



Synthesis and Characterization of Blended Polyester and Vinylester Polymers filled with MMT-Nanoclay

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ARTICLE INFO

Article history:

Received: 10 July 2015;

Received in revised form:

25 August 2015;

Accepted: 5 September 2015;

Keywords

Blending,
Mechanical properties
Thermal properties,
SEM,
DSC,
TGA.

ABSTRACT

This paper evaluates blended nanocomposites developed by in situ polymerization in which the polyester & vinylester were blended and then nanoclay dispersed with the help of probe type ultra sonicator and mechanical stirrer to ensure homogeneous dispersion of nanoparticles. Nanocomposites were then evaluated with mechanical properties like tensile strength and modulus properties from the results it was observed that, due to the substantial miscibility of polyester and vinylester was noticed from the SEM analysis and rate of tensile strength increased up to 3.5wt.% clay loading but decreases after as a function of clay. Nanocomposites were prepared by using hand layup process. SEM analysis were also studied for the specific samples to study the cross sections of fracture surfaces and it was found that interface, voids, agglomerations were played instrumental in optimization of maximum strength. FTIR analysis was also conducted to study the FTIR, DSC, and TGA were also studied to check glass bonding and structure, transition temperature and thermal stability respectively for the specific samples.

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Introduction

Advances in nanoscale research will likely have profound impact on the fields of medicine, semiconductor technology, and energy efficiency. The scope of this work, however, is concerned with the role nanoscale materials will play in composite systems. For the research scientist who is concerned with composite materials, nanomaterials possess several key attributes that have the potential to make significant impact on the state of the art. The nanoscale fillers of composite systems will do more than just enhance one aspect of a system's properties. The concept of multi-functional nanomaterials is emerging as an important research goal. For instance, ceramic nanoparticles may be embedded in a coating primarily to improve wear resistance, but these same particles may have certain luminescent properties that allow for passive wear detection. The composites containing nanoparticles display synergism in the physicochemical and physicomechanical properties yet the level of improvement maximizes up to a certain extent[1-10]. Among engineering materials, vinylester resin (VE) is a relatively cheaper than other polymers of its class and possess properties that are intermediate between epoxy resin and polyester resin. It is worth mentioning that VE and polyester resin occupy approximately 75 % of the market share making them the one of the most valuable industrial polymers. Therefore, improvement in their properties without sacrificing the basic properties of the resin is highly desirable. Vinylester resins were first introduced commercially in the early 1960s. Today, they are one of the most important thermosetting materials. Vinylester resins have been widely recognized as materials with excellent resistance to a wide variety of commonly encountered chemical environments. Vinylester resins are used to fabricate a variety of reinforced structures, including pipes, tanks, scrubbers and ducts. They are prime candidates for use in composites for transportation and/or infrastructure. Such applications include fabrication of parts for

automobiles and other surface transportation vehicles, fascia for buildings, reinforcements for bridges, etc[11-19].

In addition to these applications, vinylesters are also being used in coatings, adhesives, molding compounds, structural laminates, electrical applications and military/aerospace applications. Vinylester resins are addition products of various epoxide resins and unsaturated monocarboxylic acids, most commonly methacrylic acid. They have terminal reactive double bonds derived from the carboxylic acid used. These reactive groups can form a crosslinked network with or without the addition of a comonomer. In many industrial products, vinyl ester resins are comprised of 40-50 wt.% styrene. In dental applications triethylene glycol dimethacrylate is the comonomer. It is common to dilute the vinyl ester oligomers with a low molecular weight comonomer, such as styrene, vinyltoluene or methyl methacrylate, to reduce the room temperature viscosity of the mixture and yield a solution with a typical viscosity in the range of 200 to 2000 cps. The structure of VE as shown in the **fig.1** and the physical properties are shown in the **Table: 1** Polyester resins have a wide range of industrial relevance, such as in industrial finishes and maintenance, architectural uses, paints, and surface coatings. However, they suffer from some drawbacks, such as low alkali resistance, and low hardness. So, to overcome these drawbacks of polyester resins, blending with other suitable resins, such as vinylester resin, amino resin, silicone resin, and ketonic resin, can be performed. Polyester resins have good compatibility with a wide variety of other resins. The better compatibility comes from the relatively low viscosity of the resin and from the structure of the resin, which contains a relatively polar and aromatic backbone and aliphatic side chains with low polarity. The blending technique may be used effectively to overcome the inferior properties of both the components.

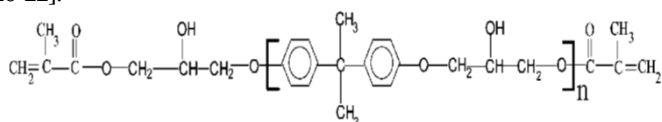
Table 1. Properties of vinyl ester resin

color	Styrene content	Specific gravity @25°C	VOC Content	Physical state	Self life
Blue	43wt.%	1.04-1.12	486 gm/l	liquid	3-5 months @ 25 °C

Table 2. Specimen names after sample preparation

Blended specimens	Clay content (Wt. %)
S1	0.0
S2	2.0
S3	2.5
S4	3.0
S5	3.5
S6	4.0
S7	5.0
S8	6.0

Miscible polymer blends produce a new improved material from less superior individual components. Again, because of the enhancement of the properties, such as the mechanical, thermal, and barrier properties, even at low concentrations, the nanocomposites of such blends have drawn much attention. Recently, extremely tough hybrid resins were produced by combining suitable vinylester. Polyesters are also commonly used as matrix materials, particularly with glass, carbon, nylon, aramid fibers reinforcement. Behavior of hybrid nanocomposites appears to be simply a weighted sum of the individual components in which there is a more favorable balance between the advantages and disadvantages inherent in any nanocomposite material. It is generally accepted that the properties of hybrid nanocomposites are controlled by factors such as nature of matrix; nature, length and relative composition of the filler, reinforcements; fibre-matrix interface; and hybrid design etc [20-22].

**Figure 1. Chemical structure of vinyl ester resin**

Therefore, in the present research focus is made on the two blending of miscible polymer such as polyester and vinylester and yet it reinforced with nanoclay. Tensile strength, tensile modulus, DSC, TGA (i.e. thermal properties) SEM (i.e. morphological properties) were studied to check the compatibility of modified blend with nanoclay.

Materials and Methods

Polyester (Ecmalon 9911, Ecmal Hyderabad, with 2% cobalt accelerator, catalyst 50% methyl ethyl ketone peroxide (MEKP) in 10% DMA solution, ratio of the resin/accelerator/catalyst:100/2/2. The resin has a density of 1335 kg/m³, Young's modulus of 450 MPa, tensile strength of 15.3MPa and elongation at break of 3.3%. In addition, exfoliated montmorillonite clay (product No.:682659; brand: Aldrich, USA; product name: Nanoclay, hydrophilic bentonite; formula: H₂Al₂O₆Si; Molecular weight: 180.1 g/mol; Appearance (Colour): Light tan to brown; appearance (form): powder; loss on drying: ≤18.0%; density: 600-1100 kg/m³; size: ≤ 25 microns), surface modified with 25-30% trimethyl stearyl ammonium, was used as filler material. The vinylester resin used was HPR 8711 grade, a Bakelite Hylam product. Methyl ethyl

ketone peroxide (MEKP), Co-napthenate and N, N dimethylamine were used as the catalyst, accelerator and promoter respectively. Tensile strength and modulus was studied using an Instron Universal Testing Machine supplied by Instron Corporation; a series-9 automated testing machine was used with a crosshead speed of 5mm/min. Testing samples were prepared in dumb-bell shapes and these dimensions are 100 X 20 X 3 mm³ based on the ASTM D 638 standards. In each case, five samples were tested and the average value tabulated. Flexural strength and modulus were tested using an Instron Universal Testing Machine with a crosshead speed of 2mm/min. The three-point bending test system was used for all samples. In each case, five samples were tested and the average value tabulated. Authors used 50KN load cell for testing further the sample sizes and 100 X 20 X 3 mm³ was cut in accordance with ASTM D 618.

The thermal characteristics TGA, DSC measured on blended polymer nanocomposites using SDT Q600 TGA/DSC (TA Instruments) at a rate of 10°C/min under nitrogen flow measurements were carried out at 20°C temperature, 40 % relative humidity. A JEOL JSM-6400 JAPAN scanning electron microscope at 15 kV accelerating voltage was equipped with energy dispersive spectroscopy (EDS) to ascertain the fiber/filler interfaces with the main modified matrix. Fractured specimen surfaces were gold-coated and the fractures surface was observed using a scanning electron microscope. The fractured surfaces were gold-coated with a thin film to increase the conductance. The FTIR spectra of the powders of the samples were run on an ABB-Bomem FLATA-2000 model spectrophotometer using KBr pellets. The concentration of the fabric powder was maintained at 1% in KBr.

Specimen preparation

A mold was prepared on par with ASTM dimensions, and it was coated with a mold releasing agent to enable the easy removal of the sample. Mould was kept on the smooth surface with the help of spirit level. Nanoclay was kept in the oven about 50° C for 1hr to remove the moisture out of it. Predetermined amounts of clays are weighed and kept aside and followed by 80wt. and 20wt. of polyester and vinylester respectively were mixed together with spatula for about 30min under the presence of temperature just above the atmospheric. Clay was added into the modified mixture (i.e. blend) with the help of mechanical stirrer for about 45 min, then followed by probe type ultra sonication for about 45min to get uniform distribution of the clay particle. Artificial cooling system was employed to control rise in temperature during the sonication process. Then the accelerator/catalyst/promoter (100:2/2/2) parts by weight was added to the modified polyester/vinylester mixture. The mixture was poured into the mould. Brush and roller were used to get the desired surface finish. The closed mold was kept under pressure 10MPa using compression mould for 24 h at room temperature. To ensure complete curing, the composite samples were post-cured at 70°C for 1 h and test specimens of required size were cut out from the sheet for further characterizations on par with the ASTM.

Results and Discussions

Fig. 2 shows assessments tensile strength and modulus of the polyester/vinylester (80/20, %w/w) nanocomposites as a function of clay content. It was observed that tensile strength and modulus were increased gradually as a function of clay content when compared with unfilled composites and the another reason was adhesion between the polyester molecules and vinylester molecules also another sign for the improved mechanical properties. The duo properties were optimized when

clay loading was at 3.5wt.% and after that clay does not impregnate properly due to fact that more clay makes more difficult to disperse the clay particles uniformly in the modified matrix. More reason was observed in the SEM analysis for sudden decrease of strength. **Fig. 4 (a-d)** shows the scanning electron microscope images various sample cross sections. It is clearly observed from the all four figures that microgram **Fig. 4(a)** is completely in brittle nature and yet it has been transformed in to ductile nature when composite receives clay gradually. From the **Fig.4(a)** it was observed that it is a plane blend of polyester and vinylester matrix and it is clearly appears that miscibility of polymers were taken places nicely and all the white spots were observed as pull outs make poor stress transfer. Whereas in the microgram **Fig.4 (d)** it was clearly observed that more voids formed due to the improper mixing left more voids in the composites.

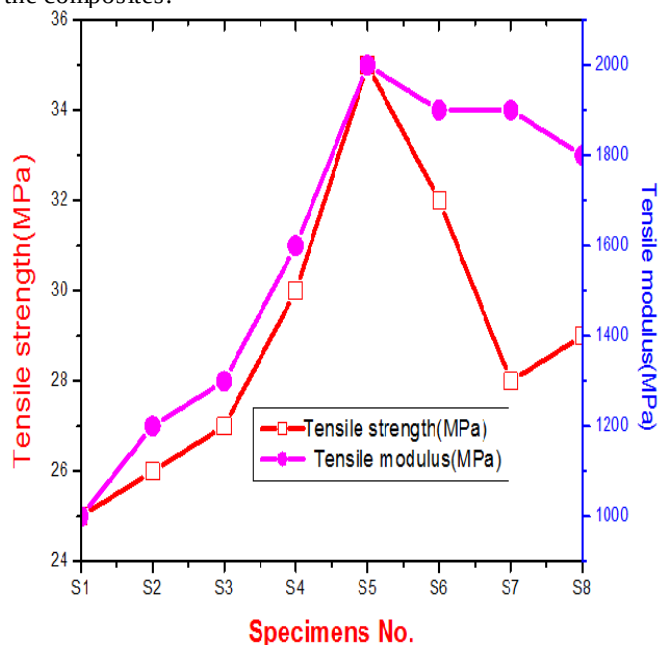


Figure 2. Variation tensile strength and modulus of polymer blended nanocomposites as a function of clay.

Fig. 5 shows the FTIR spectra of The main characteristic bands of (a) 0wt.% (b) 3.5wt.% composite (c) and 5wt% polymer blended nanocomposites. The main characteristic bands of doped blended nanocomposites are assigned as follows: the band at 3510 cm^{-1} is attributable to N-H stretching mode, $\text{C}\equiv\text{N}$ and $\text{C}\equiv\text{C}$ stretching mode for the silicate and benzen rings occur at 1900 and 1400 cm^{-1} , the bands at about 1275 and 1027 cm^{-1} have been attributed to C-N stretching mode for benzenoid ring, while the peak at 227 cm^{-1} is assigned to a plane bending vibration of C-H (mode of $\text{N}\equiv\text{Q}\equiv\text{N}$, $\text{Q}\equiv\text{N}^+\text{H}-\text{B}$ and $\text{B}-\text{N}^+\text{H}-\text{B}$), which is formed during protonation [18]. Curve (b) in **Fig. 2** indicates that the main characteristic bands of doped polymer blend and nanoclay all appear in FTIR spectra of polymer blended nanocomposite. However, the incorporation of nanoclay particles leads to the shift of some bands of modified polymer. The bands at 1900, 1400 and 1275 cm^{-1} , corresponding to the stretching mode of $\text{C}\equiv\text{N}$, $\text{C}\equiv\text{C}$ and C-N, all shifted to lower wave numbers. Meanwhile, the band at 1027 cm^{-1} which is formed during protonation obviously splits. These obvious changes reveal that the bond strengths of $\text{C}\equiv\text{N}$, $\text{C}\equiv\text{C}$ and C-N become weaker in blended nanocomposites and incorporation of nanoclay particles has effect on the doping of conducting blend. This means that there is a strong interaction between blend macromolecule and nanoclay particles. The strong interaction may be associated with the interaction of titanate and nitrogen

atom in blend macromolecule. Because clay is a transition metal, blend has intense tendency to form coordination compound with nitrogen atom in polymer macromolecule. This interaction may weaken the bond strengths of $\text{C}\equiv\text{N}$, $\text{C}\equiv\text{C}$ and C-N in blend macromolecule. Moreover, the action of hydrogen bonding between nanoclay particles and blend molecule is also contributory to the shift of bands.



Figure 3. Probe type ultra sonicator was used for homogeneous mixing of nanoclay with the modified polymer.

Fig.6 (a) reveals that pure nanoclay has silicate particles are very stable in air and almost no decomposition takes place in the range of 40-150 $^{\circ}\text{C}$ for 4wt.% clay and it was also found that curved starts going down at 324 $^{\circ}\text{C}$, and yet at this temperature there was 15% weight loss was observed. Curve 5wt.% clay loading it was observed that in **Fig. 6** represents the 14% weight loss of composite was observed at 350 $^{\circ}\text{C}$ and yet it is slightly bit higher thermal stability than 4wt.% clay loading.

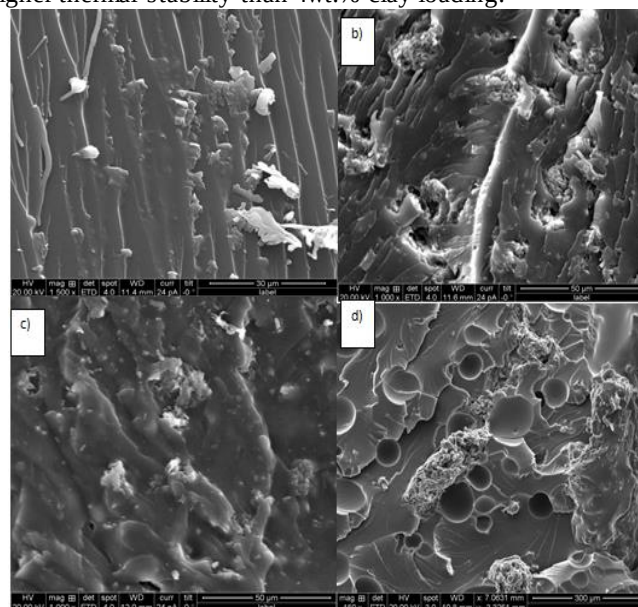


Figure 4. SEM images of various samples (a) 0wt.% ; (b) 2wt.% ; (c) 3.5 wt.% (d) 6wt.% clay loadings of polymer blended nanocomposites.

From the **Fig.6(a)** for 6wt.% clay loadings, thermal stability was slightly reduced but weight loss observed very smaller than other two clay loading and it is around 5% weight loss. Overall

at 5wt.% clay loading thermal stability was significantly good, whereas somewhat poor at remaining curves and the reason was attributed that more clay loading left more moisture as well as voids led to the decrease in thermal stability. Similar observations were made in the literature already.

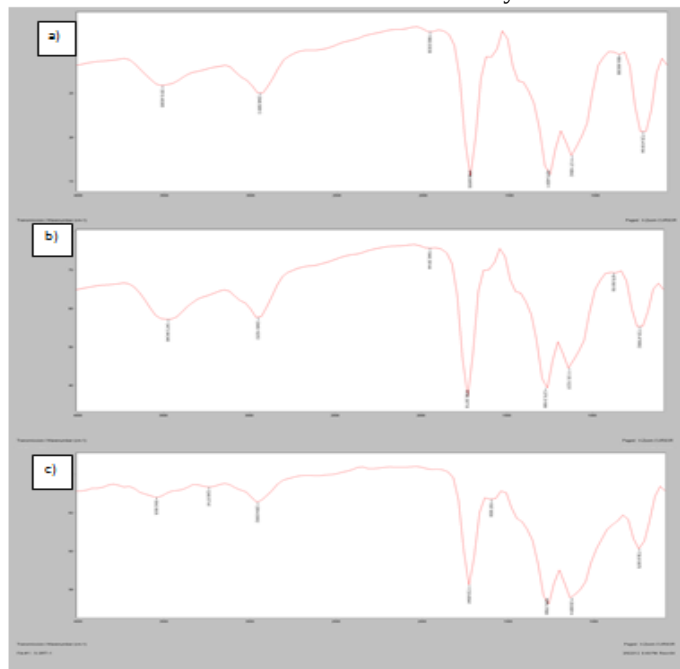


Figure 5. Fourier-transform infrared spectra of (a) 0wt.% (b) 3.5wt.% composite (c) and 5wt.% polymer blended nanocomposites

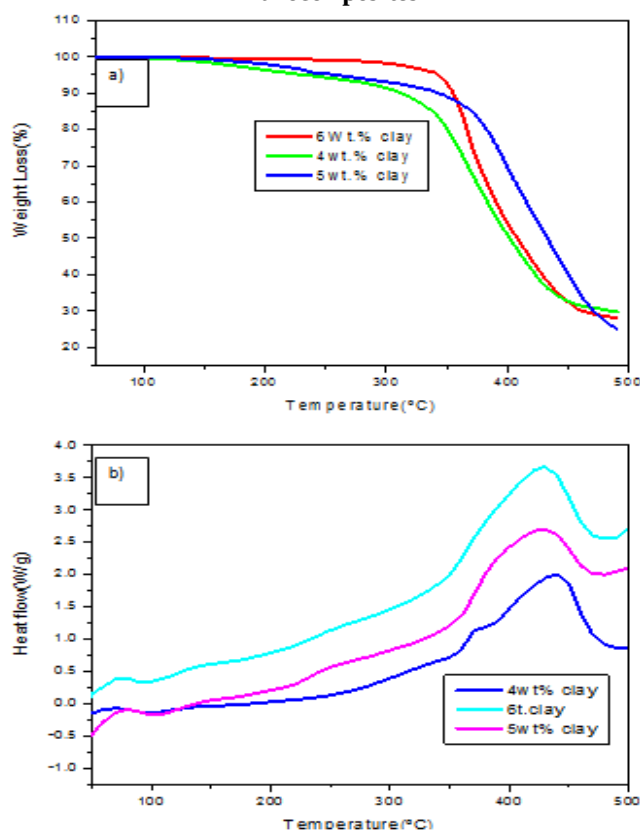


Figure 6. (a)TGA and (b) DSC analysis of polymer blended nanocomposites as a function of MMT clay.

Typical thermogram for polyester/vinylester blended nanocomposites for three different loadings viz. 4, 5 and 6wt. % clay is shown in **Fig.6 (b)**. The glass transition temperature (T_g) of blended nanocomposites was observed for different clay contents viz. for 4,5 and 6 wt. % clay contents at 436, 430,

431°C respectively as shown in **Fig. 6 (b)**. From the figures a 6°C decrease in glass transition temperature was observed when compared with for 5 wt. % clay. Whereas at 5 and 6 wt.% clay loading it was observed very small change in glass transition temperature. A number of papers have reported similar phenomena but using different fillers [10-18].

Conclusions

In this paper presented the mechanical, thermal and morphological properties of polyester/vinylester blend filled with MMT clay. Mechanical properties were optimized at 3.5 wt. % clay content. When compared with neat blend samples, 3.5 wt. % clay filled blend sample gave the following results. Thermogravimetric analysis (TGA) showed that significant weight loss was observed for small% of clay loading. Differential Scanning Calorimetry (DSC) results showed that the clay particles affected the glass transition temperature (T_g) of the nanocomposites. SEM analysis revealed that excellent adhesion and interfacing between the matrices and clay is the main reason for optimum improvement of properties. This nanocomposite can be applied in making light weight components as structural laminates, electrical applications and military/aerospace applications.

Acknowledgements

Authors would like to thank the HOD's in the Department of Mechanical Engineering, RV College of Engineering, Bangalore, Karnataka and Department of Polymer Science & Technology, SK University, Anantapur, Andhra Pradesh, India for their timely help in providing laboratories.

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