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Matrix Modification with Silane Coupling Agent for Carbon Fiber Reinforced Epoxy Composites

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Abstract: To improve interfacial adhesion between carbon fiber and epoxy resin, the epoxy matrix is modified with N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (YDH602) and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (YDH792), respectively. And the effect of matrix modification on the mechanical performance of carbon/epoxy composites is investigated in terms of tensile, flexural and interlaminar properties. The flexural properties indicate that the optimum concentration of silane coupling agents YDH602 and YDH792 for the matrix modification is approximately 0.5 wt% of the epoxy resin system, and the mechanical properties of the YDH792-modified epoxy composites is better than that of the YDH602-modified epoxy composites at the same concentration. Compared to unmodified epoxy composite, the incorporation of 0.5 wt% YDH792 results in an increase of 4, 44 and 42 % in tensile, flexural and interlaminar shear strength (ILSS) values of the carbon/epoxy composite, respectively, while the corresponding enhancement of tensile and flexural modulus is 3 and 15 %. These improvements in mechanical properties can be considered to be an indication of better fiber/matrix interfacial adhesion as confirmed by SEM micrographs of the fracture surface after interlaminar shear testing. The viscosity of the modified epoxy resin system can be reduced by incorporation of silane coupling agent YDH792, which is beneficial for fiber impregnation or wetting during liquid composite molding process.

Keywords: Composites, Matrix modification, Silane coupling agent, Interfacial adhesion

Introduction

The mechanical performance of fiber-reinforced polymer composite depends basically on the constituent materials (matrix and fiber) and the effectiveness of interface bonding between the constituents. A well-bonded interface is essential for effective stress transfer from the matrix to the fiber, which helps reduce stress concentrations and improve overall mechanical properties [1-5].

Two methodologies are generally utilized to improve the fiber/matrix interfacial adhesion: fiber surface treatment techniques and matrix modification. The fiber/matrix interfacial adhesion can be improved by changing the nature of the fiber surface with fiber surface treatment techniques, i.e. sizing. Conventional sizing, such as film former, emulsifier, antistatic agent and coupling agent, is generally designed to protect the fiber surface and to promote the adhesion between the fiber and the resin [4,6]. The fiber/matrix interaction and compatibility can also be promoted by matrix modification, such as introducing reactive sites with higher chemical affinity toward the fibers and increasing matrix toughness [3,7].

A coupling agent is a chemical that functions at the interface to create a chemical bridge between the fiber and the resin. It improves the interfacial adhesion when one end of the molecule is tethered to the reinforcement surface and the functionality at the other end reacts with the polymer-phase. Silane coupling agent, which is the most commonly used coupling agent, can be used as a sizing in fiber surface treatment, but also can be used as a reactive sites in matrix modification. Matrix modification with silane coupling agent has two main advantages: (1) silane coupling agents bear alkoxysilane groups capable of reacting with fiber surface, and they have a large number of functional groups which can be tailored as a function of the matrix to be used. This feature ensures a good compatibility between the reinforcing element and the polymer matrix; (2) silane coupling agents is generally a low-viscosity oligomer, which can reduce the viscosity of the resin system when incorporated into the matrix. Fiber/matrix interface can be improved by a reduction in resin viscosity to promote fiber impregnation or wetting [7] and hence enhance the composite mechanical properties. It is important for large-scale composite components manufacturing by liquid composites molding processes.

Silane coupling agent is generally designed to improve the fiber/matrix interfacial adhesion as a fiber-surface sizing [8-14]. Matrix modification by blending together with an reactive sites to improve the interfacial properties and mechanical behavior of fiber reinforced polymer composite has been reported in some previous works [3,15,16]. In [3] unsaturated polyester was modified with silane coupling agent to improve the mechanical properties of glass/polyester composites. Epoxy matrix was modified with hydroxyl-terminated polybutadiene to enhance the mechanical properties of short carbon fiber-reinforced epoxy composite in [15]. The influences of matrix modification on the interfacial shear strength and mechanical performance of polypropylene/glass fiber composites have been investigated by Jannerfeldt *et al.* in [16]. However, there are only a few articles relating to matrix modification with silane coupling agent to enhance

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the fiber/matrix interfacial adhesion and the mechanical properties of polymer composite, especially for the carbon/epoxy composites.

In this study, epoxy resin was modified by incorporation of silane coupling agent to improve the interfacial adhesion between carbon fiber and epoxy resin. Tensile, flexural and interlaminar shear properties of fabricated composites were investigated after resin modification. And fractured surfaces of the carbon/epoxy composites in the interlaminar shear tests were observed by scanning electron microscopy (SEM).

Materials and Experimental

Materials

An epoxy resin system, RIMR135/RIMH137 produced by Hexion Specialty Chemicals is used as matrix material which is a low-viscosity resin system for vacuum infusion molding process in wind turbine blades. RIMR135 is a modified bisphenol-A type epoxy resin and RIMH137 is a polyamine hardener. The epoxy resin is a clear liquid, and the hardener is a blue transparent liquid. The mix mass ratio of RIMR135/RIMH137 is 100:30±2. Density, viscosity and gelation time of RIMR135/RIMH137 at room temperature (~25 ^{o}C) are tabulated in Table 1.

A carbon-fiber unidirectional fabric 300CUD provided by Hangzhou Suoqi Advanced Composite Material Co., Ltd. (China), is used as reinforcement material which has a superficial density of 300 g/m^2. Other properties of fabric 300CUD are tabulated in Table 1.

Two silane coupling agents, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (YDH792) and N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (YDH602) were supplied by Trustechem Silanes Co., Ltd., China. Both are colorless liquid and 98 % concentration. Other properties of silanes are tabulated in Table 1.

Table 1. Material properties at room temperature (~25 ^{o}C)

Resin system (RIMR135/ RIMH137)	Resin	RIMR135
	Hardener	RIMH137
	Mass ratio	100:30±2
	Density	1.08-1.12 g/cm^3
	Viscosity	200-300 mPa·s
	Gelation time	250-260 min
Carbon fabric (300CUD)	Specification	CFF-I-300
	Type	Unidirectional knitted
	Carbon fiber	12k, T700 produced by Toray
	Superficial density	300 g/m^2
Silane coupling agent (YDH792)	Color	Colorless liquid
	Concentration	98 %
	Density	1.0250±0.0050 g/cm^3
	Molecular formula	$NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$
Silane coupling agent (YDH602)	Color	Colorless liquid
	Concentration	98 %
	Density	0.97-0.98 g/cm^3
	Molecular formula	$NH_2(CH_2)_2NH(CH_2)_3SiCH_3(OCH_3)_2$

Matrix Modification and Composite Laminates Preparation

Silane coupling agent was directly incorporated with the epoxy resin system to achieve matrix modification in this study. In order to determine the optimum concentration of silane coupling agent, epoxy matrix was modified by silane coupling agent which percentage increased from 0.0 wt% to 1.0 wt% of the resin system for the flexural sample preparation. Then, the matrix was modified based on the optimum concentration of silane coupling agent for the sample preparation of other mechanical testings. During manufacturing process, silane couping agent was added to epoxy matrix and mixed for 5 min at least. Thereafter, the hardener was included into the mixture, which was then subjected to stirring for 5 min at least.

Unidirectional (UD) composite laminates were manufactured by vacuum infusion molding process [17,18]. UD composite specimens $[0]_8$ with thickness of 2.3 mm were fabricated for flexural and tensile testings. And UD composite specimens $[0]_{52}$ with thickness of 15.0 mm were prepared for interlaminar shear testing. The predetermined fiber volume fraction of all fabricated composites is 58 %. To verify proper laminates fabrication and quality, visual inspection and thickness measurements shall be performed on each laminate produced. Test samples shall be clear and free of voids, dry spots, or any other contaminants. The coefficient of thickness variation shall be within 3 % of that predetermined thickness.

Flexural Test

Flexural test (Three-point bending) was performed based on the Chinese Standard GB 1449-2005 (corresponding to International Standard ISO 14125) using CMT 5105 (Electromechanical Universal Testing Machine), which is produced by MTS SYSTEMS (China) Co., Ltd. The test was carried out using a load cell of 5 kN at room temperature at a constant crosshead speed of 2 mm/min. The ratio of span to thickness of the specimen was 16:1. The flexural test was conducted to determine the optimum content of silane coupling agents for epoxy matrix modification and to verify the effects of silane coupling agent on the mechanical properties of composites laminates. Each reported data was the average of more than six successful samples.

Interlaminar Shear Strength (ILSS)

In order to verify the effects of silane coupling agents on the fiber/matrix interfacial adhesion, interlaminar shear test was conducted to determine the interlaminar shear strength (ILSS) values of the composites based on the Chinese Standard GB 1450.1-2005. The shear sample is a “T” type

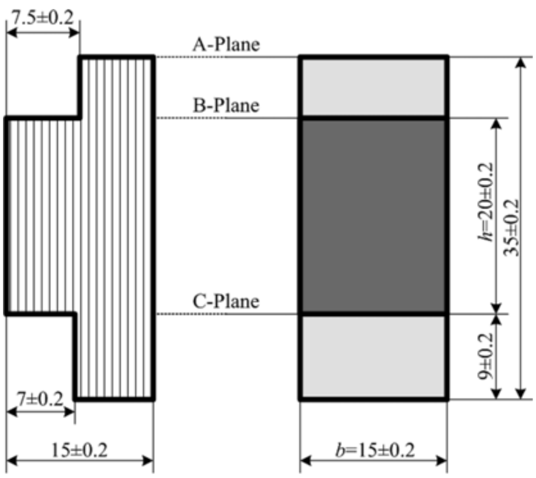

Figure 1. T type shear sample and its dimensions.

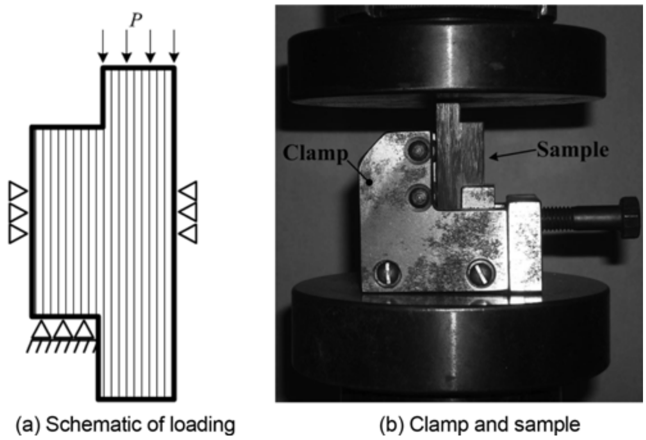

Figure 2. The setup of interlaminar shear testing system.

sample and its dimensions are shown in Figure 1. The test was conducted using the above described testing machine at a crosshead speed of 5 mm/min. All the data were averaged for at least six successful samples.

The setup of shear testing system is shown in Figure 2. The ILSS value can be calculated from the following equation.

$$\tau_s = \frac{P_b}{b \cdot h} \tag{1}$$

Where τ_s is the interlaminar shear strength (ILSS) and P_b is the maximum load, h and b is the length and the width of shear plane, respectively.

Tensile Test

Tensile test was conducted according to the Chinese Standard GB 1447-2005 (corresponding to International Standard ISO 527) using the above described testing machine. The test was carried out using a load cell of 200 kN at a crosshead speed of 2 mm/min at room temperature. The specimen length and width were 250 and 25 mm, respectively. Tensile strength and modulus of the composite were obtained. Each reported data was the average of more than six successful samples.

Scanning Electron Microscopy Analysis

Scanning electron microscopy (SEM), FEI Quanta 200, was used to observe the fractured surfaces of the fabricated composites after interlaminar shear testing. Fracture surfaces of the composite samples were coated with gold and then analyzed at 20 kV.

Viscosity Measurements

The AR2000 EX rotating rheometer (produced by TA Rheology Advantage Inc., USA) was used for the viscosity measurement of the epoxy resin system. The AR2000 EX is a controlled stress/controlled shear rate type rheometer, which is used with a stainless steel cone and plate geometry with a cone diameter of 40 mm, cone angle of 2 ^{o} and truncation of 24 μm. The controlled shear rate in the present viscosity experiments is 10 s^{-1}.

Contact Angle Measurements

The contact angles of the single carbon fiber surfaces were measured on a dataphysics OCA20 contact-angle system by sessile drop method at ambient temperature. The droplet was put on the single carbon fiber using a micro-gauge. Each of the reported contact angle was obtained by averaging five measurement results on different areas of the single fiber.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of hardener RIMH137, silane coupling agent YDH792, unmodified epoxy resin and 0.5 wt% YDH792-modified epoxy resin after curing were recorded on a Nicolet IS10 FTIR spectrometer, where samples were dispersed in KBr.

Results and Discussion

Optimum Concentration of Silane Coupling Agents

Flexural properties can be a comprehensively reflection of composite's ability to resist tensile, compressive and shear loads. So the optimum concentration of silane coupling agents was determined based on the flexural properties of the fabricated carbon/epoxy composites in this paper.

The effect of silane coupling agents on flexural strength and modulus of the modified epoxy composites is shown in Figure 3. It could be seen that the flexural strength and modulus of the modified epoxy composites increased up to 0.5 wt%, which can be related to the effect of increasing the degree of adhesion at interfaces among fiber, matrix and silane coupling agent. And significant reductions in the properties are observed by increasing concentration of silane

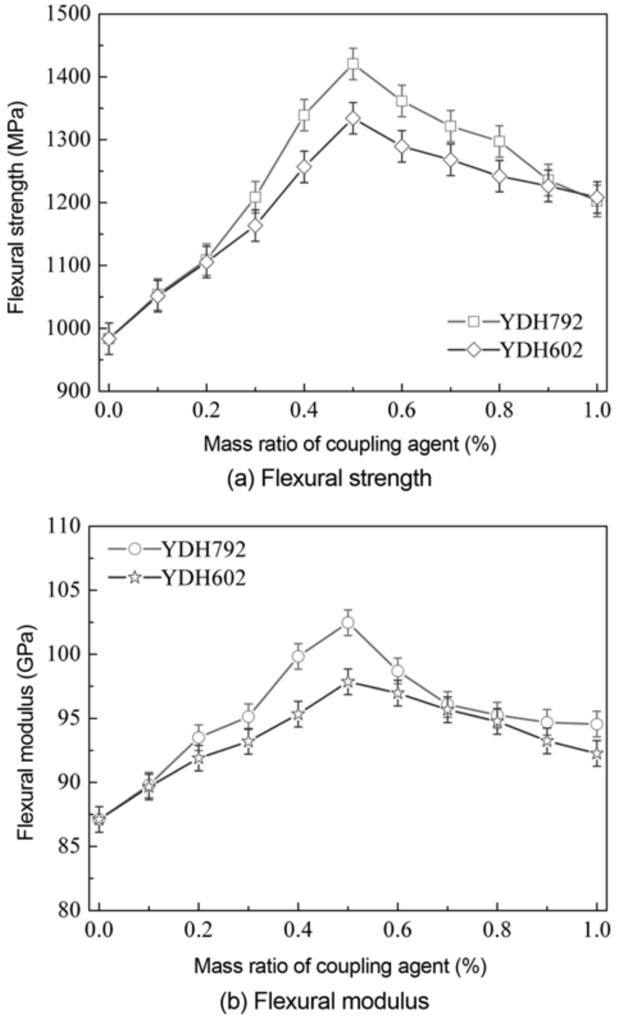

Figure 3. Flexural properties of the modified epoxy composites versus concentration of silane coupling agents.

coupling agents from 0.5 % to 1.0 wt%. This is attributed to the fact that the excess silane coupling agent can form a weak boundary layer by physical adsorption at a high silane coupling agent concentration. This excess silane layer may act deficient in the composite interphase and cause a lubrication effect [19]. Therefore, the flexural properties of the composites decrease at a given higher silane coupling agent concentration.

The experimental results indicate that the optimum concentration of the silane coupling agents is approximately 0.5 wt% of the epoxy resin system for the flexural properties of the modified epoxy composites. It is also clearly seen that the strength and modulus of the YDH602-modified epoxy composites are lower than that of the YDH792-modified epoxy composites at the same silane concentration. Based on the above-mentioned analysis, the interfacial properties and mechanical behavior of 0.5 wt% silane-coupling-agents modified epoxy composite would be presented in the following sections.

FTIR Spectra Analysis

RIMH137 is a polyamine hardener and YDH792 is an amino-silane coupling agent. Figure 4 shows the FTIR spectra of RIMH137 and YDH792. It indicates that both RIMH137 and YDH792 have amino-groups NH or NH_2 as shown in zone between 3200 cm^{-1} and 3400 cm^{-1}. The amino-molecule groups may interact and/or react with the epoxy resin following the mechanism of amine-epoxy addition polymeri-

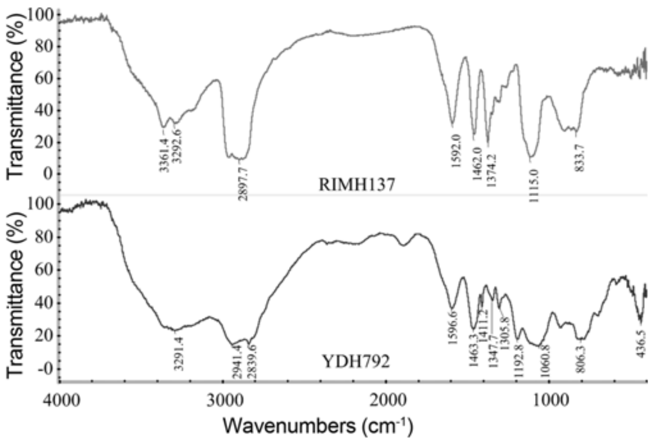

Figure 4. FTIR spectra of hardener RIMH137 and silane coupling agent YDH792.

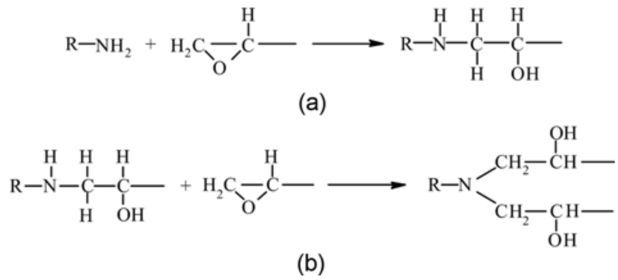

Figure 5. The mechanism of amine-epoxy addition polymerization.

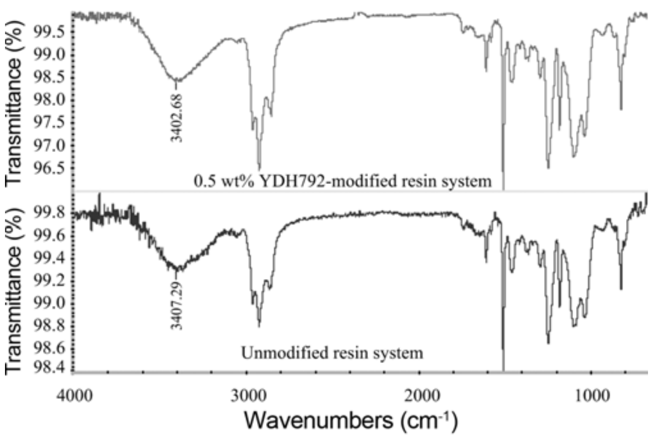

Figure 6. FTIR spectra of unmodified epoxy resin system and 0.5 wt% YDH792-modified epoxy resin system.

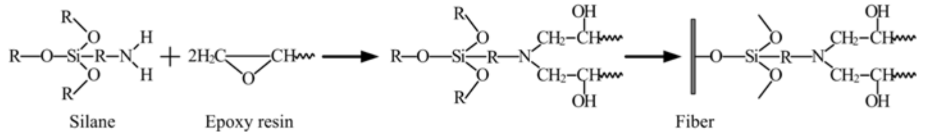

Figure 7. Coupling reaction between silane grafted fiber with epoxy resin [21].

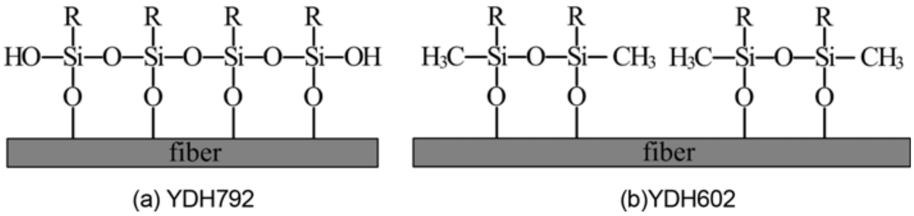

Figure 8. Network structures of YDH792 and YDH602 coupling reactions in the fiber/epoxy composites.

zation as shown in Figure 5. Figure 6 shows that the IR spectra of 0.5 wt% YDH792-modified epoxy resin system is the same as that of the unmodified epoxy resin system. It indicates that amino-silane coupling agent YDH792 can be considered as a part of hardener to react with the epoxy resin RIM135 following the mechanism of amine-epoxy addition polymerization.

As shown in Table 1, both YDH792 and YDH602 are amino-silanes, and the former has three methoxy groups and the latter has two methoxy groups. The methoxy groups of silane coupling agent may form silanols during the reactions, and oxygen linkages may be formed via OH groups on the carbon fiber surfaces, which were epoxy-sized during their production. The coupling mechanism of amino-silanes in the fiber/epoxy composites have been proposed by several authors [20-22] as summarized in Figure 7. Based on the above-mentioned coupling mechanism, the coupling reaction of YDH792 in the fiber/epoxy composites may form more complete network structure than that of YDH602 as shown in Figure 8. This may be a reason for the better modified effect of YDH792 on the flexural properties of the epoxy composites.

Interlaminar Shear Strength

The effect of silane coupling agents on ILSS values of the epoxy composites is presented in Figure 9. As shown in Figure 9, the greatest ILSS value belongs to 0.5 wt% YDH792-modified epoxy composite when compared with that of the other composites. The ILSS value of the carbon/epoxy composite without silane coupling agent is obtained to be 34.30 MPa. The ILSS values of 0.5 wt% YDH602 and YDH792 modified epoxy composites increased up to 40.13 and 48.69 MPa, this corresponds to an increase of 17 % and 42 % in ILSS value of the carbon/epoxy composite, respectively. It indicates that silane incorporation results in a better adhesion between the fiber and the resin for carbon/epoxy composite.

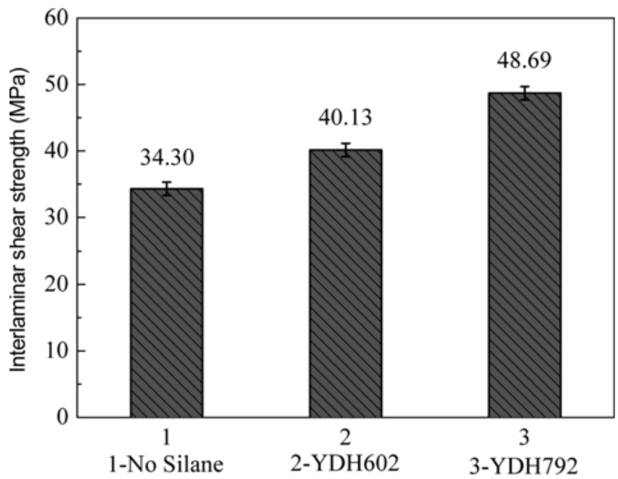

Figure 9. ILSS values of carbon/epoxy and carbon/0.5 wt% silanes modified-epoxy composites.

Flexural and Tensile Properties

Tensile and flexural strength values for unmodified, 0.5 wt% YDH602 and 0.5 wt% YDH792 modified epoxy composites are shown in Figure 10(a). It can be seen that a slight improvement in tensile strength values for carbon/epoxy composites was obtained by the matrix modification with 0.5 wt% YDH602 and 0.5 wt% YDH792, which corresponds to an increase of 2 % and 4 % respectively. It is obvious that 0.5 wt% YDH792 modified epoxy composite exhibited the highest tensile strength, which increased from 1879.27 MPa for unmodified to 1961.46 MPa for 0.5 wt% YDH792 modified epoxy composite.

Compared to unmodified epoxy composite, the flexural strength of 0.5 wt% YDH602 modified-epoxy composite and 0.5 wt% YDH792 modified-epoxy composite is enhanced by 36 % and 44 %, respectively. It is clearly seen that 0.5 wt% YDH792 modified epoxy composite showed the highest improvement in terms of flexural strength, which

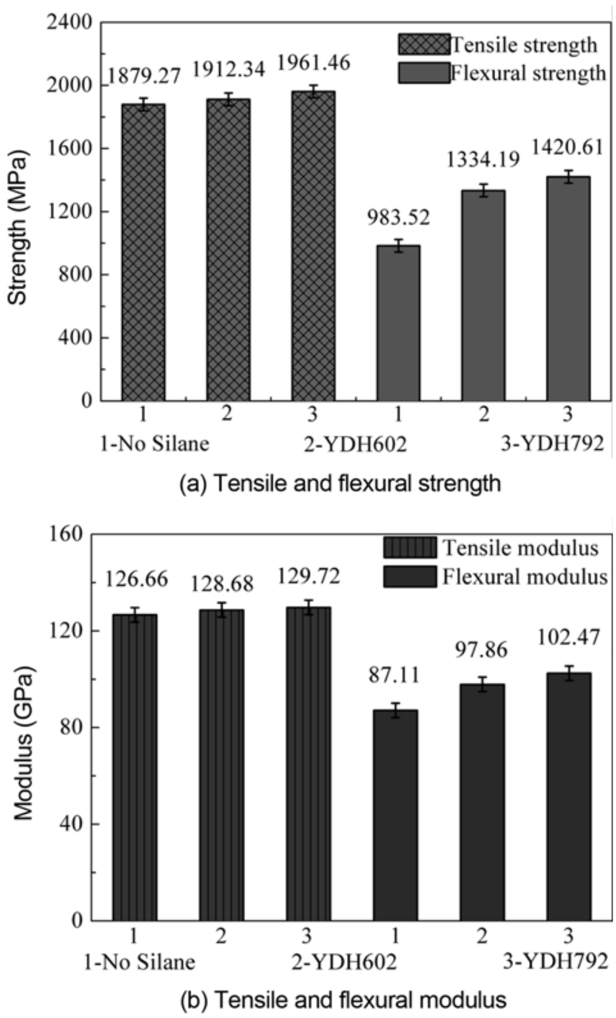

Figure 10. Tensile and flexural properties of carbon/epoxy and carbon/0.5 wt% silanes modified-epoxy composites.

increased from 983.52 MPa for unmodified to 1420.61 MPa for 0.5 wt% YDH792 modified epoxy composite.

The influence of 0.5 wt% YDH602 and 0.5 wt% YDH792 silane coupling agents on the tensile and flexural modulus of epoxy composites is illustrated in Figure 10(b). The results indicate that silane coupling agents modification of the matrix resulted in slight increase for the tensile modulus value of the epoxy composites. The improvement for 0.5 wt% YDH602 and 0.5 wt% YDH792 modified epoxy composites is 2 % and 3 %, respectively, when compared to that of unmodified epoxy composite. As shown in Figure 10(b), the flexural modulus value of epoxy composite is enhanced by 12 % and 15 % as a result of matrix modification using 0.5 wt% YDH602 and 0.5 wt% YDH792, respectively.

It can be concluded that only a slight improvement in tensile properties of carbon/epoxy composites can be obtained by the matrix modification with 0.5 wt% YDH602 and 0.5 wt% YDH792, while the silane coupling agents' modification of the matrix resulted in a larger improvement in flexural properties. The tensile properties of fiber reinforced composites mainly depend on the strength of reinforced fiber and fiber volume fraction. Therefore, there is only a slight improvement in the tensile strength values for silane coupling agents modified epoxy composites. And the enhancements in tensile properties may be explained by considering the improvement in the adhesive characteristics between carbon fiber and epoxy matrix.

The flexural properties of fiber reinforced composites depend on the fiber/matrix adhesion as well as the strength of each component. Larger increase in flexural properties may be a result of improved adhesion between fiber and matrix, pointing out a stronger interface, which allows better stress transfer between the constituents of the composite [3,23]. And the improved adhesion can be ideally reflected through flexural properties of the composites.

SEM Analysis

SEM micrographs of the fractured surface of representative specimens after interlaminar shear testing were captured to visualize the fiber/matrix adhesion in carbon fiber reinforced epoxy composites. As shown in Figure 11, the fracture surfaces show remarkable differences resulting from the change in fiber-matrix-silane coupling agent adhesion.

The surface of fracture for unmodified epoxy composite is shown in Figure 11(a). It can be seen that very little amount of epoxy resin is found to adhere onto the fiber surfaces in the facture site of the composite and the matrix between fibers is broken to pieces. The fiber surface seems to be clean, intact and free from any adhering polymer. These features suggest poor interfacial bonding between the carbon fiber and the unmodified epoxy matrix.

From the SEM micrographs of 0.5 wt% YDH602 modified epoxy composite as shown in Figure 11(b), it is clearly seen that a greater amount of epoxy resin is observed to adhere onto the fiber surfaces and the matrix between fibers is continuity, although micro-cracks can be observed in the interface between the fiber and the matrix. Compared to unmodified epoxy composite, it is evident that the interfacial adhesion between the carbon fiber and epoxy resin has been improved via modification of the resin by incorporation of silane coupling agent YDH602.

Figure 11(c) shows the fracture surface of 0.5 wt% YDH792 modified epoxy composite after interlaminar shear testing. The matrix between fibers is continuity and the fiber is obviously seen to be embedded in the epoxy resin. Moreover, it is no observations of micro-cracks in the interface between the fiber and the matrix. These suggest a better fiber/matrix adhesion in carbon fiber reinforced YDH792-modified epoxy composite than that of unmodified and YDH602-modified epoxy composites. These observations are in agreement with the previous results of tensile, flexural and interlaminar shear testing.

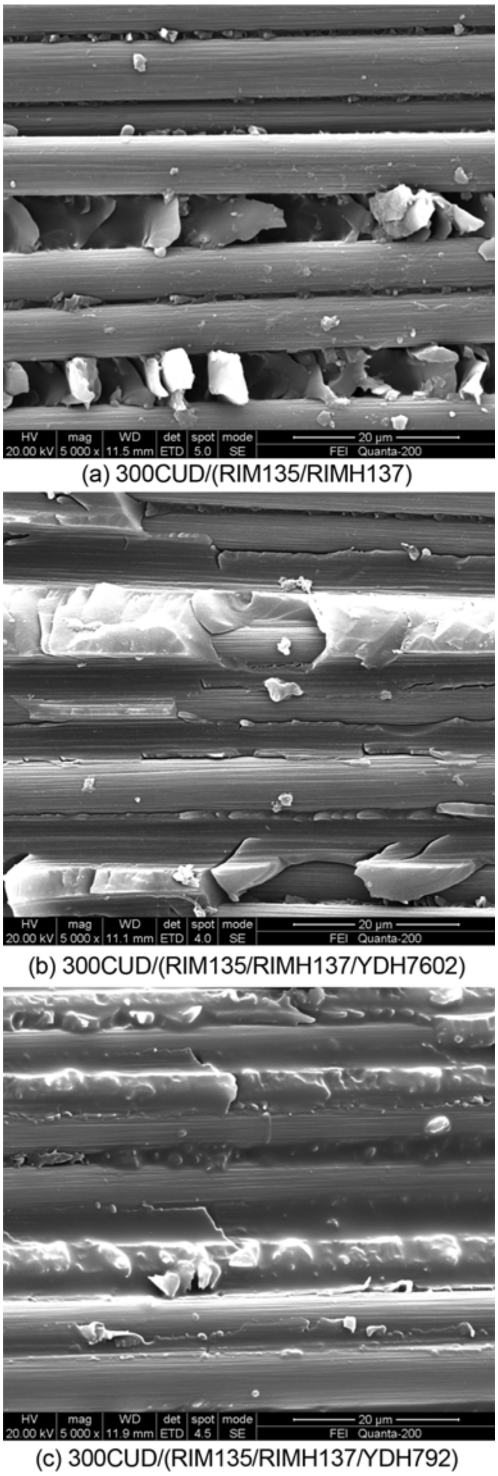

Figure 11. SEM images of fracture surface after interlaminar shear testing.

Impregnation Properties of the Modified Epoxy System

YDH792 is a low-viscosity silane coupling agent, which can reduce the viscosity of the modified epoxy resin system. Figure 12 shows that the viscosity of the modified epoxy resin system decreases with the concentration of YDH792 at room temperature. According to Darcy's law [24], the velocity of the resin flow through permeable fiber preform in the mold increases with the decreasing viscosity of the resin system at the same fluid pressure condition. It is beneficial to promote fiber impregnation or wetting during large-scale composite components manufacturing by liquid composite molding process.

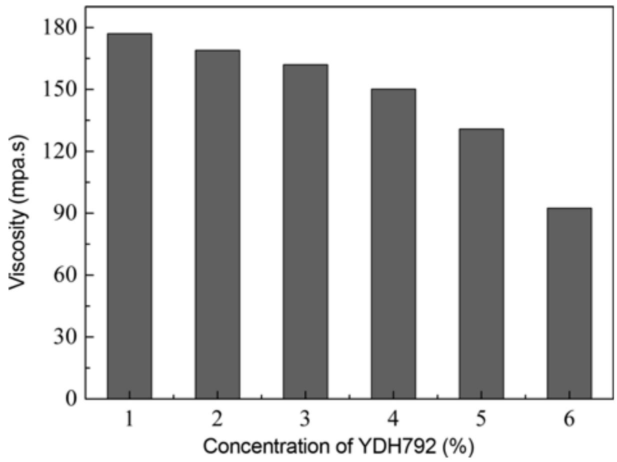

Figure 12. Influence of silane coupling agent YDH792 on the viscosity of modified epoxy resin system at room temperature.

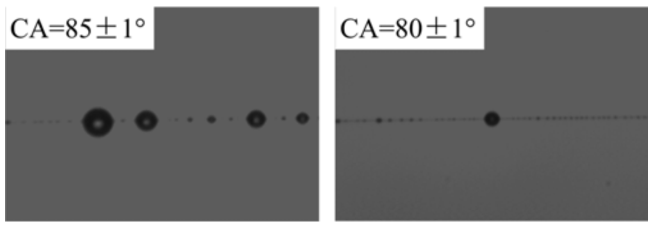

Figure 13. Contact angle of unmodified epoxy resin system and 0.5 wt% YDH792-modified epoxy resin system.

Decreasing viscosity also results in a slight decrease in the resin contact angle of the single carbon fiber surface as shown in Figure 13. The contact angle of the unmodified and 0.5 wt% YDH792-modified epoxy resin system on the single carbon fiber surface is 85±1 ^{o} and 80±1 ^{o}, respectively. It also can be considered to be an indication of better properties of impregnation or wetting for the modified epoxy resin on the carbon fiber surfaces.

Conclusion

Matrix modification by incorporation of silane coupling agents was carried out to improve the interfacial adhesion between carbon fiber and epoxy resin. The effect of matrix modification on the mechanical properties of carbon/epoxy composites was investigated in terms of tensile, flexural and interlaminar properties.

The flexural properties indicate that the optimum concentration of silane coupling agents YDH602 and YDH792 for the matrix modification is approximately 0.5 wt% of the epoxy resin system. The interlaminar results show that the incorporation of 0.5 wt% YDH602 and 0.5 wt% YDH792 resulted in an increase of 17 % and 42 % in ILSS value of the carbon/epoxy composite, respectively, when compared to the unmodified epoxy composite.

Only a slight improvement in tensile properties of carbon/epoxy composites can be obtained by the matrix modification with 0.5 wt% YDH602 and 0.5 wt% YDH792, when compared to the unmodified epoxy composite. The improvement for 0.5 wt% YDH602 and 0.5 wt% YDH792 modified epoxy composites is 2 % and 4 % in tensile strength value, and the corresponding improvement of tensile modulus is 2 % and 3 %, respectively.

The flexural strength of the modified epoxy composites is enhanced by 36 % and 44 % as a result of matrix modification using 0.5 wt% YDH602 and 0.5 wt% YDH792, and the corresponding enhancement of flexural modulus is 12 % and 15 %, respectively, when compared to that of unmodified epoxy composite.

These improvements in mechanical properties indicate that incorporation of silane coupling agent results in a better adhesion between the fiber and the resin for carbon/epoxy composite. SEM observations are in agreement with the previous results of tensile, flexural and interlaminar shear testing, which also confirmed improvement in interfacial bonding between the carbon fiber and the modified epoxy matrix.

The viscosity of the modified epoxy resin system can be reduced by incorporation of silane coupling agent YDH792. It is beneficial to promote fiber impregnation or wetting during large-scale composite components manufacturing by liquid composite molding process.

Acknowledgement

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