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Application of cold plasma technology in fiber-reinforced composite materials

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Abstract: A study is presented concerning a cold plasma technique for improving the bondability of high-strength high-modulus multi-filament polyethylene fibers to polymer matrices and the fibers impregnation with the objective to fabricate composite materials (CMs). Strong bonding between the matrixes and reinforcing fibers during the production of composites appears in the case if interaction is chemical. The value of the activation energy of the chemical interaction for very high performance polyethylene fiber was estimated. It was 1.14 eV. This allows using the cold plasma technique for producing CMs. In order to understand the effect of cold plasma treatment treated and untreated fibers were used to fabricate CMs. The strong bond between the matrix and plasma-activated fibers affects both the properties and failure mode of composite. The properties and failure modes were compared to those of CMs reinforced with untreated fibers. After plasma treatment the properties of CMs are increased. CMs are broken as a unit whole under tension. The ideas of the activating the fibers by cold plasma treatment above the activation energy of the chemical interaction may be extended over other types of the fibers and matrices to produce new types of fiber-reinforced composite materials with high physicomechanical indices.

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Today fiber-reinforced composite materials are increasingly used as lightweight constriction materials. During the development of high-molecular chemistry, copolymers with excellent physicomechanical properties have been created: Kevlar, Twaron, etc. High-oriented polyethylene fibers have also been obtained from superhigh-molecular polyethylene, which possess characteristics comparable with those of aramid fibers and have an important advantage a low density (0.95-0.97g/cm^3).

The high strength (3.4-5 GPa), high tensile modulus (110-120 GPa), high energy absorption and the low density of the high performance polyethylene (HPPE) fibers make it possible to produce CMs that combine good mechanical properties with low specific mass. For Dyneema HPPE fibers, the current strength of 3.4 GPa (340 kg/mm^2) was developed in a decade time [1]. Obviously, application of composites reinforced with HPPE fibers can be rewarding. However, the poor bondability, owing to the low surface energy (33 mJm^{-2}) and inert chemical nature of polyethylene [2], has so far limited the widespread use of HPPE fibers in mass production of the CMs. Various pre-treatments can be applied to the HPPE fibers in order to increase the bondability of the fibers to polymer matrices.

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When producing CMs reinforced with high-strength high-modulus multi-filament organic fibers such as Dyneema and Spectra HPPE fibers, one faces the challenge of the formation of the strong bond between the fibers and various matrices. The strong bond is necessary to transfer effectively the external load to the fibers and include all composite structural elements into the joint work.

A concept of a multistage physicochemical interaction between the matrix and reinforcing fibers during the production of CMs is introduced[3-6]. The interaction may be divided into three stages in every elementary part of the fiber/matrix interface: 1) a physical interaction, when the joining matters generate a physical contact, 2) a chemical interaction, which occurs only if at least one of the contacting surfaces has an energy sufficient for the chemical interaction, and 3) a diffusion interaction. The third stage is not examined in this study. In case the contacting surfaces have low energies, the interaction stops at the stage of forming the physical contact. Especially strong bonding between the fiber and matrix appears in the case if interaction is chemical. The latter is characterised by a certain activation energy value.

The objectives of this study were: to determine the activation energy for the HPPE fibers according to their chemical structure; to develop the regimes of fibers activation using cold plasma treatment; to produce composites reinforced with plasma treated and untreated fibers and to study the mechanical properties and failure modes of the CMs.

The value of the activation energy of the chemical interaction for HPPE fiber was estimated. It was 1.14 eV. Based on these estimates, conditions for the HPPE fiber activation with cold plasma are found. This allows one to use the cold plasma treatment for producing CMs.

We have developed the technology of plasma treatment of the HPPE fibers [4-6]. The non-equilibrium low-temperature (cold) plasma is applied at the reduced pressures p from 1.33 Pa to 660 Pa. The feed gases were argon, oxygen and atmospheric air. The thermal component of plasma is reduced to a minimum, due to the low density of ion current $j_i = 0.5\text{-}1\ A/m^2$ and small duration t of plasma influence on a fiber. Such plasma allows one to treat even high-oriented polyethylene fibers, which are very sensitive to heating. It does not cause the destruction of the fibers. The optimal regimes of plasma treatment were found in order to achieve activation of the fibers without degrading the mechanical strength and destroying the fibers themselves.

The study considers potential variants for changing chemical contacts at the fiber/matrix interface when imparting the energy for the second stage for the case of the production of the CMs reinforced with HPPE fibers.

As reinforcement, we used Dyneema SK-75 very high performance polyethylene fibers produced in 2000 and 2002 years. The SK-75 fibers were kindly provided by the DSM Company. We also applied Dyneema SK-60 fibers produced 10-years ago. We used SK-60 fibers in order to estimate the potentials for restoring the fiber properties by cold plasma treatment. The matrices were an ED-20 epoxy resin cured with polyethylene polyamine and the EDT-10 epoxy compound. Various curing regimes were applied: 80℃ for 2 hours, and 100℃ for 44 hours. Winding the fibers over a mandrel produced CMs specimens.

We studied the influence of plasma treatment on both the mechanical properties of the fibers and the fiber-reinforced composites. For plasma-activated SK-75 and SK-60 fibers and epoxy resin we obtained the following kinds of CMs specimens: impregnated yarns (micro plastics) and uni-directional (UD) rings. The properties were compared for the composites reinforced with plasma treated and untreated fibers.

The effect of plasma spraying was controlled by gravimetric analysis. The mechanical properties of the fibers were determined from the values of the load at break. The relative elongation of the fibers at break (ε) was measured. The changes of the fibers structure under plasma conditions were examined using X-ray diffraction analysis. The changes of the chemical composition of the treated surfaces were determined by infrared spectrophotometry of many times broken full inside reflection method. It was found that free radicals appeared on the surface of the fibers due to plasma treatment. The free radicals concentration was detected by the electron paramagnetic resonance (EPR) spectroscopy. The topographies of untreated and treated fibers surfaces were investigated by scanning electron microscopy (SEM) with a two-three thousand-fold magnification (×2000-3000).

After plasma treatment the properties of CMs are increased. The composite reinforced with plasma-activated HPPE fibers is broken as a unit whole. This is the monolithic material which all elements carry the load. The failure mode of such composite demonstrates the high joint strength between the fibers and matrix.

The plasma treatment of SK-60 fibers increased the tensile strength of the composite, σ_t, by 27% and the modulus of elasticity, E, by 37%. The plasma treatment appeared to be particularly effective for bending and shear properties of the composite thus demonstrating high increase of the interaction at the fiber/matrix interface. After the treatment of SK-60 and SK-75 fibers, the composite bending strength, σ_b, was increased by a factor of 3 (from 150 MPa to 450 MPa) and 2.5 (from 124MPa to 314 MPa), respectively. The shear strength, τ_{sh}, increased by the factors of 2.6 and 1.5 for the composites reinforced with SK-60 and SK-75 fibers, respectively. The plasma treatment of SK-75 fibers also increased the composite fracture toughness, G_{IC}, by 26% (from 3.2 kJ/m^2 to 4.0 kJ/m^2).

The application of plasma-activated HPPE fibers for reinforcing an epoxy matrix allows one to produce lightweight composites with increased properties. The concepts developed in this study on the possibility of using plasma-activated HPPE fibers in manufacturing CMs can be extended to other organic and inorganic fibers and matrices for creating new types of fiber-reinforced composite materials with high physicomechanical indices [6,7].

References

[1] Roerdink E, J van Dingenen. Past and Future of High Performance Fibres. DSM High Performance Fibers, Heerlen, The Netherlands, Polymer Fibres 2002 10-12 July 2002.

[2] Shanglin Gao, Yeguanc Zeng, Surface modification of Ultrahigh Molecular Weight Polyethylene Fibers by plasma treatment. Improving surface adhesion. Journal of Applied Polymer Science, 1993, Vol. 47, pp. 2065-2071. Ed. by John Wiley & Sons, Inc.

[3] Kudinov V V. Plasma Coatings \[in Russian, in Chinese\], Nauka, Moscow, 1977, 184p.

[4] Korneeva N V, Kudinov V V, Bazhenov S L, Solodilov V I, Pavlovskii D V, Zelenskii E S. New potentials in producing composites reinforced with superhigh performance polyethylene fibers // Proceedings of the Twelfth International Conference on Mechanics of Composite Materials.-June 9-13, 2002.-Riga, Latvia: Ed. by Institute of Polymer Mechanics and University of Latvia, 2002.-P. 96.

[5] Kudinov V V, Korneeva N V. The studies of the properties of organic fibers treated by cold plasma technology at low pressure // Proceedings of the Sixth International Conference on Composite Materials / Advancing with Composites 2003. May 7-9, 2003.-Milan, Italy: I. Crivelli-Visconti Publ., 2003. P. 359-365.

[6] Korneeva N V, Kudinov V V. Fabrication of composites reinforced with cold plasma treated Dyneema polyethylene fibers and the study of mechanical properties and failure studies // Proceedings of the Sixth International Conference on Composite Materials / Advancing with Composites 2003. May 7-9, 2003.-Milan, Italy: I. Crivelli-Visconti Publ., 2003. P. 375-380.

[7] Leone C, Caprino G, De Iorio I. Mechanical properties of fibre reinforced plastics obtained using cold plasma treated fibres // Proceedings of the Sixth International Conference on Composite Materials / Advancing with Composites 2003. May 7-9, 2003.-Milan, Italy: I. Crivelli-Visconti Publ., 2003. P. 57-66.