# Effect of Surface Modification on the Tribological Properties of Carbon Fiber/Phenolic Resin Matrix Composites (Postprint)

**Authors:** Ma Xiaolong, Ao Yuhui, Xiao Linghan, Dong Jinglong, Zhang Huixuan

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## Abstract

Surface modification of PAN-based carbon fiber (3K) was performed using concentrated nitric acid and silane coupling agent (hk550) to prepare composites with phenolic resin as the matrix. The structure and surface characteristics of the carbon fibers were investigated using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). The tensile strength of the composites was measured using a tensile testing machine, and the friction properties were measured using a micro-nano mechanical comprehensive testing system (UNMT-1). The results show that treatment with concentrated nitric acid and coupling agent can increase the surface roughness and chemical activity of carbon fibers, improve the interfacial bonding between carbon fibers and phenolic resin matrix, resulting in increased tensile strength and decreased wear rate of the composites.

## Full Text

## Preamble

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**Effect of Surface Modification of Carbon Fiber on Friction Properties of Carbon Fiber/Phenolic Resin Matrix Composites**

MA Xiaolong[1], AO Yuhui[1,3], XIAO Linghan[1,3], DONG Jinglong[1], ZHANG Huixuan[1,2]

[1]College of Chemistry and Life Science, Changchun University of Technology, Changchun 130012, China

[2]Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
[3]Jilin Province Key Laboratory of Carbon Fiber Development and Application, Changchun 130012, China

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**Corresponding author: AO Yuhui, Tel: (0431)85716471, E-mail: aoyuhui69@163.com**

## Abstract

Polyacrylonitrile (PAN)-based carbon fiber (3K) was surface-modified using concentrated nitric acid (65–68%) and silane coupling agent (hk550). The structural and surface characteristics of the modified fibers were investigated by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). Carbon fiber-reinforced phenolic matrix composites were subsequently prepared. The tensile strength and friction performance of the composites were examined using a tensile testing machine and an integrated micro-nano-mechanical test system (UNMT-1), respectively. The results demonstrated that surface modification with nitric acid and hk550 enhanced the surface chemical activity and roughness of the fibers, resulting in improved interfacial adhesion between the carbon fibers and phenolic resin matrix. Consequently, the composites exhibited increased tensile strength and reduced wear rate.

**Keywords:** composites, coupling agent, surface modification, carbon fiber, wear rate

## Introduction

Carbon fibers exhibit excellent properties including high temperature resistance, wear resistance, electrical and thermal conductivity, and corrosion resistance. Carbon fiber-reinforced composites have been widely used as friction materials due to their lower friction coefficient and self-lubricating properties compared to steel. Structurally, composites consist of three phases: matrix, reinforcement, and interface. The interface phase plays a critical role in composite performance, serving as both the connecting link between reinforcement and matrix and the medium for stress transfer. However, untreated carbon fiber surfaces are chemically inert, resulting in poor resin wettability and weak interfacial bonding, which adversely affects the friction performance of the material. Dur-

ing friction, carbon fibers easily detach from the resin matrix, causing large fluctuations in the friction coefficient and significantly reducing friction stability. Therefore, enhancing the interfacial bonding strength is key to preparing high-performance friction composites.

Surface treatment of carbon fibers to increase specific surface area and introduce active functional groups is essential for improving fiber-matrix interfacial adhesion. Numerous methods have been developed to modify carbon fiber surfaces, including chemical oxidation, electrochemical treatment, and plasma processing. Compared to other techniques, concentrated nitric acid oxidation requires simple equipment and can be performed under ordinary conditions. Subsequent treatment with a coupling agent after oxidation effectively increases surface activity and enables chemical bonding with the resin matrix, thereby improving interfacial adhesion.

In this study, PAN-based carbon fibers were surface-treated with concentrated nitric acid and hk550 silane coupling agent. SEM, FTIR, and XPS were employed to analyze the morphology and active functional groups on the fiber surface. Carbon fiber/phenolic resin composite specimens were prepared using differently treated fibers, and their fracture and wear track morphologies were observed by SEM. Friction tests were conducted using the UNMT-1 system to evaluate the friction performance of various specimens.

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## 1. Experimental Methods

### 1.1 Composite Preparation

An excess of phenol was placed in a 500 ml four-neck flask equipped with a stirrer and condenser, then heated to 80–100°C in a WC/09-05 constant temperature water bath. Formaldehyde solution (37%), catalyst oxalic acid (99.5%), and zinc acetate were sequentially added, adjusting the pH to <3. Cashew nut shell oil was subsequently introduced, and the reaction proceeded for 4 hours. After completion, water and free phenol were removed by vacuum distillation. Hexamethylenetetramine (6 wt% of resin) was added as a curing agent to the prepared phenolic resin, followed by mixing with ethanol to form a phenolic resin solution for use as a prepreg.

PAN-based carbon fiber (3K) was woven into carbon fiber cloth, which was soaked in acetone for 24 hours to remove sizing agents and impurities, then ultrasonically cleaned with distilled water for 0.5 hours and dried at 100°C. The carbon fiber cloth was immersed in concentrated nitric acid for 0.5, 1.5, and 3 hours, designated as CF-0.5 h, CF-1.5 h, and CF-3 h, respectively. After oxidation, the fibers were washed with distilled water until neutral and dried. The oxidized fiber cloths were then soaked in a pre-prepared 2% hk550 silane coupling agent solution for 3 hours, designated as CF-A-0.5 h, CF-A-1.5 h, and CF-A-3 h, followed by oven drying at 110°C to cure the silane.

The prepared carbon fiber cloths were impregnated with the phenolic resin prepreg, then placed in an oven to evaporate the solvent. This process was repeated to ensure uniform and thorough impregnation of the resin into the fiber cloth, forming composite coatings. The impregnated cloths were held in a vacuum oven at 40°C for 12 hours, then cured in a mold at 170°C and 5 MPa for 20 minutes to obtain composite specimens designated as CFRP-0.5 h, CFRP-1.5 h, CFRP-3 h, CFRP-A-0.5 h, CFRP-A-1.5 h, and CFRP-A-3 h.

### 1.2 Performance Testing

A JSM-5600 scanning electron microscope operating at 25 kV accelerating voltage was used to observe carbon fiber surfaces, composite fracture surfaces, and wear surface morphologies. FTIR analysis of carbon fibers treated with nitric acid for different durations was performed using the KBr pellet method over a scanning range of 500–4000 $cm^{-1}$. XPS analysis of fiber surfaces was conducted using an ESCALAB 250 spectrometer with Al K$\alpha$ X-ray source. Tensile properties were measured using a 3365 universal material testing machine. Friction performance was evaluated using the UNMT-1 integrated micro-nano-mechanical test system under a normal load of 10 N.

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## 2. Results and Discussion

### 2.1 Carbon Fiber Surface Morphology Analysis

[Figure 1: see original paper] presents SEM images of carbon fibers: (a) CF, (b) CF-0.5 h, (c) CF-3 h, (d) CF-A-0.5 h, (e) CF-A-1.5 h, and (f) CF-A-3 h. The untreated carbon fiber surface appears smooth with few grooves formed during manufacturing (Fig. 1a). After 3 hours of nitric acid oxidation, distinct grooves become visible on the fiber surface (Fig. 1c). With shorter oxidation times, less coupling agent adheres to the fiber surface (Fig. 1d). As oxidation time increases, the coupling agent more effectively coats the fiber surface (Fig. 1f), indicating that 3 hours of nitric acid oxidation enables hk550 coupling agent to effectively encapsulate the carbon fibers.

### 2.2 FTIR Spectroscopy Analysis

[Figure 2: see original paper] shows the FTIR spectra of carbon fibers. Fibers treated with nitric acid were washed to neutral pH with distilled water and dried before testing. The spectra reveal changes in surface functional groups before and after nitric acid treatment. As oxidation time increases, characteristic absorption peaks for -OH (3446 $cm^{-1}$) and C=O (1749 $cm^{-1}$) become clearly observable in the CF-3h spectrum. However, for fibers treated for shorter durations (CF-0.5 h and CF-1.5 h), these peaks are less pronounced. This indicates that 3 hours of nitric acid treatment effectively increases the concentration of active functional groups on the carbon fiber surface.

### 2.3 XPS Analysis

The XPS spectra in [Figure 3: see original paper] show characteristic peaks for carbon (C1s, 285 eV) and oxygen (O1s, 530 eV), the primary elements in carbon fibers. Elemental analysis of fiber surfaces after different treatments is summarized in . With increasing nitric acid oxidation time, carbon content gradually decreases while oxygen content and the O/C ratio increase due to formation of oxygen-containing groups on the fiber surface. After 3 hours of oxidation, the surface oxygen content increased by 52.7% compared to untreated fibers.

In [Figure 4: see original paper], the C1s region (280–295 eV) shows a broad carbon peak that can be deconvoluted into three Gaussian components: C-C (284.6 eV), C-O-C (286 eV), and O-C=O (288 eV). The relative contents of these functional groups for different samples are presented in . As oxidation time increases, the C-C bond content decreases while C-O-C and O-C=O bonds increase, promoting chemical bonding between the carbon fibers and coupling agent. As illustrated in [Figure 5: see original paper], the coupling agent first hydrolyzes to form silanol groups, which then form hydrogen bonds with oxygen on the carbon fiber surface and subsequently convert to covalent bonds. The remaining silanol groups react with the phenolic resin matrix, enhancing interfacial bonding strength.

### 2.4 Fracture Morphology Analysis

[Figure 6: see original paper] shows SEM images of fracture surfaces for specimens CFRP-0.5 h, CFRP-1.5 h, CFRP-3 h, CFRP-A-0.5 h, CFRP-A-1.5 h, and CFRP-A-3 h. Figures 6a–c reveal that fibers treated only with nitric acid show minimal resin adhesion, numerous voids, and extensive fiber pull-out. This indicates that during fracture, matrix cracks propagate along the interface, with insufficient load transfer from matrix to fibers, resulting in interfacial failure as the dominant failure mode. In contrast, Figures 6d–f show fibers coated with coupling agent exhibit greater resin adhesion, less fiber pull-out, fewer voids, and smoother fracture surfaces. This suggests that matrix cracks propagate only a short distance along the interface, with fracture occurring through combined transverse failure of both resin matrix and carbon fibers. The matrix can effectively transfer load to the fibers, demonstrating improved interfacial bonding between coupling agent-treated carbon fibers and the phenolic resin matrix.

### 2.5 Tensile Strength

[Figure 7: see original paper] presents the tensile strengths of various composites. Composites prepared with carbon fibers treated only by nitric acid oxidation exhibit relatively low tensile strength. In contrast, composites prepared with fibers treated by both nitric acid and coupling agent show significantly improved tensile strength due to chemical bonding at the interface and enhanced interfacial

adhesion.

### 2.6 Friction Performance

[Figure 8: see original paper] illustrates the wear process schematically. Before wear, the material surface is smooth with carbon fibers arranged in an orderly manner. During wear, the counterface moves laterally, subjecting carbon fibers to frictional forces that can cause them to detach from the phenolic resin matrix. Strong fiber-matrix interfacial bonding reduces fiber detachment through encapsulation by the resin matrix.

SEM images of worn surfaces are shown in [Figure 9: see original paper]. Figure 9a depicts the pre-wear surface morphology, which is smooth and flat. Figures 9b and 9c show worn surfaces of CFRP-0.5 h and CFRP-A-3 h, respectively, with magnified views in Figures 9d and 9e. The CFRP-0.5 h specimen exhibits severe wear, with fibers stripped and fragmented from the matrix, generating numerous fiber debris on the friction surface (Fig. 9b). In contrast, the CFRP-A-3 h specimen shows a relatively smooth worn surface, with carbon fibers remaining encapsulated by the resin matrix and only minimal fiber detachment (Fig. 9c). These results demonstrate that combined nitric acid and coupling agent treatment effectively mitigates fiber stripping during the wear process.

[Figure 10: see original paper] shows the dynamic friction coefficients of composites CFRP-0.5 h, CFRP-1.5 h, CFRP-3 h, CFRP-A-0.5 h, CFRP-A-1.5 h, and CFRP-A-3 h under a 10 N load and 5 mm/s sliding speed. Each data point represents the instantaneous friction coefficient, which fluctuates over time with varying amplitudes depending on the surface morphology and debris quantity. The average friction coefficients are presented in [Figure 11: see original paper]. During friction, carbon fibers detach from the matrix and scatter on the wear surface, acting as a lubricant. Composites with poor interfacial bonding (CFRP-0.5 h, CFRP-1.5 h, CFRP-3 h) exhibit more scattered carbon fibers, resulting in lower friction coefficients. When interfacial bonding is strong, carbon fibers remain encapsulated by the phenolic resin, and the friction surface contains more resin. Since pure phenolic resin has a higher friction coefficient than carbon fibers, composites CFRP-A-0.5 h, CFRP-A-1.5 h, and CFRP-A-3 h show higher friction coefficients.

The mass wear rate was calculated using the formula $w = \Delta m/(N \cdot T \cdot V)$, where $\Delta m$ is the mass loss, N is the normal load (10 N), T is the wear time (3 h), and V is the sliding speed (5 mm/s). The calculated wear rates are shown in [Figure 11: see original paper]. Composites prepared with nitric acid treatment alone exhibit high wear rates, while those treated with coupling agent show better interfacial bonding, reduced fiber detachment during friction, and a 39.7% reduction in wear rate, demonstrating improved wear resistance.

## 3. Conclusions

As nitric acid oxidation time increases, surface grooves on carbon fibers deepen and the concentration of active functional groups increases. After 3 hours of oxidation, the surface oxygen content increases by 52.7% compared to untreated fibers. The hk550 coupling agent effectively adheres to the carbon fiber surface, improving interfacial bonding with the phenolic resin.

Surface modification of carbon fibers using concentrated nitric acid and silane coupling agent hk550 is an effective method to enhance composite interfacial adhesion. The resulting composites exhibit increased tensile strength, higher friction coefficient, and lower wear rate. The optimal treatment of 3 hours nitric acid oxidation followed by silane coupling agent yields a composite with tensile strength of 85.79 MPa, friction coefficient of 0.43, and wear rate of 3.056 $\times 10^{-6}$ g/(N $\cdot$ m).

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*Note: Figure translations are in progress. See original paper for figures.*