

MECHANICAL, THERMAL AND DIELECTRIC CHARACTERIZATION OF IRON OXIDE PARTICLES DISPERSED GLASS FIBER EPOXY RESIN HYBRID COMPOSITE

V. R. ARUN PRAKASH*, A. RAJADURAI

Department of production Technology, MIT, Anna University, Chennai – 600 025, India

In this research an investigation was made on the mechanical, thermal, electrical properties of E-glass fiber reinforced epoxy composites dispersed with fine iron (III) oxide particles. Composites of 15 vol% glass fiber dispersed with 0.5 and 1 vol% concentration of iron (III) oxide particle were fabricated. The particulate – fiber hybrid composite was prepared by hand layup process and tested to find mechanical and thermal properties such as ultimate tensile strength, impact strength, flexural strength, hardness, and glass transition and degradation temperature. Since the used matrix material is an insulating material (thermoset plastic) dielectric properties were studied. The test results shown that there is a significant improvement in thermal and dielectric properties when the incremental in particle loading with slight marginal decrements in mechanical properties. Morphology of the composite system shows clustered distribution of iron (III) oxide particle in the matrix.

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1. Introduction

Property enhancement is a challenge in polymer materials since they are capable of serving many engineering applications like civil, mechanical, electrical, automobile and aerospace. In this trend the polymer's properties need to be changed based on respective applications. Polymers can be strengthened by addition of fiber and particles. These fiber toughened polymer composites are highly preferable in aero and automobile applications due to high strength to weight ratio. In other hand the particle added polymer composites serves in solar energy conservation, magnetic storage, magnetic shielding, and dielectric heating. Epoxy resins are more attractable because of its excellent adhesion, insulation, and chemically inactive properties. Whereas iron (III) oxide particles have better mixing with matrix due to surface porous, readily available in nature and cheaper too [1,2]. The magnetically toughened epoxy material could act as a magnetic shielding material for radio frequency identifier. The dispersed iron (III) oxide in epoxy matrix boost up heat dissipation hence the material could be used as a heating element. In order to enhance the special properties like magnetic and dielectric filler addition is a common and easy process. Due to microscopic size and surface porous the polymer-filler interaction may be partially achieved [3]. This present work evaluates the mechanical, thermal, electrical properties of hybrid composite which is strengthened by fiber and modified with particle. The hand layup process has been followed to make the composites and the properties have been unveiled by Universal testing machine (UTM), thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscope (SEM) and LCR tester. Deventra.et.al [4] reported a nominal decrement of tensile and impact strength of fiber- particle loaded epoxy composite because of particle agglomeration and affecting original molecular structure of epoxy. Apart from mechanical properties the hybrid composite are having good thermal and novel dielectric properties.

*Corresponding author: vinprakash101@gmail.com

2. Experimental procedures

2.1 Materials

The epoxy resin used in the present study was a liquid diglycidyl ether of Bisphenol-A type (Huntsman India Ltd. Mumbai, Araldite LY556) with an equivalent weight per epoxide group of 195 g/mol having viscosity of 12000 cps and density of 1.2g/cm³ at 25°C. Triethylenetetramine (TETA, Huntsman India Ltd. Mumbai., HY951), a low viscosity aliphatic amine was having viscosity of 20cps and density of 0.98g/cm³ was used as a curing agent. E- Glass fiber continuous woven mat (0-90°) with density of 2.54g/cm³ was used. Ball milled Iron (III) oxide particles with an average particle size of 800nm with density of 5.2g/cm³ were used to fabricate the hybrid polymer composite. All the chemicals and materials were used in as received condition without any post process treatments.

2.2 Sample preparation

2.2.1 Preparation of hybrid composite

A fixed quantity of 15 volume % of glass fiber with varying volume percentage of iron (III) oxide particles (0.5 and 1.0) were added to the resin at room temperature and stirred thoroughly until degassing process completed. A homogeneous mixture of resin and filler was produced at the end of stirring process. Curing catalyst (TETA) was then added by 1:8 weight ratios and stirred until a homogeneous solution was formed. The viscous colloidal suspension was poured into a silicon rubber mould with wax coating and 15 volume percentage of E- Glass woven mat (3- ply) was laid with epoxy resin matrix and entrapped air bubbles were removed by cotton roller. The excess resin was wiped out manually and gravity force is applied to get uniform thickness of composite. The curing was done at room temperature for about 24 Hrs.

2.3. Specimen preparation

The prepared E-glass fiber – filler reinforced epoxy composites sheets were taken out from mould and then specimens of suitable dimensions according to ASTM standards were cut by diamond cutter with 2500 rpm and 0.5mm/sec as feed. Five identical samples were taken out for each test. The designation and composition of composites are presented in Table 1.

Table 1. Composition and designation of composites

Material Designation	Epoxy (Vol %)	Fiber (Vol %)	Fe ₂ O ₃ (Vol %)
R	100	0.0	0.0
RI ₁	99.5	0.0	0.5
RI ₂	99.0	0.0	1.0
RF	85.0	15	0.0
RFI ₁	84.5	15	0.5
RFI ₂	84.0	15	1.0

R- Resin; F- Fiber; I₁-0.5 vol% of Fe₂O₃; I₂-1.0 vol% of Fe₂O₃

2.4. General characterization

The tensile and flexural behavior of hybrid composite were tested based on ASTM-D3039, ASTM-D790 respectively with a universal testing machine having 5 ton of loading capacity and digital encoder attached at a cross head speed of 2.5mm/min (FIE. India). The Impact behavior of composite was tested based on ASTM-D256 with a micro impact machine with maximum capacity of 20 joules (Krystal equipment Ltd. India). Five specimens were tested for each material designation. The thermal behavior of composite was analyzed with a thermo gravimetric analyzer (NETZSCH STA Jupiter 409 PL Luxx, Germany) under N₂ atmosphere. Samples were scanned from 0-600°C at heating rate of 10°C/min and sample crucible material was Al₂O₃. The hardness of composites was tested using Durometer (shore-D) as per ASTM-D 2240. Surface morphology of fractured surface of composite was analyzed using scanning electron microscope (CARL ZEISS SUPRA 55-Germany) the fractured surface of the samples was coated with gold before scanning.

The Dielectric property of composite was measured with a LCR Hi-TESTER 3532-50 (HIOKI – Japan) with operating range varies from 42Hz - 5MHz as per standard ASTM D 150.

3. Result and Discussion

3.1. Mechanical properties

The tensile, flexural and impact properties of epoxy, E-Glass fiber, iron (III) oxide hybrid composite are presented in Table 2. The addition of Glass fiber has improved the mechanical properties of epoxy resin whereas addition of iron (III) oxide particles resulted a significant decrement in strength. This is due to the reaction of particles with epoxy resin which affects the original molecular structure of epoxy and formation of more cross link makes the resin more brittle. Figure 1 shows the scheme of epoxy with iron oxide reaction. When adding iron (III) oxide particle into the epoxy resin matrix, the oxygen molecule from the particle is getting replaced by OH functional group from epoxy resin because Fe-OH bond is more stable than Fe-O bond. Since the valence of OH functional group is one each 1 set of iron particles get surrounded by six OH functional groups. Due to this action epoxy polymer chains come closer and forms a cross linked network. From the six OH three water molecules are formed and they fled away in the form of bubbles. Now again the iron particle consist of three oxygen which have link between iron and CH which is in primary polymer chain [5, 6]. When adding the curing catalyst (TETA) the CH₂-CH₂ functional group from amine reacts with the oxygen and forms cross link and also hydrogen from amine reacts with epoxide group and form another cross link hence the amount of cross links are high. The highest cross link density is the reason for high flexural modulus of epoxy after adding iron (III) oxide particle. The tensile strength, flexural strength, flexural modulus, impact energy and hardness values is listed in Table 2.

Table 2 Mechanical properties of composites

Material Designation	Tensile strength (MPa)	Flexural strength (MPa)	Flexural modulus (Mpa)	Izod Impact (Joules)	Hardness (Shore-D)
R	81	103	2245	0.93	85
RI ₁	64	74	2401	0.44	87
RI ₂	51	66	2917	0.38	88
RF	135	227	5546	8.52	84
RFI ₁	128	185	5780	7.43	88
RFI ₂	114	180	6131	6.61	88

When adding iron (III) oxide particles into resin 20 % of strength is dropped at the same time adding glass fiber to resin yield 40% of strength because of high load sharing behavior of fiber. In hybrid composite (RFI₁ and RFI₂) again the tensile strength was dropped 4% and 10% by adding 0.5 and 1.0 volume percentage of iron (III) oxide particles respectively.

The drop in strength is comparatively less than that of resin particle composite because adding glass fiber observes more loads hence stress concentration is less on the matrix. The same effect was noticed in flexural and impact test also. The flexural values for 0.5, 1.0% (by vol) particle added epoxy system was decreased 30% by and 10% and the impact strength decreased by 52% and 14% respectively. Whereas the fiber reinforced system showed significant improvement of 54% in flexural and 90% in impact energy. It is due to the role of fiber in increasing the load bearing capacity. In hybrid composites (RFI₁ and RFI₂) a decrement of 18% and 3% in flexural strength and 12% and 11% in impact energy respectively was observed. All the above tests exposed that mechanical properties were improved when adding fiber and marginally reduced on adding fillers. In hybrid composites (RFI₁ and RFI₂) the effect of filler is less on strength reduction in comparison with normal particulate composites (RI₁ and RI₂). However, there is an increase in the flexural modulus on addition of the iron oxide particles [7]. 6.5% and 23% increase was observed on adding 0.5 and 1.0 vol % of iron (III) oxide to resin. Whereas the flexural modulus

more than doubled by reinforcing with 15 vol % of glass fiber. The flexural modulus further increased on adding iron oxide along with fiber. A high flexural modulus value of 6132MPa was noticed in strength reinforced with 15 vol % glass fiber and 1.0 vol % iron oxide.

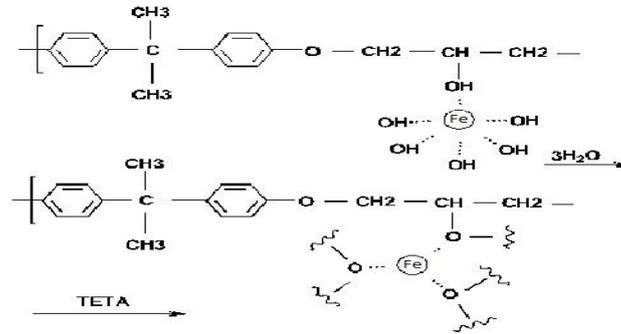


Fig.1- scheme of epoxy-iron oxide reaction

Increase in values of hardness is 2.5% and 3.5% for RI₁ and RI₂ for RFI₁ and RFI₂ it is 3.5% and 3.5% respectively. This is because of density of cross link favors improvement in hardness but in fiber loaded composite (RF) does not give any change since the surface of the composite is filled only by resin matrix.

3.2. Morphology

The SEM images of fractured surfaces of pure resin, fiber reinforced, and filler reinforced epoxy resin composites have shown in Figure 2. The image 2(a) shows fractured surface of pure epoxy. The image 2 (b) shows the fiber orientation and bonding in resin matrix. The image 2(c, d) shows the reacted phases of iron oxide with epoxy resin and reveals clustered portion of iron oxide. It is noted that the iron oxide particles grouped in some places and other areas in epoxy matrix was free. This reveals poor dispersion of particles in epoxy matrix formed cluster and increasing cross linking density. This result leads decrement in mechanical strength and unusual result in dielectric and thermal behavior [8].

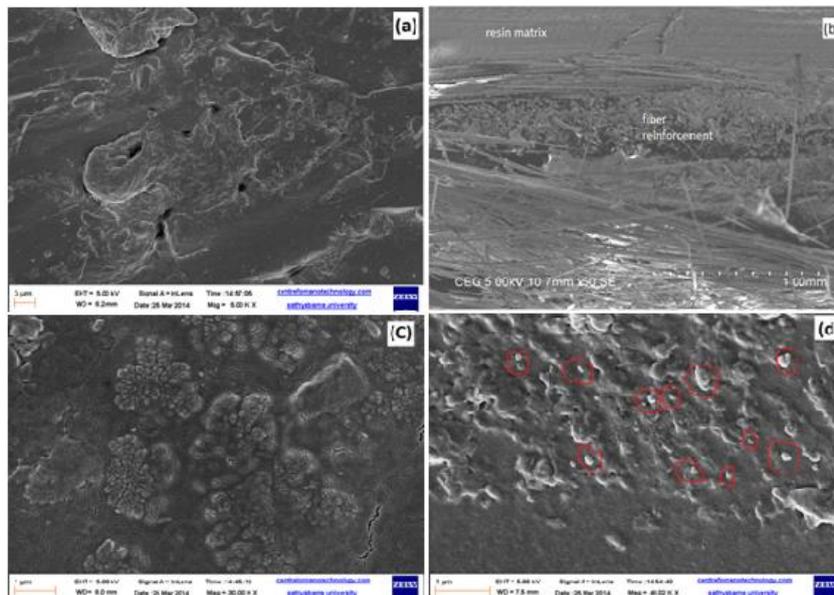


Fig. 2 Fractograph of (a) pure epoxy. (b) epoxy reinforced with fiber. (c,d) 1%(vol) iron (III) oxide filled epoxy

Table 3. Thermal properties of composites

Material Designation	T _g (°C)	Initial decomposition (°C)	Middle decomposition (°C)	Final decomposition (°C)
R	75	323	380	575
RI ₁	84	335	385	580
RI ₂	104	345	390	588
RF	73	305	360	530
RFI ₁	78	315	364	560
RFI ₂	80	320	370	565

3.3. Thermal properties

3.3.1 Thermo gravimetric analysis

Table 3 shows thermo gravimetric values of cured epoxy composites which consist of both glass fiber and iron (III) oxide particles. Initial decomposition at 300° C was noted for all composites (R, RI₁, RI₂, RF, RFI₁, and RFI₂). The percentage of mass losses during the initial decompositions is 3.98, 3.84, 3.15, 7.53, 5.19, and 3.77 respectively. The thermal stability was increased 4% and 17 % by adding 0.5% and 1.00% (by vol) iron (III) oxide filler in to the epoxy matrix this is due to the increase of cross linking density of epoxy by the affinity of iron (III) oxide particles with resin. It was reported that the addition of metal oxide fillers will increase the thermal stability of resin. Introducing more Fe-O functional group in to epoxy resin induced Fe-OH dipole attraction which attracts more epoxy primary polymer chain towards iron oxide particles. This creates clustered structure of epoxy primary link surround with iron oxide particles.

This chemical reaction liberates three water molecules and they get evacuated as bubbles. When adding hardener (TETA) into the epoxy-iron oxide solution O-CH₂-CH₂-O and CH₂-NH-R-NH-CH₂ cross links are formed. The cross linking with alkynes group increased the thermal stability of resin [9]. It is noted that there is a drop of 47% in thermal stability at 300°C when adding 15% (vol) glass fiber into the resin. The 0.5% (by vol) iron (III) oxide filler-fiber (15% vol) reinforced epoxy hybrid composite gives 23% decrement in thermal stability. The presence of metal oxides (Al₂O₃ and B₂O₃) in E-glass fiber influences the formation of moisture in epoxy matrix and evaporated in lower temperature (80° C) onwards. This gives maximum mass loss of 7.53% in fiber epoxy composite system. In composite RFI₂ thermal stability is increased by 5% on adding 1% (by vol) Iron (III) oxide particles. This is because of epoxy - iron (III) oxide solution restricts the retention of moisture in epoxy matrix and hence able to transfer heat when temperature was increased.

3.2.2. Differential scanning calorimetry

Differential scanning calorimetry test was conducted to study the glass transition temperature of composites. Table 3 shows the glass transition temperature (glassy to rubbery) of cured epoxy resin. The polymer is an amorphous polymer so glass transition temperature is very much essential to know the initial stability of polymer. The tests were conducted for all composites and the values of glass transition temperature improved 10%, 30%, 1.5%, 12%, and 18% for RI₁, RI₂, RF, RFI₁, and RFI₂ respectively. This is because when heating the epoxy molecules and secondary molecules gradually absorbs the heat, when the temperature reaches T_g the secondary group molecules gains enough energy and start rotating about the primary C-C single bond which is a back bone in polymer chain [10]. When the temperature increases the free volume (where polymer molecules are not filled) also expanded so the secondary group can easily rotate about primary C-C single bond. On adding iron (III) oxide particles cross link density is increased. The amount of free volume is less; hence the secondary links cannot rotate as much as easy as normal state. When adding iron (III) oxide particles significant improvement in glass transition temperature is observed. When adding glass fiber to epoxy resin not much different in glass

transition due to macro dimension of fiber material it does not affect the property of polymer matrix directly.

3.3. Dielectric analysis

Dielectric analysis was conducted for the resin and all composites to find the effect of particle and fiber addition. The parallel plate capacitor method was deployed where dielectric material is kept between two conductors and A.C voltage of 10mV is applied with different frequency. The polarization is needed for conducting the charges. The epoxy resin is a non polar dielectric and there is no dipole molecules are present so the dipole moment is induced by external alternating field, most of the thermosetting polymers became polarized in the radio frequency range (20 Hz-1 KHz). When field is applied with suitable frequency the polymer molecules slightly move towards the polarity. In non polar polymer all molecules are equally distributed with electrons. When external field is applied to these molecules electron density is moved towards one side as a negative and other side as a positive. The formation of induced dipoles in polymer facilitates the charge transfer [11, 15]. Figure 3(a, b) shows the dielectric loss for different frequencies and different temperatures. The dielectric loss was increased in particle loaded epoxy composite whereas in fiber not much improvement was noticed [12,13,16]. A maximum dielectric value of 5.7 was observed for material designation RI₂ when the frequency was 100 Hz. The mobility of electron in any conductor produces heat due to the resistance of mobility, the same effect was observed in the particle dispersed epoxy composite. When adding iron (III) oxide more induced dipoles are created and hence it starts conducting the charge and heat is dissipated. This is due to more resistance of dielectric medium. When frequency increases the heat dissipation decreases. At very high frequency the relaxation time for the polarized molecules is less hence a kind of disordered orientation in molecules decrease the conducting of charges [14]. The maximum dielectric loss was observed for material designation RFI₂ is 5.4 when temperature was 100°C at lower frequency itself (50 Hz). The figure 3(c, d) indicates the values of dielectric constants in different temperatures. A maximum dielectric constant of 5.55 was observed at lower frequency of 50 Hz for material designation RFI₂. In material RI₂ a maximum dielectric constant of 4.9 was observed at 100 Hz. It is noted that when temperature increases there is a decrease in dielectric constant this is due to boost up of kinetic energy of molecules. The molecules rotates freely in out of orientation, this effect affects the charge acceptance of composite. When frequency is increased, the relaxation time required for getting orientation between the molecules is very little, hence the orientation of dipolar molecules are very poor [17,18].

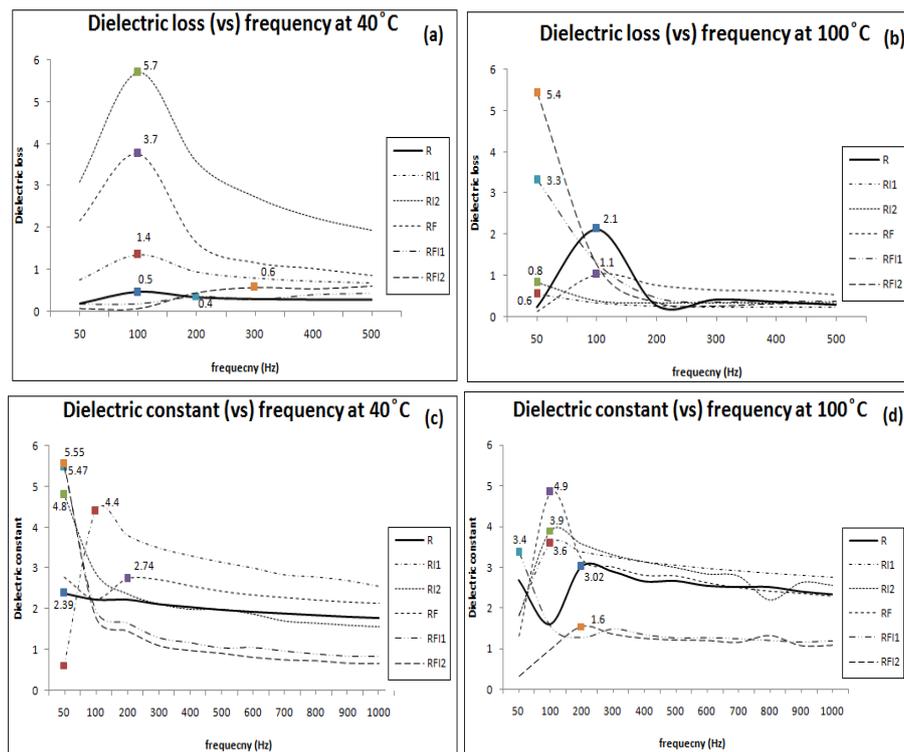


Fig.3 Dielectric properties of composites

4. Conclusions

The various compositions of E-glass fiber and iron (III) oxide particles reinforced epoxy composites were prepared successfully. Morphology of the particle loaded epoxy composites shows reacted phase of fillers with the epoxy resin improved cross linking density. Incorporation of fiber into the epoxy matrix favors improvements in mechanical properties but poor in thermal and dielectric properties. Incorporation of iron (III) oxide particles served fine improvements in thermal stability and dielectric behavior. From results greater dielectric loss has recorded by doping iron (III) oxide particles this phenomenon can be applied in dielectric heating by polymeric materials without using any other traditional heating sources. These particle dispersed polymer composites could be used as a case of thermal containers and also heating materials for low temperature applications such as smart warm devices.

References

- [1] Pedro Henrique Cury Camargo, Kestur Gundappa Satyanarayana, Fernando Wypych, *Materials Research*, **12**,1 (2009).
- [2] Thomas Hanemann, Dorothée Vinga Szabó, *Polymer Nanoparticle Composites: From Synthesis to Modern applications*, *Materials*, **3**,3468 (2010).
- [3] Xi Zhang, Ouassima Alloul, Qingliang He, Jiahua Zhu, *Strengthened Magnetic Epoxy Nanocomposites with Protruding Nanoparticles on the Graphene Nanosheets*, *Polymer*, **54**,3594 (2013).
- [4] K Devendra, TRangaswamy, *J. of Minerals and materials Characterization and Engineering*, **1**,353 (2013).
- [5] P Judeinstein, C Sanchez, *J. of Mater Chemistry* **6**,511(1996).
- [6] X Zhang, LC Simon, *In situ polymerization of hybrid Polyethylene Alumina Nanocomposites*, *Macromol. Material Eng*, **290**,573 (2005).

- [7] SL Gao, EMader, Characterization of Interphase Nanoscale Property Variations in Glass fiber Reinforced polypropylene and epoxy resin composites, *Composites A*, **33**,559 (2002).
- [8] ZhanhuGuo, Kenny Lei, Yutong Li, Thomas Hahn, *Composites Science and Technology*, **68**,1513 (2008).
- [9] ZGuo, X Liang, T Pereira, RScaffaro, HT Hahn, *Composites science Tech.* **67**,2036 (2007).
- [10] SS Park, NBernet, SDL Roche, HT Hahn. *J. Composite mater.* **37**,465 (2003).
- [11] Qi Wang, George Chen, Abdulsalam S. Alghamdi, Influence of nanofillers on electrical Characteristics of Epoxy resin Insulation. *Internat. Confer. On solid Dielectrics* (2010).
- [12] T Tanaka, Dielectric nanocomposites with insulating properties, *Dielectrics and Electrical Insulation*, *IEEE*, **12**(5),914 (2005).
- [13] S Singha, M.J Thomas, dielectric properties of epoxy nanocomposites. *Dielectric and Electrical insulation*, *IEEE trans.* **15**(1), 12 (2008).
- [14] J.P.Eloundou, Dipolar relaxations in an epoxy amine system. *J.European Polymer.* **38**,431 (2002).
- [15] Q. Wang, G. Chen, *Advances in Materials Research*, **1**(1),93 (2012).
- [16] L.D Zhang, H.F Zhang, G.ZWnag, C.M. Mo, Y. Zhang, *Phys. Stat. Sol.* **157**(2)m483 (1996).
- [17] J.K. Nelson, J.C. Fothergril, *Nanotechnology*. **15**, 586 (2004).
- [18] ZhanhuGuo, Koo Shin, Amar B. Karki *Journal of Nanopart Res.* **11**,1441 (2009).
- [19] K.Suri, S. Annapoorni, RP. Tandon. *Bull material Sci.* **24**, 563 (2001).
- [20] SVivekchand, KCKam, GGundiah, AGovindaraj, AKChellam, CNR. Rao *Jour. Of material chemistry.* **15**,4922 (2005).
- [21] R.Gangopadhyay, ADe, S. Das *Journal of Applied physics*, **87**,2363 (2000).
- [22] FMammeri, ELBourhis, LRozes, C. Sanchez, *J. Material Chemistry* **15**,3787 (2005).
- [23] T.P. Mohan, M. Ramesh kumar, R. velmurugan, Thermal stability and damping characters of high performance epoxy layered silicate nanocomposites. *International symposium of research students on material science and technology*, 2004.