مجلة جامعة بابل / العلوم الصرفة والتطبيقية / العدد (4) / المجلد (17) : 2009

The Effects of Surface Treatment on the Mechanical Properties of Carbon Fiber Reinforced Plastic

Jaleel Kareem Ahmed.
Babylon University- College of Science
Ali Hubi Haleem.
Babylon University , College of Materials Engineering
Alaa Rasheed Omran.
Babylon University- College of Science

Abstract

In the current work, the effect of carbon fiber surface treatment on mechanical properties of unsaturated polyester (CFRP) was investigated. An extreme dependence for the interaction strength in unsaturated polyester -carbon fiber system is established and its effect on the mechanical properties of CFRP and the influence of the fiber treatment on the bonded strength between fiber- resin systems is clarified. Two methods were developed in surface treatment, the first one deal with release of epoxy layer which coated carbon fiber. The second one deals with release epoxy layer and etching carbon fibers with special solution. It was found that both of methods tend to intensify the adhesion of thermosetting resin to carbon fibers owing to a more developed surface of the reinforcing fibers after surface treatment. It's found that the treatment of carbon fibers is efficient and considerably improves the mechanical properties of CFRP. Etched carbon fibers improve flexural strength of composite materials by 20% in comparison with untreated one.

Key words: Carbon fibers, Thermosetting plastic, Surface treatment, Mechanical properties.

الخلاصة

تم في البحث الحالي دراسة تأثير المعاملة السطحية لألياف الكاربون على الخصائص الميكانيكية لراتنج البولي أستر غير المشبع (CFRP). تعتمد الخصائص الميكانيكية للمادة المركبة على قوة الترابط بين ألياف التقوية والمادة الأساس. في هذا البحث تم إتباع أسلوبين في المعاملة السطحية, الأسلوب الأول تم فيه إزالة طبقة الأيبوكسي المغلفة لألياف الكاربون ,أما الأسلوب الثاني فيعتمد على إزالة طبقة الأيبوكسي وتحفير ألألياف, لقد وجد إن هذين الأسلوبين يعملان على تحسين قوة الترابط والتلاصق للألياف مع المادة الأساس وانعكس ذلك ايجابيا على الخصائص الميكانيكية للمادة المركبة. أثبتت النتائج إن تحفير الألياف يعمل على زيادة مقاومة الانحناء للمادة المركبة بنسبة 20% مقارنة بألياف الكاربون غير المقواة.

الكلمات الرئيسية: ألياف الكاربون, الراتنجات المصلدة بالحرارة,المعالجات السطحية للألياف,الخواص الميكانيكية.

1.0Introduction

The bond strength between fiber surface and matrix is the most important parameters in limiting the efficiency of composite mechanical behavior. Good bonding between composite material constituents is necessary for composite under loading and service conditions. Sufficient bonding between fiber surface and matrix allows transferring the applied load from matrix to fibers. If the interfacial surface is free from voids, then the load and stress can completely transferred, but if the bonding strength is insufficient, the load will not transferred effectively (Miller et al., 2001).

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 (Donghwan *et al.*, 2004).

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 high regions formed on fiber surface, which prevents the penetration of matrix to the depressions on fiber surface (West, 2001).

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 (Dobreva *et al.,* 2005). In earlier investigations, carboxymethylation of wood flour by an etherification reaction at room temperature with monochloroacetic acid was demonstrated (Dobreva et al., 2004; Kishi and Shiraiski, 1986; Tan and Yu, 1997; Bazarnova et al, 2004). 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 sizing and etching (Madsen, 1999).

Feldman (Feldman et al., 2003) treated Kevlar 49 fiber surface with saturated aqueous bromine solution for 15 sec. then treated with 25% NH_3 solution for 30 sec. 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 (Panigrahi and Powell, 2003) 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. (Wang *et al.,* 2003) 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 (Feih *et al.,* 2004) 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 (Donghwan and Suk, 2004) 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.

This work aims to improve the interfacial bond strength between carbon fibers and unsaturated polyester resin by removing thin epoxy layer and roughed the fiber surface by etching process 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.

2.0Carbon Fibers

In 1957, Dr. Roger Bacon created the first high-performance carbon fibers at the Union Carbide Parma Technical Center, located outside of Cleveland, Ohio. The first fibers were manufactured by heating strands of rayon until they carbonized. This process proved to be inefficient, as the resulting fibers contained only about 20% carbon and had low strength and stiffness properties. In the early 1960s, a process was developed using polyacrylonitrile (PAN) as a raw material. This had produced a carbon fiber that contained about 55% carbon and had much better properties. The polyacrylonitrile (PAN) conversion process quickly became the primary method for producing carbon fibers (Urena et al., 2007).

During the 1970s, experimental work to find alternative raw materials led to the introduction of carbon fibers made from a petroleum pitch derived from oil processing. These fibers contained about 85% carbon and had excellent flexural strength (Gojny, 2005).

The atomic structure of carbon fiber is similar to that of graphite, consisting of sheets of carbon atoms (graphene sheets) arranged in a regular hexagonal pattern. The difference lies in the way these sheets interlock. Graphite is a crystalline material in which the sheets are stacked parallel to one another in regular fashion. The chemical bonds between the sheets are relatively weak Van der Waals forces, giving graphite its soft and brittle characteristics. Depending upon the precursor to make the fiber, carbon fiber may be turbostratic or graphitic, or have a hybrid structure with both graphitic and turbostratic parts present. In turbostratic carbon fiber the sheets of carbon atoms are haphazardly folded, or crumpled, together. Carbon fibers derived from Polyacrylonitrile (PAN) are turbostratic, whereas carbon fibers derived from mesophase pitch are graphitic after heat treatment at temperatures exceeding 2200 °C. Turbostratic carbon fibers tend to have high tensile strength; whereas heat-treated mesophase-pitch-derived carbon fibers have high Young's modulus and high thermal conductivity (Dean et al., 2006).

Carbon fiber (alternately called graphite fiber) is a material consisting of extremely thin fibers about 0.005–0.010 mm in diameter and composed mostly of carbon atoms. The carbon atoms are bonded together in microscopic crystals that are more or less aligned parallel to the long axis of the fiber. The crystal alignment makes the fiber incredibly strong for its size. Several thousand carbon fibers are twisted together to form a yarn, which may be used by itself or woven into a fabric (Bowles and Frimpong, 1991).

Carbon fiber can be combined with a plastic resin and wound or molded to form composite materials such as carbon fiber reinforced plastic (also referenced as carbon fiber) to provide a high strength-to-weight ratio material. The density of carbon fiber is also considerably lower than the density of steel, making it ideal for applications requiring low weight. The properties of carbon fiber such as high tensile strength, low weight, and low thermal expansion make it very popular in aerospace, military, and motor sports, along with other competition sports (Bowles and Frimpong, 1991).

Carbon Fiber is used extensively in sailing boats, as a substitute to GRP or fiberglass hulls, or as a substitute to aluminum masts - this is because it is more flexible, stronger and far lighter. Monocoque hulls are often carbon fibre reinforced. It is also used in compressed gas tanks, including compressed air tanks. Other uses include racing vehicles, with the vehicle shell commonly composed of the material, often in combination with aramid and glass fibre. Carbon fibre is extensively used in

the bicycle industry, especially for high-performance racing bikes. Carbon fiber is used in some tennis rackets (Ammar, 1996).

CFRP is a more costly material than its counterparts in the construction industry, glass fiber reinforced polymer (GFRP) and aramid fibre reinforced polymer (AFRP), though CFRP is generally regarded as having superior properties (Ammar, 1996).

3.0 Experimental work

3.1 Materials

The fibers reinforcements are used in the preparation of composites are: Carbon plain fabric, Hyfil Ltd. U. K.). The resin used is Viapal H 265 unsaturated polyester resin based on tetrahydrophthalic acid and appropriate blends of ethylene glycol, propylene glycol, and di (propylene glycol) dissolved in styrene. The resin, promoter and catalyst were supplied by (Lonza S.P.A Company).

3.2 Carbon Fiber Pre- treatment

The carbon fibres were cut to 20 cm of length and treated according to two methods.

Method no.1

1. All weight changes of carbon fibers bundles are recorded using microbalance type (Sartorius Laboratory) model (L 220S-**D) , No.(39090002) manufactured in Germany, with an accuracy of $\pm$0.1 mg. The microbalance was calibrated frequently using standard weights. Prior to weighing, all samples were held overnight in glass desiccator 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:

   $$W\% = (W_1 - W_2) / W_1 \ldots\ldots\ldots\ldots (1)$$

   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.
2. Carbon fibers bundles are heated at 110 °C for 90 min. in holding furnace type (300), model (15 D) manufactured by (Phoenix Products Company, Inc., USA) to release the effect of humidity and to estimate moisture percentage. It was found = 2.403%.
3. Carbon fibers bundles are heated at 230°C for 90 min. to release epoxy coated layer from carbon fiber surface (de-sizing) and to estimate epoxy percentage. It was found = 1.97%
4. 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.
5. Carbon fibers bundles are washed in distilled water bath at 25°C for 10 min. to release any effect of etching solutions.
6. Carbon fibers bundles are dried at 110 °C for 90 min. and weight loose are calculated. It was found= 3.517%. This type of fiber treatment called in this paper **(etched fibers).**

Method no.2

- This type of treatment follows only steps no. 2 and no. 3. This type of fiber treatment called in this paper **(de-sizing fibers).**

3.3 Composite processing

Open mold technique was used to prepare composite samples. Wood mold with inner slot dimensions of (10 *135 mm) is polished, waxed, and has a release agent applied before the fibers and resin is applied. 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 as shown in Fig. 1.

Unsaturated polyester resin as a matrix material 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 materials were thoroughly mixed and stirred at low speed until it become uniform. The matrix material 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 80 °C for 3 hrs.

The amounts of reinforcement fibers were calculated according to the following Equation (Lukkassen and Meidell, 2003):

$$\Theta = 1/\ 1 + [(1- \psi)/ \psi]. \rho_f / \rho_m \quad \ldots\ldots\ldots (2)$$

Where Θ: 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.

The composites with untreated and treated carbon fibres were prepared for investigation. In the present paper, Volume fraction for carbon reinforcement fiber was 20%.

3.4 Test methods

3.4.1 Flexural Test

After the unsaturated polyester resin reinforced with treated and untreated composite samples were dried. Three-point flexural tests were performed in hydraulic press type (Leybold Harris No. 36110) in accordance with ASTM D790 to measure the flexural strength of the composites. A span of 100 mm was employed maintaining a cross head speed of 2 mm/min. The flexural strength was measured using the following equations (Gowda, 1999):

$$F.S = 3\ P.S/\ 2bt^2 \quad \ldots\ldots\ldots\ldots\ldots (2)$$

Where: **P**: Maximum load

S: Span length

b: Width of sample

t: Thickness of the sample

Flexural tests were performed on all unsaturated polyester resin with treated and un treated carbon fibers.

4.0 Results and Discussion

The objective of this work was to develop the bond strength between carbon fiber surfaces and unsaturated polyester. Most of the previous work used wet etching for fibers by immersion in aqueous basic solutions (Bismarck and Mohanty, 2001) (Abeel and Velde, 1999). But in this work, acidic solutions are used. No work about carbon fiber etching obtained by this route is available in literature. Therefore, initial

test was performed by heating carbon fibers bundles at 230 °C for 90 min. 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 (AGY, 2004).

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 (Tavakkolizadeh and Saadatmanesh, 2003).

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 (Tavakkolizadeh and Saadatmanesh, 2003). 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. Fig. 2 illustrates flexural strength of unsaturated polyester reinforced with treated and untreated carbon fibers. Etched carbon fibers exhibits more effective than un treated fiber; it shows improvement in flexural strength about 20% whereas, de-sizing carbon fibers exhibits improvement in flexural strength about 7% 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 tend to enlarge interlocking surface area between fiber and matrix which encourage stress transfer from matrix to carbon fiber and finally increase flexural strength. This result is in a good agreement with other investigators (Bismarck and Mohanty, 2001), (Panigrahi, and Powell, 2003) (Park and Jang, 1999).

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 flexural 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.

5.0 Conclusions

From the performance tests and results to evaluate etching effect on bonding strength between fibers and matrix it was found:

- Increase bond strength between carbon fibers and matrix due to fiber etching and desizing.
- Flexural strength values increase about 20% for etched carbon fibers and 7% for de-sizing carbon fibers in comparison with untreated fiber.

5.0 References

Abeele, K. V. D. and Velde, K. V. D, 1999, Correlation between dynamic nonlinearity and static mechanical properties of corroded E-glass reinforced polyester composites, Review of progress in quantitative nondestructive evaluation, eds, D.O. Thompson and D. E. Chimenti,Vol.19B, 1359-1366,pp.1-8.

AGY, 2004,(World Headquarters/ Americas, European Office), High Strength Glass Fibers, Technical paper, pp.1-12.

Ammar, N., 1996, Rehabilitation of steel bridge girders with graphite pultrusion (CCM report 96-26).Newark, DE, USA: University of Delaware Center for Composite Materials, University of Delaware ,pp. 126

Bazarnova, N. G., Katrakov, I. B., and Markin, W. I.,2004, Chemical modification of wood, J. Ros. Cim. Ob-va im D. I. Mendeleeva. 15(3), pp.108-115.

Bismarck, A. and Mohanty, A. K., 2001, Surface characterization of natural fibers, surface properties and the water uptake behavior of modified sisal and coir fibers, Green chemistry,3,100-107,DIO:10.1039/b100365h.

Bowles, K. J. and Frimpong, S., 1991, Void effects on the interlaminar shear strength of unidirectional graphite-fiber-reinforced composites', Journal of Composite Materials **26**(10), pp.1487-1509.

Dean D., Obore A.M., Richmond S., Nyairo E., 2006, Multiscale fiber-reinforced nano composites: Synthesis, processing and properties". Comp. Sci. & Tech. Vol. 66 pp.2135-2142.

Dobreva, D., Nenkova, S., and Vasileva, St., 2004, Modification of wood flour for polymer composites, Proceedings of the XVIII Congress of chemists and Technologust of Macedonia, PPM-40.

Dobreva, D., Nenkova, S., and Vasileva, St., 2005, Investigation of the microstructure of polypropylene composites filled with wood flour modified with monochloroacetic acid, NATO Science Ser. II 223,pp.177-180.

Donghwan, C. and Suk, H. Y.,2004, Effects of fiber surface treatment and sizing on the dynamic mechanical and interfacial properties of carbon/ nylon 6 composite , Carbon Science, Vol. 5, No.1, pp.1-5.

Feih, S. and Wonsyld, K. ,2004, Testing Procedure for the single fiber fragmentation test, Risoe National Laboratory, Roskilde, Denmark,pp.1-30.

Feldman, A., Gonzalez, M. F. and Marom, G., 2003, Transcrystallinity in surface modified aramid fiber reinforced nylon 66 composite, Macromolecular Materials and Engineering, 288, Nos.11, DOI: 10.1002/ mame.200300151, pp.861-866.

Gojny, F. H., Wichmann, M.H.G., Fiedler, B., Schulte, K.,2005, Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites - A comparative study, Comp. Sci. & Tech., Vol. 65, pp.2300-2313.

Gowda, T. M., Naidu, A. C. B., and R. Chhaya, 1999, J. Composites Part A: Applied Science and Manufacturing, Vol.30, No. 3, pp. 277–284.

Kishi, H., and Shiraiski, N., 1986, Wood –phenol adhesives prepared from carboxymethylated wood, J.Appl. Polym. Sci.32 (3), 3189-3209.

Lukkassen, D., and Meidell, A.; 2003; Advanced Materials and Structure and Their Fabrication Process, Third Edition, Narvik University, HIN.

Madsen, N. B., 1999, Modification and Characterization of The Interface in Polymer/ Inorganic Composite, Riso National Laboratory, Roskide, Denmark,pp.1-8.

Miller, T. C., Chajes, M. J., Mertz, D. R., Hastings, J. N., 2001, Strengthening of a steel bridge girder using CFRP plates, *J. Bridge* Eng. 6(6),pp. 514–522

Panigrahi, S. and Powell, T.,2003, The effect of chemical pretreatments on flax fiber bio-composites, The Society for Engineering in Agricultural , Food and Biological Systems, Paper No.RRV03- 0018,pp.1-16.

Tan, X., and Yu, Q., 1997, Study on carbomethylating modification of wood and its solubility, Chemistry and Industry of Forest Products. 17(3), pp.33-39.

Tavakkolizadeh M. and Saadatmanesh, H., 2003, strengthening of steel-concrete composite girders using carbon fibre reinforced polymers sheets. J. Struct. Eng., ASCE 129: 30–39.

Urena, A. Maria, R. G. Silvia, G. P.,2007, Carbon nano fibers reinforced adhesives for joining carbon fiber epoxy composites, http://en.wikipedia.org/wiki/Carbon_fiber_reinforced_plastic"

Wang, B. and Panigrahi, S., 2003, Modification of flax fibers by chemical treatment, The Canadian Society for Engineering in Agricultural, Food and Biological Systems, paper No.03-337, pp.1-15.

West T D 2001 Enhancement to the bond between advanced composite materials and steel for bridge rehabilitation (CCM report 2001-04). Newark: DE, USA, University of Delaware Center Composite Materials, University of Delaware, pp. 226.

Park, R. and Jang, J. 1999, Performance improvement of carbon fiber / polyethylene fiber hybrid composite, Journal of materials science, DOI: 10. 1023/ A: 1004647721380, Vol. 34, No. 12,http://www.cheric.org/research/tech / periodicats/view.php.

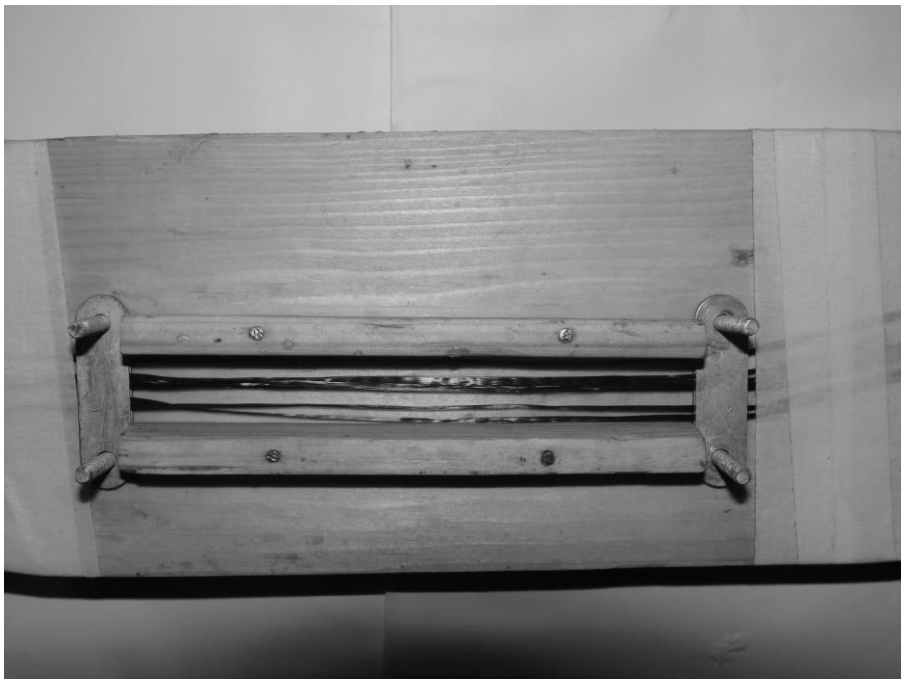

Fig. 1: Flexural sample mold for composite materials

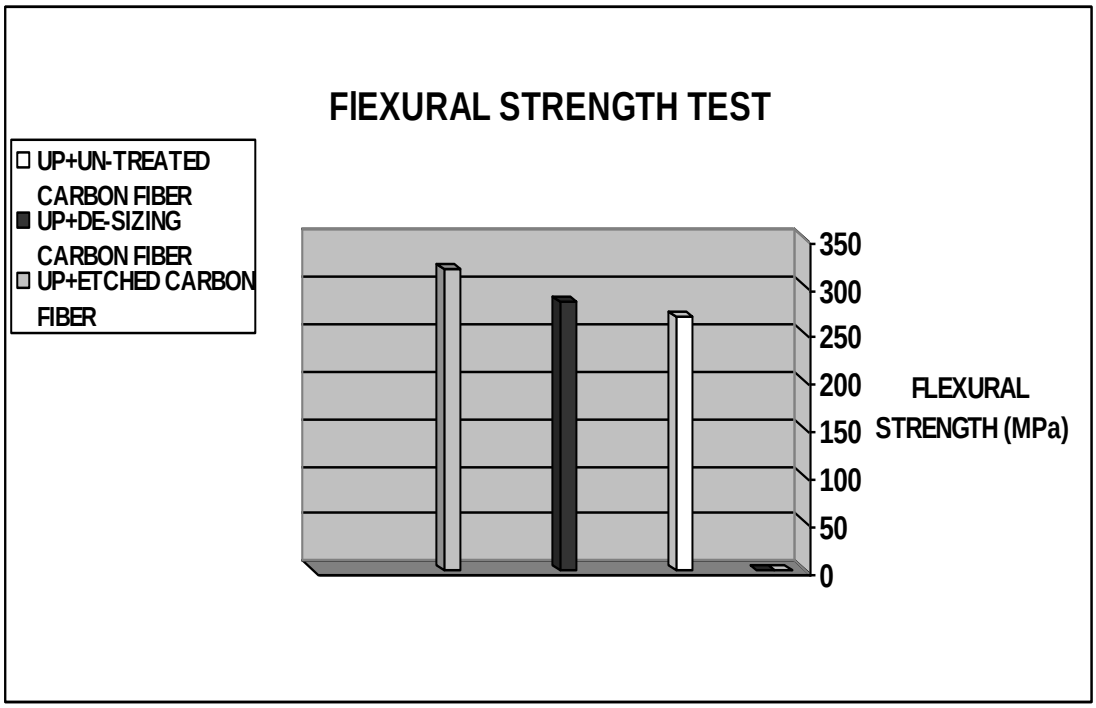

Fig. 2: Flexural strength of unsaturated polyester resin reinforced with and without etched carbon fibers.