

Surface modification of hybrid-fabric composites with amino silane and polydopamine for enhanced mechanical and tribological behaviors

Junya Yuan^{a,b}, Zhaozhu Zhang^{a,*}, Mingming Yang^{a,b}, Fang Guo^{a,*}, Xuehu Men^c, Weimin Liu^a

^a State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Tianshui Road 18th, Lanzhou 730000, PR China

^b University of Chinese Academy of Sciences, Beijing 100049, PR China

^c School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, PR China

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ABSTRACT

The poor interfacial adhesion between hybrid Nomex/PTFE fabric surfaces and polymer materials caused intrinsically by chemical inertness of Nomex and PTFE fibers severely inhibits the further application of hybrid Nomex/PTFE fabric composites. In this study, amino functionalized silane layer (KH550) was immobilized covalently onto hybrid Nomex/PTFE fabric surfaces using bio-inspired polydopamine (PDA) as a bridge to introduce substantial amino groups onto the fabric surfaces. The successful grafting of KH550 on the PDA-coated hybrid fabric surfaces was confirmed by FTIR, XPS and SEM. As a result, the tensile and bonding strength of the amino-functionalized fabric composite were obviously superior to those of the non-treated and polydopamine-coated only, which indicated that the introduction of amino functional layer brought about considerable improvement in interfacial compatibility of hybrid Nomex/PTFE fabric with the phenolic resin matrix. Besides, wear tests also showed the modified fabric composite exhibited the optimal tribological properties under varied test conditions. Most significantly, the strategy presented in this study is substrate-independent along with considerable flexibility to introduce various functional groups, suggesting promising applications for easily improving the interfacial compatibility of reinforcements with polymer matrix.

1. Introduction

Fabric reinforcements for polymer matrix composites have been extensively adopted in the high-performance manufacture fields, such as automotive, shipbuilding, aviation, aerospace, military and sports [1–3]. Among various fabric materials investigated, hybrid Nomex/PTFE fabric is primarily preferred for self-lubrication liner materials usage, as it combines the high specific-strength of Nomex fiber and excellent self-lubrication of PTFE fiber [4]. However, the inherent chemical inertness, excessive smoothness and low surface energy characteristics of Nomex and PTFE fibers result in poor adhesion properties and therefore largely limit the further application of hybrid Nomex/PTFE fabric composites.

One means to overcome this limitation is to modify the surfaces of hybrid Nomex/PTFE fabric to improve fabric/resin interfacial adhesion, which generally leads to concomitant increase in mechanical and tribological properties of the polymer composites. So far, considerable methods have been utilized to modify the surfaces of aramid fibers, including ultrasonic treatment [5], ultraviolet radiation [6], plasma treatment [7], γ -ray irradiation [8], chemical etching and grafting [9–

11]. Although most aforementioned fiber treatment methods can endorse the increases in aramid fibers/matrix adhesion to enhance composites utility, these approaches are generally restricted by high cost instruments, drastic reaction conditions and loss in fiber strength. In addition, PTFE fiber is well-known for its excessive chemical inertness and the corresponding modified method has rarely been reported. Thus, the exploration of simple and mild modification methods for both Nomex and PTFE fibers to achieve the satisfactory interfacial properties without sacrificing the fibers strength is still a challenging topic.

Surface modification using silane coupling agents is a simple and cost-effective method with considerable flexibility to introduce various functional groups [12–14]. In addition, the methods do not induce any surface flaw onto the modified fiber surfaces and, consequently, retain the mechanical strength properties of fibers after the process of surface modification. However, the lack of reactive groups on hybrid Nomex/PTFE fabric surfaces absolutely restricts the application of silane coupling agents to obtain desired functional groups. Recently, dopamine (3,4-dihydroxy-phenylalanine), an adhesive protein secreted by marine mussels, has drawn more and more attention and interest

* Corresponding authors.

E-mail addresses: zzzhang@licp.cas.cn (Z. Zhang), guofang@licp.cas.cn (F. Guo).

owing to its unique adhesion characteristics that can polymerize and adhere to almost any substrates under a quite mild and facile condition [15–18]. What's more, the consequent polydopamine (PDA) coating containing reactive groups can act as a versatile secondary platform for further functionality to satisfy various applications [19,20]. Therefore, the combination of bio-inspired dopamine polymerization and silane coupling agents grafting is an amazing surface modification strategy, as it can introduce various functional groups onto almost any substrates. Furthermore, the whole modification process is implemented under mild conditions with no fastidious preparation or expensive equipment, simultaneously preserving the strength of modified reinforcements. Thus, this method is expected to pave the way for easily improving the interfacial compatibility of reinforcements with polymer matrix.

Herein, amino-functionalized hybrid Nomex/PTFE fabric was synthesized via the combination of dopamine oxidative self-polymerization and amino functionalized silane grafting to enhance the interfacial adhesion with phenolic resin matrix. In this procedure, a thin adherent PDA film was firstly adhered to the hybrid Nomex/PTFE fabric surface via the oxygen-induced polymerization of dopamine. Subsequently, γ -aminopropyltriethoxysilane (KH550) was immobilized covalently onto the resultant PDA coating fabric by coupling with PDA reactive groups. And the obtained amino groups were further responsible for chemical interaction with the phenolic matrix [21–23]. The general procedure for preparing amino functionalized hybrid fabric was shown in Scheme 1. The interfacial adhesion properties of hybrid-fabric phenolic composites were evaluated by tensile and peeling tests, and the results showed the tensile and bonding strength of the modified fabric composite achieved 35% and 45.6% improvement, respectively, compared with the pristine fabric composite. Furthermore, the tribological behaviors of the hybrid-fabric composites were systematically investigated under various applied load and sliding speed. It was found that the modified fabric composite presented outstanding anti-wear and load-carrying capacity.

2. Experimental section

2.1. Materials

The hybrid Nomex/PTFE fabric, which was woven out of Nomex fibers and PTFE fibers provided by DuPont Plant, was satin-weave at the volume fraction of Nomex to PTFE: 3:1. The phenolic adhesive resin (resol) was purchased from Xing-guang Chemical Reagent Plant, China. Dopamine hydrochloride and Tris(hydroxymethyl)amino-methane (TRIS, 99%) were separately purchased from Sigma Aldrich and Kermel Chemical Reagent Plant (China). (3-Aminopropyl)triethoxysilane (KH550) was obtained from Alfa Aesar (China) Chemicals Co. Ltd. The rest chemicals were all of analytical grade and used as received.

2.2. Surface modification of hybrid Nomex/PTFE fabric by PDA coating and amino grafting

The hybrid Nomex/PTFE fabric was cleaned in Soxhlet extractor using petroleum ether and ethanol, respectively, and oven-dried at 50 °C. The hybrid fabric was then immersed into dopamine solution (2 mg/ml in 10 mM Tris buffer solution, pH 8.5) at ambient temperature for 20 h under continuous stirring. The treated hybrid fabric was repeatedly rinsed with deionized water to remove unreacted monomers and dried at 80 °C overnight to obtain the hybrid fabric-PDA. A possible reaction mechanism for the self-polymerization of dopamine was presented in Fig. S1. Subsequently, the hybrid fabric-PDA was added to the ethanol solution of KH550 (2 wt%, pH 9–10), which was prepared by adding KH550 in ethanol solution and subsequently thorough hydrolyzing or partial crosslinking at ambient temperature for 12 h under uninterrupted stirring, for 30 min under mild stirring. After that the fabric was thoroughly rinsed with ethanol to remove the physically adsorbed KH550 and dried to constant weight under vacuum oven to acquire hybrid fabric-PDA-KH550. The possible chemical reactions in this procedure are described in Scheme 2.

2.3. Preparation of hybrid fabric reinforced phenolic composites

The pristine hybrid fabric, hybrid fabric-PDA and hybrid fabric-PDA-KH550 were immersed into the phenolic resin adhesive solution. Repetitive immersion and drying of the hybrid Nomex/PTFE fabrics were performed until the weight fraction of hybrid fabrics reached to 70–75% in the composites. Subsequently, the obtained prepregs were affixed onto the AISI-1045 steel disks using phenolic resin as adhesive and then solidified at 180 °C for 2 h under 0.2 MPa.

2.4. Tensile and bonding strength test

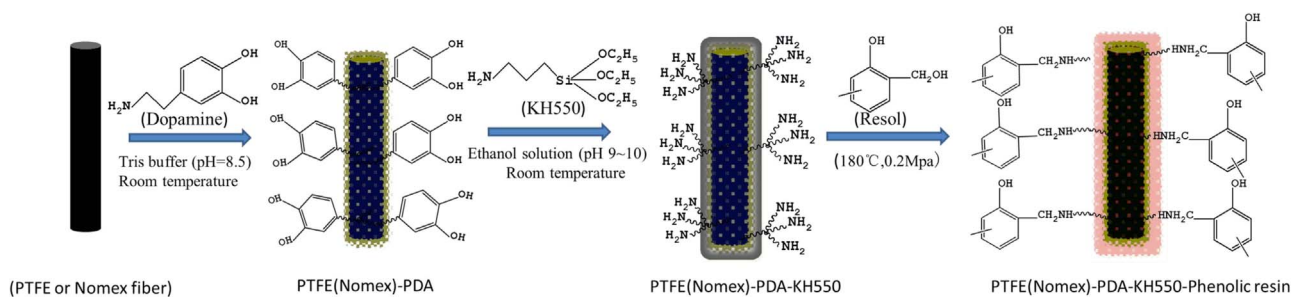
The tensile property of the hybrid-fabric composites was performed on a DY35 universal materials testing machine at a tensile rate of 50 mm/min. The dimensions of the samples used for tensile strength tests were 60 mm in length, 20 mm in width, and $250 \pm 10 \mu\text{m}$ in thickness. The tensile strength (σ_b , MPa) of the composites was obtained according to the equation as follows:

$$\sigma_b = F_p / BD \quad (1)$$

Here, F_p , B, and D refer to the maximal pull force (N), the width (m) and the thickness (m), respectively.

The bonding strength of the hybrid-fabric composites was investigated by an Electronic fabrics strength machine (YG026D) at a cross-head speed of 30 mm/min. Before performing peeling tests, the impregnated hybrid fabric was cut into given size (120 mm in length and 20 mm in width). Subsequently, the test samples were affixed onto the AISI-1045 steel plates (60 mm in length, 20 mm in width and 50 mm in adhesive length) with phenolic adhesive and cured at 180 °C for 2 h under 0.2 MPa. The bonding strength (τ , MPa) was calculated using the following relationship:

$$\tau = F / B \quad (2)$$



Scheme 1. Illustration of procedure for preparing amino functionalized PTFE and Nomex fibers.

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