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Strengthening of a Fibre-Matrix Interface: A Novel Method Using Nanoparticles

Regular Paper

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Abstract The surface of carbon fabric (CF) was treated with nanoparticles (NPs) of Ytterbium fluoride (YbF_3) (40-80nm size) in various amounts (0, 0.1, 0.3 and 0.5wt%) to improve its wettability with a Polyetherimide (PEI) matrix. The effect of treatment on the fibres of the CF was also studied by adhesion testing and fibre tow tension testing. An improvement in wettability with PEI and a slight reduction in the tensile strength of the CF was observed in these tests. Fourier transform infrared-attenuated total reflectance spectroscopy (FTIR-ATR) indicated the addition of functional groups on the fabric after treatment. Micro-Raman spectroscopy (MRS) showed a slight distortion in the structure of the CF due to the treatment. Increased roughness of the fibre surface and adhesion of NPs on the fibre surface were observed by field emission scanning electron microscopy (FESEM). Composites were developed based on untreated and surface-treated CFs by impregnation techniques. The composites were analysed for interlaminar shear strength (ILSS) and a maximum improvement of 61% was observed for the 0.3% concentration of YbF_3, followed by a slight decline in ILSS, indicating that it was the optimum dose.

Keywords Surface Treatment of Fibres, Ybf_3 Nano-Particles, Fibre-Matrix Interface, Carbon Fabric, Polymer Composites

1. Introduction

To explore the full potential of carbon fibres as reinforcements for desired composites, it is necessary to have an adequate fibre-matrix interface to ensure effective load transfer from the matrix to the fibre [1, 2]. However, carbon fibres are chemically inert in nature and therefore have poor wettability and adsorption with most matrices. There have been various reported attempts to improve their wettability [3-**9**]. Several of them are highlighted in recently published work [10]. The surface treatment of fibres may either produce chemical bonds on their surface (leading more interaction with the matrix) or roughen the surface (mechanical keying between the resin and fibre) or do both, which leads to more adhesion with the matrix. Most of the time both the effects take place simultaneously.

These reported methods have a common major drawback. They generally lead to a significant reduction in the strength of fibres. Although plasma treatment is supposed to be safe in this respect, in our earlier work almost 2.5% deterioration in strength was observed in the strength of carbon fibres due to cold remote nitrogen oxygen plasma treatment [11]. Moreover, most of the techniques are based on either complex processes (e.g., treatment by acids/alkalis/ strong oxidization agents etc.) or need exorbitantly expensive infrastructure, adding to the cost of the treatment significantly. An ideal method should lead to a significant enhancement in fibre-matrix adhesion without any damage to the strength of fibres. It should also be simple to employ and should not need expensive infrastructure, cost and manpower. Efforts in this direction are reported in this paper.

Rare earth salt (RES) treatment on carbon fibres [12-18] is a comparatively very recent technique compared to others, for example electrochemical, chemical, thermal, discharge plasma, radiation etc.

Based on chemical bonding theory, it is suggested that the RES is adsorbed on both carbon fibre and polymer surfaces through chemical bonding, which increases the concentration of reactive functional groups due to the chemical activity of rare earth (RE) elements [12]. These reactive functional groups could improve the compatibility between the carbon fibre and the matrix leading to an increase in interfacial adhesion. RES is capable of forming coordinate and ionic bonds with some functional groups of polymers and carbon fibres, such as sulfonic ($–SO_2–$), carbonyl ($C=O$), hydroxyl ($C–OH$), carboxyl ($COOH$) groups etc. [11].

As seen in Table 1 (Appendix-A), based on a literature survey compiling the issues addressed or not addressed in the respective papers, very little is reported on the full potential of RE treatment. Overall it seems that in most of the papers, Lanthanum chloride ($LaCl_3$) solution in various amounts is used for dipping the CF and modifying its wettability. Either dip time or concentration of $LaCl_3$ is selected as a variable in the treatment. Various time intervals have been used for soaking the fibres in an alcoholic solution of $LaCl_3$. RE treatment is also reported as better than air oxidation treatment of fibres [12, 13].

A more powerful RE compound was used in this work for the treatment of CF. A new RES YbF_3 (Ytterbium fluoride) was selected that is considered to be more reactive because of the addition of fluorine atom. Moreover, it was decided to modify the treatment method to make it more effective. Instead of dipping CF in a solution, boiling was found to be more effective. Proper selection of size of RE particles was also presumed be more effective. Nano-particles are known for having a very high surface area and hence a very high surface energy. Therefore, instead of micro-particles, nano-particles of YbF_3 were used in this work, since no papers are available on the exploration of NPs for fibre treatment. In this paper, optimization of concentrations was also carried out, along with fibre analysis using various techniques and studies on fibre-matrix adhesion.

2. Experiments

Carbon fabric was supplied by Fiber Glast Corporation, USA in twill weave (2x2) form. Polyetherimide (PEI) material (ULTEM 1000) was supplied by GE plastics, USA in the form of granules. Rare earth salt Ytterbium fluoride (YbF_3) was supplied by Nano-Amor, USA in a 40-80nm size.

The de-agglomeration of NPs is the most critical part of exploring their potential and depends on the selected medium, the type of probe for the sonicator, its speed, the time taken for sonication and its frequency for application, temperature etc. After trying various mediums such as water, acetone, petroleum ether etc., ethyl alcohol was found to be the most suitable for proper suspension of NPs. Suspension of YbF_3 in ethyl alcohol was prepared in three concentrations (0.1%, 0.3% and 0.5% by wt.) using a probe sonication technique by an UP200S ultrasonic processor with a cycle of 0.5 and amplitude of 75%. CF pieces (80mm x 80mm) were boiled in the suspension for half an hour, followed by thorough washing and drying in a vacuum oven. These fibres were designated as F_0, F_{Y1}, F_{Y3} and F_{Y5} respectively, where F stands for fibre and subscript Y stands for YbF_3. 0, 1, 3 and 5 stand for the YbF_3 concentrations of 0, 0.1, 0.3 and 0.5wt%, respectively used for the treatment of the fabric. The fabric pieces were sonicated again for 3 minutes at an amplitude of 75% to remove loosely adhered NPs

2.1 Tests Conducted on Fibres

Generally methods used to enhance the reactivity of inert fibres towards a matrix work by imparting the following in combination.

- Fibre surface roughening, which provides better mechanical interlocking with the matrix and therefore improves adhesion (a positive and desirable effect). Simultaneously this also imparts a negative effect on the strength of the fibre (the extent depends on the type of treatment).
- Creating reactive functional groups on the fibre surface, which are responsible for chemical reactions with the matrix and hence more adhesion (a positive and desirable effect).

An ideal method is one that has heavy weighting towards positive factors and negligible weighting for adversely affecting factors. Therefore, it becomes imperative to evaluate all the effects on the fibres as a result of a selected treatment. Virgin and treated fabrics were studied with various techniques were carried out to investigate topographical, chemical and structural changes on the fibre surfaces. Prior to every test the fibres were cleaned ultrasonically to remove any loosely adhering NPs.

2.1.1 FESEM studies- Fibre surface analysis for evaluating topographical changes on the surface

FESEM studies of untreated and treated fibres were carried out on Zeiss SUPRA 55 microscope. The results are shown in Fig. 1.

2.1.2 FTIR-ATR spectroscopic analysis to examine the inclusion of reactive functional groups on the fibre surface

In order to investigate the possible changes in the chemical composition of carbon fibres due to YbF_3 treatment, FTIR-ATR analysis was done on a Perkin Elmer SPECTRUM BX FTIR spectroscope in the mid infrared range (4000-700cm^{-1}). The results are shown in Fig. 2.

2.1.3 MRS studies to understand physical changes in the graphitic structure of fibres

A Ranishaw inVia Raman spectroscope with a 514nm He-Ne laser was used to obtain Raman spectra of untreated and treated CFs. The fibres were fixed on a microscope slide.

The intensity ratio between the D-line (1360cm^{-1}) and the G-line (1590cm^{-1}) of the Raman spectra was employed to evaluate the size of the crystalline surface of the carbon fibre samples. The results are shown in Fig. 3 and Table 2.

2.1.4 Fibre tow tension test for evaluating changes in the strength of fibres

Untreated and treated CF tows (3k) were tested under tension to investigate the effect of surface treatment on tensile strength. A tow (3k) of fabric was glued on abrasive paper at a distance of 150mm. Before starting the tension test, the paper was cut from the middle portion to allow the load to be carried on the tow only. The test was performed on a Zwick 250 Universal testing machine. The testing speed was 0.5mm/min. The maximum force taken by the fabric tow was registered. The results are shown in Fig. 4.

2.1.5 Adhesion test for evaluating the increased adhesion of the fibre with the matrix

A simple method was used to find the effect of treatment on the improvement in adhesion between the matrix and the CF. Small pieces of fabric (100mmx100mm) {untreated and treated} were accurately weighed and then dipped simultaneously in PEI solution for 3 minutes. The pieces were then carefully taken out from the solution at the same time and allowed to drip in identical conditions, followed by complete drying and weighing. The percentage gain in weight was calculated. Each experiment was repeated twice, the results of which are shown Fig. 4.

2.2 Development of composites

Composites were developed with CF and the PEI matrix based on an impregnation method, followed by a compression moulding technique [19]. After surface treatment the fabric pieces (80mmx80mm) were ultrasonically cleaned to remove any loosely adhering particles. The open strands of the pieces were sealed from all four sides with PTFE coated glass fabric tape to avoid fibre misalignment. These pieces were immersed individually in a container filled with a viscous solution of PEI (15 wt/wt % of Dichloromethane) for 12 hours. The container was properly sealed to avoid evaporation of the solvent, which was required for adequate wetting of the fibre strands with the PEI solution. The plies were taken out carefully to avoid weave misalignment and dried in the oven for two hours at 100^{0}C in stretched condition. These 20 prepregs were used to attain the desired thickness of within the range of 3.5-4mm and were stacked in a mould carefully to avoid misalignment. PTFE coated glass fabric was placed on the top and bottom of the stacked prepregs. During compression moulding, the mould was heated to attain a temperature in the range of 385-390^{0}C within 2 hours. The prepregs were then compression moulded at this temperature at an applied pressure of 7.35MPa. During the total compression time of 20 minutes four intermittent breathings (each of 2 seconds) were applied to expel any residual solvent. The composites were then allowed to cool under ambient conditions and pressure of 7.35MPa was applied. Four composites were developed with CF and the PEI matrix. One with untreated fabric and three with YbF_3 treated fabric. These composites were designated as C_0, C_{Y1}, C_{Y3} and C_{Y5} respectively, where C stands for composite and subscripts Y stands for YbF_3. 0, 1, 3 and 5 stand for YbF_3 concentrations of 0, 0.1, 0.3 and 0.5wt% respectively.

2.3 Characterization of Composites

2.3.1 Physical properties

The composites were characterized by physical and mechanical properties. In physical characterization, the density of the composites was determined as per ASTM D792 specifications. The weight and volume fractions of the CF in composites were determined by Soxhlet apparatus using dichloromethane as a solvent and keeping extraction time as 36 hours. Void contents in the composites were calculated as per ASTM D2734 standards based on the following equation

$$\text{Void content (Vol.)} = 1- \rho_c(W_m/\rho_m+W_f/\rho_f)\ldots \qquad (1)$$

where ρ_c, ρ_m and ρ_f are the density of the composite, the matrix and the fibre respectively and W_m and W_f are the weight fraction of the matrix and the fibre.

2.3.2 *Interlaminar shear strength (ILSS) tests*

ILSS tests were performed as per ASTM D2344 specifications. The span to depth ratio for the specimen was 5:1. Crosshead speed during the test was 1mm/min. Tests were performed on a Zwick 250 Universal testing machine. Five samples were tested for each type of composite.

3. Results and Discussion

3.1 *FESEM studies on fibres*

As seen in Fig. 1, the FESEM micrographs of the fibres indicate increasing amounts of NPs adhering to the surface of the fibres as concentration increases.

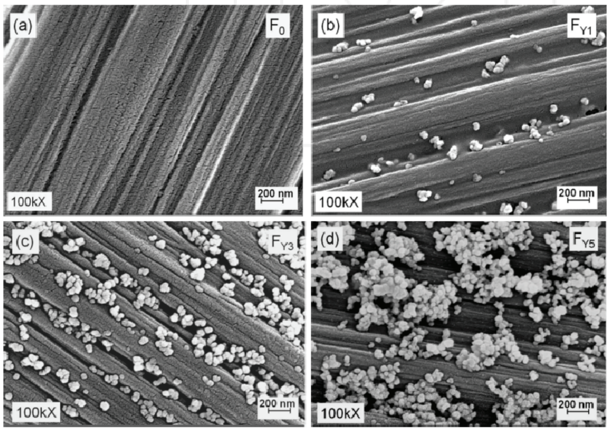

Figure 1. FESEM (100kX) of carbon fibres-(a) F_0, (b) F_{Y1}, (c) F_{Y3} and (d) F_{Y5}.

Fig. 1(b) to 1(d) show the adhered nano YbF_3 particles on the fibre surface. With an increase in concentration, the amount of particles adhering to the fibre also increased. Fig. 1(b) and 1(c) show the uniform distribution of the NPs on the fibre surface. On the other hand, Fig. 1(d) shows clustering of the particles and adherence of the particles to each other, compared to that with the fibre surface.

As per the literature, NPs in excess amounts may cause a lesser increase in the properties of composites with the formation of rare earth salt crystals on the surface of carbon fibre, which affects the bond between the fibre and the matrix [12]. This was explained based on monomolecular layer (MML) formation theory in the case of micron sized $LaCl_3$ particles. When the MML is formed; the two corresponding surfaces adhere to each other efficiently through a chemical bridge with the MML. When excess amounts exist on the interface, instead of the MML, multi-molecular layers (MTML) are formed and adhesion amongst these is based on a weak Van der Waals' force resulting in a less strong composite [12]. In present work, FESEM images have supported this theory and MML (Fig 1(c)) and MTML can be seen (Fig 1(d)) on the fibres.

3.1.2 *FTIR-ATR analysis of fibres*

Fig. 2 shows FTIR-ATR spectra of untreated, ethyl alcohol treated and YbF_3 treated CF. It was of interest to eliminate the possibility of any chemical changes due to boiling in ethanol. Therefore, one fibre specimen boiled in ethanol (without NPs) in identical conditions was also studied and the data are included in Fig. 2.

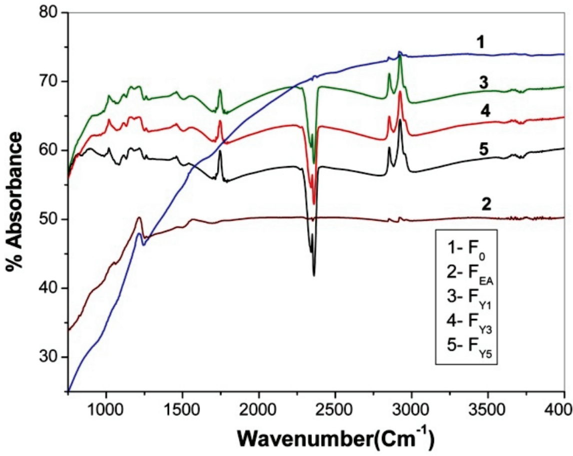

Figure 2. FTIR-ATR spectra of virgin and treated CF for various concentrations of YbF_3

Spectra of virgin CF (as received from the supplier) and ethanol boiled fibre were identical and did not show any peaks confirming the inertness of CF and also that ethanol did not affect the fibre chemically. However, for treated fibres, the presence of oxygenated polar functional groups was observed. There was a small difference in the area of peaks also. With an increase in concentration of NPs, it increased slightly. Ether, carboxyl and carbonyl groups were observed in the spectra corresponding to a wave number range of 950-1200cm^{-1} and 1650-1710cm^{-1}. These groups are responsible for the improvement in adhesion between the matrix and the fabric by increasing the chemical activity of the fibre. These could have originated during boiling with NPs, which are strong oxidizing agents. YbF_3 is from the rare earth family and rare earths are known for increased surface energy. As already discussed these particles are adsorbed on the carbon fibre surface through chemical bonding, which increases the concentration of reactive functional groups. These have a large effective nuclear charge and a strong ability to attract the electrons of other atoms around them. As per the literature, RE is first adsorbed onto the carbon fibre surface and then strongly attracts the electrons in the C-C bond of carbon fibre, resulting in the excursion of the electron cloud of the C-C bond, in turn resulting in weakening of the C-C bond [13]. Therefore, it is easier for functional groups to react with carbon fibre and more functional groups are introduced on the fibre surfaces. This process results simultaneously in two events. The first is beneficial (the incorporation of various functional groups) and the second is detrimental (a reduction in the strength of the fibres). YbF_3 is known as an oxidizing agent so CF undergoes oxidation/corrosion, leading to a reduction in strength (as discussed in Section 3.4.1).

An additional test on CF was carried out to verify if ethanol boiling has any role in altering the performance of CF. A fibre was boiled in ethanol without YBF_3 in an identical way and this did not lead to any chemical change (Fig 2) or change in surface texture or strength. This confirmed that alcohol boiling was harmless to CF. Whatever changes were seen in strength, texture and adhesion were because of YBF_3.

3.1.3 Micro-Raman spectroscopic analysis of fibres

The phases and structural changes that take place in materials were analysed by Laser Raman spectroscopy technique. The bands with an intensity of 1360cm^{-1} and 1593cm^{-1} are the main features of carbon materials and are called D bands (disordered) and G bands (graphitic), respectively. Fig. 3 (a-d) show Raman spectra of untreated and YbF_3 treated fibres.

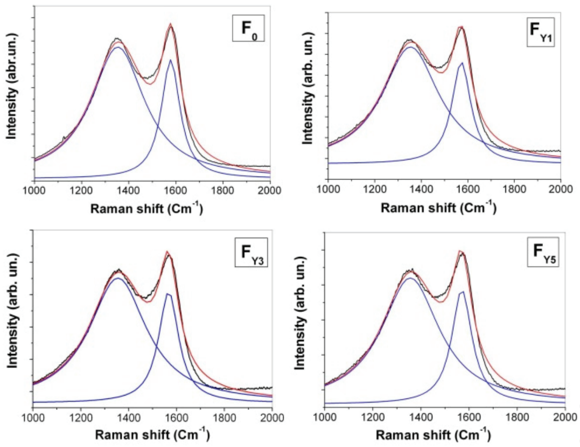

Figure 3. Raman spectra for virgin fibre and YbF_3 treated fibres.

The degree of structural disorder in the fibres was characterized by the ratio of integrated intensity of induced disorder (I_D) to the Raman allowed band (I_G). Lorentzian functions were used to obtain the intensity (I_D/I_G) ratio and the respective surface crystalline size (*La*) of the carbon fibres from the Raman spectra. The crystalline size was obtained by the following the equation.

$$La = C / (I_D/I_G) \qquad (2)$$

where La is the surface crystalline size and C is equal to 44Å.

Table 2 shows that rare earth treatments brought a slight rise (10.5%) in the I_D/I_G ratios from 3.12 to 3.45 for F_0 to F_{Y5} respectively, an indication of an increase in the degree of disorder, the slight distortion in graphitic structure of CF that would occur through the breaking of aromatic bonds and the reduction of surface crystallinity [20].

Type of fibre	I_D/I_G	*La* (□)
F_0	3.12	14.10
F_{YF1}	3.20	13.75
F_{YF3}	3.25	13.54
F_{YF5}	3.45	12.75

Table 2. I_D/I_G and surface crystalline size (*La*) of treated and untreated CF

3.1.4 Fibre tow tension test

As seen in Fig. 4, the tensile load taken by the fabric tow was reduced with an increase in concentration (approx. 5, 8 and 14% for 0.1, 0.3 and 0.5% concentrations respectively) but the increase was not linear. Reduction was at a maximum (14%) in F_{YF5}. The rate of decrease in the tensile strength of the fibres was disproportionately high beyond a 0.3% concentration. This reduction in the strength of the fibres may be due to surface roughening or damage to the fibres as confirmed by the FESEM studies.

3.1.5 Adhesion test

Fig. 4 shows the results of the adhesion test performed on untreated and treated CF. Treatment has improved the pickup of the matrix, with a maximum at 0.5%. However, the rate of increase in weight gain slowed down beyond 0.3%, indicating the possibility of saturation. Increased roughness and improved chemical reactivity of CF enhanced its wettability with the matrix and these factors were responsible for the increased adherence of the matrix with amount of NPs.

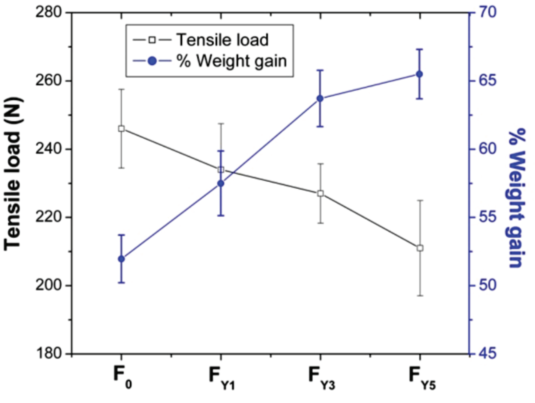

Figure 4. Maximum tensile load tolerated in the tensile test and % gain in weight in adhesion test by untreated and YbF_3 treated carbon fabric.

3.2 Studies on Composites

3.2.1 Physical and Mechanical properties

The physical properties of the composites were obtained to find the fibre weight fraction, fibre volume fraction, void content and density. It was observed that the fibre weight fraction, fibre volume fraction, void content and density of all the composites were in close range and varied between 67.15 to 68.54%, 55.58 to 56.67% and 0.48 to 0.52%, 1.54 to 1.57 respectively.

As shown by Fig. 5, ILSS for selected composites increased with the increase in concentration of YbF_3 and showed a maximum strength at 0.3% concentration. However, for 0.5% concentration, the gain in ILSS was slightly less. In the present case, the net strength of the composites is governed by two factors working in opposite directions: first an increase in fibre-matrix adhesion and second, a decrease in the strength of the fibre due to the treatment.

It was important to know the role of YbF_3 NPs in this study, if it is that of a filler in a composite or as a surface modifier for carbon fibres. NPs in composites generally lead to enhancement in properties. However, in our case NPs did not work as fillers in composites but they did stick to the fibres after the oxidation of the surface. The SEM and FESEM analyses of fibres were done after vigorous sonication. After that the FESEM micrographs showed the particles sticking. Hence, they did not contribute as a filler but as a surface modifies of the fibres.

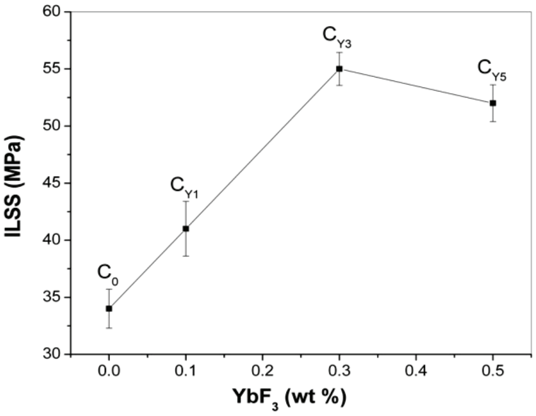

Figure 5. ILSS of untreated and YbF_3 treated fabric reinforced composites.

It is interesting to compare the benefits endowed by this method with other popular methods. In our earlier work, we have reported on the benefits of methods such as cold remote nitrogen oxygen plasma (CRNOP) treatment [21] and gamma ray radiation [22]. When the reduction in tensile strength of fibres (treated and untreated) was compared, it was observed that for treatments with CRNOP, gamma radiation and the present nano-particles method, it was 11%, 18% and 7% respectively, confirming that it was at a minimum in the NP method. Similarly the percentage increase in ILSS in other treatments with CRNOP, gamma radiation and the present method was 53%, 58% and 62% respectively.

The present method is based on the very simple technique of boiling the fabric in nano-suspension of YbF_3, which is a very cost effective technique.

4. Conclusions

Based on the studies on composites developed with a PEI matrix and carbon fabric (CF) treated with nano-rare earth particles (YbF_3) in various concentrations, the following conclusions were drawn.

- YbF_3 treatment of CF led to changes in the surface topography of fibres and inclusion of oxygenated functional groups such as ether, carbonyl and carboxyl. With an increase in treatment concentration from 0-0.5%wt, the roughness of the fibre surface increased gradually, as evident from FE-SEM studies, while tensile strength decreased as confirmed by tensile load analysis.
- A Micro-Raman spectroscopic study showed a slight rise in the I_D/I_G ratio with an increase in treatment concentration and therefore the distortion in graphitic structure as a result of chemical stressed induced during treatment.
- It was also concluded that NPs led to an enhancement in fibre-matrix adhesion as evident from the matrix pick up studies in the adhesion test. The rate of adhesion increased sharply up to 0.3% conc. dose, followed by a slow increase for the subsequent concentration (0.5%).
- The enhancement in adhesion between the matrix and the CF led to improved performance properties of all the composites.
- Overall it was concluded that YbF_3 treatment of CF is beneficial only when employed judiciously. If the treatment concentration exceeds a typical value (0.3wt% in this case), the properties of composites start falling, to the extent that occasionally 0.5wt% YbF_3 treated composites was slightly poorer in performance than the untreated one.
- FESEM studies confirmed that the YbF_3 particles adhere to the fibres in mono-molecular layer fashion, which leads to enhanced fibre-matrix adhesion. If multi-molecular layers are formed, adhesion is less and the composites developed from such fabrics show lower strength.

5. Appendix A

S. N.	Details	Matrix used	Fibre/ Fabric	Processing details	Essence	Refs.
1	RT, AO	PI	CF (PAN)	RT-CF dipped in alcoholic $LaCl_3$, 0.1-0.5wt% for 10 min. AO-450 °C for 10 sec.	Enhancement in TS, FS & tribological properties. RT better than AO, TS highest for 0.3wt% ILSS and fibre analysis not done;	[12]
2	RT, AO	PTFE	CF (PAN)	RT-same as 1 except time (3 hrs.) & (0.3 wt%) AO-450 °C for 40 min.	RT better than AO to increase TS, strain at break, bending strength and in reduction in μ and wear of PTFE composites ; Optimization of doses, ILSS and fibre analysis not done	[13]
3	RT, AO	PTFE	CF (PAN)	RT-same as [11], AO- Heated to 450 °C for 40 min.	Interfacial adhesion, bending strength and tribo- properties improved. Fibre analysis, optimization of doses, TS, & ILSS of composites - not done.	[14]
4	RT, AO	PTFE	CF (PAN)	Same as 2	Both RT and AO benefitted μ and wear; RE more efficient than AO, Fibre analysis done by XPS; Mechanical properties and optimization of doses-not done.	[15]
5	RT	PI	Short fibres of CF (pitch based)	Same as 2 except time (5 hrs.)	Wear resistance appreciably improved though not μ. Fibre analysis done by XPS and SEM; Mechanical properties & optimization of doses-not done.	[16]

RT-Rare earth treatment, AO-Air oxidation method, CF-Carbon fibre, TS-Tensile strength, FS- Flexural strength, ILSS-Interlaminar shear strength, SEM-Scanning electron microscopy, XPS-X-ray photoelectron spectroscopy, μ-Coefficient of friction, PI- Polyimide, PTFE- Polytetrafluoroethylene

Table 1. Influence of rare earth treatment in combination with air oxidation on performance properties of carbon fibres and composites

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