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Use of Chemical and Electrochemical Treatment Methods in the Liquid-Phase Modification of Carbon Fiber and Fiberglass Surfaces in the Production of Construction Materials: A Review

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Abstract—In this review, the key methods used in the chemical and electrochemical functionalization of carbon fiber and fiberglass are considered. It is shown that treating fiberglass using these methods is not effective. For the carbon filler, the best results are observed at an optimal content of functional groups on its surface, and it must be dominated by amino and hydroxyl groups, which can be achieved using amino-containing modifiers. With modification methods discussed in the review, the quality of polymer composites can be improved due to enhanced interaction in a matrix–filler system.

Keywords: carbon fiber, fiberglass, thermoplastic binder, fiber functionalization, electrochemical coating

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INTRODUCTION

The requirements for the properties of construction and functional composite materials (CMs) have been steadily rising with the aim of improving the quality and technical–technological properties of products. Using fiberglass (FG) and carbon fiber (CF) enables us to reduce weight while increasing the strength properties of products, which is of interest for application in aviation and rocketry. In this regard, more stringent requirements on FG and CF are produced in terms of the reproducibility and robustness of their property indicators [1–7].

In recent years, the demand for thermoplastic-based CMs has grown. Such materials surpass thermoset CMs in terms of resistance to impact load, heat resistance, stability to environmental factors, crack and fire resistance, and chemical inertness [8–13].

The CM properties are determined by an interfacial interaction between their components, and ensuring that this interaction takes place in FG and CF is a complicated problem, especially if thermoplastic matrices are used due to a high viscosity of the binders. Modification methods in liquid media are the most interesting from the viewpoint of increasing the interfacial interaction. These are techniques for fiber surface functionalization by chemical means such as treatment in solutions, suspensions, and emulsions with functional additives. These include fiber surface finishing, coating, and acid etching [12–20]. These fiber functionalization techniques are widely used in industry and trial production. They enable high throughput production and do not call for complex technological equipment. They are also used in manufacturing special-purpose products for aerospace, transport, and construction industries.

In this review, we analyze the situation and problems of FG and CF modification based on etching and electrochemical methods.

1. MODIFYING THE FIBER SURFACE BY ACIDS AND BASES

Fiber surface functionalization by etching in acids, bases, or their derivatives is the most widely used liquid-based method for fiber surface modification. The surface becomes enriched with functional groups and/or develops roughness [21–23] that improves the interfacial interaction in CMs [9, 13, 21, 22] (Fig. 1). In study [24], the CF surface was wetted with poly(phthalazinone ether sulfone ketone) due to the the presence of oxygen groups resulting from oxidation. For CF based on poly(ether sulfone) matrix, the strength properties of these CMs were shown in improve from 80 to 350% [25] as the extent of oxidation was increased.

However, the CM properties are determined by ratio between different types of groups. The composition of functional groups on the fiber surface depends on the nature of the oxidizing agent and its concentration, as well as the temperature and duration of oxidative treatment [9]. The fiber surface can be treated with different reagents: nitric and sulfuric acids [21,

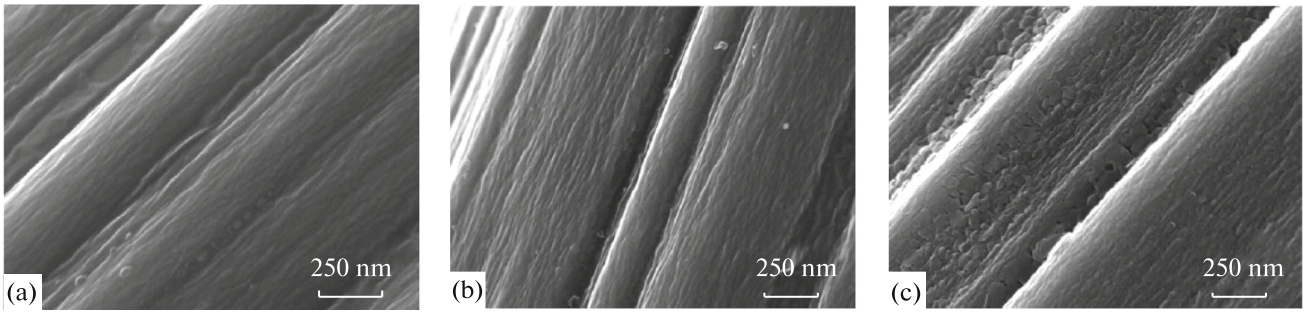

Fig. 1. CF (a) before and (b, c) after treatment in a H_2SO_4–HNO_3 mixture for (b) 15 min and (c) 4 h.

24–32], maleic anhydride [26], sodium hydroxide [21, 33], hydrochloric acid [34], hydrogen peroxide [32], and many more. Each type of oxidant gives rise to a specific range of functional groups on the fiber surface.

The nitric acid treatment of CF changes its surface substantially by enriching it with hydroxyl and carboxyl groups [29]. At the first stage, the CF surface develops functional groups whose maximum surface density reaches 2.4 group per 100 Å^2. A further increase in the number of functional groups on the CF surface is accompanied by an increase in its surface area, while its mass decreases and its mechanical strength declines [28]. Some studies showed that CF treatment with nitric acid resulted in a decrease in its surface area at the expense of a decrease in porosity and enrichment with carboxyl groups [21].

At longer exposure of CF to nitric acid, the composition and relative proportion of surface functional groups change. As a result, the fiber surface becomes enriched not only with oxygen-containing [28, 29] but also nitrogen-containing groups [22]. Treatment at 120°C for 5 h increased the strength properties of CMs based on CF and polyimide by 11–16%.

In etching CF in mixtures of concentrated nitric and sulfuric acids, the maximum functionalization was shown to occur when sulfuric acid was taken in excess. Processing CF with weak oxidants (compared to nitric acid), such as H_2O_2 and $(NH_4)_2S_2O_8$, did not alter the filler surface appreciably [32].

Treatment with bases changes the composition and structure of functional groups at the CF surface radically. Sodium hydroxide enriches CF with carbonyl and lactone groups [21]. Ammonium hydroxide increases the number of nitrogen-containing groups on the CF surface. As with acid treatment [31], the relative proportion of functional groups on the CF surface depends on the temperature and duration of processing [34, 35].

Since modifier residues on the CF surface may have a negative impact on interfacial interaction in the CM, they are removed, with the removal methods having little effect on the CM properties [27].

Unlike CF, acid and base treatment of FG results in the radical degradation of its properties. Acids do not alter the CF structure, while bases have a loosening (roughening) effect on it [36].

Thus, the treatment of CF with strong acids and bases leads to the formation of groups at its surface that cannot provide strong chemical bonding with binders. Weak chemical modifiers are incapable of providing the required level of CF surface functionalization. Treatment with ammonium hydroxide leads to the formation of amino groups at the CF surface that exhibit considerable affinity to many thermoplastic binders, suggesting that it can be recommended for use in CM fabrication. With FG, etching destroys its structure, meaning that it is undesirable to use this method.

2. ELECTROCHEMICAL MODIFICATION

In electrochemical modification, CF is used as an electrode and exposed simultaneously to an electrolyte and an electric field. This processing method increases the surface energy and roughness of CF and its affinity to CM components. One drawback is that such processing leads to the degradation of the strength of the fiber [9].

Acids, alkali, water-soluble salts, and other reagents are used as electrolytes [9, 13, 38–48]. Different functional groups and/or roughness can develop on the fiber surface depending on the electrolyte type and concentration and processing conditions [42, 43]. The variations of fiber surface properties follow a logarithmic law [34, 45–48].

Studies of the effects of electrochemical treatment on the CF properties showed that the type of electrolyte determines the composition and relative proportion of produced functional groups [44–46]. For instance, with electrochemical oxidation in the presence of ammonium carbonate, the relative proportions of functional groups produced on the fiber surface are as follows: carboxyl 30–40%, hydroxyl 10–18%, oxygen adsorbed by water 25%, and the rest are nitrogen-containing functionalities. Initially, the nitrogen on the fiber surface is present in amino groups, and the processing changes these to imides, amides, and other groups [45, 46].

In modifying CF, the use of potassium nitrate [48], potassium hydrogen phosphate [49], and sodium hydroxide solutions [50] yields predominantly carboxyl groups and their derivatives, which do not furnish a strong bonding to thermoplastic binders. To increase the relative proportion of amino and hydroxyl groups on the CF surface, it is subjected to electrochemical oxidation in acetonitrile in the presence of lithium, sodium, or potassium perchlorates, or tetraethyl- or tetrabutylammonium [51].

The other factors affecting the fiber surface properties are the duration of electrochemical treatment and the surface charge density. The fraction of oxygen-containing groups on the fiber surface increases with an increase in the charge density on the fiber [47, 52], while, with longer electrochemical treatment, the specific surface area grows, reaching as much as 1000 m^2/g [50], which diminishes the strength of material. For example, the optimal properties of the fiber surface are reached after 94 s of processing in a 0.2 mol/L ammonium oxalate at a current density of 0.6 mA/cm^2. The variation of properties of CMs based on this material also display a maximum [52]. Processing CF in a 5% sodium hydroxide solution for more than 60 s leads to an increase in the CM strength by 25–40% [50].

Technically, the extent of oxidation of fiber surface depends on the parameters of CF yarn (e.g., 3000, 6000, 12000, or 24000 filaments per yarn count) [50]. For high-density CF (i.e., at higher filament counts), diffusion processes tend to proceed slower and functionalization becomes inadequate.

The greatest compatibility between CF and most thermoplastic binders used in construction materials (e.g., polyether ether ketone, polyesterimide, and polysulfones) is achieved at the maximum extent of CF functionalization and the least surface area. For instance, in the electrochemical treatment of type *AS*1, *AS*4, and *XAS* carbon fiber, the XAS type, which has the highest number of surface functional groups, shows the highest compatibility with thermoplastic matrices [53].

Thus, the electrochemical treatment of CF enables us to produce the required range of functional groups that ensure a strong interfacial interaction. However, we must take into account that extended treatment leads to the destruction of the fiber surface. In addition, this treatment method has low productivity, which limits its application.

3. ELECTROCHEMICAL COATINGS

In contrast to electrochemical modification, electrochemical coating does not reduce the strength of the fiber. Electrochemical adsorption enhances the activity of the fiber surface by giving rise to micropores and functional groups [54–62]. This enables us to increase its affinity to a thermoplastic binder without any deterioration of its physicomechanical properties [9].

The modification of the fiber surface by applying coatings in an electric field was described in a number of works. The thickness and structure of coatings are determined, among other factors, by the solution concentration, the type of solvent, and the electric-field parameters [54–62]. This approach offers a number of advantages: a broad range of compounds can be used and their degree of polymerization on the fiber can be controlled; the thickness and homogeneity of modifying coating [13, 63–65] and its linkage to the fiber surface are also amenable to control. These include carbazole [52, 53, 56, 63–67], aniline [61, 71, 72], acrylates [60, 70–72, 74–76], pyrrole [44, 61, 77–79], acrylamides [68, 69, 73], and other compounds. Mixtures of monomers are used to fabricate copolymer coatings. Low productivity and limitations on the use of nonelectrolyte monomers are among the drawbacks of this method.

Adding –OH, $-NH_2$, and –COOH functional groups results in an increase in the surface area and the free energy of fiber surface, which ensures an improvement in its strength and interfacial interaction in CMs [80].

The formation of a coating proceeds in two stages. The first stage is determined by the reaction rate. The polymerization rate depends on the monomer concentration in solution [73, 77, 81], the potential difference between electrodes [77, 81], potential scan rate [54, 77], the solution pH, the electrolyte type and concentration [70, 74, 76], and the current density [73]. For example, as the current density is increased, the molecular weight of deposited coating decreases, while the quantity applied grows [73, 74]. With several monomers being used in combination, the structure and properties of the resulting copolymer coating depend on their ratios [59, 72, 75]. The second stage depends on the diffusion of the monomer toward a reaction site with an increase in the thickness of the coating [61, 72].

Typical coatings display an affinity to most matrices, but quite often a coating must be matched to a selected matrix. For instance, to improve the affinity between CF and the Vectra A900 liquid crystal polymer, its surface was coated with polyparaphenylene, polyphenylene oxide, and polyaniline. A CM fabricated using CF with a polyphenylene oxide coating displayed the highest shear strength (an increase by 14%) [64].

In some instances, polymer nanosuspensions and their solutions of low-molecular-weight compounds are used for fabricating the coating. For example, a polyetherimide coating with a thickness of 80–100 nm was fabricated on the fiber surface using a polymer emulsion with a particle size reaching 320 nm (Fig. 2), which improved the extent of fiber functionalization, while its heat resistance increased from 320 to 540°C [65].

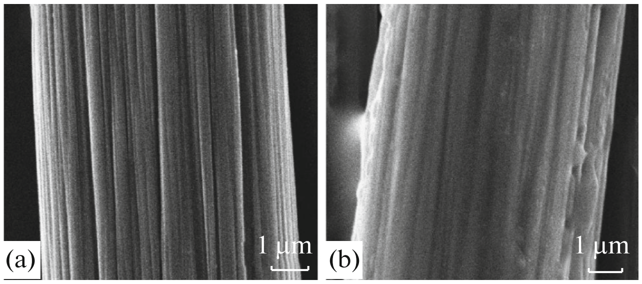

Fig. 2. CF (a) before and (b) after applying a polyimide coating [65].

With low-molecular-weight compounds [82], the linkage between monomers and the fiber is mediated by hydroxyl [83] or amino groups in acetonitrile or dimethylformamide solutions in the presence of lithium, sodium, or potassium perchlorates or tetraethyl- or tetrabutylammonium [47].

Grafting carbon nanotubes (CNTs) onto CF is another promising way to modify it. In [84], following ozone treatment, CNTs were grafted with polyethylenimine. The CNTs were then grafted onto CF through their polymer tails by using an electric current. Grafting CNTs onto CF directly by using electrophoresis was also reported [85], with ultrasonication making the distribution of CNTs across the fiber surface more uniform.

The grafting of modifying inorganic coatings, e.g., ceramic surfaces, is less common. Such coatings can consist of both a single layer and many layers. Their properties and structure are adjusted by changing current–voltage regime of the electrolysis process [86].

CONCLUSIONS

The methods of chemical and electrochemical modifications discussed here provide strong interfacial interaction between the components in CF materials. We highlight that, in order to ensure strong interfacial interaction in CMs, modifying agents capable of forming amino and hydroxyl groups on the fiber surface must be used due to their affinity to most thermoplastic matrixes. However, the greatest effect is achieved by grafting modifiers compatible with the polymer matrix onto the fiber surface by means of electrochemical reactions or electrolytic oxidation.

Acidic or alkaline etching of FG was shown to damage its surface, and electrochemical modification methods are not applicable due to the fiber's marked dielectric properties.

We note that the considered methods for electrochemical modification of the filler surface are mainly applicable to CF and can be used in the fabrication of individual special-purpose products. The fiber surface modification using acids and bases is more common when compared to the electrochemical methods and is broadly used in CF production.

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