



# CURRENT TRENDS IN MATERIALS CHEMISTRY

*Editors*

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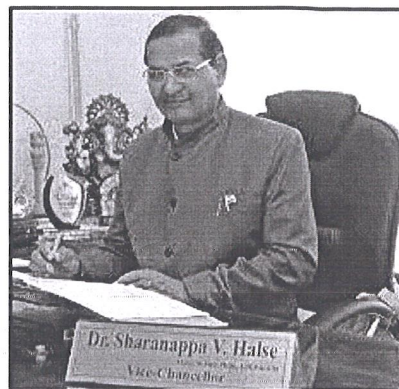
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# Message



It is my great pleasure to introduce you the book “**Current Trends in Materials Chemistry**”. This book is being published by Davangere University to highlight the rapid developments that are taking place in the field of Materials Chemistry. Materials Chemistry is rapidly emerging as a key component of contemporary science. The strongly interdisciplinary nature of the field requires input from all branches of science from crystallography, solid state physics and nanotechnology. In this book, a compiled set of chapters from researchers representing some of the highlights of materials chemistry. This book benefits scientists, researchers from academia and industry as well. I hope the book will be well received and motivates students, teachers, scientists and Engineers.

**Prof. Sharanappa V Halase**

Vice Chancellor, Davangere University,  
Shivagangothri, Davangere – 577 077.

  
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# Sea Water Durability of Vinyl Ester Resin/Clay Based Nano Composites and their Application

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## Abstract

In this paper a comparable investigation of the impacts on characteristic properties of FRP composites when presented to seawater. Similar investigation of the impacts of dipping of the composite in seawater and experimentally attempt to dissect the impact of the immersion in the mediums based on the experiment data. ILSS results achieved from the 3 point bend test, the water absorption will be estimated and reason for failure will be reported. The morphology of the failure samples were studied through scanning electron microscopy images.

**Keywords:** FRP, Sea water, ILSS, 3 point bend test, Scanning electron microscopy.

## 1. Introduction

Many of the new technology need materials with unusual blends of properties that can't be met by the traditional materials like metals, alloys, ceramics and polymers etc. The necessity for the polymeric composites has been much felt within the aircraft, offshore oil, submarine and ship building industry, as they provide the benefit of chemical stability and enormous, aren't liable to aqueous corrosion [1-2]. These are gradually utilized in civil infrastructure reestablishment applications, offshore platforms, oil development related structural facilities and marine applications.

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In all the above usage, the FRP composite is presented to dampness combined with different chemicals. The disintegration that happens in FRP during the administration life when all is said in done, is connected to the degree of dampness that is consumed. It might be conceivable that the existence of dampness in the composites, whether by itself or in mixture with other chemicals, can start adverse structural changes inside the fibre reinforcement and the matrix or the interface between the two. The absorption of dampness may make plasticization of the resin with expanding and dropping down the glass transition temperature of the resin [3-4]. This may poorly influence the fiber matrix bonding properties, results debonding at fiber/matrix interfaces, micro cracking in the matrix, fiber discontinuities, persistent cracks and a few other phenomena that may lower the mechanical property of the composites. The decrease in the glass transition temperature makes the polymer delicate and it can improve creep distortion. Due to the water ingress in the sample this may lead to volume or swelling of the sample, and this can bring stresses like thermal reactions that could cause micro-cracks. Despite these examinations, there are a few gaps in our knowledge towards the subject: for example, the interlaminar shear strength, which is a significant parameter, has not gotten a lot of consideration from this view. Besides, however the impact of water ingestion has gotten significant consideration, the impact of salt and sea water has gotten just a little consideration. This impact has gotten progressively significant because of marine applications of the glass fiber reinforced plastics (GFRP) [4-5].

Fiber Reinforced Plastic (FRP) or Glass Reinforced Plastic (GRP) is a versatile material. FRP parts can be made with generally variable properties, reliant on the type of resin matrix, level and Orientation of reinforcement; use of fillers and different added additives, just as the fabrication process and handling conditions. Subsequently, FRP parts are utilized in an expansive scope of utilizations.

FRP composites materials are shaped through the physical blend of two components, to be specific fiber and the matrix. Fibers are the strengthening components in the composite which give quality and stiffness to the composite and act as a main load carrying component [6-7]. They are generally made out of carbon, glass or aramid fibers that are presented in a specific volume fraction and bearing in a polymeric matrix epoxy. Matrix is usually a thermoset resin, for example, polyester, vinyl ester or epoxy which binds the fiber together permitting shear move among filaments and serves in as a defensive hindrance too.

Nanocomposites are composite materials comprised of matrix material and nanofillers [8-9]. Polymer-clay nanocomposites utilize a polymeric material for the matrix and clay nanoparticles for the filler. It has been indicated that nanoparticles shows superior mechanical properties of composite materials at low weight percentages more than regular composites of comparable weight parts.

The measure of increment in the extensional modulus is straightforwardly identified with the weight percentage of nanoparticles [10-12]. The extensional modulus for the most part shows a linear increment at low weight percentages and begins to level off with increase in weight percentage. This is because of agglomeration (insufficient dispersal) of the nanoparticles.

The expansion in properties of nanocomposites over conventional composites is identified with the enormous interfacial regions made by nanoparticles [13-14]. The interfacial area is where the material properties are unique in relation to those of the filler or the matrix. The variance in material properties in the interfacial region is brought about by the nanoparticles limiting the movement of the polymer chains. The enormous interfacial area and the little separation between nanoparticles because of the total number of nanoparticles considers an increase in mechanical properties than in conventional composite materials.

## 2. Materials and Method

The specifications of Nanoclays, vinylester, Glass fibre and curing agents used in the present investigation are presented in Table 1.

**Table 1** Specification of fiber and resins used

Material	Density in g/cc	Suppliers
E-Glass Fiber	2.5	Vetrotex, India.
Vinylester resin	1.05	Naphtha Resins & Chemicals , India
Montmorillonite-K10	0.7-1.1	Sigma-Aldrich

### 2.1 Fabrication of FRP

#### 2.1.1 Wet Hand Layup Method

The composite was fabricated utilizing the regular "WET HAND LAYOUT" technique [15-17]. Materials utilized are E-glass Fiber, Nanoclay and Vinyl ester. An eighteen layered structure was framed according to the ASTM standards (Table 2). The fiber and the matrix were taken in the proportion of 40:60.



Table 2 ASTM Standards for sample dimensions

ASTM Code	Mechanical Test	Sample Dimensions (mm)
ASTM-D2344	ILSS	45 X 6 X 3
ASTM-D790	Flexural	80 X 8 X 3
ASTM-D638	Tensile	216 X 19X 3
ASTM-D	Impact	64 X 12.7 X 3

### 3. Moisture Absorption Studies

Here also the effect of seawater exposure for clay loaded nanocomposites (with 0%, 2%, 4%, 6% and 8% weight additions of clay) are shown in Fig.1. The samples were taken out from seawater at regular intervals, wiped dry to remove the surface moisture and then weighed in an electronic balance to monitor the mass change behavior of moisture diffusion as shown in Table 3. The ratio of mass change (M) of the composite panel was calculated by the simple equation [17-19]:

$$M = [(m_s - m_d) / m_d] \times 100 \text{ ----- (1)}$$

Where  $m_s$  is the mass of the board after a given dipping time and  $m_d$  is the new panel mass. Dampness that the composite ingests will cause degradation in the properties of the composites in a way like that of accelerated aging. A similar investigation of seawater absorption of all the composites considered is finished by preparing a chart of Percentage dampness versus Number of days Exposure.

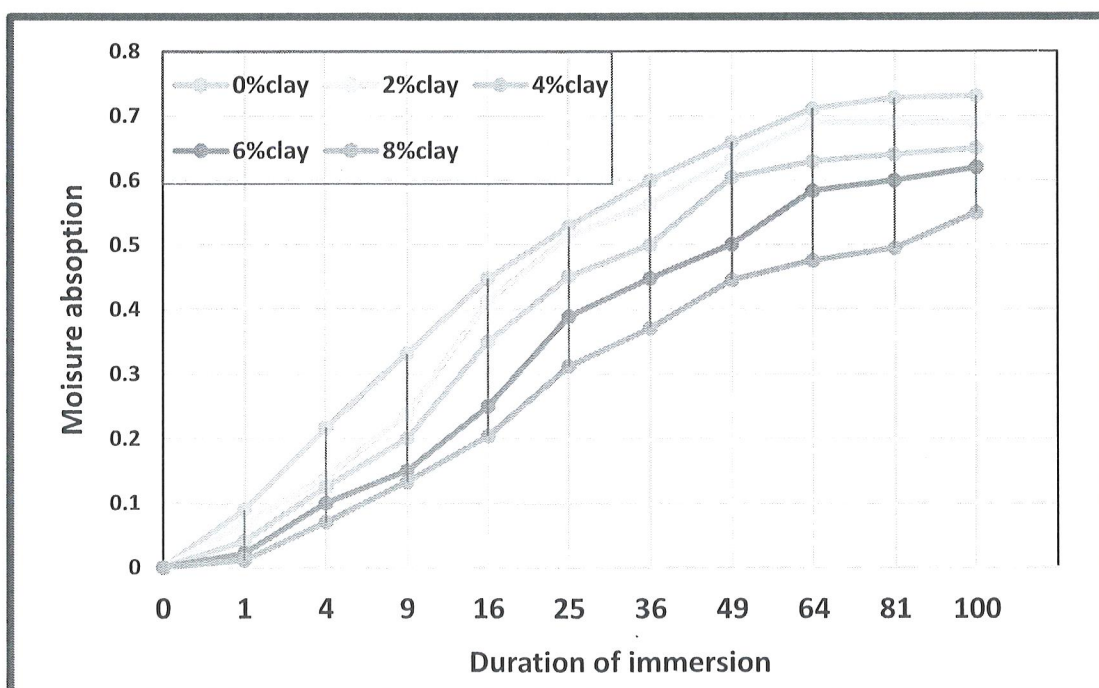


Fig. 1 Sea water absorption v/s number of days at room temperature.

**Table 3** Sea water absorption for different days

No. of days exposure	Weight % of Sea Water absorption for different composition of clay				
	0%	2%	4%	6%	8%
0	0	0	0	0	0
36	0.45	0.36	0.29	0.25	0.14
49	0.65	0.6	0.55	0.48	0.37
64	0.7	0.65	0.61	0.56	0.46
81	0.72	0.68	0.64	0.59	0.51
100	0.75	0.7	0.68	0.61	0.55

#### 4. Ultimate Tensile Strength

The percentage change in UTS for 0, 2, 4, 6 and 8 wt% of glass-vinylester-nanoclay samples after 100 days (Table 4) of exposure were 58.56, 59.12, 54.1, 57.96 and 63.66% respectively at RT. From the tensile test results as appeared in Fig.2 as the wt.% of nanoclay increased the UTS of the specimens also improved for 2wt%, 4wt% and suddenly decreases for 6 wt% and 8wt% samples. The tensile strength of the 6 and 8wt% nanoclay samples are almost same before immersion in sea water. But after days increases the strength of the 8wt% nanoclay samples decreases compared to 6wt% nanoclay samples. The 4 wt% of glass-vinylester-nanoclay samples showed the maximum increment.

**Table 4** UTS of nanocomposites for different % of clay and for different days.

% of Clay	UTS (Mpa)	UTS (Mpa)	UTS (Mpa)	UTS (Mpa)	UTS (Mpa)	UTS (Mpa)
	0 days	36 days	49days	64days	81 days	100 days
0	360.5774	283.47	255.29	210.54	183.2807	149.42
2	389.1601	301.0702	267.89	225.59	175.5965	159.07
4	470.1837	322.8421	294.56	256.63	222.21	215.78
6	333.832	224.63	214.32	188.64	162.6	140.35
8	330.9449	216.3158	198.54	169.035	151.57	120.26

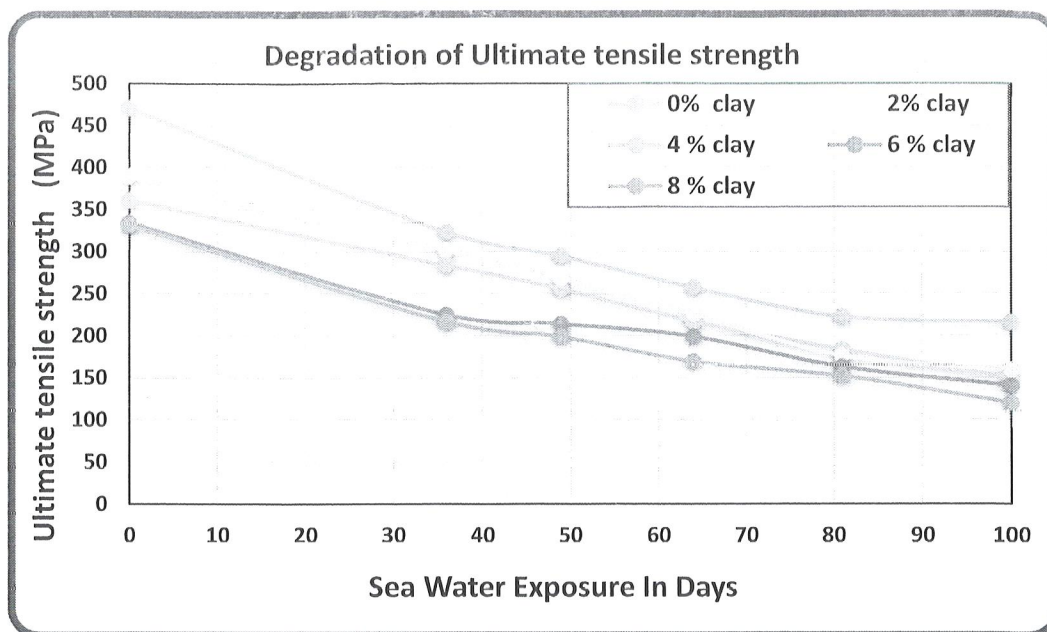


Fig. 2 Graph of UTS v/s number of days

### 5. Flexural Strength Test

The change in elasticity as a component of the length of the period of the composite system to the seawater revealed in Fig.3. Specimens after seawater exposure shows increase in degradation substantially with increase in time of exposure. All clay loaded nanocomposite specimen show flexural strength degradation (Table 5), when subjected to sea water immersion, flexural strength degradation v/s duration of immersion is shown in Fig.3. From the figure it is clear that flexural strength decreases as duration increases, Percentage drop in flexural strength for 0, 2, 4, 6 and 8wt% after 100 day's exposure were 51.29, 49.67, 44.57, 51.85, and 56.47% respectively at RT. Here the 4 wt% of nanoclay samples showed less degradation after 100 days of exposure i.e. 44.57% for 4% clay loaded nanocomposite.

**Table 5** Flexural strength of nanocomposites for different % of clay and for different days

% of Clay	FS(Mpa)	FS (Mpa)	FS (Mpa)	FS (Mpa)	FS (Mpa)	FS (Mpa)
	<b>0 day</b>	<b>36 days</b>	<b>49days</b>	<b>64days</b>	<b>81 days</b>	<b>100 days</b>
0	400	387.84	344.5	321.67	255.48	218
2	411.25	375.65	343.82	308.42	268.32	220.33
4	495	412.17	371.67	335.33	304.66	286.66
6	416.625	389.12	356.6	326.76	294.14	228.64
8	368.75	323.33	298.58	253.33	210.33	195.4

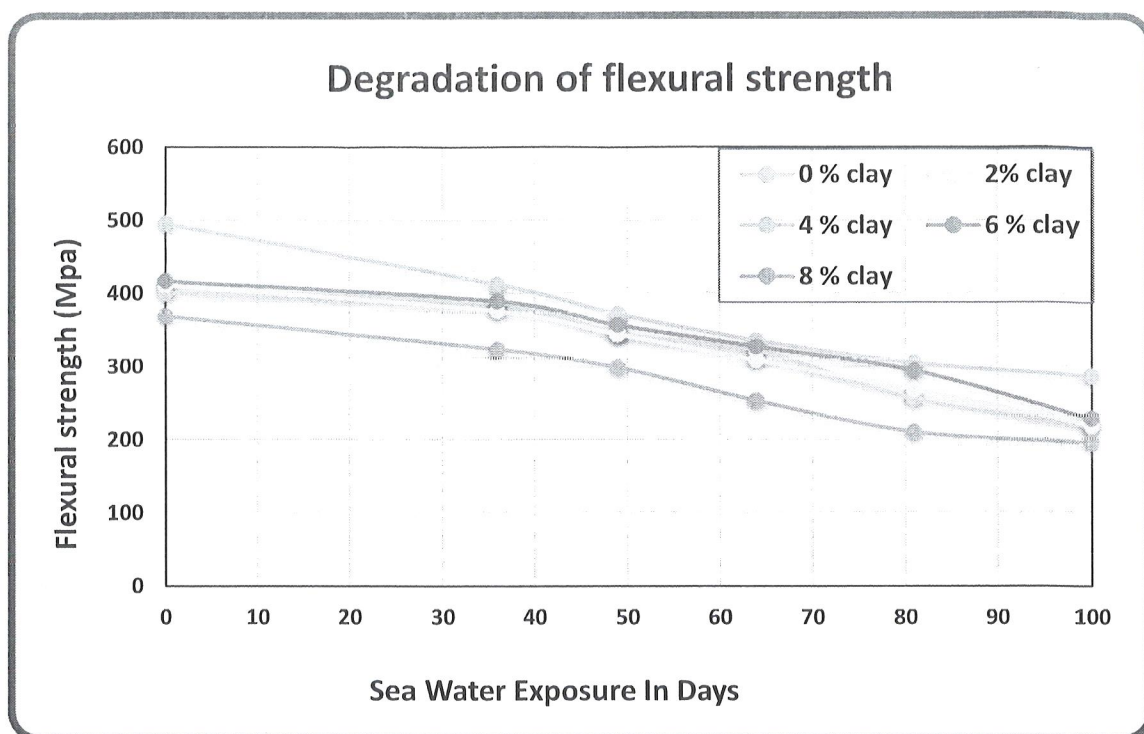


Fig.3 Overall degradation of Flexural Strength.

### 6. 3-Point Bend Test

A Similar behaviour can be seen by the PMCs in ILSS tests too 4wt% nanoclay show better performance than the others % of clay. The ILSS value of the samples as the different wt% of nanoclay (Table 6) and also the change in ILSS value as a function of duration of exposure of the composite systems to sea water is presented in Fig 4.

The percentage change in ILSS value for 0, 2, 4, 6 and 8wt % of glass-vinyl ester-nanoclay after 100 days of exposure were 70.45, 74.34, 68.97, 76.80 and 79.37 % respectively. Here the 6wt% nanoclay samples show maximum value compared to 2 and 8wt% nanoclay samples before immersion in sea water. But after 64 days the ILSS value of the 6wt% of nanoclay samples was found less the 2wt% nanoclay samples by 11.36%. After 49 days the ILSS value of 8wt% nanoclay samples showed lesser value than 0wt% nanoclay samples by 8.99%. Here also the 4 wt% of nanoclay samples showed maximum increment for glass-vinylester-nanoclay samples.

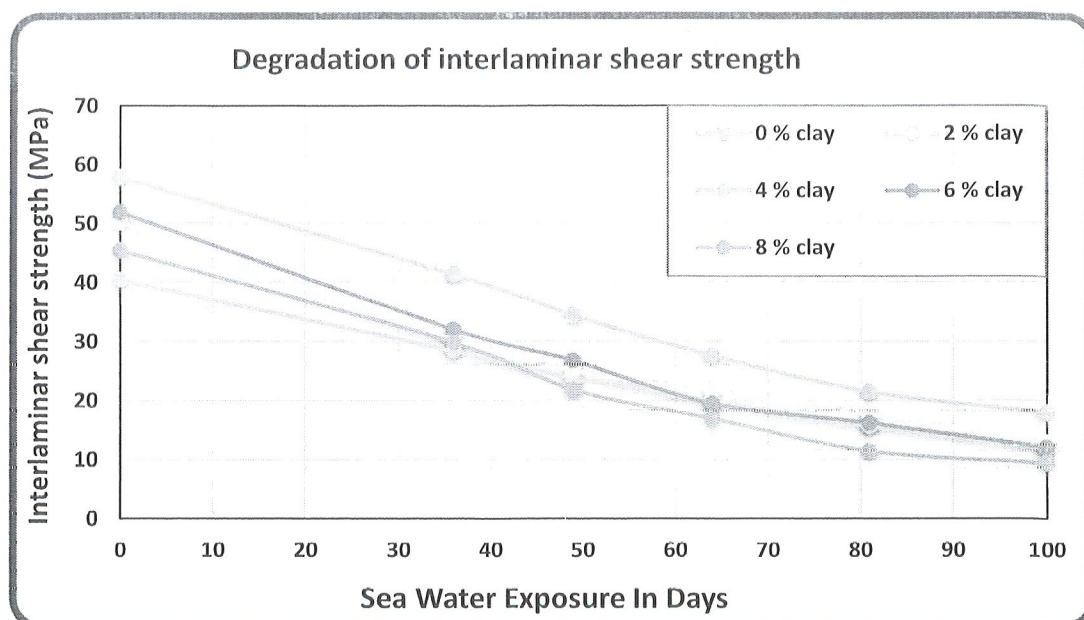


Fig 4 Graph of ILSS value v/s number of days.

Table 6 ILSS value of nanocomposites for different % of clay and for different days.

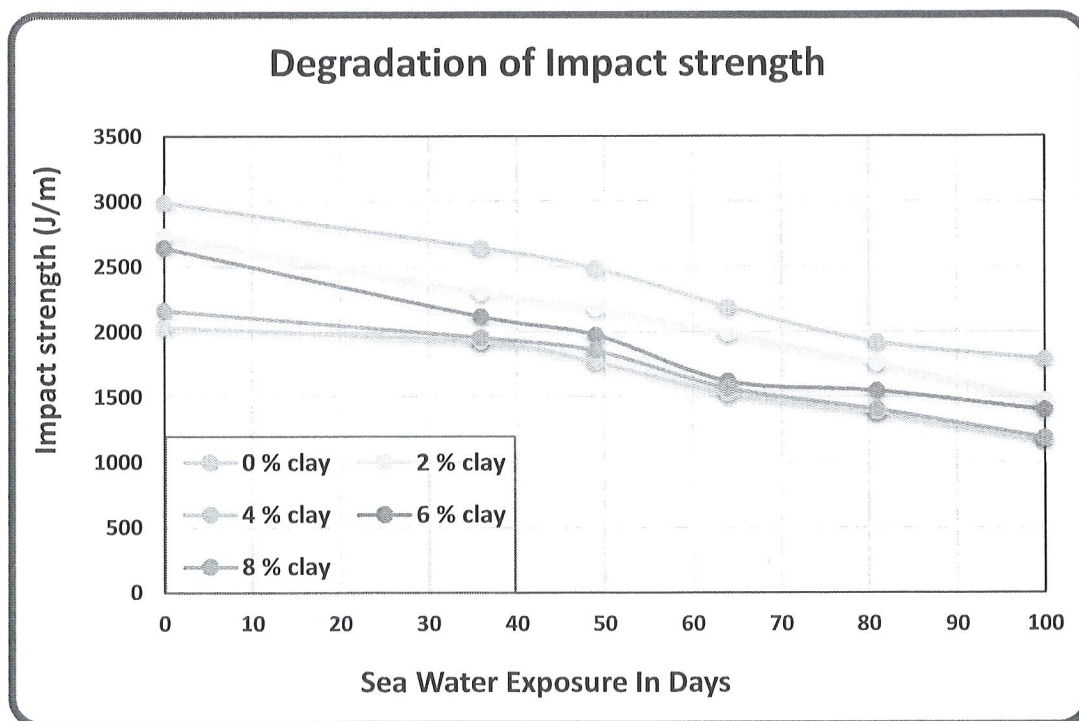
% of Clay	ILSS(Mpa)	ILSS(Mpa)	ILSS(Mpa)	ILSS(Mpa)	ILSS(Mpa)	ILSS(Mpa)
	0 day	36 days	49days	64days	81 days	100 days
0	40.375	28.43	23.75	19.93	15.62	11.93
2	50.20833	30.33	25.0833	21.66	17.67	12.88
4	57.8333	41.33	34.47	27.625	21.46	17.94
6	51.875	32.063	26.75	19.45	16.19	12.03
8	45.375	29.8333	21.79	16.9525	11.43	9.36

## 7. Impact Strength Test

The impact strength of the samples as the different wt% of nanoclay (Table 7) and also the change in impact strength as a function of duration of exposure of the composite systems in sea water is shown in Fig.5. The percentage change in impact strength for 0, 2, 4, 6 and 8wt% clay loaded nanocomposites after 100 days of exposure were 44.46, 41.54, 39.81, 47.81 and 50.50% respectively. As looking at graph the number of days increases the Impact strength decreases for all % of clay. Here also the 4wt% clay loaded samples shows maximum strength compared to other percentage samples. The maximum increment of 4% clay loaded samples is 39.81%.

**Table 7** Impact strength of nanocomposites for different % of clay and for different days.

% of Clay	IS(J/m)	IS(J/m)	IS(J/m)	IS(J/m)	IS(J/m)	IS(J/m)
	<b>0 day</b>	<b>36 days</b>	<b>49days</b>	<b>64days</b>	<b>81 days</b>	<b>100 days</b>
0	2034	1924.2	1766	1522.08	1384.82	1179.9
2	2734.56	2300	2175.86	1982.79	1753.33	1469.13
4	2990	2645	2487.6	2191.7	1921.42	1789.5
6	2643.2	2117.64	1976.09	1620.06	1546.6	1398.61
8	2164.4	1954.67	1854.4	1565.54	1403.4	1184

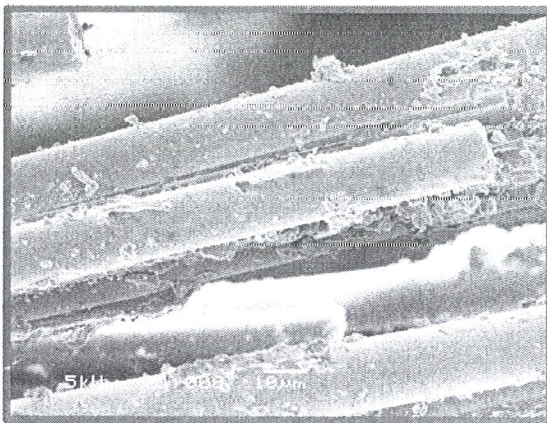


**Fig 5** Graph of Impact strength v/s number of days.

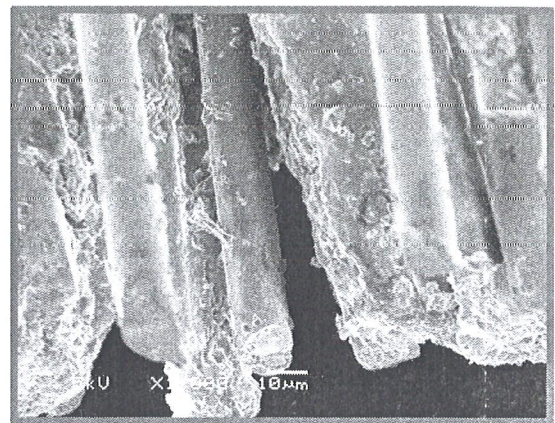
  
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### 8. Scanning electron micrograph

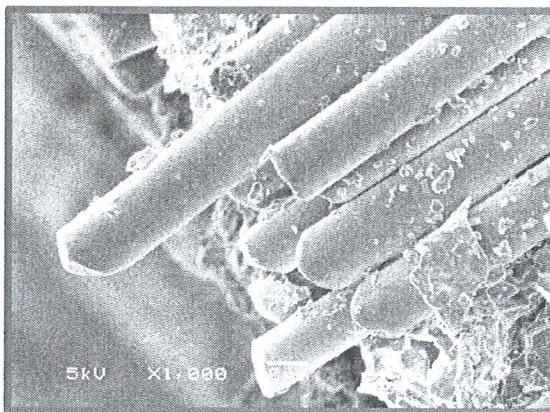
Scanning electron micrographs provide good evidence of the binding between the resin and the fiber before (Fig.7 and Fig.8) and after the exposure (Fig.9 and Fig.10). The exposure to sea water environment has led to a reduction in mechanical properties of specimens by the degradation in the fiber matrix interfacial bonding. The voids present in the matrix are the main reason for moisture diffusion. The micro cracks formed during the composite preparation or by the service condition can store the trapped water. The voids and micro cracks in the specimens can be traced using SEM images.



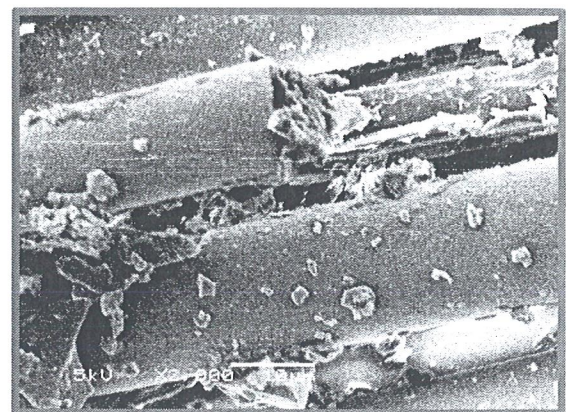
**Fig. 7 Vinyl ester/Glass 0 Days**



**Fig. 8 Vinyl ester/Glass 100 Days**



**Fig. 9 4wt%/Vinyl ester/Glass 0 Days**



**Fig. 10 4wt%/Vinyl ester/Glass 100 Days**

SEM images of tensile fractured unexposed specimen of vinyl ester/glass specimens showed the failure mode due to fiber breakage. There are many hackles can be observed on the surface of the fiber are the matrix bonded to the fiber even after the fracture. This shows that there is a strong bond at the interface between fiber and matrix before degradation.

The fractured specimens after 100 days of exposure showed fiber fracture as well as fiber pull out. After 100 days of exposure the specimens showed greater degree

of matrix plasticization in vinyl ester/glass, matrix degradation increased with duration of exposure in all the cases.

On the other hand, immersion time increased, fewer hackles can be seen at the fiber surfaces for the specimens immersed in the sea water. The relatively clean fiber surface resulted from the weak fiber-matrix bonding is observed. Vinyl ester/glass specimens causing embrittlement and micro-cracks on surface are seen, longitudinal and transverse mechanical properties show significant decrease.

## **9. Conclusions**

Nanoclay dispersion is an effective method in for resisting moisture absorption. Nanoclay acts as reinforcement- Hence improves mechanical properties. Loading of nanoclay is monotonic with respect to moisture absorption. The percentage degradation of UTS for 0, 2, 4, 6 and 8wt% of glass-vinylester-nanoclay samples after 100 days of exposure were 58.56, 59.12, 54.1, 57.96 and 63.66% respectively. The percentage degradation in flexural strength for 0, 2, 4, 6 and 8wt% of glass-vinyl ester-nanoclay after 100 days exposure were 45.5 46.42, 42.08, 45.12 and 47.01% respectively. The percentage degradation in ILSS value for 0, 2, 4, 6 and 8wt% of glass-vinyl ester-nanoclay after 100 days of exposure was 70.45, 74.34, 68.97, 76.80 and 79.37% respectively. The percentage degradation in impact strength for 0, 2, 4, 6 and 8wt% of glass-vinyl ester-nanoclay after 100 days of exposure was 41.99, 46.28, 40.15, 47.09 and 45.29% respectively. From the results 4wt% nanoclay shows the better mechanical properties. Water absorbing capacity decreases with increase in clay loading. But 4% nanoclay is the optimum level to load for a better trade off with mechanical properties.



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