PROBLEMS, DEVELOPMENTAL TRENDS, AND CURRENT PROBLEMS OF PHYSICAL CHEMISTRY

Strengthening of Fibrous Composites with Nanoparticles

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Abstract—Ways and mechanisms of strengthening polymer fiber composites by modifying matrices with nanoparticles and grafting the latter onto fibers are considered: chemical vapor deposition, electrophoretic and chemical interaction.

Keywords: polymer composites, matrices, fibers, nanoparticles

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INTRODUCTION

Polymer composites (PCs) reinforced with glass, carbon, organic and other fibers are widely used as structural materials in the aerospace, auto, and ship-building industries. The problem improving them nevertheless remains relevant, due to the constantly growing requirements for materials that technical progress imposes on them. A promising approach is using nanoparticles (NPs) to enhance fiber–matrix interface interaction [1]. It is essentially a way of combining nano- and fibrous composites that at first glance differ fundamentally: NPs first modify the properties of the matrix, which is then used to exploit the properties of the fibers.

The interface between the layers of a laminated PC is a weak link, since the interlayer region is devoid of fiber reinforcement and is destroyed by delamination and cracking of the matrix. Ways of strengthening the PC are therefore needed. One proven way of increasing the resistance of composites to damage and delamination is to raise the impact strength of the matrix, especially by introducing elasticizing agents [2]. Alternative bondless reinforcement approaches employ inline reinforcements (sometimes called micro-anchors), either through a portion of the laminate or throughout the thickness of the assembly to reduce the risk of delamination or detachment of the layers. The formation of a three-dimensional structure (3D) means that delamination or detachment requires the removal or destruction of such microreinforcements [3, 4]. NPs can be used to modify matrices [5] and create 3D structures by grafting them onto fibers [6].

MODIFYING MATRICES

Filling polymers with NPs gives them unique properties, even at low concentrations. For example, adding 5% graphene [7] or 2.5% carbon quantum dots [8] greatly improves impact toughness, and 3% montmorillonite (MMT) enhances the crack resistance of epoxy polymer [9]. A similar effect may be expected in PCs.

In [10], such NPs as colloidal silicon dioxide, carbon black, and carbon nanotubes (CNTs) were used to optimize the epoxy matrix of a composite reinforced with glass fibers. Their nanometer size allowed them to be used as reinforcing particles in glass-reinforced plastics produced by casting. An electric field was applied during curing to orient the nanofillers in the *z*-direction. The interlayer shear strength of composites modified with NPs was greatly enhanced by a maximum of 24.5% (CNT) and a minimum of 7.5% (carbon black). The fracture toughness grew by 42% upon adding 0.3 wt % CNT.

Pathak et al. [11] considered ways of strengthening CFRPs using graphene to modify their binder (Fig. 1). We can see that the maximum values of interlayer strength (ISS), bending strength (σ), and module (*E*) were at 0.3 wt %. According to the authors, the increased strength was probably due to a rise in the interface interaction between the fiber and the epoxy matrix through graphene oxide. However, we must consider its ability to improve the fracture toughness of the polymer [12]. The drop in efficiency upon an increase in the concentration of NPs is usually due to the aggregation of the latter.

A comparison of fiberglass plastics at the same applied cyclic load of 220 MPa showed [13] the fatigue life of specimens upon adding 0.1 wt % graphene and single-walled CNTs grew by three to twelve times,

Fig. 1. Dependences of the mechanical properties of CFRPs on the concentration of graphene oxide: (a) interface shear strength, (b) flexural strength, and (c) modulus. C is the concentration of graphene oxides in the epoxy binder. The data were taken from [11].

Fig. 2. Dependences of the transverse properties of (1–3) CFRPs and (4, 5) matrices on composition: (a) deformation curves, (b) modulus. (1) CFRPs with the addition of oriented CNTs, (2) undirected CNTs, and (3) with no addition; (4) matrix with the addition of CNTs; and (5) with no addition. F is load, ε is deformation. The data were taken from [14].

respectively. The high efficiency of the latter is obvious.

In [14], 1.5 wt % was added to a carbon fiber binder of multilayer CNTs oriented in the transverse direction using a magnetic field. This was facilitated by adding magnetic NPs that adhered to CNTs during curing, due to adsorption. This procedure considerably improved the transverse stiffness of CFRPs (Fig. 2).

Dvoretzskii et al. [15] suggested that when preparing a laminate with a nanomodified binder, CNTs are deposited mainly on the surface of bundles of carbon fabric and form NC layers $\sim 2 \mu\text{m}$ thick with CNT contents of ~ 0.5 – 1 wt % instead of the original 0.008%. The authors believed that the formation of such a structure of the composite from alternating unidirectional layers of microfibers and spacer mats made of NC could explain the increase in interlayer shear

strength, due to improvement of the elastic-strength characteristics of the binder layers in the gaps between fiber layers.

However, the data presented in [16] showed that the threshold of percolation in epoxy NPs lies in the range of 10^{-3} – 10^{-1} wt %. There is thus no need to allow the concentration of CNTs in the interface layer and prohibit the penetration of NPs into the interfiber space.

It was shown in [17] that the average increase in the strength and elastic modulus in bending of woven carbon composites upon adding 1.5 wt % carboxylated multilayer CNTs grew by 28 and 19%, respectively. Toughness also grew by 33%. Finite element modeling shows that fibers dominate in axial bending, while the matrix dominates in transverse bending.

The dispersion of 0.5 wt % fullerene in the CFRP matrix raised the tensile and compressive strengths by only 2–12%, but the interlayer fracture toughness grew by around 60% [18]. This effect was due to a small amount of fullerene (0.1–1 wt %) being able to improve the fracture toughness of the epoxy matrix itself.

MMT has the same effect [19]. The interlayer fracture toughness grows by 85% when 4% NPs are added to the epoxy resin, while the flexural strength is enhanced by 38% upon adding 2% MMT.

The problem of synergism was discussed in [20] using the example of carbon nanofibers (CNFs). Figure 3 shows the curves of resistance to crack growth under a quasi-static load for laminates reinforced and unreinforced throughout their thickness with 0.82 vol % CNFs and/or 0.5 vol % z -pins.

We can see that z -pins prevent CFRP delamination more effectively than CNFs. However, their joint impact is more effective. At the first stage, a frame is formed by z -pins (the growing portions of curves 3 and 4). The inhibitory effect of CNFs (curve 4) is apparent only at the stage of defining curve 3. It is curious that in this area of crack propagation, CNFs by themselves are equally ineffective (curve 2). It should be noted that the simultaneous use of CNFs and z -pins provide a much greater increase in fracture toughness. CNFs are effective for increasing interlayer fracture toughness upon quasi-static loading due to intrinsic (i.e., doubling or branching of cracks and growth of voids in epoxy resin) and external (i.e., crack bridging and pulling of CNFs) mechanisms. z -Pins cause substantial external strengthening, primarily through crack bridging.

A more efficient use of NPs than modifying matrices is processing fibers. For example, increases in interface shear strength of 45.2 and 10.14% were achieved for composites based on fibers modified with CNTs and composites based on a matrix reinforced with CNTs, respectively [21]. The effect of nanoclay reinforcement, localized at a fiber/matrix interface and distributed over a matrix and along crack paths, was investigated in numerical experiments in [22], along with mechanisms of damage and fatigue characteristics. It was found that in the first case, composites provide a longer service life and better resistance to damage than composites with NPs distributed in their matrices.

FIBER TREATMENT

Surface treatment greatly affects the roughness, surface energy, and reactive chemistry of fibers. A number of treatments have been developed.

Fig. 3. Curves of resistance to crack growth under a quasi-static load for laminates (1) not reinforced, and reinforced through their thickness while containing (2) CNFs, (3) z -pins, and (4) UNV + z -pins. E is the energy of interlayer destruction, and l is the length of delamination. The data were taken from [20].

Chemical vapor deposition (CVD) is a grafting out approach that at heavy coatings promotes the perpendicular alignment of CNTs on the surface of carbon fibers [23]. A great disadvantage of this technique is that the deposition of catalysts and exposing the fibers to high temperatures usually deteriorates their mechanical properties.

Electrophoretic grafting ensures the uniform deposition of NPs at a high rate. However, we must consider the need for such electrically conductive elements in the system as carbon fibers. The orientation of CNTs differs from the one achieved with CVD, as they mainly lie on the fiber surfaces [24].

Activation of both fibers and NPs is required for chemical grafting. For example, grafting CNTs onto carbon fiber demands carboxylation of the former, while the latter must be functionalized with amine, carboxyl, or hydroxyl groups [25].

A special place is held by modifying the surface layers of fibers by including NPs, but without grafting.

CVD

In [26], multilayer CNTs were synthesized on carbon fibers using CVD. The orientation and lengths (16.6–108.6 μm) of CNTs were determined from the silanization of the fiber surface and the growth time (30–120 min). With an increase in the latter, the specific surface area grew from 22.7 to 60.2 m^2/g . This

Fig. 4. Flexural properties of composites: (a) deformation curves, (b) strength and elastic modulus. Composite (1) without addition and with the addition of (2) nonfunctionalized and (3–6) functionalized OG; concentration, wt %: (1) 0, (2, 4) 0.5, (3) 0.1, (5) 1.0, and (6) 1.5. σ is stress, and ϵ is strain. The data were taken from [33].

increased the wettability of the fiber with the binder. At the same time, the tensile strength fell constantly. With growth for 120 min, the latter fell by around 33.5% of its initial value. A substantial increase in interface shear strength up to 175% was achieved for aligned CNTs 47.2 μm long (47.8 MPa), compared to the original fibers (17.4 MPa). However, fibers with grafted CNTs 63.5 and 108.6 μm long showed a slight drop in interface strength, due possibly to the asymmetry of the coating.

Kim et al. [27] found that the tensile strength of carbon fibers grows by more than 14% as a result of catalytic (Ni) growth of CNTs on their surface. In this case, the interface shear strength is enhanced considerably (~470%). The use of a Ni–Fe bimetallic catalyst was key in the synthesis of CNTs at a relatively low (500°C) temperature [28]. Under these conditions, diffusion of the catalyst into carbon fibers during CVD was inhibited, promoting uniform growth of CNTs only on the surface and minimizing internal structural changes in the fibers.

Electrophoresis

Song et al. [29] obtained a composite with a carbon matrix, and electrophoresis was used to apply CNTs to carbon fibers. The dispersion of CNTs on the fiber surface was uniform, and they penetrated into the bundle well. The grafted CNTs were randomly oriented and lay in a plane parallel to the fiber axis. After grafting with CNTs for 4, 8, 15, 30, and 60 s, the tensile strength of the bundle grew from 380 to 433, 455, 508, 567, and 652 MPa, respectively. In contrast, the tensile strength of composites reinforced with CNTs grown via CVD was only 268 MPa.

With CNTs incorporated into CFRPs in the same way, the interface shear strength grew by 124% [30]. Fractographic analysis revealed that in the structure of the hybrid surface, the fiber pulling length and the size of the cracks between the fibers and the matrix were reduced considerably, indicating an improvement in stress transfer and an increase in interface shear strength.

During the production process, industrial carbon fibers after such chemical surface treatments as electrolytic oxidation, acid washing, and exposure to plasma are always coated with a thin film of a sizing agent that is usually a solution or emulsion composed of polymer components and auxiliary substances. Chemical surface treatment can increase the number of active functional groups on a fiber's surface, and sizing is mainly aimed at protecting fibers from damage and increasing the compatibility between the fibers and the matrix. The sizing agent changes the surface properties of carbon fibers, along with their wettability and chemical interaction with epoxy matrices [31].

In [32], sizing was done after electrophoretic deposition. The CNT layers were protected by a polyphthalazinone ether ketone film. Introduction of CNTs into a composite reinforced with carbon fiber raised the interlayer shear strength by 35.6%.

To stimulate the dispersion of graphene oxide (GO) NPs in an epoxy matrix and improve the interface adhesion between the two, in [33] the NPs were chemically modified with cyanuric acid and diethylenetriamine. The functionalized GO was evenly distributed over the fiber surface. As a result, a considerable increase (104.2 and 100.2%) was obtained in the

Fig. 5. Change in real module $E'(1, 2)$ and $\tan \delta (I', 2')$, depending on temperature for composites reinforced with $(1, I')$ untreated and $(2, 2')$ modified carbon fibers. The data were taken from [36].

interface and interlayer shear strength, modulus, and flexural strength (Fig. 4).

As can be seen, the optimum concentration was 1.0 wt % functionalized exhaust gas in CFRP bonding layers. The ultimate deformation was in this case reduced (Fig. 4a, curve 5).

Zhang et al. [34] studied the deposition of CNTs on surfaces of glass fibers that included electrophoretic deposition and the traditional technique of dip coating. The first of these gave a more uniform and continuous distribution of nanotubes on the fiberglass surface than the second. When the fibers were mixed with epoxy resin, CNTs did not noticeably migrate from the glass fiber surface, due to entanglement of the nanotubes. As a result, the interface shear resistance of single fiber composites grew by more than 30%.

In [35], it was argued that electrophoretic deposition is a promising way of applying single-walled CNTs to nonconducting glass fabrics and making composites with large loads of NPs, expanding the possibilities of using composites made of fiberglass. Because of its insulating properties, the fiberglass was fixed on a steel plate and used as a negative electrode so that positively charged NPs could migrate to it. Another steel plate was used as the positive electrode.

Chemical Grafting

The grafting of NPs onto carbon fibers is limited by the low reactivity of graphite carbon. There is thus a need for new ways of injecting with universal functional groups (e.g., carboxylic acids that can interact with many organic and inorganic materials).

Zhao and Huang [36] functionalized silsesquioxane NPs in order to change the surface energy and increase the wettability or surface roughness of carbon fibers to improve their bond with a matrix. Fibers oxidized with nitric acid were first treated with ethylenediamine, followed by the amino groups reaction with NPs. As a result of the functionalization of carbon fibers, the interface strength grew from 46.8 to 80.6 MPa. The effect NP grafting had on the interface properties of composites upon dynamic loading is seen in Fig. 5, which shows the change in the actual modulus (E') and $\tan \delta$, depending on temperature for composites reinforced with untreated and modified carbon fibers. As is seen, E' rose from 56 to 65 GPa below T_g and from 2.9 to 4.1 GPa above T_g . The glass transition temperature of composites with untreated fibers was $\sim 139^\circ\text{C}$. T_g for modified composites was $\sim 152^\circ\text{C}$.

The high crystallinity of aramid fibers makes their surfaces chemically inert and microscopically smooth. Their adhesion to most matrices is therefore poor, and surface treatment is usually required to enhance interaction [37]. One way of doing so is the grafting of such NPs as CNTs [38, 39], GO [40], TiO_2 [41], ZnO [42].

Chen et al. [38] proposed introducing amino groups with which multilayer CNTs functionalized with COCl reacted. Kevlar fibers were treated with a solution consisting of hexamethylene diisocyanate, 1,4-diazabicyclooctane, and toluene. After grafting with CNTs, the interface strength of the composite rose from 37.5 to 49.1 MPa.

To create a layer containing amino groups on the surfaces of Kevlar fibers, allylamine and octadiene (molar ratio 3 : 1) were copolymerized in [43] using plasma. The functionalized fibers were then treated with a 10% GO solution at a pH of 6 or 9. The best

result was obtained in the second case: the average tensile strength of the modified fibers grew by ~8%, and the interface shear strength increased by 44.7%.

Surface Layer Modification

In [43], a CNT/polyacrylonitrile solution was sprayed on the surface of woven carbon fiber materials, and the CNTs were fixed in the surface layer of the fibers via heat treatment at 300°C. Composites with CNTs were fabricated by vacuum assisted resin transfer molding (VARTM) [44]. CFRPs with CNTs showed a 22% increase in tensile strength, relative to the original composite.

Rafiee et al. [45–47] developed a procedure for manufacturing fiberglass plastics using NPs with simultaneous reinforcement of the matrix and fibers by VARTM. NPs were added to the composites in two steps: one for sizing the fabric, and the other for strengthening the matrix. Glass mats were sized with a solution of a given composition using a spray gun inside a fume hood in order to ensure complete evaporation of the solvent. The use of NPs (CNTs, graphene, GO) has led to considerable improvement in the mechanical [45], thermophysical [46], and fatigue [47] properties of fiberglass.

CONCLUSIONS

This work does not claim to be an exhaustive presentation or analysis of all the results published to date on using NPs to reinforce fiber composites, especially the review by Mirabedini et al. in which CFRPs with graphene were considered for these purposes [48]. The aim of this work was to demonstrate the synergy of combining nano- and fiber composites. It was emphasized that NP grafting onto fibers is more effective than matrix modification.

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