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Improvement of the Interfacial Adhesion Between Fiber and Matrix

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In this work, the influence of carbon fiber surface treatment on mechanical properties of unsaturated polyester was investigated. Two approaches have been used in the surface treatment; the first is the desizing of the carbon fiber by the release of the epoxy layer. The second is with the release of epoxy layer and etching the fibers. It was concluded that both methods give good results on adhesion between the matrix and the fibers. It is found that the treatment of carbon fibers is efficient and greatly improves the CFRP handress. The tensile strength of composite materials increases by 30% for etched carbon fibers compared to untreated carbon fibers.SEM images confirm the results obtained.

Keywords: carbon fibers, surface treatment, desizing, mechanical properties.

1. Introduction

Carbon fiber-reinforced polymer composites have many structural applications, including aircraft, sporting equipment, automotive, and civil structures due to their outstanding mechanical properties, light weight and high thermal stabilities [1].

The interfacial and mechanical properties of a fiber-reinforced polymer composite are significantly influenced by interfacial characteristics between the reinforcing fibers and the polymer matrix. Especially for carbon fibers, the surface is an important region that plays a contributing role in the interfacial behavior with the polymer matrix. Their interfacial characteristics can be chemically or physically altered by both fiber surface-treatment and desizing. Appropriate surface-treatment may modify the fiber surface by increasing the surface area and/or by increasing oxygen containing functional groups on the surface that may provide some chemical interactions between the fibers and the matrix resin [2].

The bonding strength between fibers and matrix can be developed by fiber surface treatment; this treatment can develop the bond strength between fibers and matrix [3]. Fiber surface roughness takes an important role in increasing the bond strength between fiber surface and matrix. But the excessive roughness reduces the bond strength due to the existence of height regions formed on fiber surface, which prevents the penetration of matrix to the depressions on fiber surface [4]. For improving the mechanical properties of composite material it is necessary to optimize the interface between the fiber and matrix using certain methods for modification of reinforcing fiber [5]. In earlier investigations, carboxymethylation of wood flour by an etherification reaction at room temperature with monochloroacetic acid was demonstrated [6]- [9]. The carboxymethylated material enhances the polymer- philic character of the filler so that such composites materials are obtained much more easily.

Fiber glass surface are treated with special treatment to get good bonding strength with matrix because the inorganic glass fiber has insufficient bonding strength with organic matrix. Surface treatment includes many methods like desizing and etching [10].

Feldman [11] treated Kevlar 49 fiber surface with saturated aqueous bromine solution for 15 s then treated with 25% NH3 solution for 30 s. Scanning electron microscope images illustrated etched formation on fiber surface which tend to increase fiber surface roughness. Results show decrease in tensile strength and Young modulus in comparison with untreated Kevlar fiber reinforced composite. Panigrahi and Powell [12] performed chemical treatment to flax fibers using benzol chloride and triethoxy silane as coupling agents. Results indicated obvious increasing in the tensile strength values due to increasing bond strength between fibers and matrix for low and high density polyethylene reinforced by flax fibers in comparison with untreated samples. Further, composite samples treated with benzol chloride exhibits increase in tensile strength, impact resistance, and bending strength values in comparison with untreated samples. Wang et al. [13] treated jute fibers with chemical treatment using triethoxy vinyl silane, benzoyl chloride, and dicumyl peroxide. Results shows increase tensile strength values for composite samples treated with triethoxy vinyl silane, and with dicumyl peroxide in comparison with untreated samples but reducing tensile strength values for composite samples treated with benzoyl chloride in comparison with untreated samples. Feih et al. [14] performed surface treatment for E-glass fiber using tri-methoxysilypropyl modified Polyethylenimine (TMP) and with chloroform extracted. Test results show increasing tensile strength and interfacial shear resistance values for treated fiber reinforcing composites especially those treated with (TMP). Donghwan and Suk [3] coated carbon fibers using group of materials: epoxy, vinyl ester, poly vinyl alcohol, poly vinyl butyral, and poly etherimide, with ratios as 20, 200, and 400%. Results show decreasing the elastic modulus values for composite materials with nylon 6 matrix reinforced with treated carbon fibers in comparison with composite samples reinforced with untreated fibers.

Consequently, the objective of this work is preliminarily to improve the interfacial bond strength between carbon fibers and unsaturated polyester resin by removing thin epoxy layer and roughening the fiber surface by etching to get sufficient mechanical interlocking action. This in turn expected to increase the adhesive bond

between fibers and matrix. Mechanical properties for treated and untreated carbon reinforced composites are investigated.

2. Experiment

2.1. *Carbon Fibers*

Carbon fibers are fiber materials which contain at least 92 wt% of carbon in composition [15]. They are derived from several precursors, such as polyacrylonitrile (PAN), pitch, rayon, polyesters and polyamides. Thousands of carbon fibers with diameters ranging from 4 to 15 m are bundled together to form a tow, which may be used to produce high-performance materials as it is or in other forms (e.g. fabrics).

They have been widely used in aerospace, automotive and sport industries due to their excellent properties, such as high tensile strength and stiffness, low densities, high thermal stabilities and favorable electrical conductivity [16].

CFRP is a more costly material than its counterparts in the construction industry, glass fiber reinforced polymer (GFRP) and Kevlar fibre reinforced polymer (AFRP), though CFRP is generally regarded as having superior properties [17].

2.2. *Materials*

The fibers reinforcements are used in the preparation of composites are: Carbon plain fabric. The resin used is unsaturated polyester resin based on tetrahydrophthalic acid and appropriate blends of ethylene glycol, propylene glycol, and di-(propylene glycol) dissolved in styrene, with density of 1.2 g/cm^3.

2.3. *Pre-treatment*

The carbon fibers were cut to 20 cm of length and treated according to two methods:

First method, all weight changes of carbon fibers bundles are recorded using microbalance, with an accuracy of 0.1 mg. The microbalance was calibrated frequently using standard weights. Prior to weighing, all samples were held overnight in glass desiccator after drying in order to eliminate any effect of humidity on the fibers bundles weight determination. Fibers bundles weight change are calculated according to the following formula:

$$W\% \;=\; \frac{w_1 - w_2}{w_1}\,, \tag{1}$$

where: w_1: carbon fibers bundles before treatment (g), w_2: carbon fibers bundles after treatment (g), $W\%$: carbon fibers bundles weight loss percentage.

Carbon fibers bundles weight were measured five times and averaged to get high accuracy calculations. She was undles are heated at 110°C for 90 min, to release the effect of humidity and to estimate moisture percentage. Carbon fibers bundles are heated at 230°C for 90 mins to release epoxy coated layer from carbon fiber surface (desizing) and to estimate epoxy percentage. Carbon fibers bundles are etched by immersion in special solution consist of (12 ml H_2SO_4 + 10 ml HNO_3 + 22 ml distilled water) at 15°C for 1.5 min. Carbon fibers bundles are washed in distilled water bath at 25°C for 10 mins to release any effect of etching solutions. Then etched carbon fibers bundles dried at 110°C for 90 mins and weight loose are calculated. This type of fiber treatment called in this paper (etched fibers).

But in second method, only steps N°2 and N°3 is followed. This type of fiber treatment called in this paper (desizing fibers).

2.4. *Preparation of composites*

To give the tensile specimens according to ASTM D638. Carbon fibers bundles are fixed at the terminal of the mold through opposite holes in a unidirectional arrangement, keeping parallel fibers in a tension mode.
Unsaturated polyester resin were prepared by mixing resin with 0.5% (w/w) cobalt octoate in xylene containing 6% active cobalt as promoter, and 2% (w/w) methyl ethyl ketone peroxide as a catalyst. These compositions were thoroughly mixed and stirred at low speed until it become uniform. The mixture was poured into the mould slowly in order to avoid air trapping. The prepared composite samples were left at room temperature until they were dry. Then all samples are cured at 90°C for 5 hrs. The amounts of reinforcement fibers were calculated according to equation of Lukkassen and Meidell [18]:

$$\theta = \frac{1}{1 + \frac{(1-\psi)}{\psi} * \frac{\rho_f}{\rho_m}}, \tag{2}$$

where θ is volume fraction of fibers %, ψ weight fraction of fibers %, ρ_f fiber density in [kg/m^3], ρ_m matrix density in [kg/m^3].

After the unsaturated polyester resin reinforced with treated and untreated composite samples were dried. Tensile tests were carried out using an INSTRON machine with a load cell of 5kN. Tests were performed as specified in ASTM D638. The gauge length was 50 mm and the crosshead speed of testing was 0.5 mm.min^{-1}, five specimens were tested for each batch. The scanning electron microscopy (SEM) JSM-5610 was used to study the morphology of the different materials and observe the interface reinforcement/matrix. The specimens were quenched in liquid nitrogen, broken, mounted on sample holder, coated with a solution of gold/palladium and observed using a voltage of 10 kV. Tensile tests and SEM were performed on all unsaturated polyester resin with treated and untreated carbon fibers.

2.5. *Results and Discussion*

For developing the bond strength between carbon fiber surfaces and unsaturated polyester; Most of the work used wet etching for fibers by immersion in aqueous basic solutions [19, 20]. But in this work, acidic solutions are used. Initial test was performed by heating carbon fibers bundles at 230°C for 90 mins to release epoxy film from carbon fiber surface. It was noticed that weight reduced by 1.97% due to this treatment. Further carbon fiber bundles were immersed in (12 ml H_2SO_4 + 10 ml HNO_3 + 22 ml distilled water) at 25°C for 1.5 min, and it was found that weight reduced by 3.517% due to effect of acidic solution. Acidic solution caused obvious etching on fiber surface due to aggressive effect of such solution. The effect of etching increased proportionality with immersion time [21]. Etching forms voids and pitting on fiber surface and this lead to increase the fiber surface area which increases the adhesive bond between fibers and matrix. This increasing comes from the mechanical interfacial locking between etched fiber and matrix [22].

Its worth noting, etching must be sufficient and not excessive. If pitting is excessive, the pitting becomes deeper and this reduces penetration ability of matrix to pass through etched fibers. Over etching can remove complete layer from carbon fiber surface [25]. Etching in acidic solution (12 ml H_2SO_4 + 10 ml HNO_3 + 22 ml distilled water) at 25°C for 1.5 min seems to be sufficient for good bonding between carbon fibers and matrix according to practical work.

To examine the interfacial characteristics of carbon fiber, tensile test properties have been studied in the present work. The dynamic mechanical behavior of a composite material may be responsible for changes in the molecular mobility and the interfacial behavior between the fiber and the matrix. During measurement, a composite sample is deformed exhibiting dynamic mechanical responses by a sinusoidally oscillating stress. Tensile tests are often used to directly measure fiber-matrix adhesion in a fiber-reinforced polymer matrix composite. Tensile test is useful for examining the interfacial properties between the fiber and the matrix in a unidirectional reinforced polymer composite system, resulting in the tensile strength. Cracks are normally initiated and propagated by interlaminar shear failure.

Figure 1 present the evolution of the maximum stress as the amount function of fibers for polyester reinforced with treated and untreated carbon fibers. Etched carbon fibers exhibits more effective than untreated fiber; it shows improvement in tensile strength about 30% whereas, desizing carbon fibers exhibits improvement in tensile strength about 9% in comparison with untreated carbon fibers. The reason behind this improvement belongs to the etching process which caused obvious pitting and roughness of the fiber surface. The existence of roughness tends to enlarge interlocking surface area between fiber and matrix which encourage stress transfer from matrix to carbon fiber and finally increase tensile strength. This result is in a good agreement with other researchers [12, 19, 23] and [24].

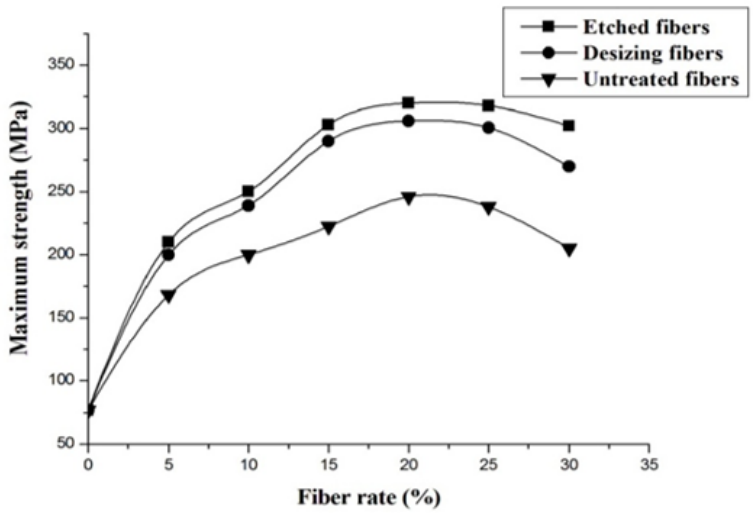

Figure 1 Fracture surface morphology of unsaturated polyester resin reinforced with A untreated B treated fiber

Figure 2 shows the SEM micrographs of fracture surface morphology of CFRP composites. The homogeneous distribution of carbon fibers could reduce the defects resulting from aggregates and therefore plays an important role in the mechanical properties of the resulting composites.

Compared with untreated carbon fibers, fewer holes were formed by etched fibers out in matrix during tensile test, which means that the interfacial adhesion between carbon fibre and resin was improved by treatement of fibers (Fig. 2 – AB1). Closer examination of the pulled carbon fibres reveals a thick layer of matrix resin attached on fibers surface, indicating a high degree of wetting and interfacial adhesion between fibres and matrix (Fig. 2 – AB2), which are consistent with the results of Fig. 1.

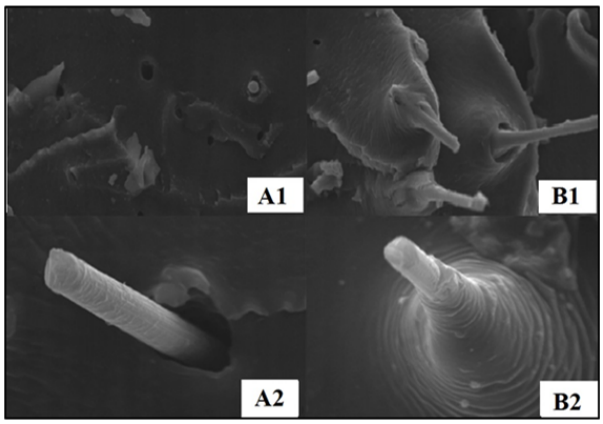

Figure 2 Fracture surface morphology of unsaturated polyester resin reinforced with A untreated B treated fiber

The morphologies of carbon fibers were studied using SEM and some of the characteristic micrographs are given in Fig. 3. For no treated fibers, it could be clearly seen that desized fibers had no more polymer patches adhered to surface compared with as-received fibers. There were longitudinal, discontinuous ridges extending parallel to the fiber axis on the surface. For the resized fibers, the longitudinal streaks on the surface became less clear. Polymer grains were found on the surface of etched fibers. When the time of sizing solution was below 1.5 min. As the time increased to 3 min, the coating became nonuniform and many sizing bridges were created between fibers. The resulting filament clumping or filament/filament cohesion must be kept to a minimum as it is unfavorable for composite processing (cf. Fig. 4) [1, 4–10] and [15–20].

The average of etching increasing proportionality with treatment time, therefore bond strength increase between fibers and matrix in case of sufficient penetration of polyester inside the fibers. But for excessive penetration the tensile strength will decrease due to over etching which cause high surface roughness which tend to lower the penetration of polyester into pitting and cause decrease in bond strength between fibers and matrix and this in turn cause decrease the stress transfer from matrix to fibers (Figs. 3 and 4).

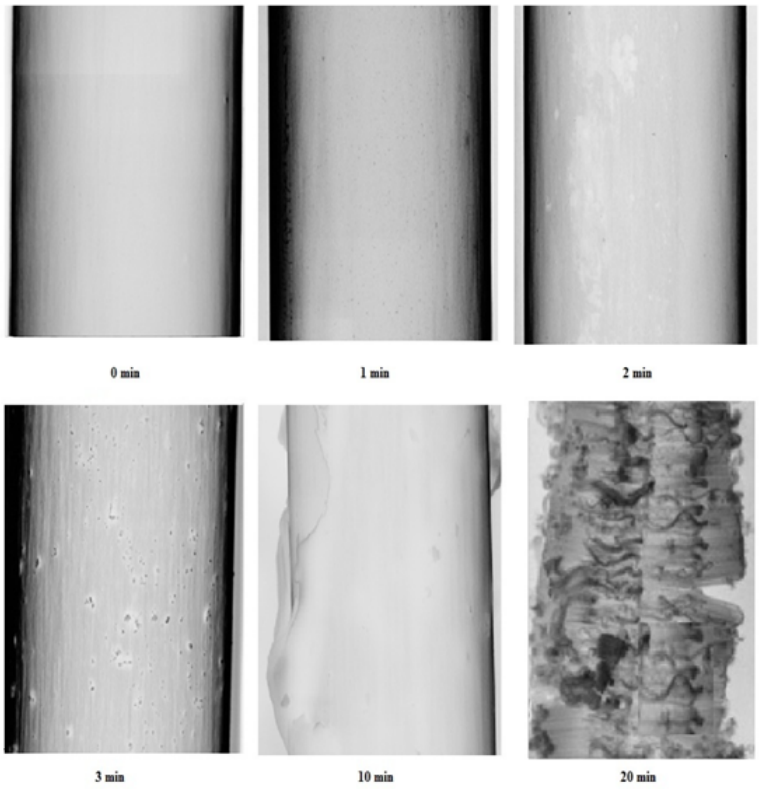

Figure 3 SEM pictures of unsaturated polyester resin reinforced with and without engraved carbon fibers

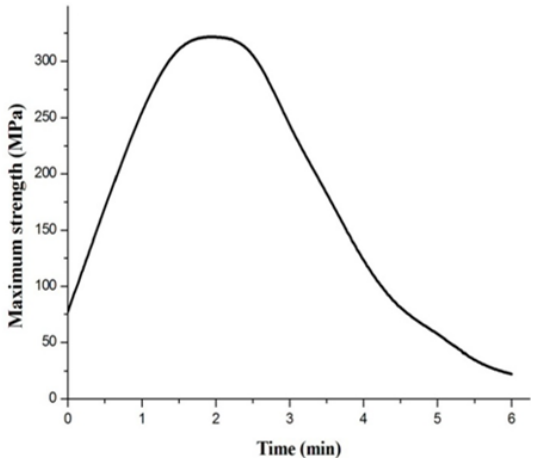

Figure 4 Tensile strength of unsaturated polyester resin reinforced with etched carbon fibers depending time

3. Conclusions

Carbon fibers are mainly used to reinforce composite materials. They make it possible to obtain structural parts having good mechanical properties: rigidity, resistance to cracking, etc., while having a low density relative to metallic materials.

In this study, the sizing and etching process may be more or reduce the rigidity of the unsaturated carbon/polyester composites, although these treatments also somewhat contribute to improving the interfacial bond between the fibers and the matrix in the composite. The tensile strength of the desizing and etched carbon fibers reinforced composite increases about 9% and 30% respectively due to increase the fiber-matrix interfacial adhesion which is enhanced with surface-treatment effectiveness on carbon fibers. The tensile test results indicate that appropriate use of desizing and etched carbon fiber composite processing may contribute to enhancing the interfacial and/or interlaminar properties of carbon fiber reinforced composites, depending on their resin characteristics and processing parameters. The results obtained are confirmed by SEM images.

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