Using Plasma-Activated High Performance Fibers with Nanocrystalline Structure in Producing New Reinforced Composite Materials

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Summary: A multifilament wet-pull-out method for estimation of physicochemical interaction between the fiber and the matrix in composite materials reinforced with high-strength high-modulus polyethylene fiber has been proposed. Controlled parameters are fiber capillary rise *h* and pull-out force *F*. The method allows one to estimate the wettability and multifilament fiber impregnation with the liquid matrix and measure fiber capillary rise and the joint strength after curing process finished. The multifilament wet-pull-out method considers a total interaction between the matrix and filaments in a complex fiber or yarn. It is the advantage of this method in comparison with the tests of individual monofilament. The method makes it possible to model the real operating conditions of CM.

Keywords: fiber capillary rise; high performance polyethylene fiber; low temperature plasma treatment; mechanical twist; modelling of technology composite material production; multifilament wet-pull-out method; wettability

Introduction

At the present time complex yarn or multifilament fiber (a single bundle of filaments) is used for reinforcing of the CM. Such fiber can consist of several thousands of the filaments. The filament strength increases with the reduction of the filament diameter and, accordingly, the strength of the complex fiber increases as a whole.

The future development of reinforced CM is based on using of multifilament fibers. These fibers have high strength and high specific properties due to small filament dimensions. For successful using of these fibers it is necessary to control physicochemical interaction at the interface. We need to obtain good impregnation of the inter-filament space of the fibers with the matrix and to distribute the fibers in the matrix according to the loads. The specific surface of the filaments increases with the reduction of the filament diameters and then its energy characteristics significantly effect on the CM properties.

Main challenges of the technology of CM production from multifilament fiber are the following: the complete impregnation of the fiber with the matrix and creation of the strong joint between the matrix and the fiber.

The strong joint is necessary to transfer effectively the external load to the fiber and include all composite structural elements in joint operation. In order to form the strong joint the multifilament fiber should be completely impregnated.

Physical and chemical interaction between the matrix and fiber leads to a good bond

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strength between them. An idea of physical and chemical stages of interaction between the matrix and reinforcing multifilament fiber during the production of CM was introduced.[1] The interaction may be divided into two stages in every elementary part of the fiber/matrix interface. The physical stage occurs when joining matters generate a physical contact. The chemical stage occurs only if at least one of contacting surfaces has the energy sufficient for the chemical interaction. In case the contacting surfaces have low energies, the interaction stops at the stage of forming the physical contact. Especially strong bonding appears if interaction is chemical.

In order to begin the interaction between the fiber and the matrix, those should come into physical contact. This contact is reached when the fiber surface is wetted with the matrix. It follows from thermodynamics, that to obtain sufficient wettability, the fiber surface energy should exceed the energy of the interface, which appear between the fiber and liquid matrix at wetting.

The structure of multifilament fiber promotes their wetting and impregnation with the matrix because it brings to the matrix capillary lifting on the clearances between the filaments. Fiber capillary rise h is used to define the wettability of one material to another. The experimental value of the h can be used for qualitative estimation of the interaction between the fiber and the matrix during the production of CM.[2]

The strong joint should appear between the fiber and the matrix in order to fabricate advanced CM. The quantitative estimation of the joint strength can be done by the pull-out method.[3] With reference to the multifilament high performance polyethylene (HPPE) fiber, a pull-out method is considered in.[4]

The objective of the paper is to combine two methods for qualitative and quantitative estimation on physicochemical interaction between the components during the production of CM.

A wet-pull-out method combined allows one to estimate the wettability and impregnation of multifilament fiber with the liquid matrix and measure the fiber capillary rise h and interfacial shear strength (IFSS) after curing process finished. Therefore, we have called proposed method a ''wet''-pull-out (from verbs to wet and to pull out).

The HPPE fiber has the unique properties. The density is slightly less than one. The tenacity can be up to 15 times that of good quality steel. Nanocrystalline structure of multifilament HPPE fiber is responsible for particularly high strength of the fiber.[5] The low density, high strength high modulus, and very high absorption energy of the fiber, which make it possible to produce, advanced CM that combine good mechanical properties with low specific mass. Obviously, application of such CM can be highly rewarding. However, the HPPE fiber possesses high inertness to the interaction with different matrices. The poor bondability, owing to the low surface energy, has so far limited the widespread use of the HPPE fiber in mass production of CM. Therefore, it was of interest to determine the sensitivity of the wet-pull-out method to this fiber and to study as activation of the fiber, mechanical twist and different matrices application effect on the indices of the method.

To improve the interfacial interaction, the HPPE or ultrahigh molecular weight polyethylene (UHMWPE) fiber was subjected to the action of different power sources, such as γ-particles, ion-beam treatment, corona, radio frequency and microwave discharges.[6] The UHMWPE fiber/matrix adhesion was measured with the monofilament (or single) pull-out[7] and microbond pull-out tests.[8]

In this study non-equilibrium low temperature plasma treatment is applied to activate the HPPE fiber and to change the fiber surface energy with the aim of obtaining a strong bond at the interface. There are considered two processes: a formation of the physical contact between the fiber and the liquid matrix at wetting and then, after curing process stopped, a

formation of the strong joint between them on the contact area. The height h at which the liquid matrix reaches inside the capillary is related to the surface tension by the Eq. discussed below.

Theory

It is known,[9,10] if the clearance between filaments is a capillary with the diameter d we have the following Eq.:

$$h = \frac{4 \times \gamma_M \cdot \cos\theta}{d\rho g}, \quad (1)$$

where h is the height the liquid matrix is lifted (or fiber capillary rise), θ is the liquid-solid contact angle, γ_M is the surface energy of liquid matrix and ρ is the density of the liquid matrix, g is the acceleration due to gravity.

As the contact angle θ is not known to us, that for the further discussion, it is reasonable to replace it. As it follows from Young's Eq:

$$\cos\theta = \frac{\gamma_F - \gamma_{FM}}{\gamma_M}, \quad (2)$$

where γ_F is the surface energy of the fiber, γ_{FM} is the energy of the interface, which appears between the fiber and liquid matrix at wetting.

As it follows from Equation (1) and (2):

$$h = \frac{4 \times (\gamma_F - \gamma_{FM})}{d\rho g}, \quad (3)$$

Thus, for improvement of wetting and impregnation of the fiber, it is necessary to increase free surface energy of the fiber γ_F, i.e. to activate the fiber.

We can change the value of γ_F and the value of d with the help of plasma treatment and mechanical twist, respectively. We did not measure wetting angle. We estimated the wetting process by the fiber capillary rise.

However, thermodynamic approach is not sufficient to the description of the fiber impregnation with the matrix. It does not consider many parameters, which affect the impregnation process and, first of all, viscosity of the liquid matrix η.

As it follows from kinetic ideas about the movements of a liquid in capillaries, that the impregnation process is well described by Poiseuille Eq.:

$$h^2 = \frac{\gamma_M \cdot d\cos\theta \cdot t}{4\eta}, \quad (4)$$

where t is the duration of the impregnation, η is the viscosity of the liquid matrix.

Substituting Equation (2) in Equation (4) we obtained:

$$h^2 = \frac{d \times (\gamma_F - \gamma_{FM}) \cdot t}{4\eta}, \quad (5)$$

As it follows from Equation (5), that for improvement of fiber impregnation, as well as from Equation (3), it is necessary to increase the surface energy of the fiber γ_F.

Experimental Part

Materials

As reinforcement, we used Dyneema® SK-75 multifilament high performance polyethylene fiber (1760 dtex) from DSM. The SK-75 fiber had a strength of 3.4 GPa, an elastic modulus of 110 GPa, a density of 0.97 g/cm^3, elongation at break of 3.8%. There are 1150 filaments in a single bundle of filaments. Dyneema® multifilament fiber or complex yarn supplied without twist.

The matrices were an epoxy resin Epicot-828 from Shell Chemical Co. cured with the mixture of metaphenylenediamine with 4,4′- diaminediphenylmethan and the same resin cured with polyethylene polyamine.

In both cases we added modifiers to the resin in order to reduce the viscosity of the matrices.

Surface Modification

Plasma Treatment

The HPPE fiber was treated by non-equilibrium low temperature argon plasma at the reduced pressure from 1.33 up to 660 Па. Plasma thermal component is reduced to a minimum due to the low density of ion current $j_i = 0.5$–1 A/м^2 and small duration of plasma influence on a fiber. Such plasma

allows one to treat even the highly oriented HPPE fibers, which are very sensitive to heating. It does not cause the destruction of the fibers.

Formation of the new chemical compounds on surface of the fiber and fiber oxidation were not observed due to argon plasma. After plasma treatment, the SK-75 fiber was wetted and impregnated with an epoxy matrix in air and cured. We used fiber in the initial state and plasma-activated fiber.

Mechanical Twist

We did from 2 to 5 the twists on the length of 1cm. We also applied untreated twisted fiber.

Adhesion and Fiber Capillary Rise Measurements

The HPPE fiber capillary rise h and interfacial shear strength (IFSS) of fiber/matrix joints were evaluated by multifilament wet-pull-out method. A scheme of multifilament wet-pull-out test and photo of experimental samples are given in Figure 1a) and b), respectively.

The samples of multifilament fiber/matrix joints were prepared in tephlon or textolite moulds (1) at room temperature. The fiber (2) was located in the middle of mould. The polymer matrix (3) was poured into the moulds as a liquid compound. As a result of wetting and capillary forces, the liquid matrix was lifted up to some height h (4) of the fiber.

Wetting and impregnation became slower as the matrix gelation began. The duration of matrix gel formation limits wetting and fiber impregnation. The samples are left for a day at room temperature. The matrix continues to cure during this day. In order to finish curing the samples were taken out from a mould and heat treated. After thermal treatment and cooling to room temperature, the samples of multifilament fiber appeared to be glued in the cured matrix layer.

We measured fiber capillary rise h after curing process finished in order to estimate wetting and fiber impregnation with the matrix.

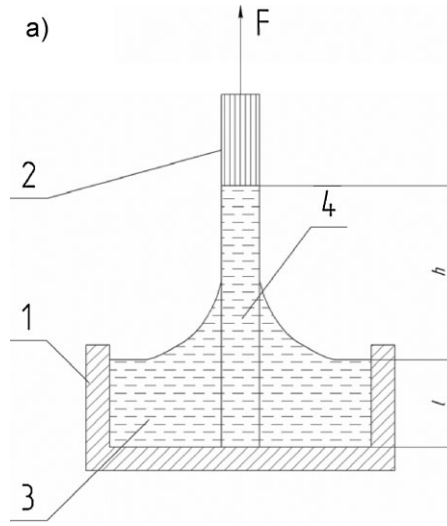

Figure 1.
a: The scheme of the wet-pull-out method: 1 - mould for resin, 2 –multifilament fiber, 3 – l – length of polymer matrix layer, 4 – h –fiber capillary rise, F - force required to pull the fiber out from the cured matrix layer. b: Samples for study the interaction between the matrix and the multifilament fiber by the wet-pull-out method.

We also measured the force F required to pull the multifilament fiber out from the cured matrix layer. We changed the force changing the length l of the layer and obtained the dependency of F (l). The layer length was changed by the way of grinding or cutting off the lower butt of the sample.

The wet-pull-out test was carried out on an Instron universal testing machine, at a cross-head speed of 5mm/min.

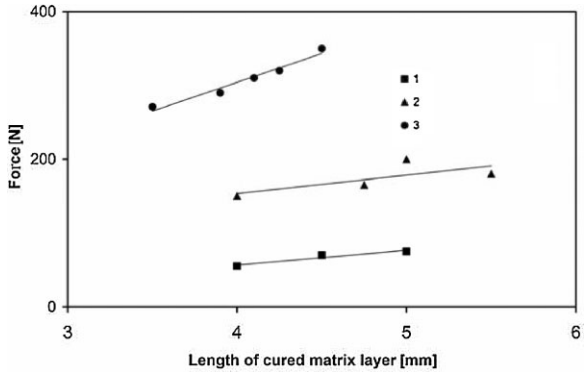

Figure 2.
Pull-out force *F* vs the length *l* of the cured matrix layer for joints of ED-20 epoxy matrix with untreated twisted (1), untreated (2), and plasma-treated SK-75 fiber (3) impregnated in air.

Results and Discussion

There is good reason to think that the diameter *D* of multifilament fiber pulled out from the matrix is constant. Then *F* determines the joint strength between the fiber and the matrix. Figure 2 shows the dependency of *F (l)*. It is linear. That is why we suggest that the joint strength for each combination of the multifilament fiber with the matrix is constant. The angle of the line slope characterizes this joint strength. Than larger is the angle, higher is the strength.

After plasma treatment of the multifilament fiber, the joint strength was increased by factor 2 in comparison with untreated fiber. This result well correlates with data from,[4,8] in which the authors also observed a twice increase of the joint strength after plasma treatment of the HPPE fiber.

The multifilament fiber is more twisted the value of fiber capillary rise *h* is lower. Fiber twisting reduced the space between filaments and the value of *h* (Figure 3, line 1) and, respectively, the joint strength decreased (Figure 2, line 1). These data confirm the kinetic nature of the phenomena at wetting and fiber capillary rise in accordance with Equation (5).

At poor bonding (Figure 2, line 1, 2) the individual filaments in the bundle de-bond and fracture and pullout producing shaving brush appearance, and the fiber looks like a brush (Figure 4a). For a ''weak'' bond all

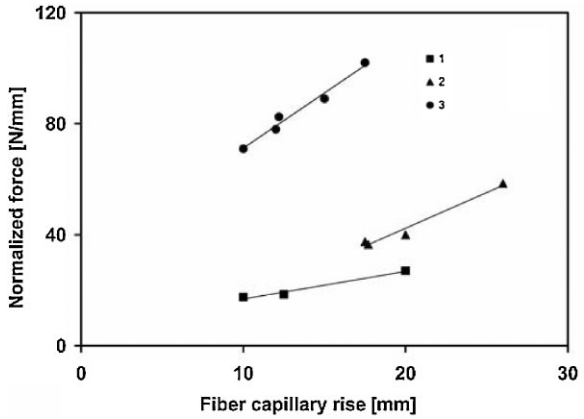

Figure 3.
Normalized pull-out force *F/l* vs fiber capillary rise *h* for the same joints as Figure 2.

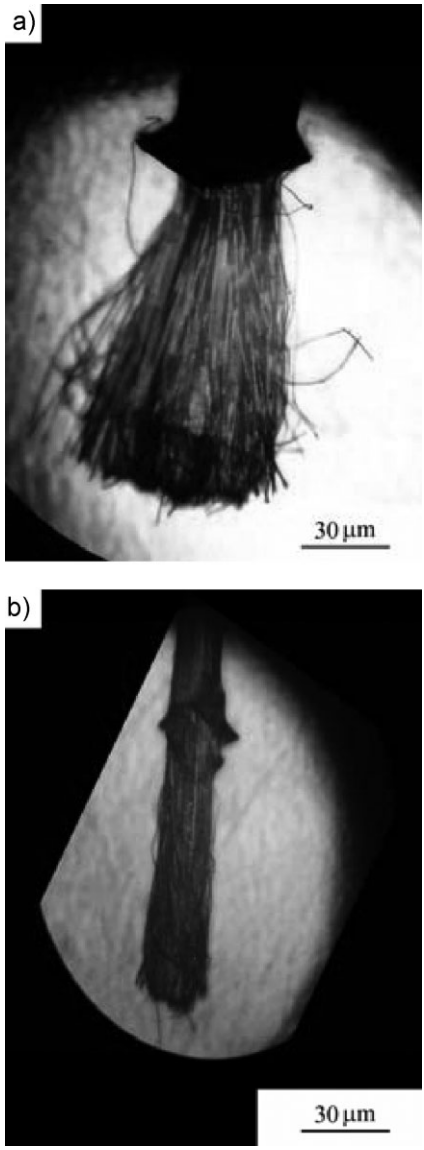

Figure 4.
a: "Brush" type mode. A type of multifilament fiber pulled out from the matrix: poor joint strength with the matrix. The fiber was plasma-untreated. b: "Kern" type mode. A type of multifilament fiber pulled out from the matrix: high joint strength with the matrix. The fiber was plasma-treated.

filaments in the bundle separated from each other.

The plasma treatment of the fiber increases the joint strength (Figure 2, line 3). The pulled out plasma-treated fiber presents the thick kern with a ridge surface emerged from filaments. The pullout process is accompanied by strong energy of feedback. A kern shoots out from the matrix at reaching the necessary force. The surface of a matrix hole in the pulled out place is clean, without traces of filaments destruction, i.e. a kern is a strong monolithic CM (Figure 4b).

Filaments in the bundle did not de-bond both for a "stronger" and a "weak" bond. For a "stronger" bond, it is a mini-composite pull-out with retained resin between the filaments firmly attached to the filaments within the bundle.

Thus, at good bonding the individual filaments do not de-bond, they fracture close to the same fracture plane of the resin. If there is any pullout it is the bundle or mini-composite that pulls out acting like a giant fiber.

At good bonding the pulled out end of the multifilament fiber looks like a kern. The surface of this kern separated from the matrix due to tangent stresses at the fiber/matrix interface. The cylindrical hole formed in the matrix.Nature of bonding is not decided in this study.

When the length of the fiber impregnated with the matrix was increased above some value, the filaments were destroyed on the surface of the kern and the dependence $F(l)$ was changed. At the even greater l the fiber did not pull-out from a matrix and failed on a free site.

The value of fiber capillary rise h indicates that the matrix and the fiber are included in physical contact in this area. However, different joint strength can be obtained on the area of contact. It is determined by a level of development of physical and chemical interaction between the fiber and the matrix.

Activation of a fiber by plasma increases wetting and fiber capillary rise h (Figure 3). However, this increase is not pronounced. For example, the value of $h = 17$ mm can be reached for untreated twisted fiber (line 1), for untreated fiber (line 2) and for plasma-activated fiber (line 3), while the joint strength is quite different.

At the same value of $h = 17$ mm, plasma activation of a fiber increases joint strength: $F/l = 23$ N/mm for the twisted fiber (line 1), $F/l = 33$ N/mm for untreated fiber (line 2), $F/l = 98$ N/mm for plasma-activated fiber (line 3).

Fiber capillary rise h has essential experimental data scatter (Figure 3). For example, in experiments with the untreated fiber (line 2) the value of h varies from 17 up to 27 mm. In experiments with the plasma-activated fiber (line 3) the value of h changes from 10 up to 17 mm.

The data scatter is evidently related to inconstancy of clearances between the filaments of the fiber and to change of viscosity η in Equation (5). Viscosity depends on many parameters of experiment: temperature, quality of used materials, duration of experiment, concentration and type of solvent, etc. However, the multifilament wet-pull-out method takes into account these variations. They are reflected in change of value F/l. The higher the value of h, the lager is the value of normalized force F/l (Figure 3, lines 1, 2, 3).

Let's estimate tangent stresses τ at the fiber /matrix interface for one of experiments:

$$\tau = \frac{F}{\pi D l} \tag{6}$$

where D is the diameter of a kern provided that it has a smooth surface.

From experiments with plasma-activated fiber (Figure 2, line 3), we have the following data: $F = 300$ N, $l = 4$ mm, $D = 0.6$ mm. Then we obtained the value of $\tau \approx 40$ MPa.

For comparison we took the data of τ for micro-composites on a basis of epoxy resin Epon 828 and radio frequency plasma-treated high performance Spectra® 1000 polyethylene (HPPE) fibers.[8] Authors achieved that plasma treatment of the monofilament taken out from complex yarn Spectra® 1000 increased the value of τ from 8.6 up to 17.4 MPa, i.e. by 102%. In contrast to the multifilament wet-pull-out method, the experiments in this work were carried out with separate monofilament of a complex yarn.

In our experiments the value of τ grows by 100% (Figure 2, lines 2 and 3), and the absolute value of τ exceeds the data[8] in 2.3 times.

The multifilament wet-pull-out method considers a total interaction between the matrix and filaments in a complex fiber or yarn. It is the advantage of this method in comparison with the tests of individual monofilament. Such total interaction between the filaments in the bundle and the matrix always takes place both at production and loading of CM. The method described corresponds to technology of CM production and approaches real operating conditions of CM.

Conclusion

In order to study physicochemical interaction between the matrix and multifilament fiber during the production of composite materials we have developed the multifilament wet-pull-out method. This allows one to estimate the fiber wetting with liquid matrix and quality the fiber impregnation with the matrix using a fiber capillary rise, and measure the fiber capillary rise and the joint strength after curing process finished. Therefore, we have called proposed method a wet-pull-out. The multifilament wet-pull-out method considers a total interaction between the matrix and the filaments in a complex fiber. Distinguishing feature of the method is testing not monofilament fiber, but multifilament fiber, which makes it possible modelling the real operating conditions of CM.

The increase of clearances between filaments in a complex fiber improves its wetting and impregnation with the matrix.

Non-equilibrium low temperature plasma activation of SK-75 HPPE fiber increases joint strength between the fiber and the matrix and allows one to obtain tangent stresses τ of $\approx$40 MPa at the fiber/matrix interface.

Abbreviations

CM: composite materials; HPPE: high performance polyethylene; UHMWPE:

ultrahigh molecular weight polyethylene; IFSS: interfacial shear strength.

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