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Original Research Article

Enhancement of the Electrical Conductivity and Interlaminar Shear Strength of CNT/GFRP hierarchical composite using an Electrophoretic Deposition Technique

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Supplementary Materials

The mechanism of chemical bond formation between the GT surface and CNTs through the silane coupling agent treatment process

The most pivotal parameters in studying the interface of GFRPs are the surface quality of the fibers and their capability to interact with polymers. During the manufacturing process of glass fibers, an aqueous emulsion of sizing material is applied on the fibers during the final stages of the process. The sizing will form a layer on the fibers' surfaces which highly affects the composite interface, and thus the strength of the composites. The layer also protects the fibers during handling and storage. The solid part of sizing mostly consists of multipurpose components like film former, surfactant, a silane coupling agent, and a small amount of lubricants and antistatic agents. The dried film holds the filaments together in a strand and prevents them from contact damages.

The silane coupling agent has a functional group on its organic tail that can be designed to react with the matrix resin. Several researchers studied the mechanism of interaction between the sizing materials and polymer resins in the interphase, and investigated the effect of sizing coupling agents on the mechanical behavior of GRPs [1–3]. Some researchers removed the sizing materials through a heat cleaning de-sizing process at high temperatures and again applied a compatible coupling agent with proper functional groups for the specified applications. In the current study, according to the manufacturer's recommendation, GTs were cleaned by heating to 500 ˚C for 1 hour and then gradual cooling to room temperature over a period of 45 minutes.

Although CNT deposition on the glass fiber surface is a physical route to provide CNT attachment, it may not be regarded as an effective interface enrichment method without strong chemical grafting of

CNTs to the fiber's surface. Introducing robust chemical bonds between the CNTs and the glass fiber surfaces after physical deposition positively affects the toughness of the GFRP composite laminates [4]. Glass fibers, as inorganic materials, interact with organic CNTs both chemically and physically. One of the most effective agents for improving the strength of heat-curable resins is a silane coupling agent, provided that the silane coupling agent contains organic functional groups which can participate in the curing reaction of the resin. Silane coupling agents react with water (hydrolysis) to form silanol groups, and oligomers are formed through partial condensation. The silanol oligomers then hydrogen bond to the surface of the inorganic material.

Finally, the inorganic material is put through a drying process and robust chemical bonds are formed through a dehydration-condensation reaction. The involved molecules have functional groups that bond with both types of materials effectively. In this study, 3-(tri-methoxysilyl) propyl amine with functional groups depicted in **Figure 1** has been used to prepare the required bonds on the surface of GT, and make it ready to interact with CNTs.

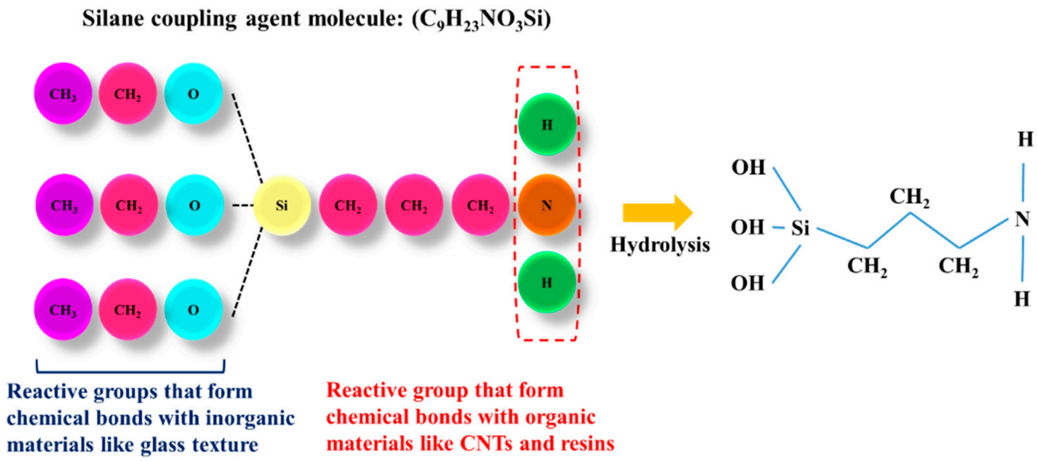

Figure 1. Functional groups in the silane coupling agent molecule.

Raw (as received) and de-sized GTs were treated with silane coupling agent to prepare specimens for EPD. 3-(tri-methoxysilyl) propyl amine diluted by 1 vol.% in solution of acetic acid and deionized water in PH equal to 4 and mixed mechanically for around 45 minutes, then, GTs were immersed in the solution for one hour. Finally, excess water was removed and the specimens were dried at 110˚C for 15 minutes. Each silane coupling agent reacts with water in a hydrolysis process in which silanol groups and oligomers are formed through partial condensation. The silanol oligomers hydrogen bond to the available OH groups on the surface of GTs. Then, a molecule of water will be removed from these bonds when the GTs are exposed to a drying process, and robust chemical bonds will appear through a dehydration-condensation reaction, as shown in **Figure 2**.

The other functional group of the coupling agents are occupied by carboxyl functional groups on the outer walls of functionalized carbon nanotubes. At this stage, EPD was employed to increase the chance of chemical bond formation due to its ability to deposit CNTs with the highest possible packing on the activated surface of the glass fibers. During deposition, ionic bonds are formed when the negative charges of the carboxyl groups on the CNTs interact with the positive charges of amidogens (NH_2) on the surface of glass fibers.

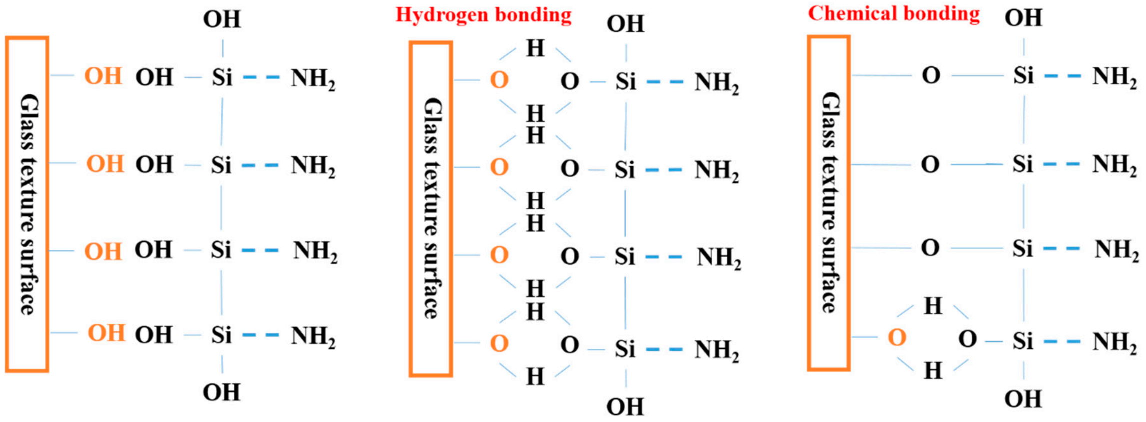

Figure 2. Chemical activation of the glass fibers' surface through coupling agent and dehydration-condensation.

The ionic bonds are converted to robust covalent bonds by losing a water molecule in vacuum oven above 120 ˚C (see **Figure 3**). At this stage, CNTs are chemically and physically attached to the surface of GTs, and the CNTs can play their role in the interaction between fibers and resin.

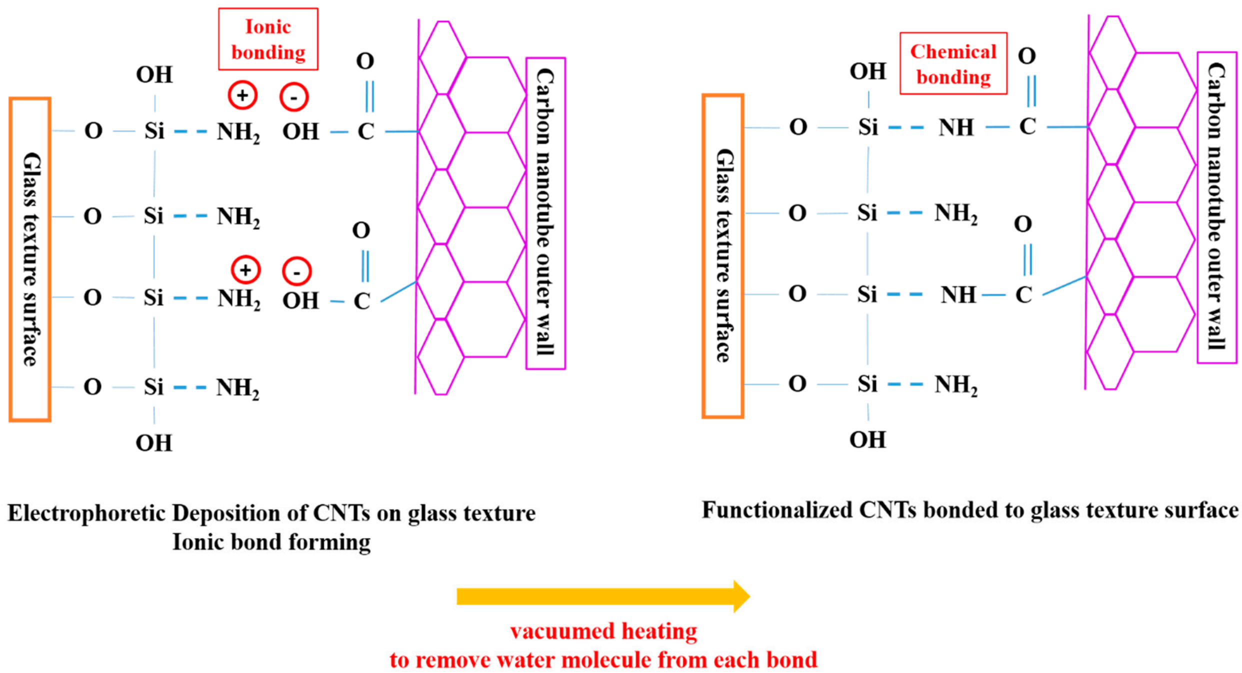

Figure 3. Bond formation between deposited CNTs on the surface of silane-treated glass fibers.

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