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Catecholamine polymers as surface modifiers for enhancing interfacial strength of fiber-reinforced composites

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ABSTRACT

Mussel-inspired catecholamine polymers (poly(dopamine) and poly(norepinephrine)) were coated on the surface of carbon and glass fibers in order to increase the interfacial shear strength between fibers and polymer matrix, and consequently the interlaminar shear strength of fiber-reinforced composites. By utilizing adhesive characteristic of the catecholamine polymer, fiber-reinforced composites can become mechanically stronger than conventional composites. Since the catecholamine polymer is easily constructed on the surface by the simultaneous polymerization of its monomer under a weak basic circumstance, it can be readily coated on micro-fibers by a simple dipping process without any complex chemical treatments. Also, catecholamines can increase the surface free energy of micro-fibers and therefore, can give better wettability to epoxy resin. Therefore, catecholamine polymers can be used as versatile and effective surface modifiers for both carbon and glass fibers. Here, catecholamine-coated carbon and glass fibers exhibited higher interfacial shear strength (37% and 27% increases, respectively) and their plain woven composites showed improved interlaminar shear strength (13% and 9% increases, respectively) compared to non-coated fibers and composites.

1. Introduction

Based on superior and balanced mechanical properties such as high strength and ductility with low weight, fiber-reinforced composites have been widely adopted in many industrial and sporting areas [1–3]. Recently, strict fuel efficiency regulation and needs for lower fuel cost have led to rapid introduction of the fiber composites in many automotive and aircraft's major structural parts by replacing conventional metals. With decreasing unit price of carbon and glass fibers, highly efficient and fast manufacturing technologies such as a high-pressure resin transfer molding and a press-based thermo-stamping are accelerating such wide range of applications in industry. To achieve material requirements reliable and compatible with practical uses, many researches have focused on improving the material property of the fiber composites. Mechanical properties of the composite are determined by the well-designed combination of reinforcing fibers and polymer matrix. Besides of the material properties of fibers and matrix themselves, an interfacial property between fibers and matrix is also crucial to control performance of the composite, since an external load should effectively transfer from the polymer matrix to the reinforcing fiber [4]. So far, there have been many trials to increase the fiber–matrix interfacial property. For good affinity with epoxy resin, conventional fibers are provided as sized-forms where fiber surfaces are coated with epoxy or silane-based coupling agents [5,6].

To reach higher adhesive strength, numerous approaches have been suggested in fiber-sizing researches for last two decades and they can be classified as two categories. One is to modify the conventional sizing agents, which are mixed with reinforcing nano-fillers such as nano-clays, SiO_2 nanoparticles, carbon nanotubes (CNTs), graphene sheets, and their hybrids [7–12]. Even though many works showed good improvements on the interfacial strength, the modification of the sizing agent usually requires unsized-fibers or desizing treatment to reach the best performance. Therefore, the conventionally sized-fibers should be desized before applying the modified sizing agent. Since most desizing processes are accompanied with high temperature annealing or strong acid treatment, unique characteristics of original fibers are likely to be degraded [13].

The second category is to directly modify the fiber surface with preserving the conventional sizing. In this case, surface pre-treatments such as plasma and ozone irradiation are occasionally carried out to increase the loading amount of reinforcing materials by adding oxygen-based functionality [14]. Physical approaches

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include various coating techniques such as a dip-coating, a pressure-driven spraying, an electro spraying, an electro-spinning, and an electrophoretic deposition [15–18]. The dip-coating and pressure-based spraying methods are very easy to apply but uniform coating morphology is difficult to be obtained. Even though the electrical field-assisted techniques are efficient and useful to control the loading amount of the sizing material and the coating quality of the fiber surface, the coating material should have high electrical mobility enough to move toward the fiber, and also the fiber should be electrically conductive to attract the sizing material. As for a chemical approach, reinforcing nano-materials such as SiC whiskers, CNTs, and ZnO nanowires can be vertically grown on the fiber surface [19–21]. By increasing the interfacial surface area, load-bearing area and crack propagation path can become lager and longer, respectively, and consequently the interfacial strength can be enhanced. Another chemical strategy is to coat matrix-compatible materials or to functionalize organic molecules on the fiber surface, which can induce further chemical interaction with the polymer resin [22].

In this work, mussel-inspired catecholamine polymer was utilized as an adhesive fiber-surface modifier to increase the interfacial strength of fiber-reinforced composites by providing an additional chemical interaction with epoxy resin, as shown in Fig. 1. Here, two catecholamine polymers, poly(dopamine) (pDA) and poly(norepinephrine) (pNE) were considered for the comparison purpose of different functionality, where pNE has one more hydroxyl functional group. pDA and pNE are polymeric forms of dopamine and norepinephrine, respectively, which mimic the repetitive catecholamine structure of 3,4-dihydroxyl-L-phenylalanine (DOPA) found in sea mussel's foot protein, *Mytilus edulis* [23,24]. DOPA has excellent attraction with various organic and inorganic surfaces, where a single molecule of DOPA exhibits very strong adhesion force, which is up to covalent bonding force. Utilizing outstanding adhesive ability, catecholamine-based materials have been used as efficient material binders and mechanical reinforcing agents [25–28]. In addition to the adhesive characteristic, Catecholamine has hydrogen-containing functional groups such as hydroxyl (—OH) and secondary amine (—NH—), which can establish hydrogen bonds with many sites in the epoxy resin and can increase the degree of cure. Consequently, catecholamine can effectively increase the interfacial strength of the composites. Using such outstanding functionalities of catecholamine polymers, many works have been reported on biomedical science, polymer chemistry, and fiber-reinforced composites [29–33], where pDA has been utilized as a surface modifier and platform for further functionalization.

Inspired by the adhesive capability and chemical functionality of catecholamine, we manufactured catecholamine-coated fiber-reinforced composites. Carbon and glass fabrics were dipped into the buffered aqueous solutions at a basic condition with dopamine and norepinephrine to coat pDA and pNE, respectively. Coating morphologies on the fiber surface were examined by scanning electron microscopy (SEM) images, and the identification and chemical structures of pDA and pNE was carried out by X-ray photoelectron spectroscopy (XPS) analysis. To examine the surface properties of catecholamine-coated carbon and glass fibers, contact angles were measured by Wilhelmy method and the change of surface free energy was investigated. The interfacial properties with epoxy of the fibers were studied by measuring interfacial shear strengths (IFSS) through the micro-droplet pull-out test of single fibers. The influence of catecholamine on matrix-dominated properties in laminated composites was also investigated by evaluating the interlaminar shear strength (ILSS) through short-beam shear tests. Furthermore, the fractured surfaces of the composites were examined by SEM image analysis.

2. Experimental

2.1. Materials

Carbon (TR30S, Mitsubishi Rayon) and glass (ER690, Hankuk Fiber) fibers were used as plain woven fabrics for conventional fiber reinforcements. Densities of carbon and glass fibers are 1.79 and 2.54 g/cm^3, respectively. For the carbon and glass fabrics, areal densities are 200 and 760 g/m^2, and yarn counts of warp and fill are 5.0 and 2.0 ends/cm (12.5 and 5.0 ends/in.), and thicknesses are 0.23 and 0.77 mm, respectively. For the catecholamine coating and composite preparation, both fabrics were cut by having 80×80 and 120×120 mm, respectively. A diglycidyl ether of bisphenol-A type epoxy resin (YD-128, Kukdo Chemicals) with an anhydride type curing agent (KBH-1089, Kukdo Chemicals) was utilized for both micro-droplet and composite samples. As for catecholamine materials, dopamine hydrochloride (H8502, Sigma Aldrich) and norepinephrine hydrochloride (A7256, Sigma Aldrich) were used. To polymerize these catecholamine monomers, a tris-buffer solution was prepared by mixing Trizma base (T1503, Sigma Aldrich) in distilled water to have pH 8.5.

2.2. Coating of pDA and pNE on carbon and glass fibers

Before coating catecholamine polymers, carbon and glass fabrics were rinsed with ethanol and fully dried. Note that ethanol

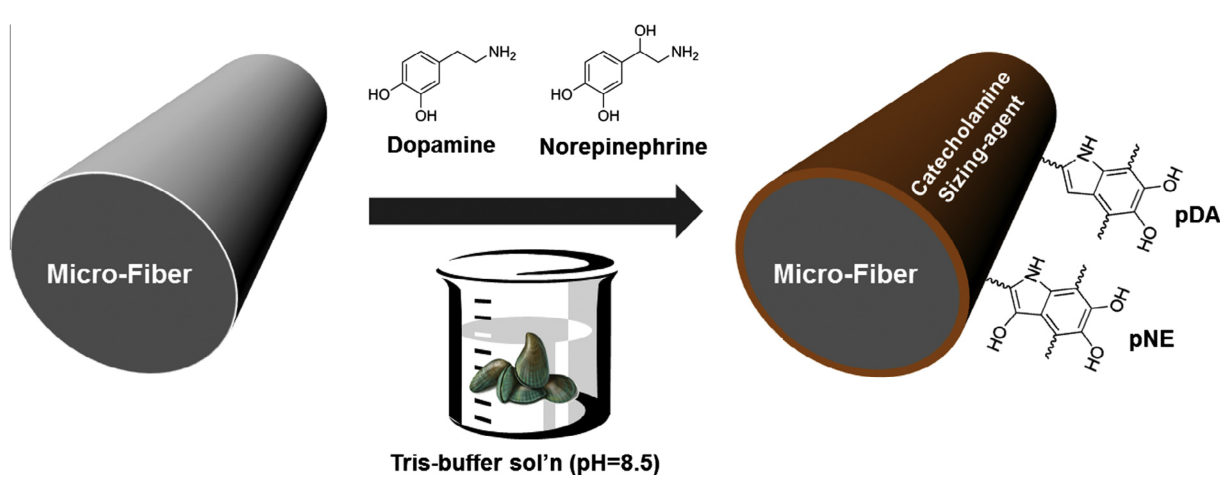

Fig. 1. Schematic illustration of coating of catecholamines on micro-fiber surfaces and chemical structures of dopamine, norepinephrine, pDA, and pNE.