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Modification of Fiber-Reinforced Plastic by Nanofillers

Martin James, Manoj George K., Cijo Mathew, Dr. K. E. George, Reji Mathew

***Abstract*— In the last 15 years, some studies have shown the potential improvement in engineering properties and performances of fiber reinforced polymer matrix materials in which nano and micro-scale foreign particles (clay, silica, rubber, etc.) were incorporated. The objective of this study is to investigate the effect of adding different percentages of nanoclays to modify a commercially available polyester resin used in engineering applications, and to enhance the mechanical properties of Glass Fiber-Reinforced Polyester (GFRP) composites.**

Keywords—**Nanocomposites; Polyester Resin; Nanoclays; Glass Fiber; Sonicator; Analysis of visco-elastic properties.**

I. INTRODUCTION

Plastics play an important role in our daily lives. Plastics can be rubbery or rigid and they can be shaped into an endless variety of objects and have a useful life of many years [1]. Thermosetting resins change irreversibly under the influence of heat into an infusible and insoluble material by the formation of covalently cross-linked, thermally stable networks. After solidified by the cross-linking, they cannot be reshaped. Unsaturated polyester resins are an example for thermosetting resins. Polyester resins are unsaturated resins formed by the reaction of dibasic organic acids and polyhydric alcohols. Polyols used are glycols such as ethylene glycol, and acids used are phthalic acid and maleic acid. The use of unsaturated polyesters and additives such as styrene lowers the viscosity of the resin. Initial free-radicals are induced by adding a compound that easily decomposes into free-radicals [4]. Catalysts used are generally organic peroxides such as benzoyl peroxide or Methyl Ethyl Ketone Peroxide (MEKP). Polyester resins are thermosetting and cure exothermically. Excessive catalyst can cause charring during the curing process, causes the product to fracture or form a rubbery material. General purpose polyester resins have good properties for most applications involving normal environments of temperature, weathering or chemical exposure [5]. Fillers are particles added to material (Plastics, composites, concrete, etc.) to lower the consumption of more expensive binder material or to better some properties of the mixture material. Mixing relatively small amount of treated nano-scale clay particles into plastics improve polymer performances including heat resistance, strength, stiffness, dimensional stability, yield stress, tensile stress, creep resistance, and toughness. Glass fibers reinforced in polymers have received considerable attention during the last century. Nano-particles are presently considered high potential filler materials for the improvement of mechanical and physical polymer properties [2].

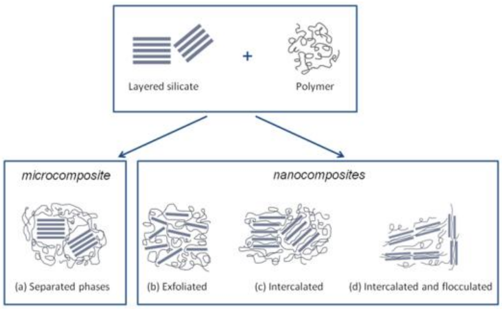

Fig. 1: Nanofillers

The latest development in polymer technology is nanocomposites whereby the addition of nano-sized fillers into the polymer, such as epoxy or polyester, can lead to a number of desirable effects. Nanocomposites are a wide range of materials consisting of more than two components, also at least one component having dimensions in the nm range. They typically consist of a macroscopic matrix with the addition of nanometer-sized particulates or filler. In nano clays, silicate layers are separated by an interlayer. Silicates layers are ~ 1nm thick, 300 nm to microns laterally. Polymer acts as interlayers on mixing. Dispersion of nanofillers in the polyester resin matrix is a challenge [7]. Fiber-Reinforced Plastic (FRP) is a composite material made of a polymer matrix reinforced with fibers. The fiber used is glass, carbon, aramid, kevlar, paper, wood, asbestos, etc. Polymers used are epoxy, vinylester, polyester, and phenol formaldehyde resin. FRP's commonly used in the aircraft, aerospace, automotive, marine, sports goods, home appliances and construction industries. Glass reinforced polymers are having high specific strength, high specific stiffness, light weight and, corrosion resistance. They help in improved surface quality and aerodynamics, reduction in components by combining parts and forms into simpler moulded shapes, pedals can be moulded as single units combining both pedals and mechanical linkages simplifying the production and operation of the design. Fiber mats are web form non-woven mats of glass fibers. Fiber mats are manufactured in cut dimensions with chopped fibers, or in continuous mats using continuous fibers [8]. Since glass fiber possess inorganic nature and resin possess organic nature, in between adhesion will be less. In order to improve adhesion between those two, modified clays are mixed with polyester resin. Studies conducted during the last decade reveal that adding small amounts of foreign particles (like clay or silica) of nanosize significantly improves the engineering properties

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of the polymers. The mechanical properties such as impact strength, tensile strength, flexural strength, and hardness have been studied according to ASTM standards [3]. The improvement of the mechanical properties of polyester/nanoclay nanocomposites are analysed by preparing polyester resin with nanoclay content (1.0, 1.5, 2.0 wt%) for unmodified, mercapto and dialkyl nanoclays. Initiator and accelerator are widely used to bring about faster curing of the unsaturated polyester resin. Curing temperatures are fixed according to the specified limit for composites. Glass fiber-reinforced plastics are fabricated with respect to the modified polyester resin with nanoclays [6].

II. MATERIALS AND METHODOLOGY

In chemistry all clay minerals may simply be described as hydrous silicates. Organically modified nanoclays have become an attractive class of organic-inorganic hybrid materials because of their potential use in wide range of applications such as in polymer nanocomposites.

TABLE I: NANOCLAY

Supplier English India Clay Limited, Thiruvantahapuram			
Properties	**Unmodified**	**Dialkyl**	**Mercapto**
Appearance	White/Off White Powder	White/Off White Powder	White/Off White Powder
Brightness (ISO) Min.	86 +/- 0.5	86 +/- 0.5	86 +/- 0.5
Median Particle Size (D 50%)	100 +/- 0.5 nm	100 +/- 0.5 nm	100 +/- 0.5 nm
Below 0.5 Micron (Mass%)	100	100	100
Plate Thickness (SEM)	<80 nm	<80 nm	<80 nm
300 Mesh (Max.)	10 ppm	10 ppm	10 ppm
pH (10% Slurry)	7.5-8.0	8-8.5	8.0-8.5
Bulk Density	0.2-0.3 g/cc	0.2-0.3 g/cc	0.2-0.3 g/cc
Hegman Grind	6.5+	6.5+	6.5+
BET Specific Surface Area	28-30 m^2/g	28-30 m^2/g	28-30 m^2/g
Oil Absorption	45-50 g/100g	48-50 g/100g	48-50 g/100g
Moisture	<1w/w%	<1w/w%	<1w/w%
LOI	14-14.5 Ww/w%	14-14.5 Ww/w%	14-14.5 Ww/w%

In plastics, Grade 2 is given for polyester resin, and here we are using General Purpose (GP) polyester resin of Grade 102. Styrene acts both as a cross-linking agent and as a viscosity reducer so that the resin can be processed without the evolution of any by-products. The initial free radicals are induced by adding a compound that easily decomposes into free-radicals, i.e. catalyst. Optimal temperature range of conventional catalyst system for unsaturated polyester is 25-35°C for MEKP and cobalt naphthenate. Cobalt (II) naphthenate is a mixture of cobalt (II) derivatives or salts of naphthenic acids, acts as accelerator. Glass fibers are amorphous solids. Selected glass fibers are Chopped Strand Mat (CSM) of 300 g/cm^2 and Woven Roven Mat (WRM) of 610 g/cm^2. Emulsion bond type WRM is used here instead of powder bond type. The various factors such as clay percentage, clay material, curing temperature, accelerator and catalyst compositions are considered here for the experiment. Silica paste is the most common anti-adhesive agent used in moulding operation. It is white in colour and diluted using water. A purpose built mould was designed for producing the dog bone resin specimens for tensile testing according to the recommendations of ISO 527 standard. The mould was made in acrylic sheet [4]. Moulding operation is carried out for different clays and their percentages in a pre-manufactured mould according to the size of test specimens. At first polyester resin is measured at the weighing machine for the required amount and accelerator and catalyst are dropped down to the beaker for the corresponding ratios. Then, the mixture is poured over the mould cavity and set for curing. For modifying resin, clay must be added before the reaction occurs. Samples are left to cure at room temperature for 24 hours. After 24 hours, samples were post cured for one day at 80°C in an electric oven. Samples are taken away from the mould and tested for mechanical properties.

Fig. 2: Nanoclay

Pristine polyester resin is mixed with accelerator and catalyst, stirred well using a glass rod, poured into the mould cavities and kept for 24 hrs for curing. While mixing clay with resin we have to use mechanical stirrer as well as sonicator. Mechanical stirrer and sonicator are used for the proper dispersion of the nanofiller into the matrix. Mixing of clay and resin will take more than 1hr and it produces high frequency sound, temperature, and foam. External cooling system was employed by submerging the beaker containing the mixture in an ice bath to avoid temperature rise during the sonication process. Moulding can be done by pouring the resin clay mixture into the shapes provided on the mould. The mixture is then added to polyethylene terephthalate mould, which was coated with Teflon based mould release agent to aid in demolding. Clay was dried in an oven at a temperature of 80°C for 24 hrs. Take 1% clay of resin (i.e. 2 g clay of 200 g resin) and measure it by using weighing machine. Collect it into a mortar and add styrene in order to dissolve it. Gently mix it using the mortar rod. Take 200 g of resin in a 600 ml beaker and add this clay in to it. Stir it well with a glass rod and using mechanical stirrer mix the resin and clay for 15 minutes on 1000 rpm at ambient temperature conditions. In order to avoid the foams generated, mix it again for 15 minutes using sonicator. The amplitude of sonicator must be fixed at 80%. Hand lay-up technique is used in this study since it is effective, economic, good surface finish and easy fabrication. The random chopped strand glass mat or woven roving is cut to fit the open mould contour and impregnated with the catalysed resin using a brush in successive piles. The hand lay-up method is labour intensive and is suitable for low rate of production. The quality of the product is highly dependent on operator skill in removing air bubbles and voids and safety will be followed by maintaining good operating

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ambience. For reinforcing the polyester matrix, E-glass (chopped glass-fibre mat and glass woven [0/90]) fabric were used. The process of hand lay-up was continued until the composite consisted of 3-4 layers of CSM glass fiber with a thickness of 2-3 mm (ISO 1268).

Fig. 3: Hand Lay-up Method

Take 4 OHP sheets and apply silica paste on one side and keep it for drying. Take 2 tiles with smooth coated straight surface. Then, fiber glass (CSM of 300 g/cm^2 and WRM of 610 g/cm^2) are cut it into 3 pieces according to the size of the tile. Pour pristine polyester resin or modified resin of 200 g in to the beaker. Here, resin/accelerator/catalyst ratio is 200:2:2. Push the TARE button on the weighing machine and add 2 g of accelerator into the resin using a dropper and stir well using glass rod for 4-5 min. without forming air bubbles. Add 2 g of catalyst (hardener) into the resin mixture using a dropper . Apply gel coat with roller or 3" brush, which was used to impregnate the nanocomposite. Take the cut piece of CSM or WRM and place it over the resin mixture coated on the OHP sheets of the tile. Again, brush the mixture over the mats. Close the mould and keep it under pressure by putting a weight over it for 24 hrs at room temperature for curing. To ensure complete curing, modified nanocomposite samples were post-cured at 80ºC for 24 hrs. Take out the composite produced and machine it in industries according to the standard test specimen sizes for tensile, impact and flexural tests. Depending on whether it is a roughing or a finishing operation, the parameters can be adjusted for either a higher cutting rate or a better cut quality. Glass fibers must be handled with most care, and should use hand gloves and goggles and also clean the work premises neatly after completing the experiment.

Fig. 4: GFRP Sheet and Tensile Test Specimen

Compare results of resin added with different clays (Unmodified, mercapto modified, dialkyl modified) and different compositions (1wt % – 2wt %) with standard base resin composite.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

Various tests are conducted for the mechanical and thermal properties of moulded polyester resin and fabricated GFRP's. Graphs showing trend and area under the curve are plotted using OriginPro8 software. Tensile strength measures the force required to pull something to the point where it breaks. Tensile strength of a material is the maximum amount of tensile stress that it can get before breaking. Area underneath the stress-strain curve is called toughness. Flexural strength is defined as a material's ability to resist deformation under-load. Transverse bending test is most frequently employed and which uses a three point flexural test technique. Flexural strength represents the highest stress experienced within the material at its moment of rupture.

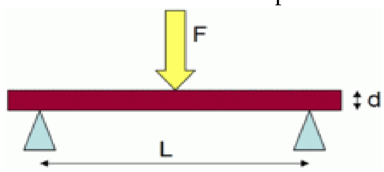

Fig. 5: Beam under 3 point bending.

Drop-weight impact tests have been carried out for glass-polyester laminates for a range of diameter to thickness ratios. Analysis of the impact response using a mainly graphical methodology allowed further characterisation of the behaviour. Damage occurs in two stages, hidden internal delamination damage and perforation failure. Shore D Durometer was employed for measuring surface hardness. For plastics Grade D is selected and its unit is SHORE, i.e. SHORE D. Tests are conducted according to ASTM D 2240 specifications and minimum 6 mm thickness of the specimen is needed for the test to conduct. Thermo-gravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature or as a function of time. TGA gives information about physical phenomena and chemical phenomena. Scanning Electron Microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. Electrons interact with atoms in the sample, generates various signals that can be detected and that contain information about the sample's surface topography and composition.

A. *Tensile Strength*

TABLE II: Tensile Test Results

TENSILE TEST									
Clay Type							GFRP		
Temperature	Cured at 30°C			Cured at 80°C			Temperature	Cured at 30°C	Cured at 80°C
Clay %	UM	DAL	MC	UM	DAL	MC	Clay %/Fiber	CSM	WRM
Units	N/mm^2	N/mm^2	N/mm^2	N/mm^2	N/mm^2	N/mm^2	Units	N/mm^2	N/mm^2
0	32.51	32.51	32.51	37.8199	37.8199	37.8199	WRM	245.487	251.985
1	48.06	46.7679	37.3109	53.62	52.3959	42.6291	CSM	93.0349	100.282
1.5	44.2884	34.9939	46.1221	50.6357	41.3548	50.634	CSM1%UM	115.415	130.718
2	44.06	33.0338	42.165	50.5119	34.6193	49.3888	CSM1%DAL	94.5393	104.14

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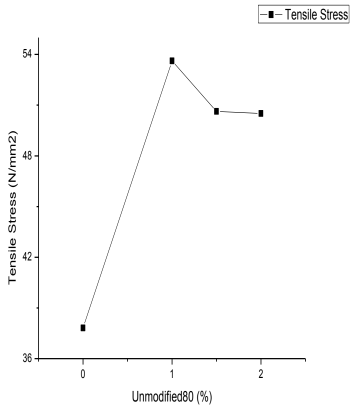


Fig. 6: Tensile strength variations for different clay loading of unmodified clay cured at 80°C.

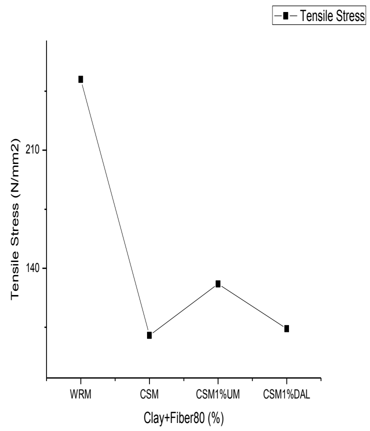


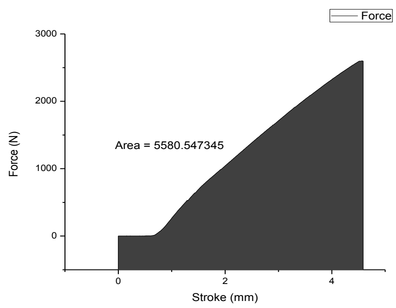
Fig. 7: Tensile strength variations for different GFRP's cured at 80°C.

Tensile strength increases with the addition of nanoclays into the pristine resin. Fiber reinforcement also increases the tensile value to great extent and will get improved on post-curing at 80°C. In GFRP fabricated with CSM, tensile strength value is found high for 1% unmodified clay, post cured at 80°C.

B. Toughness

Area under the stress-strain curve for GFRP fabricated by polyester resin with 1% unmodified clay cured at 80°C is much higher than GFRP fabricated with pure polyester resin. Therefore, it is tough material for the industrial applications.

Fig. 8: GFRP fabricated by polyester resin with 1% unmodified clay cured at 80°C



C. Flexural Strength

TABLE III: FLEXURAL TEST RESULTS

FLEXURAL TEST									
Clay Type							GFRP		
Temperature	Cured at 30°C			Cured at 80°C			Temperature	Cured at 30°C	Cured at 80°C
Clay %	UM	DAL	MC	UM	DAL	MC	Clay %/Fiber	CSM	WRM
Units	N/mm^2	N/mm^2	N/mm^2	N/mm^2	N/mm^2	N/mm^2	Units	N/mm^2	N/mm^2
0	67.6526	67.6526	67.6526	104.461	104.461	104.461	WRM	162.369	199.198
1	103.683	101.12	76.473	123.624	123.034	115.543	CSM	132.505	176.315
1.5	86.1644	62.6657	91.4874	108.453	96.1136	122.09	CSM1%UM	153.849	176.961
2	85.3738	51.5691	89.4635	103.063	108.419	93.265	CSM1%DAL	146.491	171.926

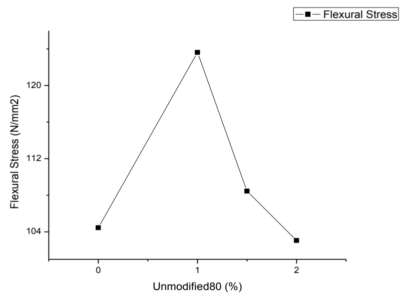


Fig. 9: Flexural strength variations for different clay loading of unmodified clay cured at 80°C.

Flexural strength increases with the addition of nanoclays into the pristine resin. Flexural strength value is found high for clay loading of 1% unmodified clay. Flexural strength of the polymer composite increases with increase in polyester and fiber contents.

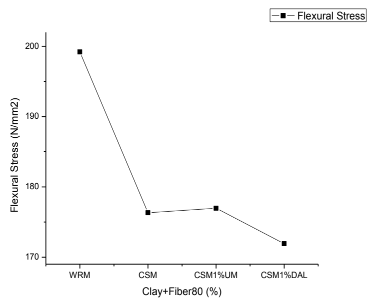


Fig. 10: Flexural strength variations for different GFRP's cured at 80°C.

Fiber reinforcement also increases the flexural value to great extent and will get improved on post-curing at 80°C. Flexural strength value is found high for GFRP fabricated with WRM than CSM. In GFRP fabricated with CSM, flexural strength value is found high for 1% unmodified clay post-cured at 80°C.

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D. Impact Strength

TABLE IV: IMPACT TEST RESULTS

IMPACT TEST						
Clay Type				GFRP		
Temperature	Cured at 30°C			Temperature	Cured at 30°C	Cured at 80°C
Clay %	UM	DAL	MC	Clay %/Fiber	CSM	WRM
Units	KJ/m²	KJ/m²	KJ/m²	Units	KJ/m²	KJ/m²
0	3.41	3.41	3.41	WRM	85.1	93.71
1	10.97	7.48	5.03	CSM	102.58	108.64
1.5	8.18	4.36	7.57	CSM1%UM	119.37	131.54
2	7.25	6.2	4.64	CSM1%DAL	111.01	123.69

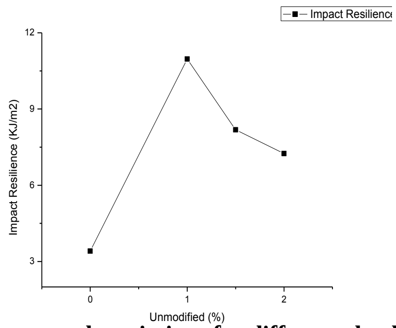

Fig. 11: Impact strength variations for different clay loading of unmodified clay cured at room temperature.

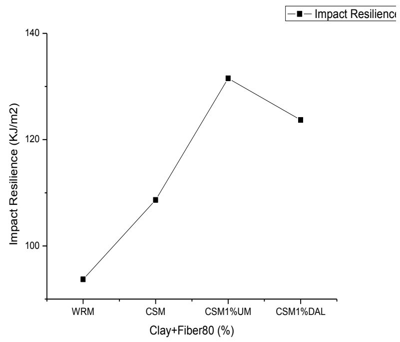

Fig. 12: Impact strength variations for different GFRP's cured at 80°C.

Impact strength increases with the addition of nanoclays into the pristine resin. Fiber reinforcement also increases the impact value to great extent and will get improved on post-curing at 80°C. Impact strength value is found high for a clay loading of 1% unmodified clay. CSM has more impact than WRM. GFRP fabricated with CSM and 1% unmodified clay, which is post-cured at 80°C, shows more impact strength value.

E. Surface Hardness

TABLE V: SURFACE HARDNESS

HARDNESS TEST									
Clay Type							GFRP		
Temperature	Cured at 30°C			Cured at 80°C			Temperature	Cured at 30°C	Cured at 80°C
Clay %	UM	DAL	MC	UM	DAL	MC	Clay %/Fiber	CSM	WRM
Units	SHORE D	SHORE D	SHORE D	SHORE D	SHORE D	SHORE D	Units	SHORE D	SHORE D
0	82	82	82	84	84	84	WRM	86	88
1	93	86	88	94	87	87	CSM	88	90
1.5	88	84	87	91	86	87	CSM1%UM	94	95
2	86	84	86	89	85	85	CSM1%DAL	91	92

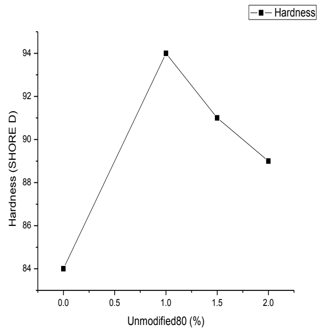

Fig. 13: Hardness variations for unmodified clay cured at 80°C

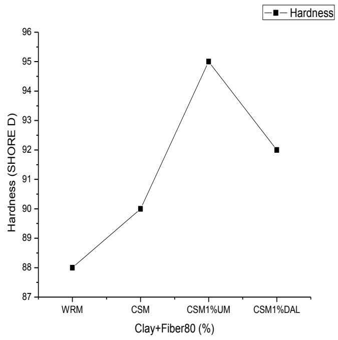

Fig. 14: Hardness value for different GFRP's cured at 80°C

Surface hardness value increases with the addition of nanoclays into the pristine resin and will get improved on post-curing at 80°C. Fiber reinforcement also increases the hardness value to great extent. Chopped Strand Mat fabricated with 1% unmodified clay post-cured at 80°C is much harder than other reinforcements.

F. Themo-Gravimetric Analysis (TGA)

The thermal characteristics of the polyester/clay blended nanocomposites were studied using themo-gravimetric analysis. TGA was used to investigate thermal decomposition behaviour of the nanocomposite blend.

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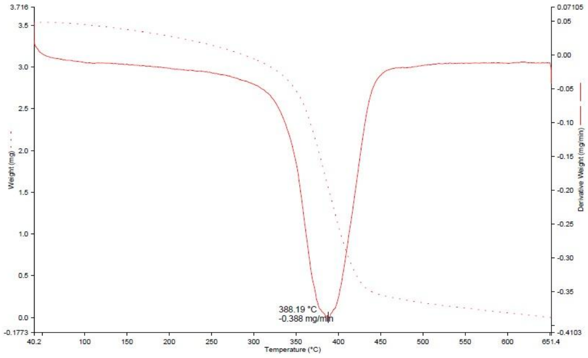

Fig. 15: TGA analysis of polyester resin with 1% unmodified clay

Degradation temperature for pure resin is 377.41°C and for polyester resin with 1% unmodified clay is 388.19°C. While adding nanoclay content to polyester resin more than 11°C of degradation temperature happens. Therefore, better thermal stability can be achieved. Degradation rate for pure resin is -0.718 mg/min and for polyester resin with 1% unmodified clay is -0.388 mg/min. Since degradation rate is reducing with the addition of nanoclay, melting rate will be low for the nanocomposite.

G. Scanning Electron Microscopy (SEM)

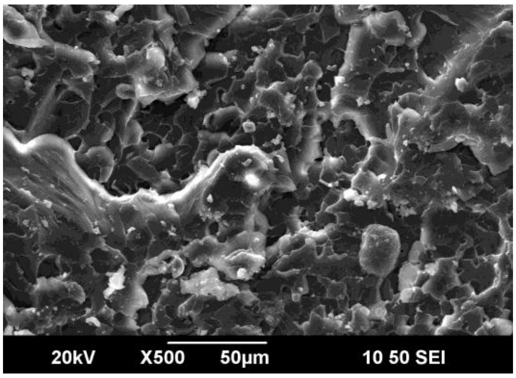

Fig. 16: SEM micrograph of polyester resin with 1% unmodified clay

Magnification at X500 reveals that clays mixed with the resin are at nm range. Brittle fracture can no longer be seen as the clay content is gradually increased from 0.5wt% to 1wt% as a result of which, strong ductile nature of the composite was observed, which is still an indication of good dispersion of nanoparticles that brought out maximum improvement of mechanical properties at 1wt% clay loading. Also, the fracture behaviour was studied by SEM.

IV. CONCLUSION

It was understood that addition of various clays to the polyester resin, could improve the thermal and mechanical properties of the resin. Improved mechanical strength can be achieved by glass fibre reinforced polymer with 1% unmodified clay post-cured at 80°C. Polyester clay nanocomposites showed remarkable improvement in tensile, flexural and impact properties. Thermal stability and barrier properties were significantly improved by the incorporation of clay particles to polyester systems. Reinforcement of the resin matrix with fibers will improve toughness considerably.

V. ACKNOWLEDGMENT

The successful completion of the present research endeavour was made possible by the generous, enthusiastic and inspiring guidance of my dear supervising teacher Dr. K.E. George, former Head of Polymer Science & Rubber Technology Department, CUSAT.

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AUTHOR BIOGRAPHY


Martin James has received his B.E. degree in Mechanical Engineering from Karpagam College of Engineering, Coimbatore (Anna University- 2008). He has 3 years of industrial experience in Power Plant construction field. He is doing M.Tech in Production and Industrial Engineering in M.A. College of Engineering, Kothamangalam (M.G. University- 2013).


Manoj George K. got his Bachelor’s degree in Mechanical Engineering from NSS College of Engineering, Palakkad, under University of Calicut. He took his Post Graduation from the School of Engineering, Cochin University. He is working as Vice-Principal in Mangalam College of Engineering, Ettumanoor, Kottayam.


Cijo Mathew has received his B.Tech degree in Mechanical Engineering from M.A. College of Engineering, Kothamangalam (2003) and M.Tech degree in Production and Industrial Engineering from M.A. College of Engineering, Kothamangalam (2006). He is working as Professor in M.A. College of Engineering, Kothamangalam.

Dr. K.E. George has received his Ph.D from Cochin University of Sciene and Technology. He took M.Tech from IIT Madras and B.Sc. Engineering from Calicut University. He is working as Principal in Albertian Institute of Science and Technology, Cochin.

Reji Mathew has received his B.Tech degree in Mechanical Engineering from College of Engineering, Trivandrum (1985) and M.Tech degree in Thermal Science from College of Engineering, Trivandrum (1987). He is working as Professor in MACE, Kothamangalam.