

# Understanding the Performance of Epoxy Nano Composites — A Physico-Chemical Approach

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**Keywords** : epoxy resin, nanocomposites, MMT clay, insulation, breakdown, contact angle

High performance polymer nanocomposites are emerging as a new class of materials for its demanding applications as insulating material. Epoxy resin is an indispensable material for insulation systems in power equipments like dry type transformers and rotating machines. The epoxy resin is used not only as insulating material but also as structural material because the material is cost-effective. Recent times epoxy resin added with organically modified clay as filler finds major application. The selection of clay as reinforcing material is extremely appealing because of cost, high thermal inertness, and environmentally friendly characteristics. It is believed that consistent improvements in properties of clay loaded polymeric system can be achieved by minimizing clay aggregation, promoting the formation of chemical bonds between polymer and clay and achieving exfoliation of clay. The researchers in the world over are trying to understand the electrical, thermal and mechanical properties of epoxy nanocomposites insulating materials and the database is scanty.

Having known all this, in the present work, it is planned to carryout a methodical experimental study, to evaluate the performance characteristics of the epoxy nanocomposite, an epoxy resin containing different proportion of MMT clay and the results of the study were compared with epoxy resin without filler content. The basic characteristic of the epoxy nanocomposite were analyzed through certain physico-chemical diagnostic studies.

The improvement in breakdown voltage for the nano filled epoxy resin material could be due to several factors viz.

- (1) Increase in surface area of the nano particle, which alters polymer behaviour
- (2) Changes in space charge distribution in the insulation structure
- (3) Scattering mechanism.
- (4) Improvement in dielectric properties viz., volume resistivity, permittivity and  $\tan(\delta)$ .

Based on the study, it is observed that the breakdown strength of epoxy nanocomposite is high compared to epoxy resin under AC and DC voltages. The breakdown voltage of epoxy nanocomposite is high under positive DC voltage compared to Negative DC voltage

The WAXD studies indicate that intercalated structures are formed in above certain weight percentage of clay in epoxy resin. It is observed that increase in percentage of nano clay in epoxy resin shows increase in hydrophobic characteristics of the material. This is realized from the contact angle measurement. Diffusion of water in epoxy nanocomposite is less compared to pure epoxy resin material. The TG-DTA studies indicate that degradation of material occurs in the temperature range 300-500°C.

Tensile strength and elastic modulus of the material is increased by addition of small percentage of nano clay in base resin material. It is realized that the flexural strength of the material and the impact strength of the material shows considerable improvement in its property by addition of small amount of nano clay in epoxy resin material, indicating that the mechanical properties improved considerably by addition of nano clay in epoxy resin.

The Heat Deflection temperature analysis indicates that increase in weight percentage of epoxy nanocomposites shows increase in its value and above certain limit the characteristic improvement in its value is drastically reduced.

The DMA studies indicate that storage modulus of the material increases with increase in percentage of nano clay in epoxy resin, for a given frequency. A slight increase in the storage modulus was observed when the frequency of the signal is increased. It is realized that glass transition temperature increases with increase in percentage clay content of the material. It is shown for epoxy nanocomposites,  $\tan(\delta)$  increases with increase in frequency. The activation energy of the material increases with increase in percentage of clay in epoxy nanocomposites.

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In the present work, the electrical and mechanical properties of epoxy nanocomposite materials were studied. The hydrophobicity of the insulating material was analyzed through contact angle measurement. The diffusion coefficients of the material with different percentage of clay in epoxy nanocomposites were calculated. The exfoliation characteristics in epoxy nanocomposites were analyzed through Wide Angle X-ray Diffraction (WAXD) studies. The thermal behaviour of the epoxy nanocomposites was analyzed by carrying out Thermo gravimetric Differential Thermal Analysis (TG-DTA) studies. The tensile test, flexural test, impact test were carried out to understand the mechanical characteristics of the material with different percentage of clay. Heat deflection temperature of the material was measured to understand the stability of the material for intermittent temperature variation. The Dynamic Mechanical Analysis (DMA) results indicated that storage modulus of the material increases with small amount of clay in epoxy resin. The activation energy of the material was calculated from the DMA results. The short time insulation breakdown studies of nanocomposite material indicate that the breakdown voltage increases with small percentage of nano clay in epoxy resin. Also, it was shown that the positive DC breakdown voltage is higher than the negative DC voltage, irrespective of the percentage of nano clay in epoxy resin.

**Keywords :** epoxy resin, nanocomposites, MMT clay, insulation, breakdown, contact angle

## 1. Introduction

High performance polymer nanocomposites are emerging as a new class of materials for its demanding applications as insulating material. During operation of power equipment, the insulation is not only subjected to electrical stress but also to thermal stress due to heat generated by the current carrying conductor and mechanical stress due to force exerted by the flow of high current / vibrational stress arising from the mechanical movement of electrical machines. Thus, multi-stress ageing of insulating material occurs. However, because of the polymer matrix, it must withstand the mechanical strength and tribological loads, it is usually reinforced with fillers forming composite material. In general, the composite materials contain two phases: the base matrix and the dispersed phase.

Nanocomposites are named when the disperse phase particle size is less than 100 nm. Reinforcement of polymeric resin with nanoclay platelets as fillers has resulted in light weight materials with increased modulus and strength, decreased permeability, less shrinkage, increased heat resistance, decreased flammability and good electrical insulation characteristics<sup>(1)-(4)</sup>.

Epoxy resin is an indispensable material for insulation systems in power equipments like dry type transformers and rotating machines. The epoxy resin is used not only as insulating material but also as structural material because the material is

cost-effective. Recent times epoxy resin added with organically modified clay as filler finds major applications<sup>(5)-(9)</sup>. The selection of clay as reinforcing material is extremely appealing because of cost, high thermal inertness, and environmentally friendly characteristics. It is believed that consistent improvements in properties of clay loaded polymeric system can be achieved by minimizing clay aggregation, promoting the formation of chemical bonds between polymer and clay and achieving exfoliation of clay. The researchers in the world over are trying to understand the electrical, thermal and mechanical properties of epoxy nanocomposites insulating materials and the database is scanty.

Having known all this, in the present work, it is planned to carryout a methodical experimental study, to evaluate the performance characteristics of the epoxy nanocomposite, an epoxy resin containing different proportion of MMT clay and the results of the study were compared with epoxy resin without filler content. The basic characteristic of the epoxy nanocomposite were analyzed through certain physico-chemical diagnostic studies especially through Wide angle X-ray Diffraction (WAXD) studies and heat deflection temperature (HDT) and Thermo gravimetric–Differential Thermal Analysis (TG-DTA). Contact angle ( $\theta$ ) measurement was used as a measure of hydrophobicity of the material. Water aging was carried out to understand the diffusion coefficient of the material. In addition, to understand the mechanical properties of the material, the tensile test, flexural test, impact test and Dynamic Mechanical Analysis (DMA) were carried out. The electrical insulation characteristics were analyzed through short time breakdown voltage test under AC and DC voltages.

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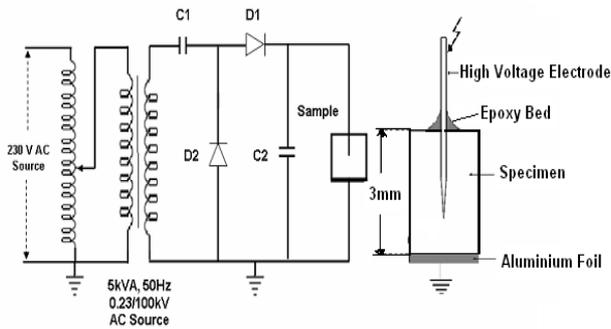


Fig. 1. Experimental setup

## 2. Experimental Studies

**2.1 Synthesis of Epoxy Nanocomposite** Epoxy nanocomposite synthesized by mechanical shear mixing of organo clay in the resin bath at room temperature. The mechanical shear mixer is used to disperse the clay in epoxy resin matrix. The high shear mixer consist of impellar with rotates at the high speed of 2000 rpm. The clay mineral used in this study was organophillic MMT procured from southern clay products Inc. (Gonzales, Texas) under the trade name of Garamite 1958. The Table 1 shows the physical properties of Garamite 1958<sup>(10)</sup>. After uniform mixing of clay particles in epoxy resin (DGEBA, CY205, Ciba Geigy Inc), 10 wt% percentage of Tri Ethylene Tetra Amine (TETA) hardener is added and then casted in a mold of required dimension and then degassed. The hardner used is of room temperature curing type and for stabilization, the mold was kept in oven at 75°C for three hours, after 24 hrs of processing. The Montmorillonite (MMT) clay belongs to a family of 2:1.layered silicates. The crystal structure of MMT clay consists of two fused silica tetrahedral sheets sandwiching an edge shared octahedral sheet of either aluminium or magnesium hydroxide. Epoxy nanocomposites with different percentage of clay (~1-10 wt%) were prepared.

**2.2 Short Time Breakdown Voltage Test** In the present work, the Needle-Plane configuration was used to understand the breakdown characteristics of the material under AC and DC voltages. The dimension of the sample used in the 30×30×3mm. A schematic diagram of the experimental setup and the electrode configuration used in the present work are shown in Fig.1 for the DC voltage test. If the sample is connected directly to the transformer without the rectifier circuit, the AC voltage test can be carried out. The radius of curvature of the needle electrode is 50µm. The high voltage is connected to the needle electrode and the bottom layer of the specimen attached with aluminium foil and grounded.

The gap distance between the needle tip and the ground electrode is 0.5mm. The space between the pin and the dielectric was effectively sealed with the cold setting araldite and the specimens were immersed in filtered, degassed mineral transformer oil to avoid surface flashover and ready for voltage application. The AC and DC voltage is applied to the sample at the rate of 500V/sec till breakdown occurs. The average of 10 breakdowns is arrived as the breakdown voltage of the material. The test was carried out at room temperature.

### 2.3 Physico Chemical Analysis

**2.3.1 Wide angle X-ray diffraction (WAXD)** In the present work, WAXD measurements were carried out with Philips

Table 1. Properties of clay particle

Colour	Off White
Bulk Density g/cc	1.5-1.7
Weight loss at 1000°C	37%
D spacing at $d_{001}$	17.2

x-ray diffractometer to obtain finger print identification of MMT clay and to understand exfoliation/intercalation properties of the epoxy nanocomposite. A scan rate of 2° per minutes at 2000 cycles using  $\text{CuK}_\alpha$  radiation of wavelength 1.542Å was applied. A radial scan of Bragg angle (2θ) vs. intensity was obtained with an accuracy of  $\pm 0.25^\circ$  at the location of the peak.

### 2.3.2 Thermo gravimetric differential thermal analysis

The thermal behavior of the material was characterized using TG-DTA studies. The TG-DTA study provides the temperature at which the maximum degradation occurs. A transparent observation on the thermal behavior could be realized. The study was carried out with Netzsch STA 409C equipment. The experiments were performed in nitrogen atmosphere, in the range 25 to 800°C, at a heating rate of 20°C/min. Alumina was used as a standard catalyst.

**2.3.3 Tensile and flexural test** Tensile test is carried out to understand the ability of a material to resist breaking under tensile stress. The breaking load and the elongation at break lengths, and the tensile stress were measured in the present work. In general, the ability of the material to resist deformation under a load is its flexural strength. For materials that do not break the load at yield, typically measured at 5% deformation/strain of the outer surface, is the flexural strength or flexural yield strength. The test was carried out using instron machine at the cross head speed of 1mm/min following ASTM-D638 standards

**2.3.4 Impact test** In the present work, the impact test is carried out to understand the variation in toughness of the material due to aging. This test was carried out in the Frank model machine of 50 J capacity. Important factors that affect the toughness of the material includes low test temperatures, extra loading and high strain rates due to wind or impacts and the effect of stress concentrations such as notches and cracks.

**2.3.5 Heat deflection temperature (HDT) test** The heat deflection temperature is a measure of a polymer's resistance to distortion under a given load at elevated temperatures. The deflection temperature is also known as the 'Deflection Temperature Under Load' (DTUL) or 'Heat Distortion Temperature' (HDT). It is used to determine short-term heat resistance. It distinguishes between materials that are able to sustain light loads at high temperatures and those that lose their rigidity over a narrow temperature range.

**2.3.6 Dynamic mechanical analysis (DMA)** The visco-elastic measurement of both storage modulus and mechanical loss tangent were performed on Netzsch DMA-242C through three point bending mode. Experiments were carried out over a wide frequency range (2,5,10 and 20 Hz) in the temperature range -100 to 190°C under controlled sinusoidal strain, at a heating rate of 2°C/min under a flow of nitrogen. All experiments were performed on a 60×10mm rectangular sheet at different frequencies. The visco-elastic properties, such as, storage modulus ( $E'$ ) and the mechanical loss tangent ( $\tan\delta$ ) were recorded as a function of temperature and frequency. Dynamic mechanical analysis was carried out over a wide range of temperature and frequencies, which permits the determination of the viscoelastic

behaviour of the material and provides valuable insight into the relationship between structure, morphology and proportional properties of nanocomposite material.

### 3. Results and Discussion

#### 3.1 Short Time Breakdown Voltage Test on Epoxy Nanocomposite

Breakdown of polymer dielectrics is affected by several factors, such as degree of crystallinity, accumulation of bulk charge, interfacial area, type of bonding, temperature and free volume. Figure 2 shows the characteristic variation in short time breakdown voltage of epoxy nanocomposite material with different percentage of nano clay material, under AC and DC voltages. It is observed that the AC breakdown voltage is less than the DC breakdown voltage. Under AC voltages, the charges injected in one half cycle get swamped out in the next half cycle. Constant injection and extraction of charges in the medium cause local temperature variation and aid the process of breakdown. Under DC voltages, the charges inhibit the breakdown process due to charge accumulation near the defect site counteract the applied electric field, thereby requires higher voltage to cause breakdown.

It is observed that increase in percentage of nano clay in the epoxy nanocomposite shows increase in breakdown voltage (up to 5wt% of nano clay), under AC and DC voltages. Zilg et al.<sup>(11)</sup>, observed an increase in breakdown voltage of the polypropylene nano composite material. J. K. Nelson et al.<sup>(12)</sup>, observed epoxy/TiO<sub>2</sub> nano composite shows no variation in breakdown voltage up to 10 Wt% of TiO<sub>2</sub> and above which slight reduction in breakdown voltage is observed.

The improvement in breakdown voltage for the nano filled epoxy resin material could be due to several factors<sup>(13)</sup> viz.

- (1) Increase in surface area of the nano particle, which alters polymer behaviour.
- (2) Changes in space charge distribution in the insulation structure.
- (3) Scattering mechanism.
- (4) Improvement in dielectric properties viz., volume resistivity, permittivity and tan( $\delta$ ).

Due to increase in the surface area of nano particle, interfacial area leads to a significant volume fraction of polymer surrounding the particle having high interaction zone. Since the interaction zone is much more than for micro composites, the polymer has significant impact on its functional properties. Also because of high packing density, the accumulated charge is reduced and

threshold field at any point is reduced and the space charge distribution is altered<sup>(14)</sup>. When the material is packed with nano materials, the fillers acts as a scattering site. The electrons injected from the high voltage electrode or formed by different mechanism in solid insulation get accelerated by the applied field. Due to dispersed nano particles, the electrons transfer the energy to the nano particles and lose its momentum involving in reaction. Since the particles are so closely packed, the electrons cannot gain momentum to involve in the process of breakdown. For it to cause damage to the insulation, it requires additional voltage to cause any catastrophic failure of insulation. Thus the epoxy nanocomposite has improved breakdown strength compared to the normal epoxy, under AC and DC voltage. H.Z. Ding et al.<sup>(15)</sup>, has shown that in epoxy resin treeing resistance is enhanced in nano composites. It is realized that the dispersion of nano particle in polymeric system which might activate submicron defect, which could result in increase in the size of electrical tree formation and hence improve the resistance of electrical tree growth and therefore the insulation lifetime.

Roy et al.<sup>(16)</sup>, have emphasized that the interaction zone around the particle is quasi-conductive, which partially overlaps in the nanocomposites. These overlapped zone acts as site of charge dissipation, return, which can be expected to increase the breakdown strength of the material under DC voltages. When the percentage of clay content is increased above certain weight percentage, the chance of formation of aggregates/clusters in the structure is high. These loose clusters or unexfoliated nano particles in the matrix acts as additional crack initiation sites by splitting up easily under applied electrical stress causing reduction in breakdown voltage.

#### 3.2 WAXD Studies of Epoxy Nanocomposite

WAXD pattern of the epoxy nanocomposites is shown in Fig.3. It is observed that organo clay shows peak at 5.2° of the 2 $\theta$  value correspond to the d spacing of 17 Angstrom, which is attributed to the reflection from the d<sub>001</sub> plane. It is observed that neat epoxy and the epoxy nanocomposite (up to 5 wt % of nano clay) did not show any sharp diffraction peaks in the WAXD pattern, indicating that the structure is exfoliated<sup>(8)</sup>. To achieve an exfoliated clay nano composite structure in the epoxy matrix is to make the epoxy chains to enter into the intergallery region, and the ammonium ion in the intergallery region catalyze the chain formation at a rate that is equal at the extra gallery polymerization. The polymers are intercalated if the free energy change,  $\Delta G$ , associated with separation of the silicate layer and incorporation of the polymer chains from the bulk is negative. As the weight percentage is increased above 5%, the diffraction patterns show the formation of intercalated nanocomposites. If the orientation of stacks is in random, then also the d<sub>001</sub> peak reflection is absent in the XRD pattern<sup>(17)</sup>.

#### 3.3 Thermal Analysis of Epoxy Nanocomposite

To understand the influence of nano clay on the thermal stability of the material, TG-DTA studies were carried out. Fig.4a shows TGA spectra of epoxy nanocomposite material. The TG curve shows gradual weight loss above 290°C for the epoxy/epoxy nanocomposite material. The lack of weight decrease at a temperature lower than 290°C indicates that there is no release of any molecules from the host during heating. Fig.4b shows DTA spectra of epoxy nanocomposite material. Generally exothermic peaks involving with weight loss, no weight change and weight gain are known to be result from combustion, crystallization and

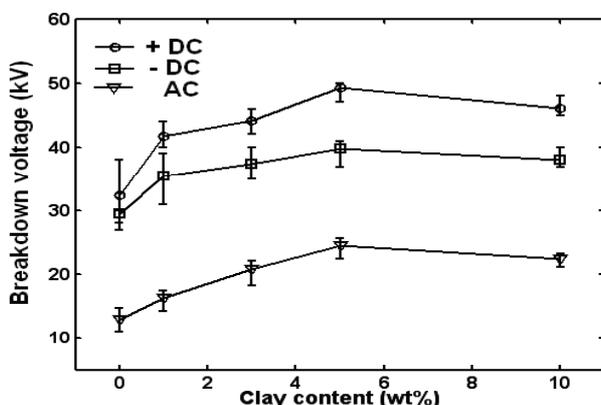


Fig. 2. Variation in breakdown voltage of epoxy nanocomposite under AC and DC voltages

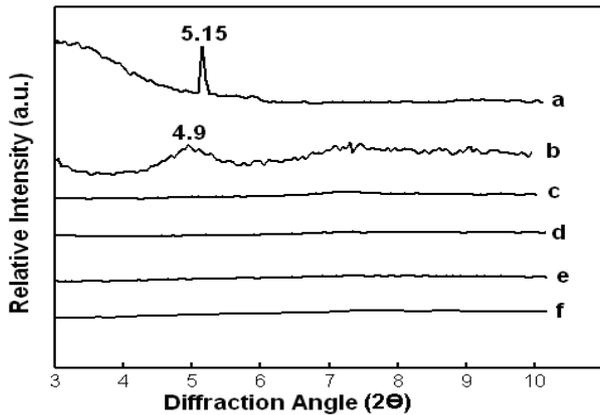


Fig. 3. WAXD pattern of epoxy nanocomposite : (a) Clay, (b) 10Wt.%, (c) 5Wt.%, (d) 3wt.%, (e) 1 wt.%, (f) Epoxy

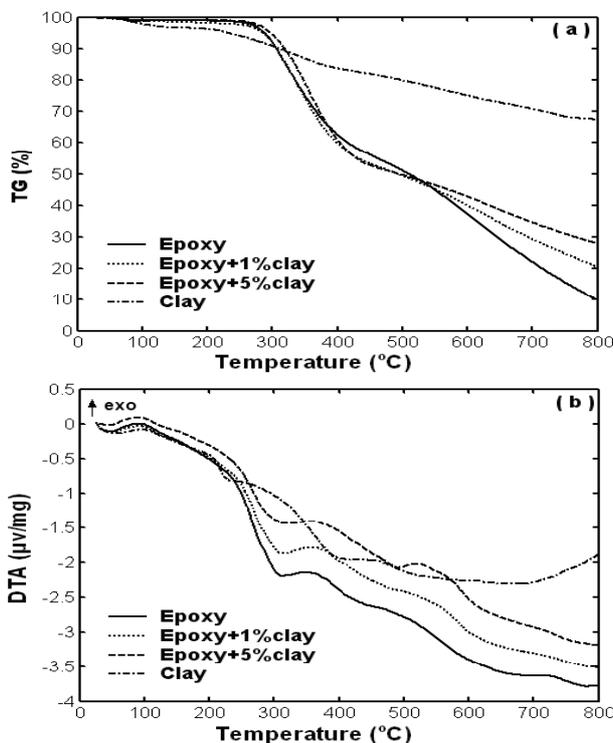


Fig. 4. TG-DTA pattern of epoxy nanocomposite : (a) TG Pattern, (b) DTA Pattern

oxidation respectively. Also, the endothermic peaks involving with weight loss indicate decomposition or dehydration. In the present study, the DTA curve indicate a endothermic dent at around 300°C and exothermic peaks at around 350°C and 500°C, with weight loss of material. This indicates that decomposition and combustion of material occurs at temperature above 300°C. Also it is to be noted from the TGA studies that increase in weight percentage of nano clay in epoxy resin shows reduction in weight loss of material at high temperature.

**3.4 Hydrophobicity Characterization of Epoxy Nanocomposite** The measure of contact angle of a water droplet is an indirect measure of hydrophobicity of the material. When particulate or fibers are used for reinforcement, flame retardancy or for improving the mechanical properties,

understanding wetting phenomena has considerable value in relation to material performance. The contact angle ( $\theta$ ) depends on the surface energy of the material. In the present work, the static contact angle was measured by liquid droplet method<sup>(18)</sup>. The size of the drop was about 1.5mm in diameter. The contact angle is measured using the following equation,

$$\theta = 2 \tan^{-1} \left( \frac{2h}{d} \right) \dots\dots\dots (1)$$

where d is the diameter of the liquid drop and h is the height of the liquid drop. After the solution is placed over the surface of the specimen, the contact angle ( $\theta$ ) is measured within 5 seconds. For each specimen, the contact angle were measured at six different locations and average of it considered as the contact angle. The hydrophobicity of a specimen could be analyzed by measuring the contact angle variation of the specimen. In general, if the contact angle of the material is above 90<sup>0</sup>, it is the indication that the material is hydrophobic and if the value is less than 90<sup>0</sup> it is the indication that the material is hydrophilic. Figure 5 shows variation in contact angle of the specimen aged in water at different temperatures with time. It is observed that increase in aging time of the specimen shows a reduction in the contact angle, irrespective of temperature of the water bath. It is also noticed that the contact angle variation is less as the temperature of the water bath is increased. Comparing the contact angle of pure epoxy resin with epoxy nanocomposite, it is observed that epoxy nanocomposites has high contact angle. Also, increase in weight percentage of nano particle in epoxy resin shows increase in contact angle, indicating increase in hydrophobicity of the material. It is also observed that reduction in contact angle of epoxy nanocomposite is less compared to pure epoxy resin, with water ageing.

Figure 6 shows weight gain in epoxy nanocomposites due to aging of specimen in water at room temperatures. It is observed that an increase in weight up to certain time period and then it saturates irrespective of temperature. To explain its mechanism, the water molecules are absorbed at the surface of the resin and will fill the surface voids and crazes and then penetrate into the epoxy resin, The energy that is required for the molecule to penetrate the resin will depend on the available volume for their motion. The diffusion process therefore depend on movement of water molecule through the matrix aided by the existence of free volume. Subsequently, further increase in the concentration of absorbed molecule will require the polymer chains to be separated and this will involve lot of energy. Therefore rate of sorption decreases as the matrix approaches saturation and is controlled by the capability of the network to rearrange to accommodate the increased number of water molecules. However, the absorbed water can plasticize the polymer matrix, create new free volume and it facilitates the motion of the polymer matrix allowing stress relaxation and change in physical dimension of polymer. Such characteristics were not observed in epoxy nanocomposites.

When diffusion is driven by the concentration gradient and if there is no chemical change between liquid and material, this would result in mass change and the rate of absorption will be initially linear with t<sup>0.5</sup>, where ‘t’ is the time of absorption. Hence,

$$\frac{\Delta m(t)}{\Delta m_{\infty}} = 2 \sqrt{\frac{Dt}{l^2}} \left\{ \sqrt{\frac{1}{\pi}} + 2 \sum_{n=1}^{\infty} [(-1)^n \cdot \text{ierfc} \left( \frac{nl}{2\sqrt{Dt}} \right)] \right\} \dots\dots\dots (2)$$

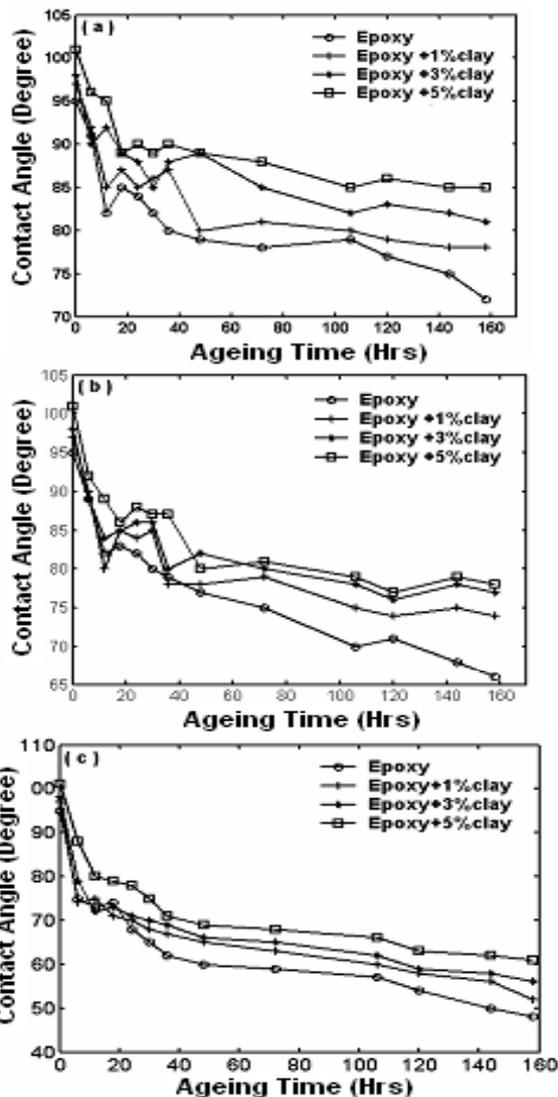


Fig. 5. Variation in contact angle in epoxy nanocomposite due to water ageing : (a) T= 30°C, (b) 60°C, (c) 90°C

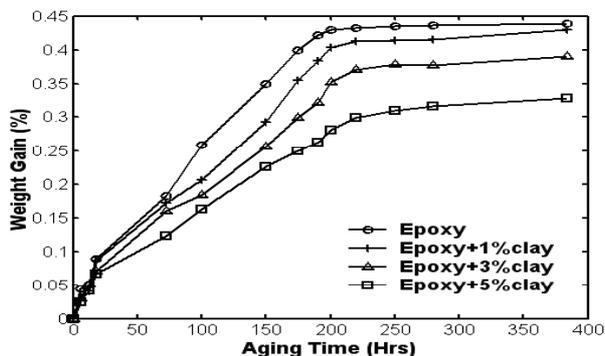


Fig. 6. Variation in weight gain in epoxy nanocomposite due to water ageing at room temperature

where  $D$  is the diffusion coefficient,  $l$  is the thickness of sheet,  $n$  is the number of sheets, 'ierfc' is the integrated complimentary error function,  $\Delta m(t) = m(t) - m(0)$  and  $\Delta m_{\infty} = m_{\infty} - m(0)$ . In this,  $m(t)$  is mass at time 't',  $m(0)$  and  $m_{\infty}$  are initial mass (at

Table 2. Diffusion coefficient of epoxy nanocomposites

Material	At 30°C X10 <sup>-12</sup> (m <sup>2</sup> /sec)	At 60°C X10 <sup>-12</sup> (m <sup>2</sup> /sec)	At 90°C X10 <sup>-12</sup> (m <sup>2</sup> /sec)
Epoxy	0.3906	3.4778	10.295
Epoxy+1%clay	0.2745	2.8410	7.4437
Epoxy+3%clay	0.2179	1.2271	5.663
Epoxy+5%clay	0.1243	0.9632	4.721

time  $t=0$ ) and after infinite time respectively. Crank (18) formulated the final equation to calculate diffusion coefficient and if the linear dependency in plot  $\Delta m(t)/\Delta m(\infty)$  vs  $t^{0.5}$  is not observed, then the diffusion constant is obtained by equating  $\Delta m(t)/\Delta m_{\infty}=0.5$ . Simplifying the equation we get

$$D = \frac{\pi L^2}{64t_{0.5}} \dots\dots\dots (3)$$

where  $L$  is thickness of the specimen. Table 2 shows the variation in the diffusion coefficient of the material aged in water at different temperature. It is observed that at increase in aging temperature relatively increases the diffusion coefficient of the material. Also increase in percentage of nano filler in epoxy shows reduction in diffusion coefficient of the material, for a given temperature. In general, due to high surface area of nano filler, it have good adhesion and reduces molecular motion in the matrix, thereby mitigating migration of water into the polymer matrix. Indirectly it indicates that the epoxy nanocomposite is hydrophobic in nature with increase in percentage content of nano filler in the base resin material.

**3.5 Mechanical Test of Epoxy Nanocomposite**

Tensile strength is important for a material that is going to be stretched or under tension. The stress needed to break the sample is the tensile strength of the material. The stress-strain curve obtained during tensile strength reveals the mechanical nature of the material. The stress-strain behavior of the epoxy nanocomposites under uniaxial tension is shown in Fig.7. It is realized that as the clay content is increased, the strain for failure is reduced. Figure 8 shows the tensile strength of the material as a function of percentage of clay in epoxy nanocomposite material. It is observed that up to certain weight percentage of nano clay in epoxy resin, a reduction in the tensile strength of the material. It is realized that the reduction in tensile strength could be due to formation of fine voids in the epoxy nanocomposites. When the percentage of nano clay is increased, the packing density of the material is increased thereby the formation of voids is reduced thereby the tensile strength is increased. Yasmin et al.(13), suggested that under tensile loading, cracks can initiate from tiny voids and can initiate failure process at lower strains. Figure 9 shows the variation in elastic modulus of the epoxy nanocomposite material with different percentage of clay content. It is observed that elastic modulus increases with increase in percentage of clay content. An improvement of 61% is observed with an addition of 1% of clay content, whereas a maximum of 155% observed with an addition of 5 wt% of clay. Although the rate of increase at the beginning is dramatic, it decreases as the clay content is increased. This improvement in strength of the material is due to complete exfoliation of the clay and good dispersion of nano clay particles that restricts the mobility of polymer chains under loading. This reduction in elastic

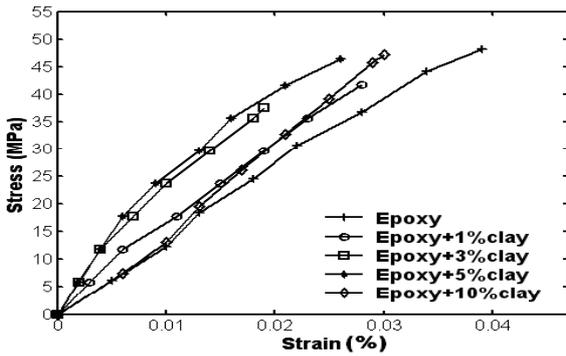


Fig. 7. Stress strain behaviour of epoxy nanocomposite

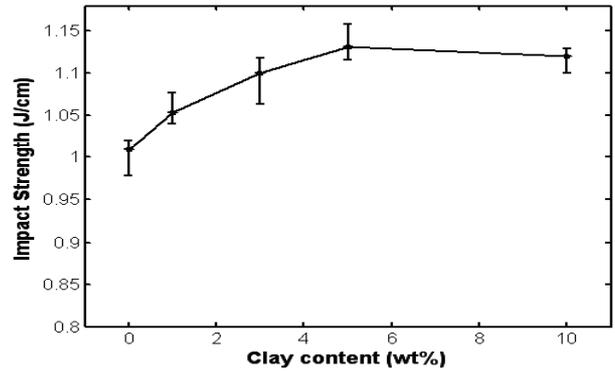


Fig. 11. Variation in impact strength of the epoxy nanocomposite

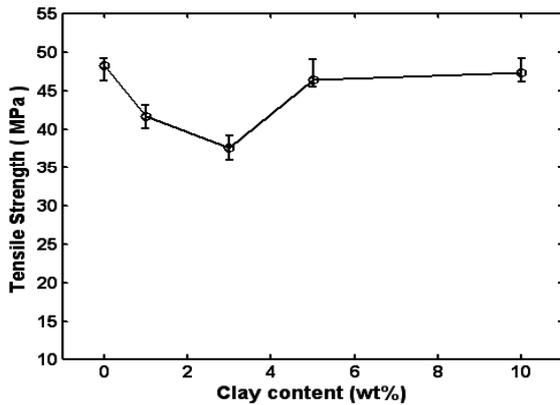


Fig. 8. Variation in tensile strength of the epoxy nanocomposite

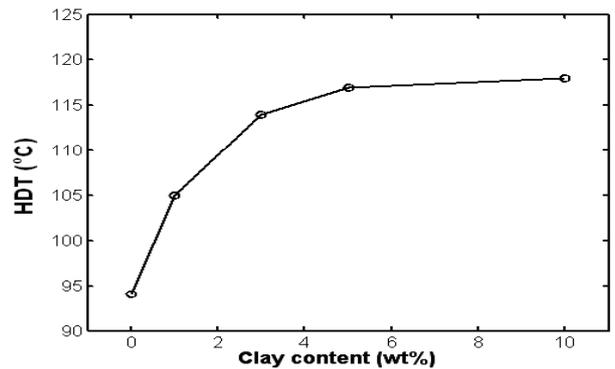


Fig. 12. Variation in heat deflection temperature of epoxy nanocomposites

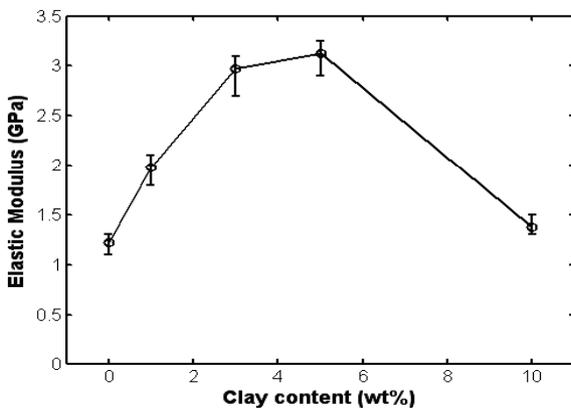


Fig. 9. Variation in elastic modulus of epoxy nanocomposite

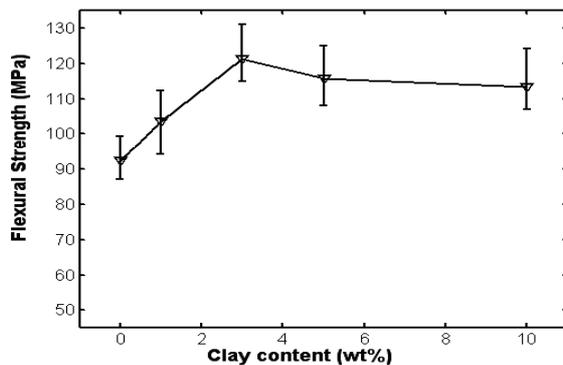


Fig. 10. Variation in flexural strength of the epoxy nanocomposites

modulus could be due to the presence of unexfoliation structure in the material. The formation of unexfoliated structures in epoxy nanocomposites could be realized from XRD studies.

The mechanical test measures the behaviour of the material subjected to simple bending loads and determines the extent to which they can be bent before they break and the relationship between stress and deflection. The ability of the material to resist deformation under load is the flexural strength of the material. Figure 10 shows variation in flexural strength of the material as a function of percentage variation of nanocomposite in epoxy resin. It is realized that increase in flexural strength of the material up to certain percentage of nano clay in epoxy nanocomposite and above which a reduction in value is observed. It is realized that increase in flexural strength of the material could be due to the presence of layered silicate layer so that it increases the bending strength of the epoxy nanocomposite material

The impact test provides the value of toughness of the material. In this test, a hammer strikes and breaks the specimen. The amount of energy absorbed in the test is a measure of impact toughness. Figure 11 shows variation in impact strength of the material as a percentage of nano clay in epoxy resin. It is realized that the impact strength increases with increase in percentage of clay up to certain weight percentage of nano clay in epoxy resin, above which it is realized a slight reduction in impact strength but much higher than the pure epoxy resin material.

Figure 12 shows variation in heat deflection temperature of the epoxy nano composites. In this the deflection temperature is the temperature at which a test bar, loaded to the specified bending stress, deflects by 0.25 mm. It is realized that HDT increases up to

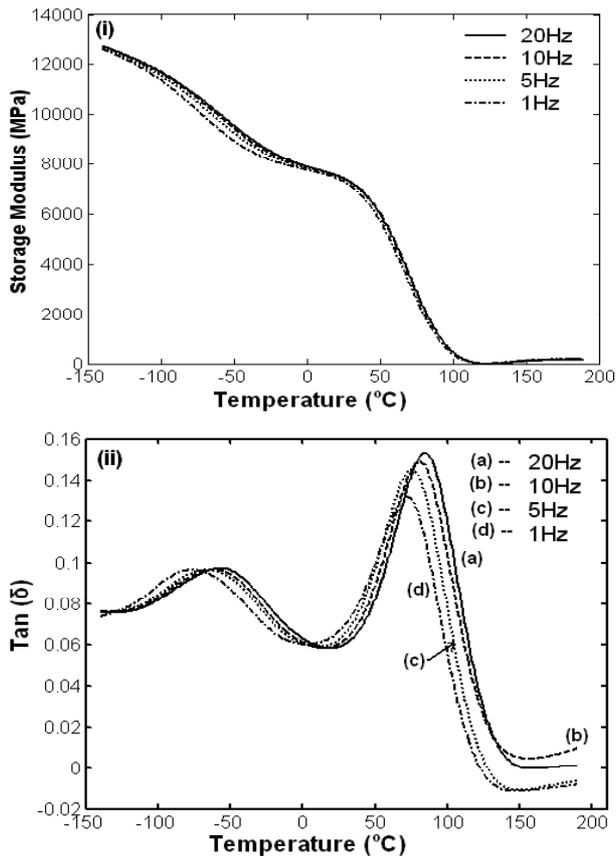


Fig. 13. Dynamic mechanical analysis of epoxy nanocomposite with 3wt% clay : (i) Storage modulus, (ii) tan(δ)

certain percentage of nano clay in epoxy resin material above which not much variation in its value is observed.

**3.6 DMA Study of Epoxy Nanocomposite** In DMA technique an oscillatory force is applied to a sample and the response to that force is analyzed. Figure 13(i) shows the variation in storage modulus of epoxy nanocomposite material (with 3wt% of MMT clay) at different temperatures, measured at different frequencies. It is observed that as the frequency increases, the storage modulus of the material increases with respect to temperature. Fig.13(ii) shows the variation in mechanical tan(δ), which is a dimensionless parameter and conveys no physical magnitude. It is a measure of the ratio of energy lost to the energy stored in a cyclic deformation, is the loss tangent, which is high at high frequencies, in the range studied. Also from Fig.13(ii), it is observed that the relaxation peak temperature is increased by about 10°C when the frequency is increased from 1 to 20 Hz in all the specimens used in the present study. It is observed one relaxation peak at about -50°C and another relaxation peak at about 90°C. It could be possible to relate the temperature at which the relaxation process is observed with the frequency of excitation ( $f$ ) by the Arrhenius equation<sup>(19)</sup>,

$$f = f_0 \exp\left[\frac{-E_a}{RT}\right] \dots\dots\dots (4)$$

where  $f_0$  is a constant,  $f$  is the test frequency,  $R$  is the gas constant and  $E_a$  is the activation energy for the relaxation process. According to the above equation, a plot of  $\log f$  vs  $1000/T$  should give a straight line with a slope that is directly related to the

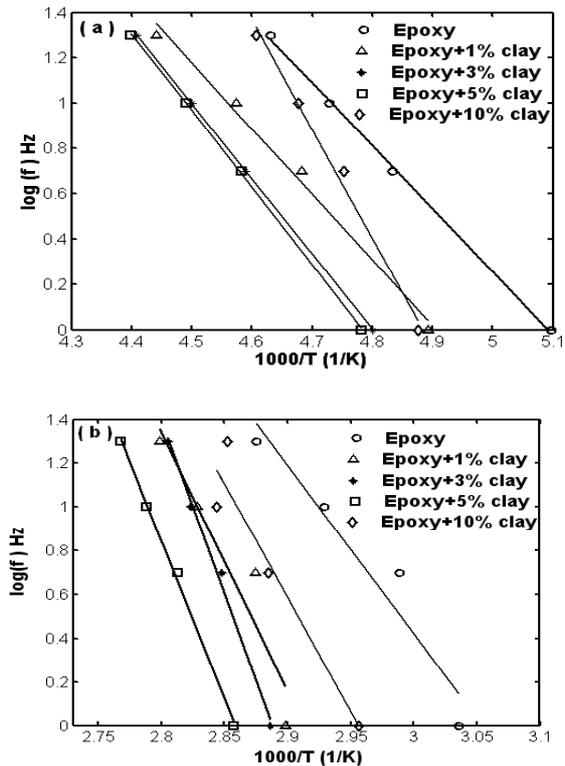


Fig. 14. Calculation of activation energy of epoxy nanocomposite : (a) at low temperature, (b) at high temperature

Table 3. Activation energy of epoxy nanocomposite

Material	At high temperature kJ/mol	At low temperature kJ/mol
Epoxy	147.465	53.099
Epoxy +1%clay	226.635	56.186
Epoxy +3%clay	278.799	62.732
Epoxy +5%clay	304.767	64.830
Epoxy +10%clay	200.317	92.586

apparent activation energy for the relaxation process of the material, shown in Fig.14. Activation energy is the energy for the molecule moves from one balanced position to another balanced position. It represents the relation between the mechanical loss factor and temperature. Calculated activation energies at low temperature and high temperature are shown in Table 3. It is observed that the activation energy of the material increases with increase in percentage of nano clay in epoxy resin material, at low and high temperatures.

Figure 15(i) shows the variation in the storage modulus of the epoxy nanocomposite insulation material (with different weight percentage of nano clay in base resin), measured at one frequency. It is observed that increase in percentage of nano clay in epoxy resin increases the storage modulus of the material upto certain percentage of loading and a reduction in storage modulus is observed above it. Fig.15 (ii) shows the variation of tan(δ) or loss

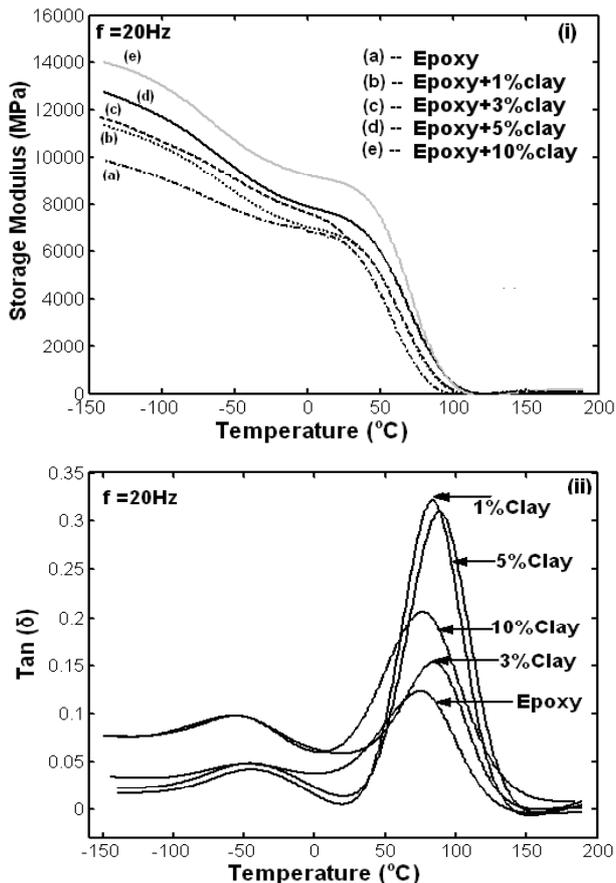


Fig. 15. Dynamic mechanical analysis of epoxy nanocomposite : (i) Storage modulus, (ii)  $\tan(\delta)$

factor of the different percentage of clay in epoxy nanocomposite, measured at one frequency. It is evident that glass transition temperature increases with increase in percentage of nano clay in epoxy resin up to certain percentage of clay content in epoxy resin. Above that, it is realized drastic reduction in its value is observed.

#### 4. Conclusions

The important conclusions arrived based on the present study are the following.

- (1) It is observed that the breakdown strength of epoxy nanocomposite is high compared to epoxy resin under AC and DC voltages. The breakdown voltage of epoxy nanocomposite is high under positive DC voltage compared to Negative DC voltage
- (2) WAXD studies indicate that intercalated structures are formed in above certain weight percentage of clay in epoxy resin.
- (3) Increase in percentage of nano clay in epoxy resin shows increase in hydrophobic characteristics of the material. This is realized from the contact angle measurement. Diffusion of water in epoxy nanocomposite is less compared to pure epoxy resin material.
- (4) TG-DTA studies indicate that degradation of material occurs in the temperature range 300-500°C. Tensile strength and elastic modulus of the material is increased by addition of small percentage of nano clay in base resin material.
- (5) It is realized that the flexural strength of the material and the impact strength of the material shows considerable

improvement in its property by addition of small amount of nano clay in epoxy resin material, indicating that the mechanical properties improved considerably by addition of nano clay in epoxy resin.

(6) Heat Deflection temperature analysis indicates that increase in weight percentage of epoxy nanocomposites shows increase in its value and above certain limit the characteristic improvement in its value is drastically reduced.

(7) The DMA studies indicate that storage modulus of the material increases with increase in percentage of nano clay in epoxy resin, for a given frequency. A slight increase in the storage modulus was observed when the frequency of the signal is increased. It is realized that glass transition temperature increases with increase in percentage clay content of the material. It is shown for epoxy nanocomposites,  $\tan(\delta)$  increases with increase in frequency. The activation energy of the material increases with increase in percentage of clay in epoxy nanocomposites.

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