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Thermal and Chemical Etching of Carbon Fiber

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ABSTRACT

In this work both of desizing and etching (thermally and chemically) for carbon fiber surface was performed. To investigate their effect on the mechanical properties on the fiber and it's composite. Acetone and ethanol are used for desizing, as well as heating up to 380℃ . Etching of fibers is one of the suggested methods to improve adhesion between carbon fiber and matrix. Etching of carbon fiber under atmosphere as a function of temperatures for (380,400,420,500,520) ℃ and nitrogen gas as a function of temperatures for (500,520,540,560,580,600) ℃. The result shows that nitrogen gas give the best etching comparing with atmospheres and this reflects on the mechanical properties of the composite material. Nitric acid, sulphuric acid and hydrogen peroxide are used for chemical etching. Scanning electron microscope (SEM) and contact angle tests on desized and etched carbon fiber show better mechanism for adhesion. The mechanical properties of the treated composites was higher values than those of untreated composites.

Keywords: *Carbon Fiber, Desizing, Etching*

1. INTRODUCTION

Carbon fibers are currently being used as the reinforcement for both thermoset and thermoplastic matrix composites [1]. Carbon fiber/polymeric matrix composites is a class of advanced materials that have been established for a variability of applications in areas of high technology, such as aerospace, automobile, air craft, defense industry, and sporting goods[2,3 and 4]. Carbon fibers are superior by having the highest stiffness and tensile strength as well as a rather low density [5]. The carbon fibers have poor wet and adsorption ability with most resins because the carbon fiber surface is non-polar and compound of highly crystallized graphitic basal planes with inert structures [6 and 7].

Carbon fibers are widely used as reinforcements in epoxy resin composites. High modulus carbon fibers are widely used as reinforcement for advanced composite materials. As for composites, the resulting mechanical properties not only depend on the reinforcement and matrix materials but also have relationship with the interfaces between fibers and matrix, which are stated to be important in improving composites performance [4, 3 and 8]. An increase in the surface polarity or active sites for van der Waals linking and hydrogen bonding can improve the interfacial adhesion between the fiber and the surrounding polymer matrix, leading to better stress transfer from the matrix to the fiber materials [8 and 9].

To improve the wettability of carbon fibers and interfacial adhesion of composites, several techniques for surface treatment on carbon fibers have been applied, including plasma, electrochemical oxidation, wet chemical and thermal treatment. These treatments on carbon fibers improved interfacial wetting and adhesion force of the final composites to some extent and enhances the ILSS [3, 7, 10, and 11].

The factors contributing to adhesion could be due to chemical reaction, van der Waals forces, electrostatic attraction, acid-base interaction including H-bond, or mechanical interlocking [9].

The sizing materials (generally, 0.5–1.5 wt. %, sizing is usually applied to the fibers to produce a layer approximately 0.03 μm thick on a 7μm fiber) [12, 13 -14]. The mechanical properties of the carbon fiber reinforced resin matrix composites depends not only on the properties of reinforcing fiber and matrix, but also on the fiber/coatings and coatings/matrix interfacial properties as shown in Figure (1**)** [6].

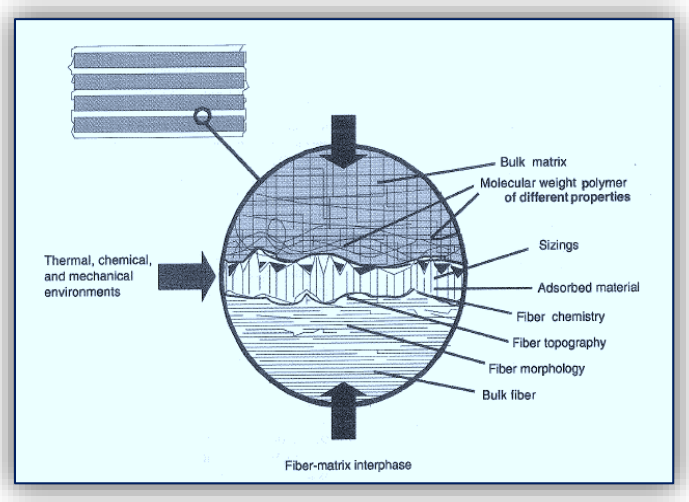

Figure (1); shematic digram of the fiber-matrix interphase [15].

In this research, the surfaces of the carbon fibers were chemically and physically adjusted by nitric and sulphuric acid, in addition to heat treatment under nitrogen and air atmospheres. The untreated and treated surfaces of the carbon fibers were exposed to detailed characterization. The chemical and physical aspects of the surfaces were inspected by scanning electron microscopy (SEM), contact angle, tensile strength.

2. MATERIAL& EXPERMENTIAL

2.1. Materials

Unidirectional woven CF (kind 300 C/60) was obtained from Sika Ypi Co., Ltd / Turkey. Resin used in this research is Epoxy was obtained from CMCI (Construction Material Chemical Industries). EPOMORT 1000 LV, ISO 9001 Certified company.), supplied by Saudi Arabia.

2.2. Determination of purity of carbon fiber

This is done by ignition carbon fiber at 700°C and from the weight loss, the purity was 100%.

2.3. Desizing

A - Solvent: Acetone and ethanol were chosen as the solvent for desizing (epoxy sizing). Immerse a certain weight of fiber in acetone (or ethanol) for 24 hours with heating up 50°C,washing by acetone, dried at 110 ◦C for one hours ,weight loss were found 1.098% and 1.7% for acetone and ethanol respectively.

b –Thermal treatment: Drying fibers at 110 °C for 90 min. fibers were held overnight in glass desiccator to eliminate any humidity, Certain weight of fiber with high accuracy measurement (average of five weights), then fibers are heated at 380 °C for 60 min. to desizing and to determine epoxy percentage, cooling in glass desiccator and calculating the weight loss, In order to investigate the sizing percentage. Sizing was found 1.75%.

2.4 Surface treatment of carbon fiber (etching).

Oxidation treatments can be applied by thermal and solution (chemical) treatments.

A. Thermal treatment

1. Weight loss percent as a function of temperature under atmospheres

Certain weight, drying at 110°C for 90 min to remove humidity. Fibers must be put in tension and separate so that the heat reaching for all fibers, then, modified by heating at five different temperatures (380, 400, 420, 500, and 520 ºC) for one hr. to activate fibers for reinforcement composite.

2. Weight loss percent as a function of temperature under nitrogen atmospheres.

Fibers were modified by heated in holding furnace at six different temperatures (500,520,540,560,580 and 600 ºC) for one hour each. To activate the fibers for reinforcement composite.

B. Chemical treatment: Strong acidic treatment is another wet method for CF modification which corrodes its surface and/or introduces perforations, to improve fiber/matrix interlocking [16].Oxidation of carbon fiber by separately nitric acid, sulphuric acid or hydrogen peroxide.

1. Nitric acid: The oxidation treatments of fibers were performed in nitric acid (69-71) %, Treat the fiber in concentrated acid for different time (30, 60, 90 and 120) minutes, rinsed in distilled water, then drying and calculating the weight loss.

2. Hydrogen peroxide: Hydrogen peroxide (H_2O_2) was chosen as oxidation for carbon fiber, using (50%) hydrogen peroxide, made in Spain. Treat the fiber in hydrogen peroxide for 24 hours, after that washing and drying the fibers.

2.5 Samples Preparation for testing

Aluminum mold was used for these tests, composite was made by setting the fiber inside the mold and pour the resin mixed with its hardener on it. Epoxy as a matrix material were arranged by mixing resin with its hardener in a ratio (2:1) by volume. These materials were carefully mixed and stirred at speeds (400 rpm) for 6 min. until it develop uniform matrix material was filled the mold gradually so as to avoid air trapping, and the arranged composite specimen were left at room temperature until dryness, Then cured at 90°C for 4 hrs.

3. RESULT& DISCUSSION

3.1 Determination of carbon fiber: Carbon fibers are ignited at 700°C for 60 min. to determine its purity .In this work ignition method is used to determine the purity of the used carbon fiber. At temperature neighborhood of 500°C, carbon reacts with oxygen to yield practically pure carbon dioxide [17].

3.2 Desizing:

Two techniques were used to remove the size from the fibers both solvent extraction and heat treatment [18] sizing is organic material (epoxy),that is prevent direct contact between fiber and matrix even its epoxy ,this is lead to effect on adhesion between them. On one hand, it must remove the size material from carbon fiber when produced composite materials with matrix other than epoxy. Even in case of epoxy it is necessary to desizing the fiber to activate its surface.

A. By solvent: Both acetone and ethanol were chosen as the desizing solvents because they are polar solvents. Acetone boils at 56°C and ethanol at 78°C; thus both solvents are easily removed. The size material could not be eliminated completely by acetone. This is due to the fact that size materials reacts with the fiber resulting in an insoluble polymer or a chemical interaction between the fiber and the size material take place result in preventing dissolution and remove of the size as well as diffusing in the fiber [18].

B. By heat treatment: fiber heated nearly at 380°C, in such temperature epoxy materials oxidized to carbon dioxide and water vapor. This is agree with reference [5].lower than 380 °C, it seems not all epoxy removed comparing with the solvents technique, this push us to raise the temperature up to ~ 380°C at this temperature the result of Wt. % size equal to 1.7 % which is in very agree with literature value 1.75% .generally 0.5-1.5 Wt. % is applied to the fiber to produce 0.03 μm thick on a 7 μm fiber [12, 13, 14]. As expected the result, heating led to essentially complete size removal [18].

3.3 Etching of carbon fiber

A) Thermal etching of carbon fiber

1- Heat treatment of carbon fiber under atmosphere

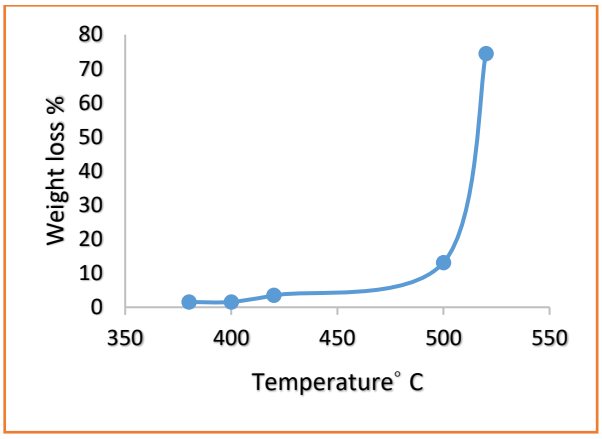

Figure 2; Heat treatment of carbon fiber under atmosphere.

The Figure 2 shows the loss of weight of fibers as a function of temperature. The results show that the losing of weight began at 400 ºC with decomposing of size material and appearing of pure shine carbon fiber, which coming from damage sizing of epoxy that covering of carbon fibers and then keep on losing sharply at temperature more than 500 ºC. It is coming sublimation of carbon. By heating attack surface of fiber the create groups contain oxygen because of interaction carbon with air. This groups are hydroxyl group, carbonyl group, carboxylic group and CO_2 .

2. Heat treatment of carbon fiber under nitrogen gas

The aim of this study is to look about the physical change on morphology of the fiber since nitrogen gas is chemically inert so no reaction or group formation take place on the fiber Figure.(3) shows weight loss starting near 500 ºC and increase sharply at 600 ºC, this is due to

1- Carbon starts sublime near 500 ºC, at temperature neighborhood of 500 ºC, carbon reacts with oxygen to yield practically pure carbon dioxide [17].Nitrogen gas contains traces of oxygen, this traces attack carbon at that temperature.

2- Size material starts for self-oxidation near 380 ºC due to the presence of oxygen in its chemical structure.

3- This confirm by Fig.2 which shows very sharp increase in weight loss near 500 ºC comparing with Fig.3 shows a simple increment at~ 600 ºC.

4- nitrogen slightly attack carbon at high temperature forming cyanogen gas (CN)2 with melting point of -28 ºC and boiling point of -21 ºC [19]

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B) Chemical etching of carbon fiber

1. Nitric acid

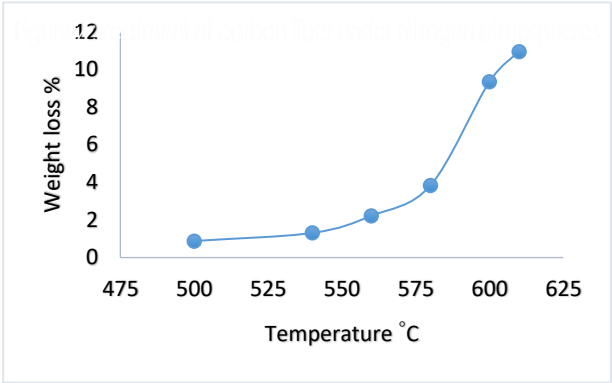


Figure 3; Heat treatment of carbon fiber under nitrogen.

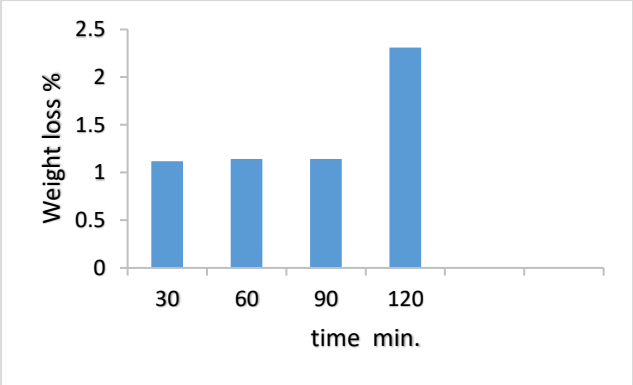


Figure 4; Weight loss by concentrated nitric acid as a function of time.

Figure (4) shows constant weight loss (1%) for the first 90 minutes, then a jump 2.25 % after 120 minutes, it seems that carbon fiber resists this strong acid. Nitric acid have used as oxidant to introduce various of acidic functional groups (carboxyl and phenolic) on surfaces of fibers, aiming to increase the fiber/matrix adhesion through a combination of increased acid-base interactions, chemical bonding and/or improved mechanical interlocking on the fiber surface [20].

2-Carbon fiber treatment by 50 % hydrogen peroxide

Hydrogen peroxide (H_2O_2) was chosen as oxidant for carbon fiber, The weight loss was found to be 0.558% which indicates no action of peroxide on the fiber comparing with sulphuric and nitric acids.

3.4 Contact angle

The increased surface energy of the carbon fiber can help to improve the interfacial adhesion of composites [21].an increase in the surface polarity or active sites for van der Waals linking and hydrogen bonding can improve the interfacial adhesion between the fiber and the surrounding polymer matrix, leading to better stress transfer from the matrix to the fiber materials. Therefore, the decreased surface energy, especially the polar component of surface energy on carbon fiber's surface after sizing suppresses surface wettability or even decreases the interfacial adhesion between fiber and matrix possibly [22].

Figure 5 shows the contact angle decreases with increasing temperature. i.e. wettability increase with temperature due to the destroying the glass Water insoluble coat (epoxy) as well as increasing reaction groups on carbon fiber with temperature, which interact with polar molecule.

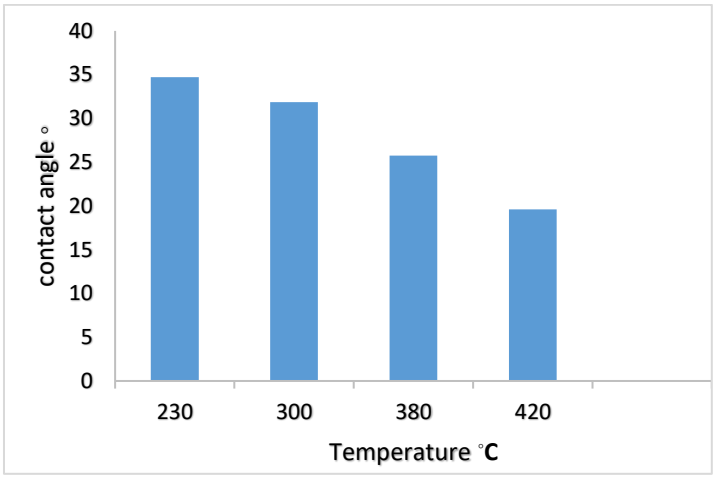


Figure 5; Variation of contact angle as a function of temperature under atmosphere

Figure 6 shows the main action of the heat is to remove epoxy coating and may be at high temperature, nitrogen attack carbon fiber to form carbon nitride attacks the surface of the fiber to activate it as well as there is always traces of oxygen in the nitrogen gas.

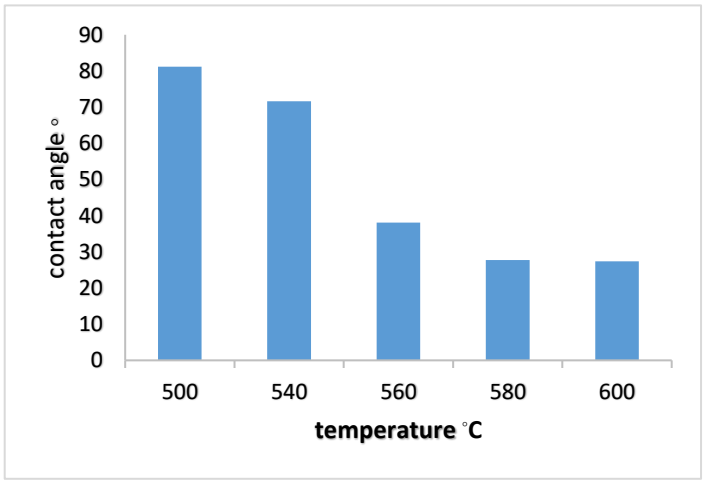


Figure 6; Variation of contact angle as a function of temperature under nitrogen gas

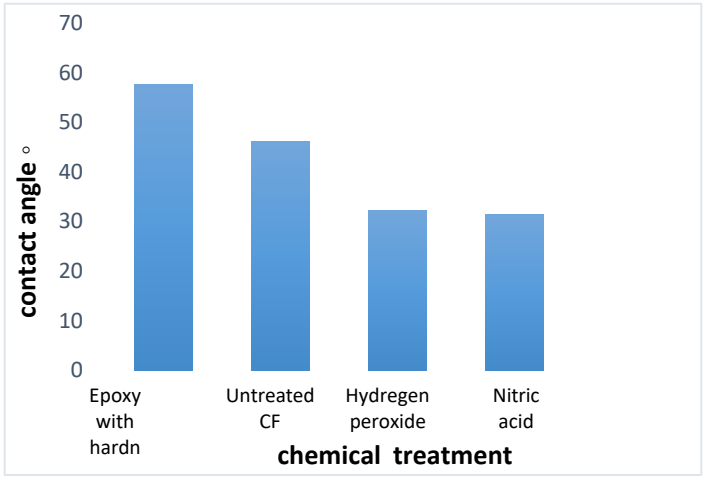
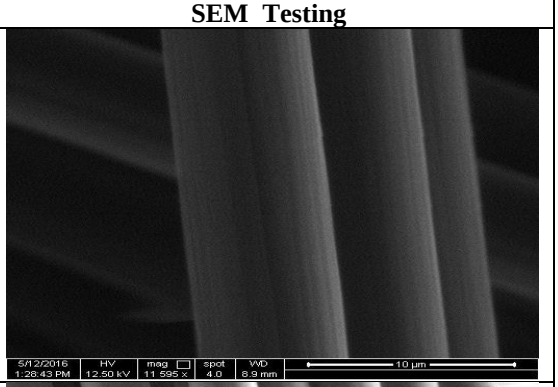
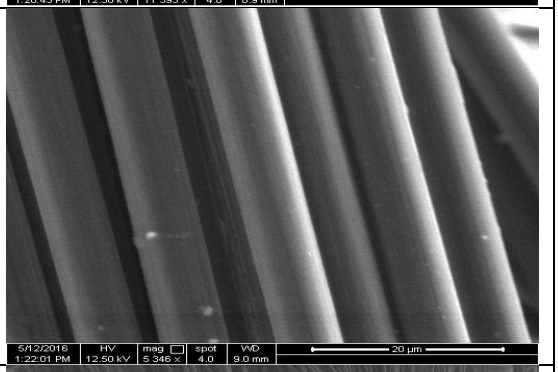
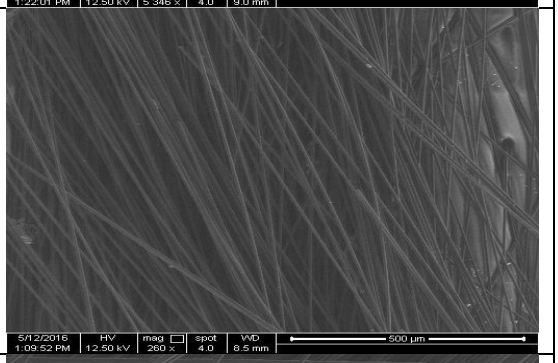
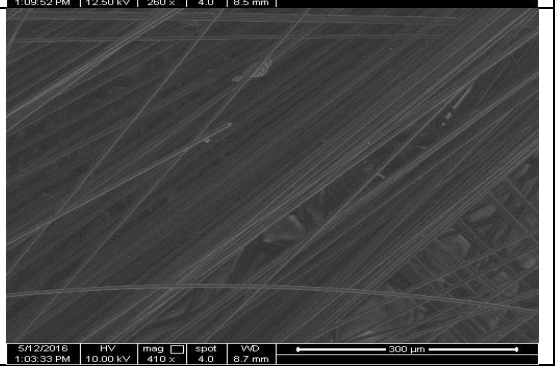


Figure 7; shows the variation of contact angle under chemical treatment

3.5 Scanning electron microscopy (SEM)

Table 1; Show a SEM image of carbon fiber sample

Sample	SEM Testing
(a) Untreated carbon fiber	
(b) desizing (acetone)	
(c) 420℃ under atmosphere	
(d) 520℃ under nitrogen	

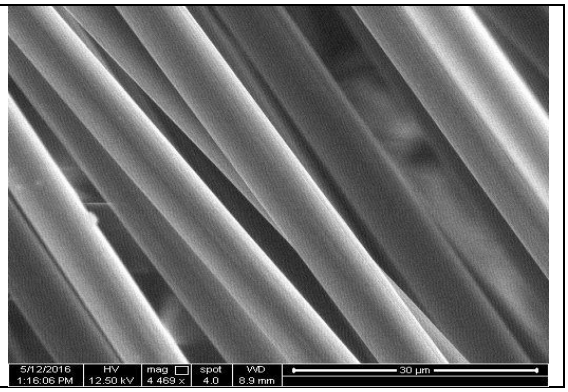
(E) **treatment by nitric acid**	

Table 1 (a) shows a SEM image of untreated carbon fiber sample. Obviously, this fiber's relative smoothness was attributed to the wet spinning procedure working to produce the Polyacrylnitrile (PAN) fibers used as raw material in carbon fiber processing [20].

Table 1 (b) shows an image of a carbon fiber sample treated with acetone for 24 hours. No important variances are noticeable and the sample shows a moderately smooth surface and little defects. Removing the sizing of the fiber change in the appearance due to removing sizing material of fiber result in absorption of the acetone and swallow of the fiber and high reflectness of incident light comparing in untreated.

The sizing increases fiber surface smoothness and the longitudinal streaks on sized fibers become shallower, which resulted from streaks on fiber surface were covered during the sizing process. Increasing the fibers surface roughness could enhance the mechanical interlocking Therefore, the smooth surface of the samples after sizing has negative effect on mechanical interlocking [22].

The micrograph of the carbon fibers which treated under air oxidation Table 1 (c) shows that this treatment created better modifications on fiber surface, with improved roughness and etching more transversely oriented along the fiber's axis. Under heat treatment of fiber for example at 420℃ under air oxidation, some of the fiber are cut and become more random.

While under nitrogen gas at 520 ℃ no change appeared in the fiber. The macrograph of heated of carbon fiber under air show that there is a major change on the surface of fiber result increasing roughness. Show that heat treatment under nitrogen the result increase the superficial roughness of fiber surface as shown in Table 1 (d). Heat treatment could affect the physico-chemical properties as well as the morphology of carbon fibers [12].

The micrograph of the carbon fibers treated with nitric acid Table 1 (E) shows that this treatment created better modifications on their surface, Most of the nitric acid treatments resulted in very little change in fiber surface morphology, but a significant decrease in diameter with treatment time was observed. The action by fuming nitric acid gave friable surface with low defects.
These samples were selected for an additional complete analysis because these treatments heighten the probability of presenting polar groups and adjusting the roughness of carbon fiber surfaces.

3.6 Mechanical properties

As the temperature of the treated fiber increases more epoxy coating remove as well as polar group on the carbon surface formed result in a good adhesion and mechanical interlocking with the matrix as shown in the Tables (2 and 3).

Table 2; Tensile strength for treated carbon fiber under air oxidation.

Sample of composite	Elastic modulus (GPa)	Tensile strength(MPa)
epoxy	0.01	4
Untreated fiber	0.015	9
desizing	0.02	14
At 400 ℃	0.06	29
At 420℃	0.07	42

Table 3; Tensile strength for treatment carbon fiber under nitrogen gas

Sample of composite	Elastic modulus (GPa)	Tensile strength(MPa)
Pure	0.01	4
Untreated fiber	0.015	9
Desizing	0.02	14
HNO_3	0.03	27
H_2O_2	0.15	17

Table 4; Tensile strength for treatment carbon fiber under chemical treatment.

Sample of composite	Elastic modulus (GPa)	Tensile strength(MPa)
Pure	0.01	4
Untreated fiber	0.015	9
Desizing	0.02	14
500 ℃	0.27	59
520℃	0.09	78

Table 2 Indications that the tensile strength values of the composites with air oxidation of carbon fibers are increased by compared to that without treatment .it is proved that the better interfacial adhesion can be obtained through surface modification. The reasons attribute that the air oxidation was used as method to etching carbon fiber, which increase the interlock between the fiber and matrix, leading to the increase of tensile strength of composites, which can effectively transfer the stress from matrix to fiber, so the fiber bring more reinforcement .therefore, the tensile strength of the composite reinforced by air oxidation of carbon fiber are considerably improved.as well as the elastic modulus value doublet at 400℃ and bath more increase at 420℃ .

Table 3 indicates that the tensile strength of carbon fibers treated with thermal treatment under nitrogen condition increased more than that of fibers treated with heat treatment under air oxidation, since nitrogen gas is chemically inert so no sever etching take place.

Table 4 Indicates that the acid has removed the sizing and it is no longer acting as a factor in the transverse tensile strength. It's presence in the acid after removal apparently does not affect the fiber surface groups that are implanted.

4. CONCLUSIONS

1- Desizing of carbon fiber accompanied by heat treatment improve the mechanical properties (elastic modulus and tensile strength) of the resulting composite.

2- The above heat treatment under inert atmosphere gives better composite mechanical properties.

3-Thermal etching better than chemical etching

4-Etching of carbon fiber under enactive atmosphere give more freedom with temperature change than under atmosphere

5- Under air etching lower contact angle (high wettability) obtained than in case of etching under inactive atmosphere due to the formation of active groups on the fiber surface by the former.

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