

## FUNCTIONAL COATINGS FOR POLYMER COMPOSITES

A. Babik<sup>1</sup>, L. Hoferek<sup>1</sup>, D. Janova<sup>2</sup>, V. Cech<sup>1</sup>

<sup>1</sup>*Institute of Materials Chemistry, Brno University of Technology  
Purkynova 118, CZ-61200 Brno, Czech Republic*

<sup>2</sup>*Dept. of Structural and Phase Analysis, Brno University of Technology  
Technicka 2896/2, CZ-61669, Brno, Czech Republic*

### ABSTRACT

The development of high-performance polymer composites is tightly bound with the functional surface modification of reinforcements. A new method, based on the principle of the fiber-bundle pull-out test, was used to analyze the interfacial properties between the long fibers in the form of a bundle and the polymer matrix. The pull-out test can be used for a relative comparison of different surface modifications if the bundle geometry is unknown. Glass fibers coated by plasma polymer films of tetravinylsilane were tested to determine the interfacial shear strength as a function of RF power and film thickness that was varied from 50 nm to 10  $\mu\text{m}$ . SEM micrographs of pulled-out (debonded) fiber bundle were used to characterize adhesion at the interlayer/fiber and polymer/interlayer interfaces.

### KEYWORDS

Thin films, plasma-enhanced chemical vapor deposition (PECVD), polymer composites, scanning electron microscopy (SEM)

### 1. INTRODUCTION

New helical coupling plasma system for continuous surface treatment and modification of fiber bundles has been developed using the RF (13.56 MHz) pulsed plasma of glow discharge technique [1]. The pulsed mode means, that plasma was controlled by changing the ratio of time, when plasma was switched on ( $t_{\text{on}}$ ) to the time when plasma was switched off ( $t_{\text{off}}$ ). Afterwards we can define the effective power  $P_{\text{eff}} = t_{\text{on}}/T \times P_{\text{total}}$ , where the period was defined as  $T = t_{\text{on}} + t_{\text{off}}$  and the total power of generator was  $P_{\text{total}} = 50 \text{ W}$  [2].

Low-temperature plasma is a suitable technique used for surface modification of materials [3] and plasma-enhanced chemical vapor deposition (PECVD) is a useful technique able to prepare engineered interlayers on surface of composite reinforcements [4].

The surface of reinforcements has to be modified to improve wettability and adhesion to the matrix for sophisticated composites. The surface modification of reinforcements is a useful way to influence the chemical and physical structures of their surface layer, tailoring fiber-matrix stress transfer, but without influencing their bulk mechanical properties [5]. Silane coupling agents are applied to glass fiber surface to promote their adhesion to the polymer matrix. However, modern surface analytical studies have shown that the coatings are usually heterogeneous, with thickness varying from less 10 nm to more than 1  $\mu\text{m}$  [6]. The formed siloxane bonds are hydrolytically unstable, which results in worsening of mechanical properties of the composite in the presence of water and, eventually, in failure of the material. This problem may be resolved with plasma surface modification [7].

### 2. EXPERIMENTAL

Plasma polymer films were deposited on a bundle of unsized glass fibers (GF) using tetravinylsilane monomer (TVS, purity 97%, Sigma Aldrich) at different powers

ranging from 0.1 to 10 W using RF (13.56 MHz) pulsed-plasma system and film thicknesses that were varied from 50 nm to 10 microns.

Glass fibers (E type, 1200 tex, 19  $\mu\text{m}$  diameter) were used as reinforcements and polyester resin was the matrix. This polyester resin was cured from oligomers on the base of isophthalic acid with mixture of styrene, initiators, stabilizer and separator. Curing was carried out in the oven with programmable temperature regime at 140  $^{\circ}\text{C}$ .

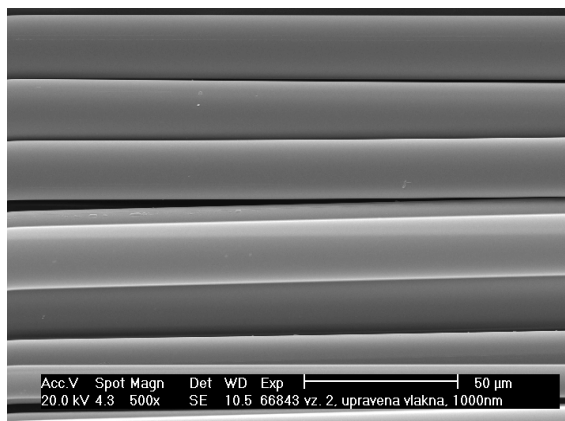
The composite samples were tested by fiber-bundle pull-out test [8] to determine the interfacial shear strength. The bundle was terminated by the disk at the bottom side and by a polymer dumb bell (ISO 527) at the other side. Such a specimen was subjected to a tensile test using a universal testing machine (Z010/TH2A, Zwick). The dumb-bell-shaped part of the specimen was hold by grips and the disk was hold by a test fixture using a specific edge. The experiment consists of an increasing normal force, which is applied to the fiber bundle in order to pull it out of the polymer disk. The design of the sample was constructed with respect to results of finite element analysis (FEA). The tensile test was employed to evaluate adhesion at the fiber-matrix interface. The maximum applied load,  $P_{\text{max}}$ , corresponds to a debonding of the fiber bundle embedded in the polymer disk; the contact area between the bundle and the disk can be expressed through the disk height,  $h$ , and the bundle perimeter,  $\pi d$ , where  $d$  is the bundle diameter. In a similar manner to the microbond technique, the interfacial shear strength can be calculated as the maximum applied load divided by the contact area using the relation:

$$\tau_{\text{int}} = P_{\text{max}} / (\pi h d) . \quad (1)$$

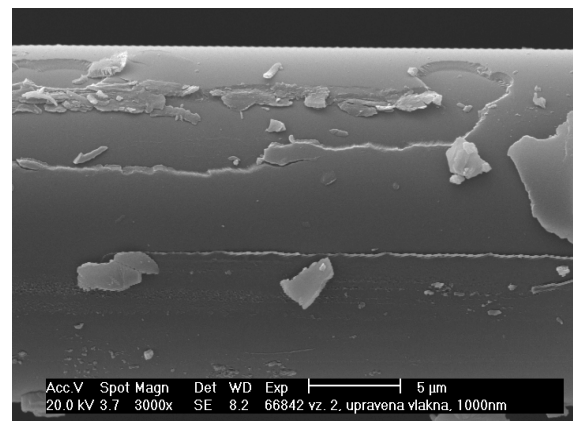
The coated fibers and pull-out bundles were observed by scanning electron microscopy (SEM) to investigate film uniformity, and characterize adhesion of plasma polymer interlayer to the surface of glass fibers and polymer matrix.

### 3. RESULTS AND DISCUSSION

Unsize glass fibers and fibers with plasma coatings were observed by SEM to investigate film uniformity. The deposited plasma coatings on fibers were uniform (Figure 1) unlike industrially sized fibers using wet chemical processes. Surface of plasma coated GF is smooth without impurities and defects. In the detail (Figure 2), an evident rupture of the coating is observed on the fiber surface close to the cut fiber end. This means that the plasma coating is spread on the whole surface area of GF.



**Figure 1.** Deposited plasma coatings on glass fibers.



**Figure 2.** Rupture of the coating on surface of glass fiber.

Prepared composite samples with unsized and plasma modified glass fibers were tested by universal testing machine. Displacement rate was 1 mm per minute and the force response was measured. The tensile test was ended when the bundle of glass fibers was pulled-out from polymeric disk of composite sample.

Results of fiber-bundle pull-out test for composite samples with unsized fibers and plasma coated reinforcements at different powers ranging from 0.1 to 10 W are given in Table 1.

**Table 1.** Results of fiber-bundle pull-out test.

RF power (W)	$h$ (mm)	$P_{max}$ (N)	$P_{max}/h$	$\tau_{int}$ (MPa)
Unsize	4.90	235	48	17.0
0.10	4.91	354	72	24.1
0.50	4.90	331	68	23.9
2.5	4.94	343	69	24.4
5.0	4.93	339	69	24.5
10.0	4.92	385	78	27.6

( $h$  is the height of polymeric cylinder,  $P_{max}$  is the maximum applied load for pulling-out the bundle of tested glass fibers from disk, and  $\tau_{int}$  is the interfacial shear strength calculated using equation (1)).

Results of fiber-bundle pull-out test for composite samples with unsized and plasma coated fibers at the film thickness that was varied from 50 nm to 10  $\mu$ m are given in Table 2.

**Table 2.** Results of fiber-bundle pull-out test.

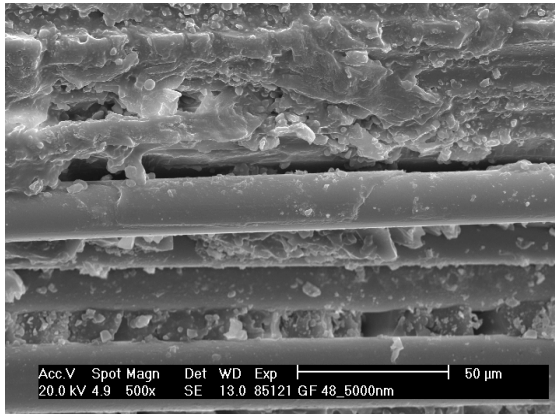
Thickness (nm)	$h$ (mm)	$P_{max}$ (N)	$P_{max}/h$	$\tau_{int}$ (MPa)
Unsize	4.90	235	48	17.0
50	4.99	293	59	20.8
100	4.96	340	69	24.4
500	4.95	375	76	27.0
1000	4.94	343	69	24.4
5000	4.89	452	93	32.9
10000	4.86	534	110	38.9

Pull-out bundles were observed by SEM to characterize adhesion of TVS interlayer to surface of glass fibers and to polymer matrix. In SEM micrographs, we observe that the fibers are coated by thin polymer film and covered by cured polyester resin. A good adhesion of polymer matrix to the glass fiber and no signs of cracks are evident in micrographs (Figure 3). In the detail, we can observe the rupture of the coating on GF surface evidencing the cohesion failure (Figure 4).

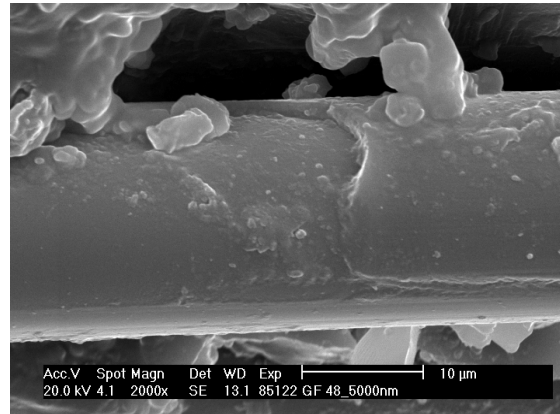
#### 4. CONCLUSION

Plasma surface modification is an effective technique to influence physical and chemical properties of interphases in fiber reinforced polymer composites. The tensile strength of single fibers is sensitive to both the plasma treatment and plasma polymerization. Strong adhesion is promoted by increasing the surface energy of fibers, as a result of plasma modification, decreasing contact angle of the matrix, and thus the wettability of fibers by the polymer matrix is improved. The organosilicon plasma polymers are widely recognized for preparation controlled interphase in composites. The functional coating serves as suitable interlayer to

improve compatibility between the glass fiber and the polymer matrix resulting in enhanced composite performance. The composite samples were tested by fiber-bundle pull-out test to determine the interfacial shear strength as a function of RF power and film thickness that was varied from 50 nm to 10 microns. A significant increase of the interfacial shear strength by 102% was found for the increased film thickness and a weak descent by 10% was related to the enhanced power. SEM micrographs of pulled-out (debonded) fiber bundle were used to characterize adhesion at the interlayer/fiber and polymer/interlayer interfaces.



**Figure 3.** Micrograph of plasma modified glass fibers embedded in polyester resin after fiber-bundle pull-out test.



**Figure 4.** Detail of plasma coated glass fiber embedded in polyester resin using SEM image.

*Acknowledgements:* This work was supported in part by the Czech Science Foundation, grants no. P106/11/0738, P205/12/J058 and 104/09/H080, the Czech Ministry of Education, grant no. ME09061 and the Technology Agency of the Czech Republic, grant no. TA01010796.

## REFERENCES

- [1] V. Cech, N. Inagaki, J. Vanek, R. Prikryl, A. Grycova and J. Zemek, *Thin Solid Films* 502, 181 (2006).
- [2] V. Cech, J. Studynka, N. Conte, V. Perina, Physico-chemical properties of plasma-polymerized of tetravinylsilane, *Surface & Coating Technology* 201, 5512 (2007).
- [3] N. Inagaki, *Plasma Surface Modification and Plasma Polymerization*. Lancaster : Technomic Publishing Company, Inc., 1996.
- [4] V. Cech, *Compos. Interfaces* 14, 321 (2007).
- [5] J-K. Kim and Y-W. Mai, *Engineered Interfaces in Fibre Reinforced Composites*, Amsterdam, Elsevier, 1998.
- [6] D. W. Dwight, Glass Fiber Reinforcement, in: *Comprehensives Composite Materials*, Amsterdam: Elsevier, 2000, Ed. Kelly A., Zweiben C. Volume 1. p 231 – 261.
- [7] V. Cech, New Progress in Composite Interphases: A Use of Plasma Technologies. In *Proceedings of FRC 2000*. 2000. Newcastle, GB: Woodhead Publishing Ltd, s. 246.
- [8] V. Cech, P. Janecek, T. Lasota, J. Bursa, *Compos. Interfaces* 18, 309 (2011).