REVIEW

Effect of Fiber Sizing on Mechanical Properties of Carbon Reinforced Composites: A Review

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1. Introduction

Carbon fibers are one of the most important choices for the industry in the area of fiber reinforced composites. The market of composite industry is expanding day by day because of the increased demand of the materials which have good strength to weight ratio. The production of carbon fiber has a very sophisticated procedure which has evolved in a very long span of approximately 60 years. The most critical component involved in the industry of carbon fibers is carbon fiber sizing or size. The sizing is a coupling agent coating which is coated over a carbon fiber to enhance the binding capacity of fiber to the resin. The term sizing is often used to get rid of confusion between size the coupling agent and the size relating dimension. It has been found in many studies that the unsized carbon fiber gives poor mechanical properties in comparison of sized carbon fibers. The carbon fiber sizing influence both long term and short term performance of the composites [1-4,22].

In recent years, Carbon fiber reinforced composites (CFRP) have been used for many offshore and marine applications. Composites are exposed to salt and high moisture conditions, hence sizing and interface play an important role. The performance of the composites in these critical environmental conditions have been a big issue. So it becomes important to make such fibers and fiber interphase which can work under intense weather conditions without or less degradation in the properties [5-6].

Commercially produced carbon fiber comes with a thin polymeric film which protects the fiber from damage due to friction between adjacent fibers during handling, transportation and textile processing and also provides good wettability during composite manufacturing. Sizing also acts as an adhesion promoter between the fiber surfaces to matrix. Recent work on the sizing has demonstrated that
the polymeric sizing on carbon fiber reinforced composites can improve the durability and life span of composites.

2.1 Effect of Fiber Sizing on Carbon Fibers

The adhesion between the fibers and matrix is very important to have good mechanical properties as the fibers take maximum load and the load transfers from fiber to matrix through interphase, so it is very important to have a strong interphase. Different sizing chemicals are employed on the fibers to alter the surface morphology of the fibers. Different research works have been conducted in past to develop the sizing technology and to get compatible sizing chemicals for fibers and different polymer resins. The manufacturers keep the knowhow of sizing chemistry secret and researchers are trying to understand this technology and modify the sizing for the practical applications.

2.1.1 Carbon Fiber Sizing Technology

To develop a good sizing technology and to develop these apparatus have not been an easy task as sizing needs to be employed at the time of manufacturing of fiber itself. Broyles et al. [1] developed a sizing apparatus which could be used to coat carbon fibers with aqueous water-dispersible polymeric interfaces of poly vinyl pyrrolidone. A high level of fiber spreading achieved by controlling fiber tension and application of rollers.

2.1.2 Characterization of Carbon Fiber Reinforced Composites

It is very much needed to characterize the composites whenever there is a change in the morphology of fiber. Different techniques are employed to characterize the composites. Cho et al. [2] conducted dynamic mechanical analysis (DMA) on unidirectional and bidirectional woven carbon/nylon 6 composites. The results of DMA and short beam shear tests indicate an enhancement in interfacial and inter laminar strength of woven composites. The authors also found that glass transition temperature (Tg) increased as the fiber matrix adhesion increased. Dilsiz and Wightman [3] compared the unsized fibers with Ultem polyamide and PU sized fibers. In the study it was evident that the sizing reduces the surface energy and acid-base sites. X-ray photoelectron spectroscopy (XPS) analysis showed that there is a decrease in hydroxyl groups on the carbon fiber surface. Single fiber fragmentation test showed the direct relation of surface energies to change the fiber matrix adhesion. Epoxy has also been used as a sizing agent. The effect of different molecular weight sizing on the performance of carbon fiber was studied by Zhang et al. [4]. The sizing agent were epoxy 601, epoxy 6101 and epoxy 618 which are different in molecular weights. As the diameter of carbon fibers is in few microns so it is not feasible to study the surface of fiber from optical microscope for this purpose scanning electron microscopy (SEM) is a very important technique. Atomic Force Microscopy (AFM) and scanning electron microscopy (SEM) analysis showed that the sizing agent affects the surface topography. Interfacial shear strength (IFSS) results indicated that epoxy 6101 gave better results in comparison of other two. Yao et al. [5] compared of sizing effect on T700 grade carbon fiber on interfacial properties of carbon/epoxy and carbon/bismaleimide (BMI) composites. Fourier-transform infrared spectroscopy (FTIR) analysis showed that the coupling agents are chemically reactive. Sizing react with bismaleimide and epoxy resin matrix. Micro droplet test indicated that desized fiber shows lower interfacial strength in epoxy resin than that of sized fibers, however, the trends in the case of BMI were reversed. This is also indicated by the chemical reactions, as the reaction between epoxy and sizing was sufficient in case of epoxy but partial reaction took place in case of BMI. Modification in surface roughness as well as chemical properties can be seen from the results of AFM and XPS analysis.

Some of the other techniques are also employed to modify the surface characteristics. Downey and Drzal [6] used the impact of UV-ozone on the fiber surface treatment with aromatic and aliphatic epoxy sizing. These sizing is used to enhance toughness of diglycidyl ether of bisphenol A (DGEBA)/ meta-phenylene diamine (mPDA) based carbon-epoxy composites without compromising static mechanical properties and glass transition temperature. The results showed significant increase in mode I fracture toughness as well as improved transverse flexural strength. Yuan et al. [7] modified the interface between carbon fiber and epoxy matrix. A modified polyacrylate sizing agent was applied on the fibers. The sized carbon fiber increase the wettability and decreased the surface roughness due to smooth sizing layer. Inter laminar shear strength increased by 14.2%. Liu et al. [8] synthesized a modified epoxy emulsifier (MEE) for preparing an aqueous epoxy sizing agent, the carbon fiber surface is evenly wrapped with tiny particles to increase the surface roughness. SEM, AFM and XPS analysis also showed the increase in activated carbon atoms on the surface of carbon fiber. The results of single fiber fragmentation test suggested interfacial shear strength increased by 70-76%. Han et al. [9] used polydopamine (PDA) as sizing on the carbon fiber surface. The authors observed that by implementing PDA as the sizing the behaviour of the crack
propagation becomes smooth whereas in the case of neat carbon fiber the curve is not uniform and it's like the teeth of a saw blade. They also reported that single fiber pull out test shows that the interface never failed in case of sized fiber the fracture took place in epoxy resin only. The SEM images of the neat and sized fiber also confirms that the surface of sized fiber is quite rough in comparison of neat fiber surface as shown in figure 1.

Figure 1. SEM image of (a) CF and (b) PDA-CF surface

Sizing deposition ratio also affects the properties of composites. Stojcevski et al. [10] reported the effects of sizing deposition ratio on the properties of composites. The deposition ratio of unsized, 1:10, 1:15 and 1:20 parts of water and altering electrochemical oxidation with oxidation current 0 A, 2 A and 3.4 A on several fiber types. Two epoxy resin systems were used in the analysis and their effect on interfacial shear strength (IFSS) was studied. Epoxy RIMR935 with hardener RIMH 937 at 1:04 parts by weight ratio. Epoxy Bisphenol A diglycidyl ether (DGEBA) was mixed with 4,4′ Diaminodiphenylmethane (DDM) at a ratio of 1:0.3 by weight. Single fiber tensile test, fiber fragmentation test, AFM, contact angle and surface free energy were used to characterization of composite. The results showed that the unsized, unoxidized have least interfacial shear strength (IFSS).

Carbon nano tubes (CNT) have also been incorporated in sizing to enhance the adhesion between the fiber and the matrix. Zhang et al. [11] modified the carbon fiber surface by introducing carboxyl-functionalized carbon nanotubes (CNTs-COOH) and the amine-functionalized carbon nanotubes (CNTs-NH₂) in carbon reinforced composites. The results showed the betterment in the mechanical properties while CNTs-COOH, while CNTs-NH₂ gave adverse effects on mechanical properties as shown in figure 2. Yu et al. [12] studied the long term moisture effects on the interfacial shear strength. Multi walled carbon nanotubes and silane coating was applied on the fibers. The increase in interfacial shear strength was 14.5% and 26.3% by using silane and CNT respectively. Also these strengths were maintained for 120 day immersion test in de-ionized water and simulated sea water.

The improvement in mechanical properties of carbon/epoxy composites by using hybrid Poly Urethane (PU)/silane coupling agent is studied by Mao et al. [13]. The silane coupling agent concentration affects the shear strength of composite and wettability of carbon fiber. If the sizing concentration was more than 3% the resin accumulated on the surface of fiber which reduced the mechanical properties again. Kobayashi et al. [14] studied the resin impregnation behaviour at different sizing content and found resin impregnation improved with decreasing sizing content. This impregnation causes larger permeability. Sizing agent on the fiber surface increased the resin flow among the fibers. It was also found that the sizing content which was optimized with epoxy does not provide good results with PA 6.

It becomes very important to analyse the surface of the carbon fiber while manufacturing a composite as the interfacial shear strength depends on the adhesion between the fiber and the matrix. Dilsiz and Wightman [15] did the surface analysis of sized and unsized fibers and found the thickness of poly(thioarylene phosphine oxide) (PTPO) thickness is greater than the thickness of poly(etherimide) (Ultem) sizing. The practical applications of carbon fiber and vinyl ester composites are restricted beacause of poor adhesion between the fiber and matrix which leads to lower IFSS. To resolve this issue N-(404-diaminodiphenyl methanee)-2-hydroxypropyl methacrylate (DMHM) may be used as a sizing agent which can improve interfacial shear strength by covalently bonded carbon fiber and vinyl ester resin [16]. Zegaoui et al. [17] incorporated various concentrations of silane treated carbon fiber in cyanate ester/ benzoxazine resin. 3-glycidyloxypropyltrimethoxysilane (GPTMS) was used as a sizing agent. FTIR studies showed that the treated carbon fiber had effectively reacted with the matrix, SEM micrographs confirmed the changes in the morphology of composites. At 20% treated carbon fiber filled composites had best mechanical properties. Ozkan et
al. [19] studies the effects of carbon fiber sizing on the short carbon fiber reinforced polycarbonate composites. Sizing materials were epoxy/phenyox, phenoxy and polyimide. 1%, 2% and 3% by wt.% sizing is used on the carbon fiber, while the weight percentage of carbon fiber was kept constant at 30%. It was observed that tensile strength and modulus of sized carbon reinforced polycarbonate composites were higher than the unsized fibers. From the TGA analysis it was evident that the sizing material was stable at the time of composite processing.

2.1.3 Sizing on Recycled Fibers

The disposal of composites after the completion of life is a big issue in the application of composites. So composites can be collected after their lifetime and fibers can be extracted from these composites for recycling. Recycled fibers are available for free or at a very low cost. These fibers can be used in composites for secondary structural applications as the stiffness and the strength of composites decreases after the primary use. To again impart strength and stiffness to the fibers the coupling agents are applied on the fibers. The length of the recycled fibers is in millimeters so these fibers can be used a randomly oriented 2D mat or single direction aligned mat [19].

2.1.4 Effect of Sizing on Fatigue Properties

The study of the fatigue properties of a composite is very important. As in most of the applications the composites are not subjected to only static loading but also to dynamic loading which can be repeating in nature. So in these cases fatigue failure becomes predominant. In fatigue loading material fails well below its yield or ultimate strength so fatigue can be very detrimental to a structure. The fatigue limit is the value of stress which a sample can withstand for one million revolutions. The studies are conducted to find the fatigue life of composites. Broyles et al. [20] studied the effect of phenoxy polyhydroxyether (PKHW35) and poly vinyl pyrrolidone (PVP K17) as the sizing material in the composite of carbon fiber and vinyl ester. The stress levels of 75%, 65%, 55% and 45% were applied in compression to draw S-N diagram. From the studies it was concluded phenoxy sized composites gave about 60% increase in fatigue limit of the composites in comparison of unsized fiber while PVP gave an increase of just 20%. From this study is also concluded that sizing not only affects the static mechanical properties but also improve fatigue properties. Tsai et al. [21] incorporated silica nano particles (SNP) in the sizing HS-1 and Neoxil-965 as the emulsion of different weight percentages. The DCB specimen were used as the fatigue crack growth test at room temperature. The displacement ratio used was 0.1 at a frequency of 10 Hz using a sinusoidal wave form. The sizing had no effect on the fatigue limit but the mode I fracture energy increased by 101%.

Table 1 consists of the list of common sizing chemical used for carbon fiber. GPTMS is also a very effective sizing chemical for glass fiber [22]. GPTMS can be used as a common fiber sizing for glass fiber and carbon fiber reinforced hybrid composites.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Sizing</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Poly vinyl pyrrolidone</td>
<td>1,20</td>
</tr>
<tr>
<td>2</td>
<td>Polylamide and PU</td>
<td>3,19</td>
</tr>
<tr>
<td>3</td>
<td>Epoxy</td>
<td>4,8</td>
</tr>
<tr>
<td>4</td>
<td>Polyaclate</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>Poly dopamine (PDA)</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>4,4’ Diaminodiphenylmethane (DDM)</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>Carbon Nanotubes</td>
<td>11</td>
</tr>
<tr>
<td>8</td>
<td>Poly(thioarene phosphine oxide) (PTPO)</td>
<td>15</td>
</tr>
<tr>
<td>9</td>
<td>N-(404-diaminodiphenyl methane)-2-hydroxypropyl methacrylate (DMM)</td>
<td>16</td>
</tr>
<tr>
<td>10</td>
<td>3-glycidyloxypropyltrimethoxysilane (GPTMS)</td>
<td>17</td>
</tr>
<tr>
<td>11</td>
<td>Phenoxy polyhydroxyether</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>HS-1 and Neoxil-965</td>
<td>21</td>
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</tbody>
</table>

3. Conclusion

The current study shows the different compounds used as sizing on carbon fiber. The methods to characterize the interface also discussed. The primary function of fiber sizing is to enhance the adhesion between the fiber and the matrix material and to protect fibers from the neighbouring fibers. Sizing also affects the glass transition temperature and morphology of fiber surface. The discussed methodology can be used for recycled composites and the recycled fibers can be used in the secondary structural applications.

References


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