Hygrothermal degradation of mechanical properties of nanoclay based stainless steel and glass fibre-epoxy laminate

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Abstract. Fibre metal laminates (FML’s) are the multilayer composite laminates of metallic sheets and fibre reinforced plastic (FRP) composites. The stacking sequence of metallic sheets and FRP prepgs in FML’s vary as per the type of fibre metal laminate and its application. FML’s are the most suitable materials for shipbuilding, aerospace and aeronautical structural use due to better mechanical properties over traditional materials. In the present research, the mechanical properties of nanoclay based stainless steel and glass fibre-epoxy laminate (SS FML) have been investigated. Hygrothermal conditioning of specimens was performed in two aqueous environments at 40 °C and 70 °C for three months. After hygrothermal conditioning, tensile, flexural, compression and Izod impact tests were performed as per ASTM standards. It is concluded that the nanoclay addition in the epoxy matrix of SS FML improves its mechanical properties drastically. It is due to the fact that the nanoclay in the epoxy matrix improves the interfacial bonding between the composite layers. It is observed that the mechanical properties were reduced more in distilled water due to the salts available in seawater that reduces the moisture absorption in epoxy matrix of SS FML. It is also noticed that the temperature has the considerable effect on the degradation of mechanical properties. Higher temperature of water softens the epoxy, results in highest degradation in distilled water at 70°C.

1. Introduction
Fibre metal laminates (FML’s) are the multilayer composite laminates of metallic sheets and fibre reinforced plastic (FRP) composites. FML’s are the popular materials for shipbuilding, aerospace and aeronautical structural use due to better mechanical properties over other materials [1,2].

Aramid Fibre Reinforced Aluminium Laminate (ARALL) was the initial fibre and metal laminate developed in Netherland in 1978 by the Faculty of Aerospace Engineering (Delft University of Technology). They concluded that the fatigue crack growth resistance of multilayered composite laminate was superior than one thick monolithic sheet [3,4]. Jayabal et al. [5] experimentally investigated the flexural, tensile and Izod impact strengths of woven coir and woven coir–glass fibre reinforced polyester composites and concluded that the mechanical properties of woven glass fibre polyester composites were superior than woven coir polyester composites.

Flexural strength degradation of polyester and jute fibre based composite laminates was investigated by Akil et al. and it was found that the reduction in flexural strength and the amount of moisture ingestion was less for specimens immersed in seawater as compared to distilled water [6].
The corrosion resistance of FML’s with stainless steel AISI 304 or mild steel EN 10130 DC01 and Glass fibre-epoxy layers has been experimentally observed by Sarlin et al. in two environments. The specimens contained mild steel exhibited low peel strength and corrosion resistance as compared to stainless steel based FMLs [7].

Khalili et al. performed the experimental investigation to compute damage tolerance, Izod impact strength and stiffness of glass fibre reinforced composite (GRP) and FML’s contained aluminium alloy or stainless steel. The mechanical properties of FML’s contained stainless steel layers were found to be superior than FML’s with aluminium alloy and GRP [8].

Botelho et al. evaluated hygrothermal reduction in compressive and tensile strengths of fibre glass-epoxy laminate and fibre glass-epoxy-aluminium laminate (Glare). It was found that reduction in tensile strength for Glare was less than fibre glass-epoxy laminate and compressive strength reduction for both laminates was equivalent [9]. The compression resistance of glass fibre-epoxy laminate was evaluated by Ning et al. and found that delamination in fibre-epoxy layers was the major failure criterion for specimens during tests [10].

Various research studies [11, 12] have been conducted to find out the reduction in properties of FML’s due to controlled temperature conditioning in different environments and temperatures. The effect of nanoclay addition on the degradation of mechanical properties of FML’s has not been studied yet. The aim of current research study is to determine the degradation in mechanical properties of nanoclay based stainless steel and glass fibre-epoxy laminate (SS FML) due to hygrothermal conditioning in distilled water and seawater at 40ºC and 70ºC.

2. Materials and method of SS FML preparation

2.1. Materials used
MasterBrace 4500, epoxy resin and E-glass fibre [13,14] UD (SikaWrap-430 G) with thickness 0.172 mm, areal weight of 445 GSM, density 2.56 g/cm3 were selected for inner FRP fabrication. Stainless steel AISI 304 sheet (0.4 mm thick) has been used as outer layers of fibre metal laminate [15]. An adhesive with cured thickness 0.1 mm was used for interfacial joint between composite and metal sheets. A nanoclay powder (Closite 15 A) has been selected due to its hydrophobic nature [16].

2.2. Method of preparation
The stacking sequence of stainless steel and glass fibre-epoxy laminate (SS FML) is shown in figure 1. Fibre metal laminate (FML) sheets were prepared using hand layup process. The detailed process to fabricate FML sheets without nanoclay is explained in our previous studies [11, 12]. To produce FML sheets containing nanoclay, the nanoclay need to be mixed in the epoxy matrix of inner FRP layers. GF/E and SS FML sheets with the addition of 2 % nanoclay powder (closite-15 A) by weight of epoxy resin were also prepared [16]. Such a weight percentage (i.e. 2 %) shows significant improvement in mechanical properties. Due to high viscosity of epoxy resin, manual mixing of nanoclay powder is quite difficult. So a mechanical stirrer and a hot oil bath (figure 2) were used for proper mixing of nanoclay.

Oil bath was used to reduce the viscosity of epoxy resin by heat it up to 60 ºC. Proper mechanical stirring (1000 rpm for 15 minutes) of epoxy at this stage resulted better dispersion of clay powder. High speed shear homogenizer (20000 rpm for 20 minutes) was used to break the lumps of clay particles and to disperse the clay particles throughout the epoxy resin. Due to the high shear mixing, air bubbles entrapped in the epoxy. Air bubbles were removed by putting the jar in to a vacuum chamber for 15 minutes. After that the jar containing epoxy and nanoclay mixture was put under ultrasonic probe for at least 15 minutes. Sonication was done to break intermolecular interactions and for evenly dispersing nano-particles in epoxy resin. After preparation of epoxy resin, the same procedure was adopted as described in [11, 12] to produce SS FML with nanoclay. After preparation
of FML sheets containing nanoclay, four types of test samples were cut from prepared sheets. The specifications of the test samples are listed in table 1.

![Figure 1. Stacking sequence of SS FML](image)

![Figure 2. Oil bath setup along with mechanical stirrer](image)

### Table 1. Details of specimen dimensions and ASTM standards used

| Sr. No. | Type of Specimen | ASTM used             | Length  | Width  | Thickness |
|---------|------------------|-----------------------|---------|--------|-----------|
| 1       | Tensile          | ASTM D3039/D3039M – 14| 250 mm  | 15 mm  | 3.5 mm    |
| 2       | Flexural         | ASTM D790-15e2        | 127 mm  | 12.7 mm| 3.5 mm    |
| 3       | Compression      | ASTM D695 – 15        | 25.4 mm | 12.7 mm| 12.7 mm   |
| 4       | Impact           | ASTM D256–10e1        | 63.5 mm | 12.7 mm| 3.5 mm    |

### 3. Experimentation

Two types of waters i.e. seawater (SW) and distilled water (DW) were utilized for environmental degradation study. Seawater was prepared artificially as per ASTM D1141-98. The flexural, tensile, compression and impact specimens were kept in temperature controlled chambers contained seawater and distilled water at 40°C and 70°C for three months (90 days). The four chamber water bath setup is shown in figure 3.

![Figure 3. Four chamber water bath setup](image)
3.1. **Tensile test**

The specimens for the tensile tests were prepared and tested as per ASTM D3039/D3039M – 1 [17, 18]. The specimens were tested on 50 kN UTM (universal testing machine - EZ50) with controlled crosshead speed of 2 mm/min. To determine the reduction in tensile strength, specimens from water chambers were tested after every 10 days up to three months and ultimate tensile strengths were recorded. SS FML specimens were failed due to the failure of internal glass fibre laminate and thereafter the outer metallic skins were failed with significant strain.

3.2. **Compression Test**

Compression test samples were prepared from the SS FML sheets as per ASTM D695 – 1 [6,19]. The compression tests were conducted on 50 kN universal testing machine with controlled crosshead speed of 1.3 mm/min using standard compression test fixture. The average compressive strength values were computed using five randomly selected specimens from water chambers after 10 days up to three months. The stacking sequence of tensile, flexural and Izod impact specimens was similar to each other. However, the number of glass fibre-epoxy layers in compression test specimen were higher than tensile, flexural and Izod impact specimens, due to its geometrical difference with them.

3.3. **Flexural test**

Three point bend tests were performed on samples prepared from SS FML sheets using EZ50 universal testing machine. Test samples were prepared and tested on standard three point bend test fixture with controlled crosshead speed of 1.5 mm/min as per ASTM D790-15e2 standard [5]. Flexural tests were performed on five randomly selected flexural specimens from water chambers and average flexural strengths were recorded.

3.4. **Izod impact test**

Izod impact tests were performed on pendulum type impact testing machine (Model IT-30-D made by fuel instrument & engineers Pvt. Ltd.) The capacity and the least count of the impact testing machine were 300 Joule and 0.5 Joule respectively. Impact test specimens were arranged from SS FML sheets and tested edgewise with bottom end fixed in fixture as per ASTM D256–10e1 standard [5].

4. **Results and discussion**

4.1. **Tensile Strength Degradation of SS FML**

The tensile tests were performed on five randomly selected SS FML specimens from four water chambers after each 10 days up to 90 days. The average values of ultimate tensile strength have been reported. Figures 4 and 5 represent the trend of tensile strength degradation of SS FML (containing nanoclay in its matrix phase) in seawater and distilled water at 40°C and 70°C respectively. It was observed that the tensile strength of SS FML was drastically improved by the nanoclay addition in the epoxy matrix. It was happened due to the dispersion of nanoclay particles in to the microscopic cavities in the epoxy resin layers. The addition of nanoclay in the epoxy resin enhanced the adhesion between the epoxy layers and results in higher tensile strength.

It was also observed that tensile strength (TS) of SS FML containing nanoclay was reduced more in distilled water as compared to seawater at both temperatures. In seawater (SW) at 40°C, the TS was reduced continuously till 50 days, and after that the reduction in TS was very less. On the contrary, the TS in distilled water (DW) was dropped even after 50 days. However, at 70°C, the TS of SS FML in seawater was decreased up to 70 days and thereafter the TS was nearly constant.

4.2. **Compressive Strength Degradation of SS FML**

The compression tests were performed on five randomly selected SS FML specimens from the water chambers after every ten days for three months. The compressive specimens both conditioned and unconditioned were failed due to delamination between glass fibre and epoxy layers. Figures 6 and 7
display the decreasing trend of compressive strength of SS FML containing nanoclay after hygrothermal conditioning in seawater and distilled water at 40°C and 70°C respectively. It is observed that the compressive strength degradation in distilled water was higher than that of seawater. It is due to the high salt content of seawater, which decelerates the moisture absorption rate. It can also be seen that the degradation of compressive strength at 70°C was higher than at 40°C, due to the softening of matrix phase at higher temperature. At high temperature, the matrix of composite becomes soft, which results in the more moisture absorption and hence more degradation in compressive strength.

4.3. Flexural Strength Degradation of SS FML

The flexural strength degradation behaviour of SS FML containing nanoclay is shown in figures 8 and 9. It is clear that the flexural strength was reduced continuously till 70 days during hygrothermal conditioning and after that the reduction is very less. It is also observed that at 70°C, the maximum flexural strength degradation was happened in distilled water. Unconditioned flexural specimens were failed due to inner composite laminate breakage. While the conditioned flexural specimens were failed due to delamination in fibre-epoxy layers as well as at metal composite interface. This is due to the weakening effect of epoxy and adhesive due to moisture absorption during environmental conditioning.

4.4. Impact Energy Degradation of SS FML
The Izod impact tests were performed after every ten days on SS FML specimens containing nanoclay as described in section 3.4. Both conditioned and unconditioned specimens were failed due to shear out of metal and inner composite at the notch. The delamination between inner composite layer and at metal composite interface was observed for conditioned specimens. The degradation behaviour of impact energy absorption of SS FML owing to environmental conditioning is illustrated in figures 10 and 11. It was observed that at 70°C, the impact energy reduction was highest in distilled water.

5. Conclusions
The four types of mechanical tests were performed on the SS FML specimens containing nanoclay as per the ASTM standards. The effect of addition of nanoclay in the epoxy subsystem of SS FML, on the mechanical properties has been evaluated. Hygrothermal conditioning was performed for 90 days and tensile, compression, flexural and Izod impact tests were also performed on the conditioned specimens of SS FML.

Tensile, flexural, compressive strengths and Izod impact energy absorption was improved drastically by the nanoclay addition in the epoxy subsystem of unconditioned SS FML. After hygrothermal conditioning, the mechanical properties of conditioned specimens of SS FML were reduced up to 70 days in seawater and thereafter a constant trend has been observed. The specimens immersed in distilled water show reduction in
mechanical properties even after 70 days. The reduction in mechanical properties was highest for SS FML specimens in distilled water at 70 ºC and lowest in seawater at 40 ºC. The mechanical properties of SS FML have been drastically improved due to the dispersion of clay particles in to epoxy matrix. The dispersed clay particles enhanced the interfacial bonding between the inner composite layers, which result in the improvement of mechanical properties of SS FML. The clay particles dispersed and occupied the microscopic cavities in the epoxy layers. It also reduces the water absorption and thus the hygrothermal degradation.

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