused by the polymer structure in the matrix, which was the presence of other silicate components such as illite and quartz that produced undesired structure of the system (exfoliated or intercalated). Besides, there were some other factors that affected the activation energy of the system, which was polymer chain. It is known that longer polymer chain is less stable than shorter polymer chain as the energy required to break the bond is lower in long polymer chain than shorter chain. As seen in the EDX analysis, the presence of other contents in Sabah bentonite resulted in a lower crosslink density of the polymer. Therefore, it led to longer polymer chain for the system compared with others due to the space of crosslink area in the composite. This result is similar with those reported by Arridge and Speake (1972) and Grillet et al. (1991) in their study of curing and crosslink behavior of epoxy, which showed different crosslink densities when there were unwanted components and contaminants in
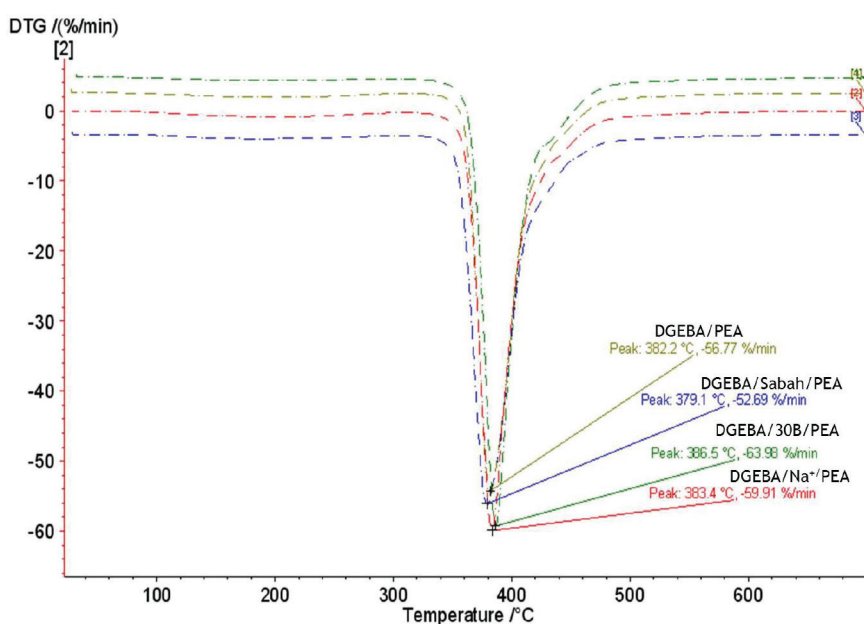

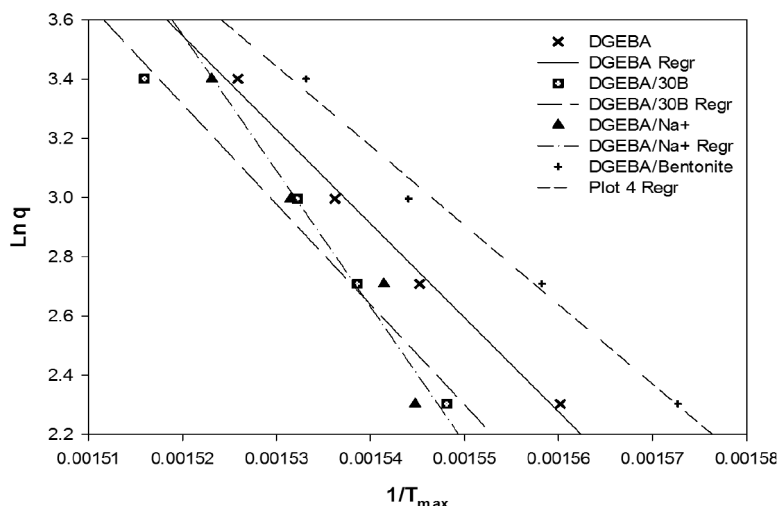FIGURE 2. DTG curves for DGEBA/MMT system
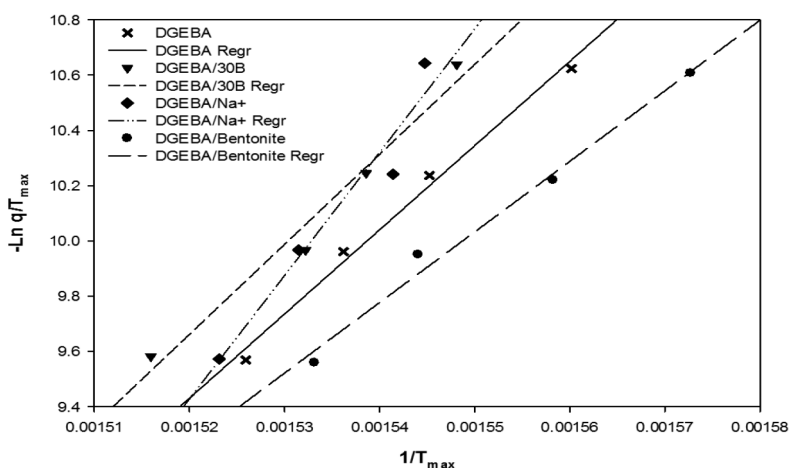
FIGURE 3. Flynn-Wall-Ozawa plot

FIGURE 4. Kissinger plot

the matrix. In DGEBA/30B/PEA, the surface treatment with ammonium salt produced more organophilic Cloisite 30B, which eased the binding of DGEBA resin and nanofiller surface it, hence making it a longer chain. The summary of activation energy required by the system to decompose is presented by the bar chart in Figure 5.

SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY DISPERSE X-RAY ANALYSIS (EDX)

Every sample should be coated with gold to increase the electron conductivity through the surface of the sample. Figure 6 shows the SEM result for each sample. As can be seen in Figure 6(a), DGEBA/PEA with no filler showed clear and smooth crack propagation for 100× magnification (Scale 20 μm). Figure 6(b), 6(c) and 6(d) shows the aggregation of nanofiller for DGEBA/30B/ PEA, DGEBA/Na+/PEA and DGEBA/Sabah/PEA samples, respectively. The aggregated structure of the filler on the sample was obviously seen. This result influenced the

thermal stability of epoxy. From Figure 6(b) with 500× magnification (scale of 10 μm), aggregated particles were randomly arranged in every space, forming exfoliated or intercalated structure. The same result was obtained for DGEBA/Na+/PEA sample, which clearly showed the aggregated particles with 5000× magnification (scale of 1 μm). Meanwhile, DGEBA/Sabah/PEA sample at 10000× magnification (scale of 200 nm) showed the exfoliated filler in the structure. All the results can be probably proven by TEM analysis (not shown) to ensure their exfoliated or intercalated form.

The component in the system can be determined using EDX analysis. The amount of atomic number and mass percentage are summarized in Table 4 for each filler type. As expected from the EDX analysis, Sabah bentonite contained other components such as calcium, magnesium, ferum, zinc and bromine. Carbon and oxygen atoms obtained were from the epoxy, whereas silicon and aluminium atoms obtained were from the montmorillonite
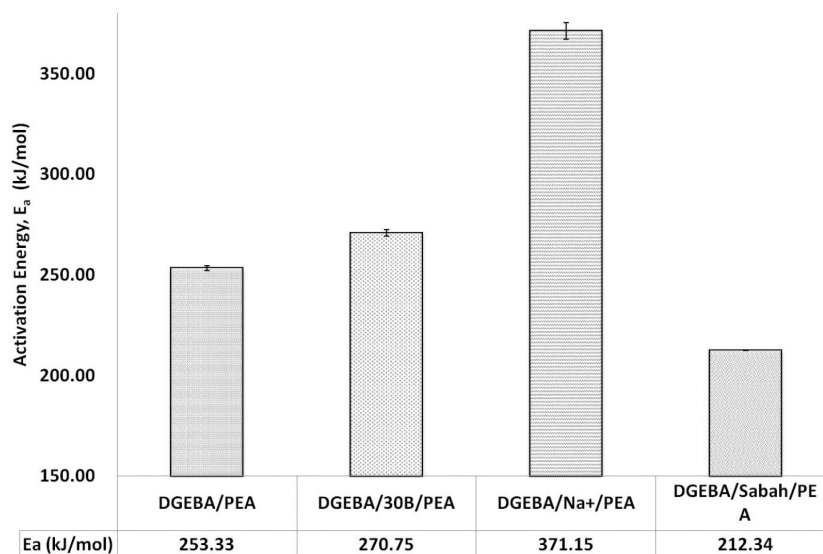
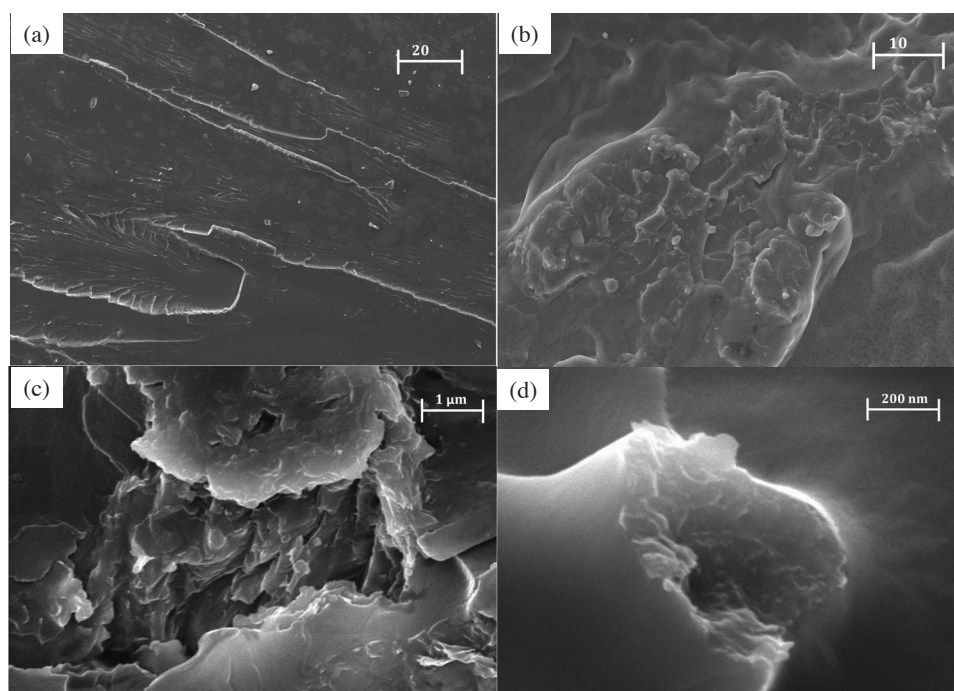FIGURE 5. Activation energy of different nanofiller contents

	DGEBA/PEA	DGEBA/30B/PEA	DGEBA/Na+/PEA	DGEBA/Sabah/PEA
Ea (kJ/mol)	253.33	270.75	371.15	212.34

FIGURE 6. SEM analysis for a) DGEBA/PEA, b) DGEBA/30B/PEA, c) DGEBA/Na$^+$/PEA and d) DGEBA/Sabah/PEA

filler. Some of the Na$^+$ in the DGEBA/Na$^+$/PEA originated from the natural montmorillonite did not go through surface modification. The increase of thermal stability of DGEBA/MMT system due to the presence of aluminium and silicon was proven by the EDX result.

FTIR

There were differences for FTIR spectra of DGEBA/MMT for samples containing Cloisite Na$^+$ and Cloisite 30 fillers at different range of wavelength numbers from 4000 to 3600 cm^{-1}, 3000 to 2800 cm^{-1}, 2400 to 2300 cm^{-1} and in the range of 1800 to 1700 cm^{-1} for DGEBA/Sabah/PEA. The increase of peak at 2873 cm^{-1} band was due to the bending of OH bond in carboxylic acid group. Meanwhile, the bands at 1500 and 1601 cm^{-1} represented the asymmetric stretching of benzene ring. Since the sample contained montmorillonite, the increase of peak at 2357 cm^{-1} band could be related to the presence of P-H bond that was represented by the band at 2400 cm^{-1}, which demonstrated the variety change of the peak. At 2967 cm^{-1} the band represented the peak of CH stretching bond from alkane RCH$_2$CH$_3$ group. It was related to the stretching of CH$_2$ and CH$_3$ bands at 1455 cm^{-1} with rocking of C-H at 1361 cm^{-1} band. Lastly, the

TABLE 4. Component composition in DGEBA/MMT systems

| Type	Component	Mass (%)	Atomic (%)
DGEBA/PEA	Carbon	66.40	72.47
	Oxygen	33.60	27.53
DGEBA/30B/PEA	Carbon	78.98	84.72
	Oxygen	17.76	14.23
	Silicon	2.54	1.16
	Aluminium	0.72	0.34
DGEBA/Na$^+$/PEA	Carbon	32.02	41.35
	Oxygen	50.10	48.57
	Silicon	12.16	6.72
	Aluminium	4.97	2.86
	Sodium	0.75	0.51
DGEBA/Sabah/PEA	Carbon	41.89	52.09
	Oxygen	44.64	41.67
	Silicon	8.08	4.30
	Aluminium	2.19	1.21
	Calcium	0.11	0.04
	Ferum	1.18	0.31
	Zinc	0.44	0.10
	Bromine	1.46	0.27
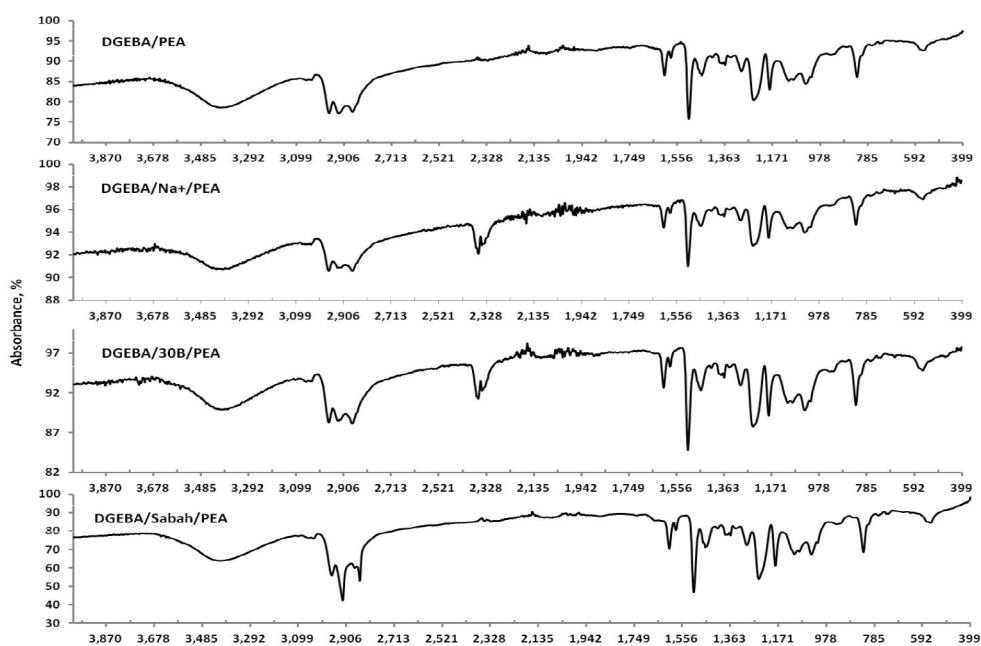
FIGURE 7. FTIR spectra for DGEBA/MMT systems

analysis showed that there was a C-Br bond stretching related to alkyl halide CH$_2$X (C-H Wag) at 1246 cm^{-1} band as presented in Figure 7.

CONCLUSION

From the research, in can be concluded that the incorporation of nanofiller into the polymer matrix changes the thermal stability of the system. The introduction of thermally stable materials, which are aluminium and silicon, into the system can enhance the exposure of material to high temperature. The use of different types of montmorillonite can also change the thermal stability through several factors, which are polymer chain length and the dispersion of the structure, which are related to the sample preparation method. This experiment shows that sample DGEBA/Na$^+$/PEA requires higher energy to break the polymer bond to decompose. Although the initial decompose temperature of DGEBA/Na$^+$/PEA occurred earlier than DGEBA/30B/PEA, the breaking of the polymer bond took longer time than other samples. It can be concluded that Cloisite Na$^+$ filler produces stable system than others. Meanwhile, the system

containing Sabah bentonite filler gives the lowest thermal stability due to the presence of impurities in its structure. However, it may have other advantages that need to be discovered in further studies, such as mechanical properties and water absorption.

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