

## COMPOSITE FIBER MATERIALS

### MODIFICATION OF SURFACE OF REINFORCING CARBON FILLERS FOR POLYMERIC COMPOSITE MATERIALS BY PLASMA TREATMENT (REVIEW)

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*The problem of increasing the adsorptive and adhesive interaction at the phase boundary between a matrix and a reinforcing fibrous filler in the creation and application of carbon-filled plastics was investigated. A promising way of achieving this aim is to develop methods for surface treatment of the carbon reinforcing fillers and, particularly, to modify the surface of the carbon fibrous materials by plasma treatment.*

The production technology of carbon fibrous materials (CFM) and polymeric composite materials (PCM) based on them is continually improving on account of the demand of aerospace, aviation, and other specialized technologies for novel materials with unique properties. The advantages of CFMs include high strength, sorption activity, and low density. It is these qualities that have determined the widespread use of the materials in both military and civil branches of industry (with expansion of the range of civil and dual-purpose products) [1].

Polymeric composite materials are multicomponent systems of complex structure with a clear interface between the components. Their properties depend to a significant degree on adhesive interaction between the reinforcing filler and the polymeric binder. Study of the adhesive strength at the interface is an essential stage for creating PCMs that have specific and controllable characteristics and for forecasting the behavior of materials during use under various conditions and also for investigating the mechanisms by which they are destroyed [2]. For this purpose it is necessary to determine how the properties of the PCM depend on the adhesive strength and the parameters that determine and control it.

Adhesion at the interface between the CFM and the polymeric matrix is mainly determined by mechanical bonds that result from contact between the polymer and the surface relief of the fibers, by chemical bonds between the surface of the CFM and the polymeric matrix, and to a small degree by bonds due to Van der Waals forces [3]. The degree of adhesion is affected substantially by the surface condition of the reinforcing filler in so far as the effective area of contact between the filler and the matrix at the interface is determined by the specific area of the surface and its relief. A major role here is played by morphological formations with sizes of 10-100 Å [4]. As known, carbon fibers have a fairly smooth surface. Apart from the surface relief, the chemical composition of the surface layer of the fiber (because of the specific nature of their production the surface of carbon fibers is chemically inert) and the surface energy are also important [5]. For PCMs the nature and composition of the binder, the formation conditions, and the storage [6] and application [7] temperatures are also important.

It is known that because of increase in the ineffective length of the fibers insufficient adhesive interaction and a large number of defects at the interface [8] between the fibrous filler and the polymeric matrix lead to poor realization of the strength of the fibrous filler in the material. Conversely, in the case where the adhesion is sufficient the effect of the reinforcing filler in the PCM becomes stronger owing to more uniform distribution of the stresses and elimination of surface defects in the filler [4].

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An important task in the creation and application of reinforced plastics is to find improved methods of increasing the adsorptive and adhesive interaction at the interface between the matrix and the reinforcing fibrous filler by surface treatment of the filler and also to study the dependence of the physical and mechanical characteristics of the PCM on the strength of interaction between the matrix and the filler. A promising way of achieving this aim is to modify the surface of the CFM by various physical, mechanical, and chemical methods with and without change in the structure of the reinforcing filler.

Modification involves directional change of properties as a result of additional treatment of ready-made CFMs. Here efforts are made to preserve essential characteristics of the material while simultaneously introducing new or eliminating undesirable characteristics. The modification is divided between bulk and surface treatments according to the depth of penetration. In the case of increased adhesion of the reinforcing carbon fillers for PCMs it is not necessary to modify the whole volume, and treatment of the surface layer is sufficient.

Physical (structural) modification involves directional change of the physical and most of mechanical characteristics of the materials achieved by transformation of their supermolecular structure by physical actions (vibrational treatment, magnetic field, ultrasonic treatment, heat treatment, high frequency currents, low-pressure plasma,  $\gamma$  radiation [9], etc.). The chemical structure of the material does not change during physical modification.

Chemical modification involves directional change of the properties of the material by introducing fragments of various low-molecular or high-molecular modifying agents into the macromolecules.

Among the various methods for surface modification of carbon reinforcing fillers the most widely used are dressing [10-12] and reducing or oxidizing treatment in a liquid or gaseous medium (hot air, ozone, nitrating mixture, hydrogen peroxide, sodium hydroxide, potassium permanganate, etc.), or electrochemical treatment [13] (with sodium hydroxide, ammonium bicarbonate, sulfuric, nitric, or organic acids, or salts as electrolyte). In addition, chemical grafting of various functional groups onto the surface of carbon fibers, catalytic growth of carbon nanofibers [14] or nanostructures [15, 16], and so forth are becoming more widespread.

One of the most interesting and promising methods of modifying the surface of the reinforcing filler for PCMs and for carbon, in particular, is plasma treatment. This makes it possible to change both the mechanical and the chemical characteristics of the material (surface energy, wettability, adhesion, specific surface area, functional groups, etc.) over wide limits.

Plasma is the name for a gas in which a significant part of the atoms or molecules are present in an ionized state while the concentration of electrons and negative ions is equal to the concentration of positive ions. A plasma does not have electric charge but has high electroconductivity [17].

Plasma modification of polymers has been studied since the 1980s. Since that time the necessary vacuum equipment created specifically for the realization of plasma chemical processes has been produced in many developed countries. From the ecological stand point modern plasma chemical methods are preferred to chemical modification, which uses such aggressive reagents as acids, hydroxides, alkaline-earth metals and their compounds, etc.

An important feature of plasma chemical modification is the fact that only the surface being treated and a very thin surface layer, the thickness of which according to various estimates is between 100 Å and several micrometers, are subjected to treatment. The bulk of the polymer is unaffected and retains the mechanical, physicochemical, and electrophysical properties of the material being modified.

Depending on the parameters of the plasma treatment, the relief of the surface layer can be both developed and smoothed out. Relief can develop in particular as a result of the different rates of erosion of neighboring sections of the surface being treated (etching relief) [18]. During treatment of the surface of CFM by plasma of specific composition (in which gaseous compounds of the plasma particles with the surface atoms are formed) the nonuniformity of the surface relief can reach several tens of micrometers. Smoothing of the relief (ionic polishing) can be observed when sputtering of the surface elements is not accompanied by its nonuniform erosion. Cones and pores can form on the surface depending on the conditions of plasma treatment [19].

Plasma spraying of various materials (metals [20], alloys, ceramics, organic materials, etc) has become widespread and has a series of advantages: the large range of materials that can be sprayed, the possibility of varying the spraying regimes, the high density, and the strength of adhesion of the coating to the base [17]. There are two main types of plasma spraying of metals: the metal being sprayed is delivered to the plasmatron in the form of wire or in the form of a powder [21].

Less widespread is the use of plasmochemical treatment of reinforcing fillers in order to produce a polymer coating identical or compatible with the polymeric matrix on their surface. This is of particular interest in the production of PCM based on polytetrafluoroethylene because of its chemical inertness and also of the high viscosity in the process [22].

A feature of plasmochemical spraying is the fact that the properties of the obtained coating do not depend on the properties of the material being treated. Moreover, plasma spraying gives the possibility of single-stage cleaning of the surface and production of a coating with various thicknesses and strength by varying the process conditions. In most cases the thickness of the coating is selected experimentally according to the optimum depth of diffusion of the polymeric matrix.

The effect of plasma treatment of the carbon fiber (CF) surface in oxygen on the mechanical properties of PCM with a polypropylene matrix was studied in [23]. It was established that treatment of the surface of the CF by a low-pressure plasma leads to an increase in the amount of oxygen-containing groups and in the surface energy and, as a consequence, improved physicochemical properties in the PCM (tensile strength, bending strength, etc.).

A promising direction of study in the plasma treatment of the CFM surface by spraying is the production of a coating in which the functional groups will form covalent chemical bonds with the matrix material as a result of plasma curing, thereby creating a high degree of adhesion at the matrix–filler interface [24].

There are published data about increasing the adhesion interaction in PCM samples based on carbon fibers of Russian manufacture and an epoxide binder. The effect is achieved by grafting a specific type of functional groups (mostly amino groups) onto the surface of the filler [25].

Treatment of the carbon fibers with hydrofluoric acid, as a result of which the amount of oxygen-containing carboxyl and hydroxyl functional groups is increased, was investigated in [26]. The efficiency of high-temperature and chemical oxidative treatments of the surface of carbon fibers based on a polyacrylonitrile precursor was compared [27]. It was shown that high-temperature treatment has a large effect on increasing the surface area. The tensile strength of the CF is also increased. Oxidation of the carbon fiber surface with nitric acid increases the adhesion interaction between the reinforcing filler and the high-molecular polyethylene matrix as a result of the formation of active functional groups on the surface of the fiber. The elasticity modulus of the PCM based on modified carbon filler is three times higher than for the carbon-filled plastic based on untreated carbon fibers.

One way of increasing the adhesion of the filler to the polymeric matrix is to clean the surface of the filler from random and manufacturing contaminants and also from adsorbed water and weakly bonded layers formed during heat treatment in the production of carbon fibers by ion-plasma purification [28].

The effect of electrochemical treatment at various intensities in softened water on the chemical and physicochemical properties of the surface of undressed CFs was investigated [13]. It was shown that active oxygen-containing groups are not formed on the surface of the fibers as a result of this treatment. In this case the defective surface layer of CF formed during carbonization, which is characterized by an increased content of sodium compounds and by a more amorphous structure than the bulk fiber, is removed.

Thus, during development of a method of modifying the surface of CFM by plasma treatment it is necessary to create conditions leading to optimum interaction for each matrix–filler pair over the interface.

In addition to the methods examined above there are also nontraditional methods of modifying the surface of CFMs, such as low-temperature ozonation, the action of oxygen and inert glow-discharge plasma, and high-frequency and superhigh-frequency discharges. An advantage of these methods is the absence of losses of carbon material as a result of burning and the possibility of predicting the properties of the modified carbon fiber (porosity, specific surface area, amount of oxygen-containing groups) [29].

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