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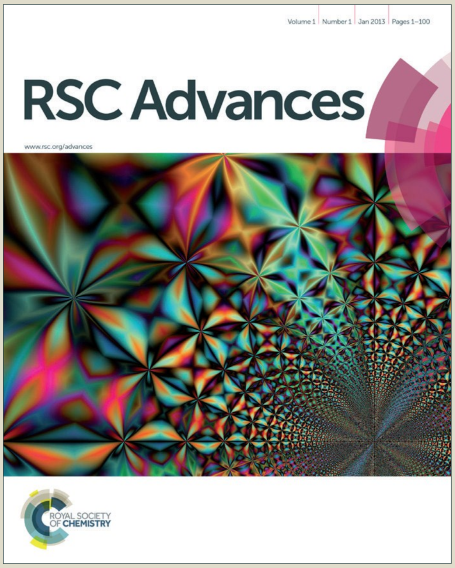

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Novolac Cured Epoxy Resin/ Fullerenes modified clay Composites: Applied in Copper Clad Laminate

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Abstract

Functionalized inorganic layered material based on modification system composed by Benzalkoniumchloride-N-methyl pryrrolidine-Fullerene (BEN-(C_{60}-O)), were designed and fabricated in this paper, aiming at developing high performance fire retardant epoxy composites without halogen and phosphorous. BEN-(C_{60}-O) modifier used to utilize enlarge the inter-layer distance of layered material. Based on functionalization of montmorillonite type clay (CL88), a series of the novolac cured epoxy resin/BEN-(C_{60}-O)-CL88 composites have been developed. The structural morphology and dispersion properties of composites were investigated by wide-angle X-ray diffraction, and transmission electron microscopy. Composite reached V0 rating in UL-94 vertical burning testing. Furthermore, the incorporation of BEN-(C_{60}-O)-CL88 into novolac cured epoxy led to a significant reduction in peak heat release rate, total heat release and total smoke production, which exhibited superior fire resistance over its counterparts at the equivalent filler loading. Additionally, composite shows good thermo mechanical properties than that of novolac cured epoxy resin.

Keywords: Inorganic layered material, Fullerene, Montmorillonite, Burning test, Epoxy resin.

1. Introduction

In recent years Epoxy based polymer nano sized composites have been focused on development of special properties such as mechanical, [1-3] thermal, [4] gas barrier properties, [5] flammability resistance [6-7]. Among all properties fire-resistance is one of

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the most important properties. Epoxy has a fatal drawback of high flammability, which has severely restricted the application fields required a remarkable flame-retardant grade. Thus, to improve the fire resistance that needs to pay much attention that to the general electronic products and printed circuit board (PCB). Since many years various phosphorus, [8-9] silicon, [10-12] boron-containing compounds, [13] halogenated compounds have been incorporated into epoxy resins to improve the flame retardancy. Although halogenated-epoxy compounds are used in PCB to improve the thermal and fire resistant properties, [14-16,6] but this kind of material produces large amount of smoke and toxic material like dioxin during combustion. The arising of nano sized composite technology has provided a revolutionary new solution to flame retardant polymer materials which need to be replaced as far as the environmental pollution is concerned. Novolac cured resins have been widely used for the purpose of impregnating the fiberglass to prepare the high frequency printed circuit boards (HFPCB).

The preparation of polymer/layered inorganic nano sized composites (PLN) extensively studied past two decades that of clay material with C_{60}, both of which have attracted considerable attention to enhance the thermal stabilities and flame retardancy of polymer matrix with a small amount [17] of layered inorganic material. In consideration structure of fullerene, it may act as a barrier slowing down heat release and hindering transfer of combustion gases into the flame zone and energy feedback as a layered inorganic compound. Accordingly, we suppose that fullerene can be used as layered nanofillers into polymer matrix to enhance thermal stability and flame retardancy. Recently, Fullerenes-clay composites have been synthesized by D. Gournis et. al. in which the water-soluble fuller-pyrrolidines were intercalated clay through ion exchange process.[18]

For the preparation of nano sized composites, the compatibility between polymer and inorganic layered material must be considered. In our continuous research regarding polymer/layered material composites, [5, 19-23] we has been reporting novolac cured epoxy resin/modified clay composites which is applied in copper clad laminate. In order to improve properties of copper clad laminates, first, the CL88 was treated by bifunctional modifiers i.e. mixture of benzalkonium chloride (BEN) and fullerene-pyrollidine (C_{60}-O).

Further novolac cured epoxy resin/BEN-(C_{60}-O)-CL88 different weight% composites are successfully prepared by *in situ* cross-linking polymerization method. Among all epoxy composites novolac cured epoxy resin/BEN-(C_{60}-O)-CL88 3wt% was applied to make copper clad laminate (CCL). Prepregs were prepared by impregnating five woven fiberglass sheets with a pure novolac cured epoxy resin and also with the novolac cured epoxy resin/BEN-(C_{60}-O)-CL88 3wt% composites as described in the experimental section. The properties like water uptake, adhesion, coefficient of thermal expansion (CTE), and thermal stability measured also compared with pure novolac cured epoxy resin.

2 Experimental

2.1 Materials

CL88 (trade name CO_2), was supplied from CHINA GLAZE GROUP, with the cation exchange capacity (CEC) of 200 meq/100g of clay and it's chemical formula is $[Ca_{0.37}Na_{1.28}(Al_{1.98}\ Fe_{2.02})Si_8O_{20}(OH)_4 \cdot 1.46\ H_2O]$. Fullerene ($C_{60}$) was purchased from (AdvaNanoBio CO., Ltd. 75 wt%). Benzalkoniumchloride (BEN) used as a compatibilizing agent was purchased from Showa Chemicals. The Novolac cured epoxy resin and solvent propylene glycol methyl ether (PM) were purchased from ITEQ Cooperation (Taiwan). N-methyl glycine (sarcrosine) and paraformaldehyde were purchased from (TRADE Mark Lot. 95 wt %) and (Aldrich 95%), respectively. Solvents were used as received without further purification. A is bisphenol-A novolac resin and B is phenolic novolac cure resin. These two types of resin are mixed together which is so called novolac cured epoxy resin used in this study.

2.2 Preparation of water soluble N-methyl pryrrolidine-C_{60} (C_{60}-O) [16]

2.416g (27.6 mmol) of N-methyl glycine (sarcrosine) and 2.07g (69 mmol) of paraformaldehyde were added to 10g (13.8 mmol) fullerene (C_{60}) containing 500ml toluene solution. The resulting mixture was heated for 2h at 120~130°C and then the solvent was removed in vacuum. N-methyl pryrrolidine-C_{60} (C_{60}-O) was formed.

2.3 Preparations of modified clay BEN-(C_{60}-O)-CL88

In the preparation of BEN-(C_{60}-O)-CL88, first, 4g of clays in 200ml of distilled water kept in stirring for overnight at room temperature. Consequently in another beaker, 20ml of 0.2M HCl aqueous solution was added to 3.196g of N-methyl pryrrolidine-C_{60} (C_{60}-O) and 14.6g of BEN, resulting solution was stirred for 24h at room temperature. The mixture solution was stirred, centrifuged, and washed with deionized double-distilled water several times to remove the chloride ion and finally freeze dried.

2.4 Preparations of BEN-(C_{60}-O)-CL88/novolac cured epoxy composites

First, propylene glycol methyl ether (PM) in a ratio of clay/solvent = 0.1, was added separately to the various weight fraction of modified clay (1wt%, 3wt%, or 5wt %) and resulting mixture was stirred overnight. Then the in each case required amount of novolac resins was added to each solution and stirred for another 24h. The solution was outgases in a vacuum oven for a period time. All samples were cured at 190℃ for 3h.

2.5 Preparations of copper-clad laminate

Among all epoxy composites, 3wt% modified clay incorporated epoxy chose to prepare copper-clad laminates. The typical procedure is as follows, Modified clay (3wt %) of 15g was first mixed with the solvent propylene glycol methyl ether (PM) in a ratio of clay/solvent = 0.1 and stirred for 24h. Then the novolac epoxy resins of 8.07g were added to the modified clay stirred for another 24h. Then the solution was soaked in the five pieces of glass fiber sheet separately and dried in oven at 170°C for about 3 min. followed by stacking these sheets together. Then the stacked fiber glass sheets were hot pressed at high temperature (~ 190°C) and pressure (~300 to 400 Psi).

2.6 Characterization of layered materials/novolac cured epoxy composites

After curing all the slurries at 190°C for 3h, samples make it in the thickness, length, and width within 2.5, 40, and 25 mm, respectively. Wild-angle X-ray diffraction (WAXD) patterns of the samples were recorded by a PANalytical, PW3040/60 X'Pert Pro with Cu K_α radiation (45 kV, 40 mA) and wavelength λ= 1.54 Å. The scan angle covered $2° < 2\theta < 80°$for clays and composites at a scan speed of $3°\text{min}^{-1}$. Thermo-gravimetric analyzer

(TGA, Thermal Analysis, and TA Q50) was used to measure the amount of modifying agent intercalated into the clay layers and decomposed temperature of composites. Thermogravimetric analysis (TGA) was carried out using SII TG/DTA6200 thermo-analyzer instrument at a linear heating rate of 10°C/min under a nitrogen flow. The dynamic mechanical analysis (DMA) measurements were performed with a TA-Q800 instrument in the air at a scanning range of 30°C to 250°C with a heating rate of 3°C/min. The detailed vision of the morphology and microstructures of the composites dispersion of clay were characterized by using the transmission electron microscopy (TEM JEM2010, 200 KV, and JEOL). Finally, limiting oxygen index (LOI) test was carried out according to ASTM D2863 and Peak heat release rate (PHRR) by using cone calorimeters (Atlas Technology Corp. CONE 2 instrument). UL94 test is carried out by ASTM D3801 method.

2.7 Characterization of novolac cured epoxy resin/clay composites in copper clad laminates

Physical and mechanical properties of different weight % of modified clay containing epoxy composite we have been characterized. It has been observed that the material doping with 3wt% of modified clay into the epoxy polymer shows the excellent physical and mechanical properties. Therefore, we expected that these composites could have been applied in copper clad laminates. We measured the important properties of copper clad laminates (CCL). These are as follows:

2.8 Water uptake

The CCL was cut into 2 inch in the width and length. The sheet was then dried in oven at 70^{o}C to remove the water if any in the sheet followed by measuring the weight. Then it was kept in the pressure cooker containing water and heated at 120^{o}C for 3h. Then weight of CCL was measured and the difference of weight is the amount of water uptake. The same procedure was followed for all other composites and pure novolac cured epoxy resin to get water uptake value and then compared with the water uptake value with pure novolac cured epoxy resin.

2.9 Dipping

The same width and length of CCL, as taken in the determination of water uptake, was suspended in the solder bath at 288^{o}C temperature for 10 min. The surface of CCL was checked about one time per minute. If there is no blister on surface over 10 min, the CCL pass the test.

2.10 Adhesion

After final stage both side of CCL was covered with copper-foil. The peel strength between the surface of copper clad laminate and copper-foil is measured by using Shimadzu AGS 500 G tester with a load cell of 500g. The CCL was then etched in 15 mm in width and 100mm in length and the copper foil was pulled out to separate it from the CCL and the tensile strength was measured. The operation condition is 50.8 mm/min. The same process was applied in the case of pure novolac cured epoxy resin and all other composites and compared with the storage module of pure novolac cured epoxy resin.

2.11 Coefficient of thermal expansion (CTE)

Thermomechanical analysis (TMA) is one of the important characterization techniques in the field of thermal analysis. In the TMA technique, a number of different probe configurations are offered in order to optimize the test conditions for a specific sample and/or application. The most commonly used TMA probe is the expansion probe. This probe rests on the surface of the test specimen under low loading conditions. As the sample expands, during heating, the probe is pushed up and the resulting expansion of the sample is measured. The apparatus used in this study is a Perkin-Elmer TMA7 equipped with classical expansion quartz probe. Its weight is fixed at 50 mN and the displacement sensibility is 50 nm. The thermal calibration of the instrument was performed with zinc and indium. The heating rate was 10°C/min. The CCL samples of both pure novolac cured epoxy resin and the novolac cured epoxy resin/modified clay (3wt%) composites were cut into (ca. 5×5×5 mm) in length, width and thickness and dried before measurement.

Results and discussion

3.1 Characterization of fullerene and modified clay

To prove that the interlayer spacing of the clay was indeed expanded by the introduction of C_{60}-O, we employed X-ray diffraction to determine the d_{001} spacing. The characterization of C_{60}-O and modified clay determined by wide-angle powder X-ray diffraction (WAXD). Figure 1 (A) shows the WAXD of powder C_{60} and C_{60}-O. In Figure 1(A), the new peak observed at 2θ =19.57° is (211) phase of the N-methyl pryrrolidine. The d-spacing of pristine CL88 is about 12.63 Å, but when CL88 was intercalated with the mixture of N-methyl pryrrolidine-C_{60} (C_{60}-O) and BEN, the d-spacing is increased to about 19.81 Å as shown in Figure 1(B). The variation of d-spacing is caused by the orientation of the C_{60}-O and BEN, of which the theoretical molecular sizes is 7~7.5 Å and 13~ 24 Å, respectively. The thickness of brucite-like clay sheet is 2.54nm and average diameter of CL88 is 500-600nm. C_{60}-O and BEN structures are schematically representation in Figure 2.

FT-IR spectra of pure C_{60} and modified C_{60} shown in Figure 3 (A), the bands appeared at 3445 and 2918 cm^{-1} are due to free water and $–CH_2$- asymmetric stretching frequency for C_{60}. The vibrational bands above ~1000cm^{-1} are predominantly due to displacements tangential to the C_{60} surface. The medium band appeared at 2931 cm^{-1} and weak band at 2768 cm^{-1} in the modified C_{60} (C_{60}-O) are assigned to $\upsilon_{(-CH2)}$ and $\upsilon_{(N-CH3)}$, respectively. Raman spectroscopy has been used to evaluate the effect of the modifier on the properties of the C_{60} being used. In Figure 3 (B), the Raman spectrum of a C_{60} and C_{60}-O shows, Except for the partial contribution of the background signal, both the C_{60} samples exhibit similar D-band (~1,300 cm^{-1}) and G-band (~1,600 cm^{-1}) peaks, which are associated with disordered and fullerene carbon, respectively. The D-band/G-band peak intensity ratio of C_{60} and C_{60}-O are 2.529 and 4.420 respectively, it is indicating that additional disorder is introduced during the modification process.

The thermal stability of pristine CL88 and the modified CL88 has been investigated and the important results presented in Table 1. The decomposition temperature of pure CL88 is 450°C. Weight loss observed at 230°C in the TGA curve of modified-CL88 is due to loss of crystalline water and decomposition of BEN. The decomposition temperature of C_{60}-O is ~340°C. Figure 4 shows the 5% decomposition temperature (T_{5d}) of C_{60}-O is increased to about 390°C after intercalation. This is the evidence of the intercalation of C_{60}-O into the clay layer. The above results reveal that the modified clay is successfully synthesized. TGA not only measure the thermal stability of modified clays but also determine the amount of modifying agent intercalated into the clay layer and the result shows that the intercalated amount of BEN is 27.09% and that of C_{60}-O is 47.41%.

3.2 Morphology of novolac cured epoxy resin modified clay composite

The pure novolac cured epoxy resin and novolac cured epoxy nano sized composites containing CL88-(C_{60}-O)-BEN 1, 3 and 5wt% morphology was confirmed by XRD and TEM, results are shown in Figure 5, 6. XRD patterns of pure novolac cured epoxy resin shows two broad peaks at $2\theta = \sim 4.4°$ and 19.5°. After incorporation of 3wt% and 5% of CL88-C_{60}-O-BEN in the novolac cured epoxy, the characteristic peak of clay completely disappeared, this is evidence that the clay is well dispersed in the novolac cured epoxy polymer matrices. However, XRD patterns cannot be considered as conclusive evidence of monolayer exfoliation because they detect average diffractions from the overall X-ray irradiated sample area. Therefore, TEM is the best way to describe the morphologies of composites. Among all samples we choose 3wt% composite, the dispersion of clay in novolac cured epoxy composites shown in Figure 6 which indicates mostly intercalated and partly exfoliated morphology. The dark black spot represents the fullerene.

3.3 Solution Gel Time Measurement

Table 1 shows the solution gel (SG) time of the slurries as the precursor of novolac cured epoxy resin/CL88-(C_{60}-O)-BEN composites with 3wt% of modified clay. The solution gel time for pure epoxy is longer than 1,500 seconds. SG time is decreased to 262.2 seconds when 3wt% of modified clay containing epoxy resin. SG time longer than 1,500 seconds is defined as non-reactive while the shorter SG time indicates good reactivity. This is because the incorporation of layered material in the epoxy polymer affects the cross linking reaction i.e, the reaction between the layered material and epoxy resin become fast that decreases the SG time.

3.4 Thermal stability of epoxy composite

The thermal stability of the functionalized BEN-(C_{60}-O)-CL88 and BEN-(C_{60}-O)-CL88 based epoxy composites has been investigated in Figure 7 (A). In Table 1 summarized the 5% weight-reduction temperature (T_{5d}) of pristine pure novolac cured epoxy and novolac cured epoxy composites. It is found that the thermal stability of pristine novolac cure epoxy is 395°C, whereas T_{5d} for novolac cured epoxy/BEN-(C_{60}-O)-CL88 3wt% composites is slightly increased to 398°C. Thermal stability increased due to the introduction of organic structures in the modifiers. The incorporation of the functional BEN-(C_{60}-O)-CL88 led to an increase in the char yield at 800°C. Pure EP has 0% residue at 800°C, whereas epoxy/BEN-(C_{60}-O)-CL88 1wt%, epoxy/BEN-(C_{60}-O)-CL88 3wt%, epoxy/BEN-(C_{60}-O)-CL88 5wt% composites has 0.5, 1.5 and 2.1% residues respectively.

3.5 Mechanical Properties

Differential Scanning Calorimetry (DSC) of pure novolac cured epoxy and novolac cured epoxy/BEN-(C_{60}-O)-CL88 3wt% composite results are summarized in Table 1. DSC thermograms shown in Figure 7 (B) the glass transition temperature (T_g) of pure epoxy is 188.1°C whereas T_g for novolac cured epoxy/BEN-(C_{60}-O)-CL88 3 wt% composites is decreased to 184.2°C. The lower T_g was attributed to the enlarged free volume arising from the interface between fillers and epoxy resin, which provides more space for polymer chain segments to move even at a lower temperature.

The thermomechanical properties of epoxy composites are measured by dynamic mechanical analysis (DMA). Storage module (E') generally increases with increasing the crosslinking density. When the modified clays contain curing agent the storage modulus, E' is increased from 1950.60 to 2186.1Mpa pure novolac cured epoxy and Novolac cured epoxy/BEN-(C_{60}-O)-CL88 3wt% respectively. Also the glass transition temperature (T_g) of composites can be estimated by plotting tan δ versus temperature curves (Figure 7 (C)) from DMA. From the result T_g of pure novolac cured epoxy is higher (194.4°C) than that of the corresponding epoxy composites (197.2°C). This might be due to fact that the clay inhibits the growth of polymer chain and consequently that become short.

3.6 Burning behaviour

The LOI is the minimum percentage of oxygen in an oxygen-nitrogen mixture that will initiate and support for 3 min candle like burning of a polymer sample. The fire-resistance properties of novolac cured epoxy composites are listed in Table 2. From the LOI results it is observed that after incorporation of modified clay in epoxy resin LOI value increased pure epoxy resin and epoxy composite LOI values 22.5 and 30 respectively. Pure epoxy polymer and novolac cured epoxy resin/BEN-(C_{60}-O)-CL88 3wt % composite the total heat released is decreased from 92.01 to 86.45 MJ/m. UL94 test was carried out for both the pure novolac cured epoxy and novolac cured epoxy resin/BEN-(C_{60}-O)-CL88 3wt % composites. The results are summarized in Table 2. The nano sized composites passed the UL94-V1 test. In the case of epoxy composites, the increasing LOI value is due to the incorporation and dispersions of CL88, which provides the layer silicate and the C_{60}-O which contains a number of C=C groups. During the combustion, the pathway to the air into the composites is increased by the layer silicate and the hydroxyl group producing the mist, and we expect that C=C groups acts as a free radical capture. However, it was noted that adding BEN-(C_{60}-O)-CL88 into novolac cured epoxy resulted in a great improvement in fire resistance and the UL-94 V0 rating was achieved in vertical burning test.The excellent improvement of fire-resistance property of these composites used to applied to make a printed circuit board.

Cone calorimeter tests were carried out for measuring the burning behavior of polymeric materials in bench-scale tests. It is found that pure epoxy burnt very rapidly after ignition and the peak heat release rate value is 599.03kWm^{-2}. Compared with pure epoxy, epoxy composites burnt relatively slowly and the peak HRR decreased from 567.77 kW m^{-2}. The improved fire retardancy of epoxy composite led to good dispersion of modified clay in the epoxy matrix; secondly, C_{60} species improved the char yield of epoxy composites during combustion. Pure epoxy have been released a total heat of 92.01 MJm^{-2}, the epoxy composite had released heat 86.45MJ m^{-2}. The significant reduction in THR meant more organic structures in the epoxy resin participated in the carbonization process and kept in the condensed phase, rather than converted to “fuel” in the gas phase. This was also evidenced by the increased char residues.

A coefficient of thermal expansion (CTE) is very important parameters for evaluating the usage stability and reliability of electrical/electronic substrate. It can be easily measured by TMA using the expansion probe. The CTE is a quantitative assessment of the expansion of a material over a temperature interval. The CTE values are measured below T_g value on copper clad laminates containing novolac cured epoxy resin with 3wt% modified clay. The copper clad laminate of pure novolac cured epoxy has CTE value of 62.10 ppm/°C and the CTE value is decreased to 60.60 ppm/°C for novolac cured epoxy/ BEN-(C_{60}-O)-CL88 3wt% composites below T_g (α_1) in the thickness (Z) direction (Table 1). In addition, the water uptake was decreased from 0.34% for pure novolac cured epoxy to 0.26% for composites using BEN-(C_{60}-O)-CL88 as modified clays (Table 1). This result is very desirable especially in the electronic applications wherein water absorption is detrimental to dielectric performance. As per thermal stability, the durable time in 288°C solder bath was significantly increased over 10 min.

3. Conclusion

A series of nano sized composites that are composed of novolac cured epoxy/modified-fullerenes-clay (BEN-(C_{60}-O)-CL88) has been synthesized and characterized by WAXD, TGA, DMA and TEM. Due to the introduction of BEN-(C_{60}-O)-CL88 moiety, the obtained thermosets had high T_g and exhibited excellent thermal stability and improved flame retardant properties with the evaluation of LOI measurement and UL-94 vertical test. The material has highly flame retardant due to the presence of clay and fullerene which acts as a free radical capture. The copper clad laminates containing modified clays pass the strict tests, such as low water uptake, low coefficient of thermal expansion, high thermal stability, and strong copper adhesion and all these improved properties are due to the presence of modified clay using modified C_{60}-O and BEN. BEN acts as a compatibilizing agent as well as a curing agent. This result suggests that the novolac cured epoxy resin/clay composites with balanced properties can be potentially applied in the electrical/electronic industries may apply to make copper clad laminates.

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Caption and legends

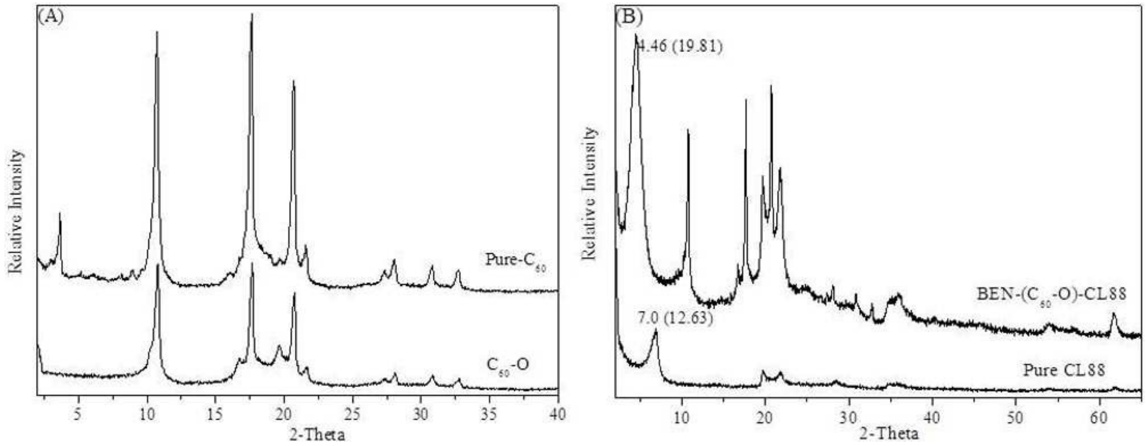

Fig. 1 WAXS graphs for (a) C_{60} and C_{60}-O (b) pure CL88 and modified CL88

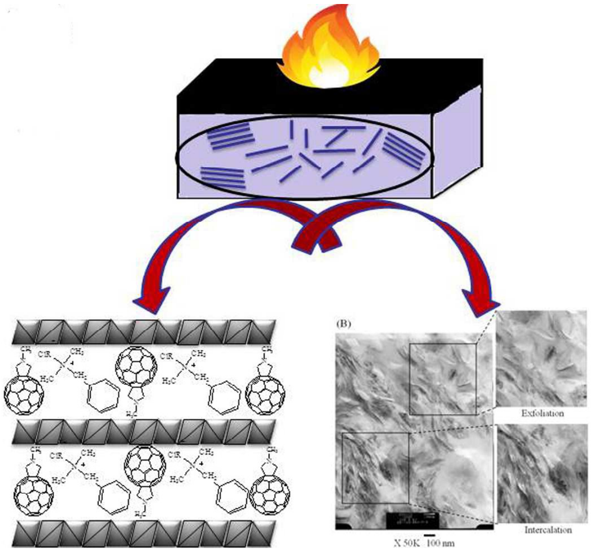

Fig. 2 Schematic representation of Modified Clay material, epoxy composite morphology and burning behavior.

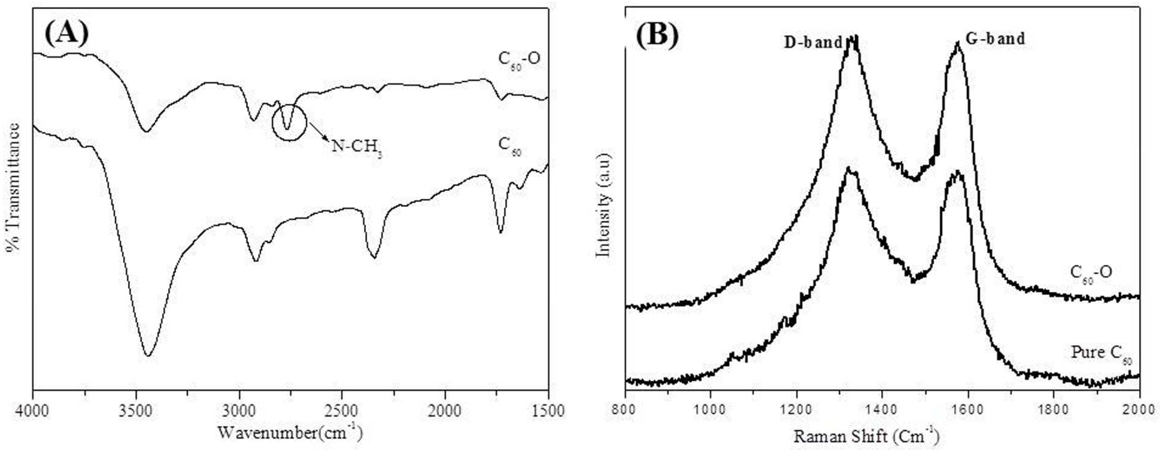

Fig. 3 (A) FT-IR, (B) Raman spectra of C_{60} and C_{60}-O

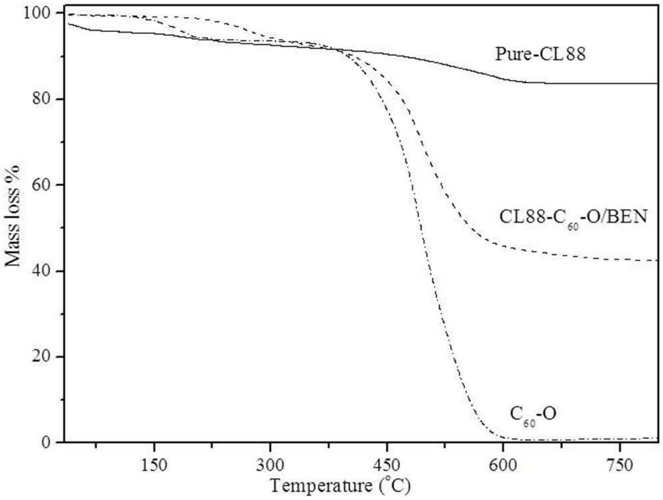

Fig. 4 TGA curves of C_{60}-O, pure CL88and BEN- (C_{60}-O)-CL88.

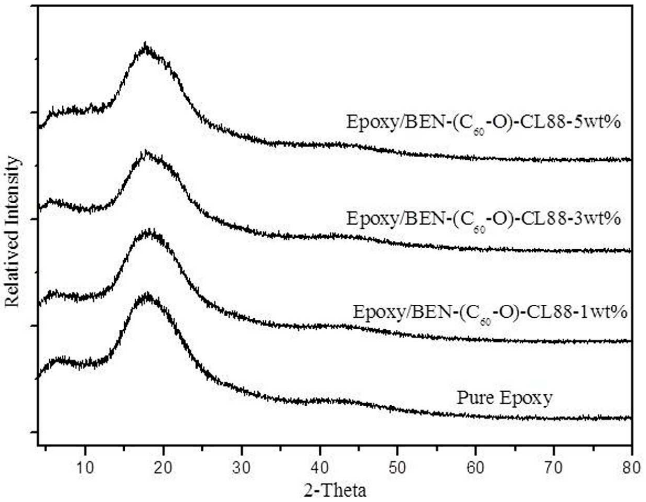

Fig. 5 WAXD of pure novolac epoxy resin and BEN-(C_{60}-O)-CL88/Novolac cured epoxy composites.

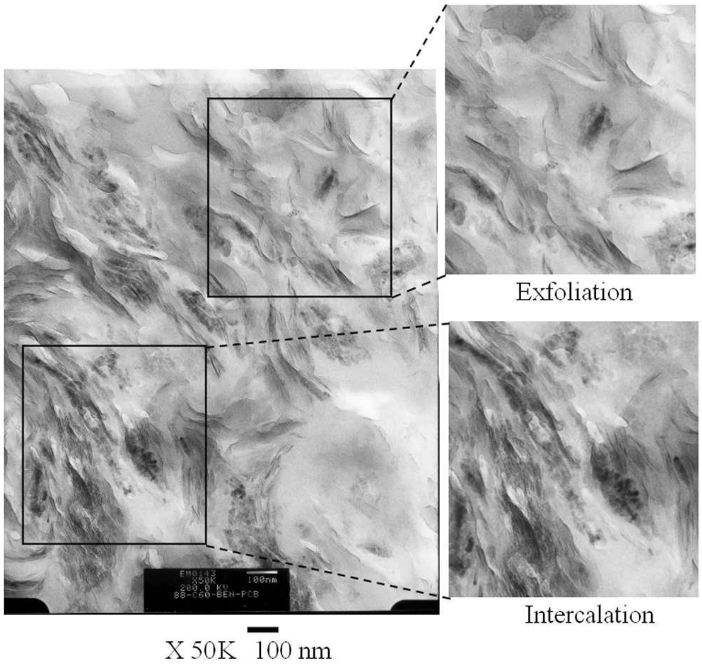

Fig.6 TEM image of BEN-(C_{60}-O)-CL88/Novolac cured epoxy 3 wt% composites.

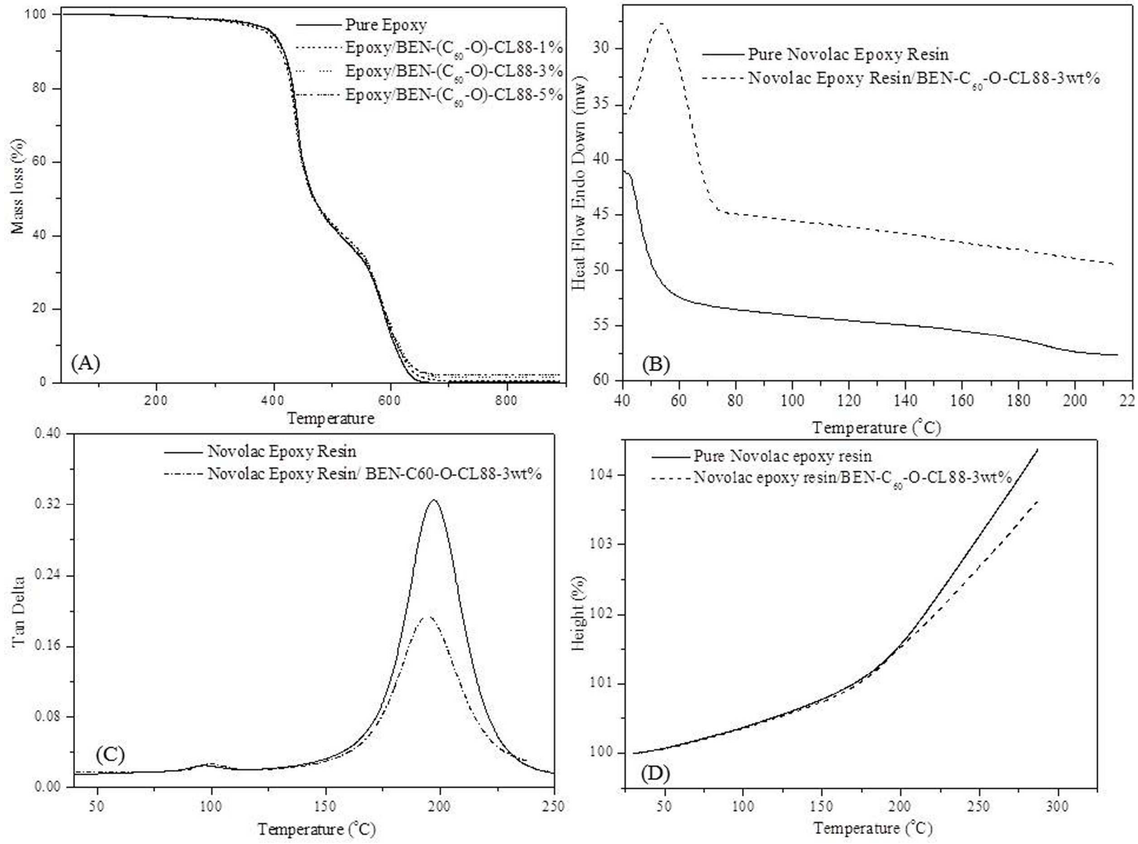

Fig. 7 (A) TGA, (B) DSC, (C) DMA, (D) TMA curves of pure enovolac cured epoxy and BEN-(C_{60}-O)-CL88/Novolac cured epoxy composites.

Table 1. TGA and Solution Gel time results of Novolac Pure-Epoxy, and epoxy composites

Sample	T_{5d}(℃)	Char yield	SG(sec.)
Novolac Pure- Epoxy	395.6	0	>1500↑
CL88-C60-O/BEN-1wt%	389.7	0.5	461
CL88-C60-O/BEN-3wt%	395.6	1.5	262
CL88-C60-O/BEN-5wt%	398.0	2.1	170

Table 2. DMA, LOI, UL94 and Combustion parameters obtained from the cone calorimeter test results of EP and EP composites

Sample	Novolac Pure- Epoxy	Epoxy/CL88-C60-O/BEN-3wt%
Storage module(Mpa)	1950.86	2186.1
Tg	194.4	197.2
LOI	22.5	30
UL-94	V-1 test is not achieved	V-1 Test is passed
pHRR (kW m^{-2})	599.03	567.77
THR (MJ/m^2)	92.01	86.45