Influence of plasma modification on free surface energy of synthetic fibrous materials

Y A Timoshina, E F Voznesensky, A E Karnoukhov, I V Krasina, G R Rakhmatullina, E A Pankova and Shagivalieva R R
PNTVM Department, Kazan National Research Technological University, Kazan, 420015, Russia

ybuki@mail.ru

Abstract. The results of experimental studies of the effect of plasma modification in various plasma-forming gases on the acid-alkaline properties and free surface energy of samples of synthetic fibrous materials are presented. The effect of changes in the free surface energy of fiber samples on their adhesion to an epoxy binder in a composite material is studied.

1. The Introduction
Currently, fibrous polymer composite materials are widely used in the strategic areas of modern technology, industry, sports, medicine, construction, etc. The properties of the produced polymer composite materials depend on the technological conditions of production, the choice of the starting components and their ratio, the strength of the adhesive bond between them. The acid-alkaline characteristics often affect the formation of interfacial bonds, along with diffusion, mechanical and electrical factors. In this case, the best interaction is achieved when one of the materials to be joined has predominantly acidic properties, and the other alkaline.

Various modification methods are used to change free surface energy (FSE) and acid-alkaline characteristics of substrate and the adhesive to improve the adhesive interaction between them. One of these methods is the modification of non-equilibrium low-temperature plasma (NELTP), which allows you to adjust the surface properties of synthetic materials depending on the choice of plasma-forming gas and plasma modification parameters [1-5].

2. Materials, methods and equipment
The use of NELTP in the processes of modification synthetic materials ultra-high molecular weight polyethylene (UHMW PE) fiber samples. An experimental radio-frequency plasma installation of a low-pressure capacitive discharge [6] was used to modify synthetic fibrous materials.

The graphical method for estimating the components of free surface energy, based on the Owens-Wendt equation, was used to determine the dispersion and acid-base components of the FSE samples. This was used to evaluate the effect of plasma modification on UHMWPE fiber samples. In this method, the determination of the FSE energy occurs by constructing a linear approximation based on measurements of the contact angles of the surface by the test material with test liquids [7]. The wetting angle, characterizing the degree of wettability of the material, was determined on a Kruss Easy Drop DSA 20E instrument using the sitting drop method. The effect of changes in the FSE on the adhesion properties of the fibers was evaluated using the values of the normalized value of the breaking load of the micro composite using the universal testing machine AutographAGS-X100 (Shimadzu).
3. Results
During the NELTP modification of UHMW PE fibers, the following processing parameters were varied: discharge power $W_d = 0.4–2.2$ kW; processing time $t = 60–600$ s; pressure in the working chamber $P = 10–30$ Pa; plasma-forming gas flow rate $G = 0.01–0.04$ g/s; plasma-forming gas: air, argon, argon/nitrogen, argon/propane-butane. The results of the determination of the dispersion and acid-alkaline component of the FSE are presented in Table 1 and in Figure 1.

Table 1. FSE of UHMW PE fiber samples

| Sample                  | The dispersion component of the FSE, $\gamma_s^d$ mJ / m$^2$ | The acid-alkaline component of the FSE, $\gamma_s^{AB}$ mJ / m$^2$ | FSE, mJ / m$^2$ |
|-------------------------|-------------------------------------------------------------|-----------------------------------------------------------------|-----------------|
| Source                  | 17.78                                                       | 13.98                                                           | 31.76           |
| Modified in air         | 17.55                                                       | 11.11                                                           | 28.66           |
| Modified in argon       | 17.58                                                       | 11.34                                                           | 28.92           |
| Argon / Nitrogen modified | 17.39                                                      | 9.88                                                            | 27.27           |
| Argon/Propane-Butane modified | 17.98                                                      | 15.41                                                          | 33.39           |

The experimental data indicate that the plasma modification of UHMW PE fibers leads to a change in the acid-alkaline and dispersion components of the FSE samples (Table 1). For plasma-modified samples in a plasma of argon, air and argon/nitrogen, a decrease in the FES occurs, and for a sample modified in a plasma-forming medium of argon/propane-butane, an increase in the FES is compared with the initial sample (Figure 1).

Figure 1. Change in the FSE of UHMW PE fibers after plasma modification in various plasma-forming gases

Further, adhesion properties were evaluated for all samples by determining the bond strength of the fiber with the epoxy matrix using the wet-pull-out method. The results of determining the normalized value of the breaking load of the microcomposite are presented in Figure 2. The highest increase in the adhesive strength of UHMW PE fiber with epoxy resin is also observed for a sample modified in argon/propane-butane plasma (Figure 2). When processing fiber in a given plasma-forming gas mixture, the normalized breaking load of a microcomposite made on its basis is 65.29 N/mm, which is 1.5 times higher than the value for the starting material. For samples modified...
in a plasma of argon, air, and argon / nitrogen, an increase in the adhesive properties to the epoxy binder does not occur.

![Figure 2](image_url)

Figure 2. Change in the normalized value of the breaking load of the microcomposite after plasma modification of UHMW PE fibers in various plasma-forming gases

4. Conclusions

A number of studies have shown that NELTP modification of synthetic materials in various plasma-forming gases leads to changes in the acid-base and dispersion components of the FSE samples. Increasing the FSE and, consequently, the adhesive properties of the UHMW PE samples fibers modified in the plasma an argon/propane-butane, can be explained by the appearance in the plasma processing adhesively-active functional groups on the surface of the polyethylene fibers.

References

[1] Sergeeva E A, Zheltukhin V S, Abdullin I Sh 2011 Modification of synthetic fibrous materials and products by non-equilibrium low-temperature plasma. Theory, models, methods (Kazan: KSTU) p 252

[2] Timoshina Y A, Voznesensky E F, Tskhay E S, Sysoev V A, Krasina I V, Kulevtsov G N 2019 Modification of surface of textile materials with silver nanoparticles in the radio-frequency induction plasma discharge of low pressure Journal of Physics: Conference Series 1328 p 012083

[3] Timoshina Y A, Voznesensky E F, Tskhay E S, Sysoev V A, Krasina I V, Kulevtsov G N 2019 Surface activation of polyamide fibers by radio-frequency capacitive plasma for application of functional coatings Journal of Physics: Conference Series 1328 p 012084

[4] Timoshina Y A, Trofimov A V, Miftakhov I S, Voznesensky E F 2018 Modification of Textile Materials with Nanoparticles Using Low-Pressure High-Frequency Plasma Nanotechnologies in Russia 13 pp 561-564

[5] Timoshina Y A, Tskhay E S, Voznesensky E F, Rakhmatullina G R, Tikhonova V P, Sharifullin F S 2019 Modification of a surface of synthetic fibrous materials by silver nanoparticles with application of plasma processing Journal of Physics: Conference Series 1058 p 012039

[6] Abdullin I Sh, Zheltukhin V S, Sagbiev I R, Shaekhov M F 2007 Modification of nanolayers in radio-frequency plasma of low pressure: monograph (Kazan: KSTU) p 356

[7] Kraus E, Boundrit B, Bastian M 2015 Analysis of the surfaces of polymers treated with low-pressure plasma from the point of view of the acid-base approach Bulletin of the Technological University 4 pp 71-76