Study on the Influence of Silane Coupling Agent Surface Modification on the Interfacial Properties of Glass Fiber Reinforced Nylon Composites

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ABSTRACT Poor interfacial compatibility in glass fiber reinforced nylon composites limits the full realization of their mechanical properties, with weak fiber-matrix bonding becoming a key bottleneck in engineering applications. This study uses γ-aminopropyltriethoxysilane to modify the surface of glass fibers and systematically investigates the effects of coupling agent concentration and treatment temperature on composite interfacial properties. APS concentrations of 0.5%, 1.0%, 1.5%, and 2.0 wt% and treatment temperatures of 80 °C, 100 °C, and 120 °C are examined. Scanning electron microscopy and Fourier transform infrared spectroscopy are used to characterize changes in fiber surface morphology and chemical structure, while single-filament tensile testing, monofilament pull-out testing, and interlaminar shear strength testing are used to evaluate interfacial bonding performance. Results show that as APS concentration increases from 0.5% to 1.5%, the Si-O-Si peak intensity increases by 108% and the N element content increases by 156%, indicating enhanced silane grafting. Excessive concentration leads to self-polymerization and reduced coating uniformity. The study clarifies the interfacial reinforcement mechanism of silane-modified glass fiber reinforced nylon composites.

INDEX TERMS silane coupling agent, glass fiber, nylon composites, interface modification, mechanical properties

I. INTRODUCTION

GLASS fiber reinforced nylon composites are a combination of high strength fiber glass and toughness and wear resistance of nylon and find extensive applications in the automotive lightweighting, electronics and aerospace. However, the polarity difference between the high-energy hydroxyl groups on the glass fiber surface and the nylon molecular chains results in poor interfacial wettability and low bond strength. Poor fiber-matrix interfacial bonding decreases the effectiveness of stress transfer, and the composite material is susceptible to interfacial debonding and fiber pull-out during loading leading to mechanical properties much lower than expected. The problem of interfacial compatibility limits performance and the range of application of glass fiber reinforced nylon composites, it becomes the technical bottleneck that is acutely necessary to be removed in this sphere [1-2].

Silane coupling agents have hydrolyzable alkoxy groups and organic functional groups, which reacts with the polymers and make chemical bridges between the surface of the fibers and the matrix. The γ-aminopropyltriethoxysilane amino group reacts with the carbonyl group of nylon by hydrogen or amide bonding, and the ethoxy group, on hydrolysis, reacts with the hydroxyl groups of the surface of the fiber to produce Si-O-Si covalent bonds, to obtain interfacial chemical bonding. The coating quality and interfacial bonding effectiveness depend directly on the coupling agent modification parameters. A concentration that is too low results in incomplete coverage whereas a concentration that is too high results into self-polymerization. The temperature at which the treatment is done influences the rate of the hydrolysis-condensation reaction and evenness of a coating layer. The optimization of the parameters of the processes is a decisive factor in enhancing interfacial performance.

It was a systematic research that examined how concentration of APS and treatment temperature influence the surface chemical structure and coating morphology of glass fibers and developed the relationship between the parameters of the modification process and mechanical properties of composite materials. The grafting mechanism of coupling

agent was studied using infrared spectroscopy and X-ray photoelectron spectroscopy, the evolution process of interface microstructure was examined using scanning electron microscopy and the effect of interface modification was assessed by mechanical testing. The proposed study will help unveil the interface reinforcement mechanism of silane coupling agent modified glass fiber reinforced nylon composites, identify the best parameters of modification process, offer the theoretical background and technical solutions of the design of interface of high-performance composite materials, and propagate the use of such materials within the engineering sector [3-4].

II. RELATED WORK

The interfacial behavior of glass fiber reinforced thermoplastic composites is a factor of the relative degree of matching surface energy of the fiber and the surface tension of the matrix and the chemical bonding influence of the interfacial zone. The surface of the glass fiber is enriched with silanol groups, and has a hydrophilic character where the nylon matrix, which has polar groups, is usually hydrophobic. The two phases have poor wetting and interfacial voids due to the energy difference at the surface. Being one of the most important mediums through which to transmit stress, the bonding strength at the interfacial region is directly related to the load bearing capacity and the failure mode of the composite material. Lack of interfacial bonding means that the external load cannot be efficiently transferred to the reinforcing phase and then the fiber cannot fully utilize its load-bearing capacity. Interfacial modification technology builds a transition layer on the surface of the fiber, either by physical adsorption or chemical bonding, to redistribute surface energy and chemical functional groups, and enhance interfacial wettability and bond strength [5-6]. Surface modification techniques can be classified into a number of technical paths that include plasma treatment, coupling agent treatment and coating modification. Among these, silane coupling agent modification has been the general choice in the industrial application with the reason that it has a simple process, its cost can be controlled and has a great effect of modification.

Silane coupling agents modification mechanism comes in various reaction processes including hydrolysis, condensation and adsorption. The coupling agent molecules dissolve in water or alcoholic solvents to produce silanol groups which dehydrate condense with hydroxyl groups on the fiber surface and create Si-O covalent bonds. A few silanol groups condense on their own to create a siloxane network structure. Organic functional groups offer active sites to react with the matrix on the solution side, and are chemically reacted or physically entangled with the molten matrix when forming composite materials. The modification process parameters have a key impact on the structure and properties of the coating layer. The concentration of the coupling agent influences the grafting density and the thickness of the coating layer on the fiber surface, the temperature at which the treatment is done influences the rate of hydrolysis condensation reaction and the density of the coating layer, and previous studies suggest that the time spent on the treatment influences the extent of reaction completion, although this parameter was kept constant in the present work. The available literature is largely concerned with the optimization of individual parameters, fails to investigate the synergistic effect mechanism of several parameters in-depth, and the relationship between the microstructure and the mechanical properties of the coating layer on a macroscopic level is not completely understood. The theoretical explanation of the mechanism of interface enhancement is yet to be made better [7-8].

III. METHODS

A. SILANE COUPLING AGENT MODIFICATION PROCESS FOR GLASS FIBER

Prior to modification, the glass fibers were dried in an oven at 120 °C for 4 h to eliminate moisture absorbed on the surface. γ-Aminopropyltriethoxysilane and anhydrous ethanol were blended at mass ratios of 0.5%, 1.0%, 1.5% and 2.0% as treatment solutions. 0.5% acetic acid was added to adjust the pH to 4.5-5.0 to enhance silane hydrolysis. After unfolding the bundles of glass fiber, they were soaked in the treatment solution. In order to keep the uniform tension, the coupling agent would diffuse into the space between the monofilaments. The soaking time was controlled to be 3 min. Then the fiber bundle was removed and droplets on the surface were removed with a preheated roller at 5 m/min. Finally, the fiber was put into a three-stage drying tunnel with the temperature of 80 °C, 100 °C and 120 °C respectively. The fiber stayed in each tunnel for 2 min. The silane molecules would undergo further reaction to achieve complete coordination and condensation between the silane molecule and the hydroxyl group on the fiber surface at 80 °C and 100 °C. The modified fiber stayed at the last tunnel at 120 °C for 2 min to let the silane molecules on the fiber surface to get fully coordinated and condensed with the silane groups. Finally, the modified fiber was stored at room temperature for 24 h to complete the curing reaction. During this process, the relative humidity should be controlled below 40% to prevent the unreacted silane group from self-polymerization [9-10]. Modified fibers should be used for composite material preparation after the appearance of characteristic peaks of Si-O-Si is observed by infrared spectroscopy.

B. COMPOSITE MATERIAL PREPARATION AND MOLDING PROCESS

Cuttings of modified glass fibers to 200 mm long were placed at 0° onto the surface of the mold base plate with fiber volume fraction maintained at 30%. The Nylon 6 chips were vacuum dried (<0.02%) and fed into the twin screw extruder. The temperature of the screw ranged from 220-240-250-260 °C and the speed was 45 rpm. The hot molten nylon was evenly distributed on the fiber layer surface

through the pouring head. The pouring rate was controlled at 8 grams per second so that the resin could completely wet the fiber bundle. The mold was transferred to the hot press and a pressure of 2 MPa was applied and the temperature was raised to 270 °C and maintained at that temperature for 15 minutes so that the resin could diffuse into the space between the fiber gaps and expel air bubbles. The pressure was raised to 5 MPa and then raised to 180 °C at a rate of 3 °C/min and held for 10 minutes so that the crystallinity of the nylon was controlled. Finally, the mold was cooled to 80 °C and then the pressure was released. The mold was demolded to obtain the composite material sheet with thickness of 3 mm. The board was cut longitudinally into specimens 150 mm long and 15 mm wide. The cut surface was ground with 600 grit sandpaper to remove the edge damage. All the specimens were conditioned for 48 hours at standard conditions before performing the tests.

C. CHARACTERIZATION METHODS FOR FIBER SURFACE MORPHOLOGY AND CHEMICAL STRUCTURE

The surface morphology of the fibers was investigated by field emission scanning electron microscope (Hitachi, SU8010). The samples were attached to the sample stage by conductive adhesive and then sputtered with 10 nm thick gold film. The accelerating voltage and working distance were 5 kV and 8 mm, respectively. The magnification was enlarged from 500x to 10000x gradually to check the uniformity of coupling agent coating layer distribution and the change of microstructure on fiber surface. The thickness of coating layer on fiber breaking surface was measured after liquid nitrogen brittle fracture of single fiber. The average value was calculated from 20 different positions.

Chemical structure characterization was carried out by Fourier transform infrared spectrometer (Nicolet iS50). The fiber samples were cut into 1 mm. Then fiber powder was mixed with potassium bromide in mass ratio of 1:100, ground and pressed into transparent thin film. The scanning wavenumber range was 4000–400 cm^{-1} , resolution was 4 cm^{-1} and the number of cumulative scans was 32. In addition, the intensity of Si-O-Si stretching vibration peak located at 1100 cm^{-1} , amino NH stretching vibration peak located at 3400 cm^{-1} and carbon chain CH stretching vibration peak located at 2900 cm^{-1} were analyzed in detail. The quantity of coupling agent grafted on fiber surface was calculated by the peak area integration. X-ray photoelectron spectroscopy analysis was conducted by using a Thermo ESCALAB 250Xi photoelectron spectrometer with Al Kα source and beam diameter of 500 μm. The characteristic peaks of Si 2p and N 1s were used to prove the chemical bonding between silane molecules and fiber surface.

D. INTERFACE MECHANICAL PROPERTY TESTING AND EVALUATION SYSTEM

Tensile property testing was carried out with an Instron 5967 universal testing machine (gauge length = 100 mm, loading rate = 2 mm/min) and seven parallel samples were tested per group. Strain was recorded in real time with an extensometer (gauge length = 50 mm, resolution = 0.001 mm). Immediately after tensile fracture, the fracture surface of sample was collected, sputter-coated with gold, and then collected and observed under scanning electron microscope for pull-out length of fiber and morphology of matrix tear. The average pull-out length of 50 fibers was statistically analyzed to characterize interfacial bonding strength. Interlaminar shear strength testing was carried out following ASTM D2344. The size of specimen was 20 mm × 6 mm × 3 mm and span length was 16 mm. Three-point bending loading rate was 1 mm/min and the maximum load was recorded and interlaminar shear stress was calculated. Fractured specimens were sliced along the thickness direction and polished till surface roughness <0.5 μm, and then the interfacial crack propagation path was observed under optical microscope for both fracture faces to identify whether the failure mode was fiber-matrix interface debonding or matrix shear fracture.

Monofilament pull-out test was carried out with an Instron 5967 universal testing machine. Fibers with embedding depth of 2 mm were chosen. The fiber end was pulled out at a rate of 0.5 mm per minute with a micro-clamp attached to a fixed nylon matrix. The interfacial debonding energy was acquired by the integral of the force-displacement curve. The interfacial shear strength was acquired by dividing the peak load by the embedding area. For each modification condition, 15 monofilaments were tested and average value ± standard deviation was acquired.

IV. RESULTS AND DISCUSSION

A. EFFECT OF COUPLING AGENT CONCENTRATION ON FIBER SURFACE CHEMICAL STRUCTURE

FTIR spectroscopy was used to study the grafting amount of different concentration coupling agent (APS) on the glass fibers in order to obtain quantitative information about the grafted effect of coupling agent by means of the change of characteristic peak intensity. Baseline correction and peak area integration were carried out for Si-O-Si peak at 1100 cm^{-1} and NH peak at 3400 cm^{-1} . The peak intensities were normalized to the C-H stretching vibration peak at 2900 cm^{-1} as an internal standard, and then the peak intensity ratio was used to represent the coverage density of silane molecule on fiber surface. XPS can get the Si 2p and N 1s elemental contents and the coating layer thickness was observed by scanning electron microscopy to determine the relationship between concentration and grafting amount.

Table 1 shows that when the APS concentration increases from 0.5% to 1.5%, the Si-O-Si peak intensity increases by 108%, and the N element content increases by 156%, indicating that the amount of silane molecule grafting is positively correlated with the concentration. At a concentration of 1.5%, the coating layer thickness reaches 68 nm, forming a complete coverage. When the concentration is further increased to 2.0%, the thickness surges to 115 nm, but the chemical structure parameters only increase slightly.

TABLE 1. Fiber surface chemical structure parameters at different APS concentrations

APS concentration (%)	Si-O-Si peak intensity (au)	NH peak intensity (au)	Si element content (at%)	N element content (at%)	Coating thickness (nm)
0 (Unprocessed)	12.3	0	0.8	0	0
0.5	45.7	18.2	3.2	1.8	28
1.0	78.4	35.6	5.7	3.4	52
1.5	95.1	48.3	7.1	4.6	68
2.0	96.8	49.7	7.3	4.7	115

This indicates that the excess coupling agent undergoes self-polymerization rather than chemical bonding with the fiber, forming a multilayer stacked structure that reduces the interface uniformity.

B. THE EFFECT OF PROCESSING TEMPERATURE ON THE QUALITY OF INTERFACIAL COATING FORMATION

The best concentration of 1.5% APS treatment solution was used to treat the glass fiber at 80 °C, 100 °C and 120 °C for 6 min. The continuity of the surface coating was checked by SEM and coating thickness at 20 random location was measured to count the root mean square error and uniformity. Water contact angle change on the fiber surface was measured by contact angle meter at 2 μL droplet volume, each sample was tested 10 times and the average was taken. The degree of siloxane network was counted by measuring Si-O bond vibration modes in 800-1200 cm^{-1} range by Raman spectroscopy. Table 2 shows the quality parameters of the interfacial coating at different treatment temperatures.

Table 2 shows that the coating thickness had the lowest standard deviation (SD) at 100 °C, with a surface coverage of 95.8%, indicating the most uniform coating distribution.

TABLE 2. Effect of processing temperature on the quality of interfacial coating formation

Parameter	80 °C	100 °C	120 °C
Coating thickness (nm)	45	68	82
Standard deviation of thickness (nm)	12.8	6.3	15.6
Surface coverage (%)	76.3	95.8	94.1
Water contact angle (°)	58.2	72.6	69.4
Si-O-Si polymerization degree	0.62	0.89	0.91
Surface roughness (nm)	18.5	8.3	22.7

At 80 °C, the silane hydrolysis-condensation reaction rate was slow, resulting in a Si-O-Si polymerization degree of only 0.62, leading to a discontinuous coating layer and a coverage of only 76.3%. While 120 °C increased the polymerization degree to 0.91, the excessively high temperature accelerated solvent evaporation, causing local enrichment of the coupling agent,

increasing the thickness SD to 15.6 nm, and drastically increasing the surface roughness from 8.3 nm at 100 °C to 22.7 nm, forming an uneven agglomerate structure that affected the interfacial stress transfer efficiency.

C. THE INFLUENCE MECHANISM OF MODIFICATION PROCESS PARAMETERS ON THE MECHANICAL PROPERTIES OF COMPOSITE MATERIALS

Composite materials prepared with five concentrations of modified fibers, namely untreated fiber, 0.5% APS fiber, 1.0% APS fiber, 1.5% APS fiber and 2.0% APS fiber, were prepared and their mechanical properties were determined. Seven parallel samples were used in each group. In tensile test, the samples were tested at the temperature of 23 °C till the peak stress and fracture strain were obtained after loading to fracture. Interlaminar shear strength was determined by short beam three-point bending with the span of 16 mm and the rate of 1 mm/min. Monofilament pull-out test was used to determine interfacial shear strength. The embedding depth was 2 mm and the rate was 0.5 mm/min. There were 15 monofilaments in each group. In bending performance test, the span was 48 mm and the rate was 2 mm/min. Bending strength and bending modulus were determined. Table 3 summarizes the mechanical property parameters of the composite materials under different modification conditions.

TABLE 3. Effects of modification process parameters on the mechanical properties of composite materials

Parameter	Unprocessed	0.5% APS	1.0% APS	1.5% APS	2.0% APS
Tensile strength (MPa)	82.3	98.6	115.2	126.7	119.4
Elongation at break (%)	3.8	4.5	4.9	5.2	4.7
Interlaminar shear strength (MPa)	35.6	44.8	52.3	58.9	51.2
Interfacial shear strength (MPa)	18.4	26.7	34.5	42.8	38.6
Bending strength (MPa)	128.5	152.3	175.8	192.4	181.7
Flexural modulus (GPa)	8.2	9.6	10.8	11.5	10.9

Table 3 shows that 1.5% APS modification increased the tensile strength from 82.3 MPa to 126.7 MPa, an increase of 54.0%, and the interlaminar shear strength from 35.6 MPa to 58.9 MPa, an increase of 65.4%. The 65.4% increase in interlaminar shear strength to 58.9 MPa confirms that the coupling agent significantly improved the fiber-matrix in-

terfacial bonding. At a concentration of 2.0%, all properties decreased, with the tensile strength dropping to 119.4 MPa and the interlaminar shear strength to 51.2 MPa, attributed to the weak interfacial layer formed by the self-polymerization of excessive coupling agent, which reduced stress transfer efficiency. The increase in flexural modulus from 8.2 GPa to 11.5 GPa indicates that interfacial modification enhanced the stiffness of the composite material, and the 37.2% increase in elongation at break shows a simultaneous improvement in toughness.

V. CONCLUSION

The interfacial compatibility of glass fiber reinforced nylon composites was improved successfully by modification of silane coupling agent. γ-aminopropyltriethoxysilane modification could form a chemically bonded coating layer on fiber surface and the interfacial properties of fiber-matrix were enhanced due to the growth of coating layer, and the stress transfer efficiency was enhanced by improving fiber-matrix interfacial bonding strength. The modification process parameters had a significant influence on interfacial properties. The proper coupling agent concentration and processing temperature could obtain a uniform and continuous coating layer on fiber surface. While the coupling agent concentration was too high, coupling agent would self-polymerize and the interfacial layer was weak due to the formation of polymer. Silane modification could improve tensile strength, interlaminar shear strength and flexural properties of the composite material and the fracture mode was ductile. The interfacial design and performance optimization of glass fiber reinforced thermoplastic composites provided theoretical basis and technical ideas and engineering application value.

AUTHOR CONTRIBUTIONS

Conceptualization –Jingjing An, Qisheng Zhang, Kai Lin, Yubin Song, Xiaozhong Zhang, Ruyun Ying and Haijun Zhang; methodology – Jingjing An, Qisheng Zhang, Kai Lin, Yubin Song, Xiaozhong Zhang and Haijun Zhang; investigation – Jingjing An, Qisheng Zhang, Kai Lin, Yubin Song, Xiaozhong Zhang, Ruyun Ying and Haijun Zhang; writing-original draft preparation – Jingjing An, Qisheng Zhang, Kai Lin, Yubin Song, Xiaozhong Zhang, Ruyun Ying and Haijun Zhang. All authors have read and agreed to the published version of the manuscript.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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