

This article is a post-print copy of H. Cui, M. R. Kessler: Pultruded Glass Fiber/Bio-based Polymer: Interface Tailoring with Silane Coupling Agent, *Composites Part A: Applied Science and Manufacturing*, 2014, 65, 83-90. doi:10.1016/j.compositesa.2014.05.021.

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## **Pultruded glass fiber/bio-based polymer: Interface tailoring with silane coupling agent**

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### **Abstract**

Economical glass fiber reinforced polymer composites were developed from biorenewable resins utilizing a highly automated pultrusion process. The composites were successfully pultruded with a self-built table-top pultrusion machine. The interfacial interaction of the composites was significantly improved after surface modification with a silane coupling agent. The optimum silane concentration was determined by testing the mechanical properties of the pultruded fiber reinforced composites. Composites reinforced with fibers that were treated with a 3% silane solution exhibited the best properties in both DMA and flexural tests.

### **Keywords**

- Glass fibers;
- Interface/interphase;
- Surface treatments;
- Pultrusion

### **1. Introduction**

The applications of fiber reinforced polymer (FRP) composites have grown significantly since 1960s because of their excellent overall properties which are either comparable to or better than many traditional metallic materials. FRPs possess superior properties in terms of light weight, high specific strength and stiffness, excellent environmental resistance, high electrical insulation, and low thermal expansion [1]. Over the years, FRP composites have found increasingly wide applications in a variety of fields, such as in the aerospace, transportation, construction, chemical engineering and electrical industries. In the early days, advanced composite materials were mainly used in military and government aerospace industries where cost is not a major concern. In recent years, the application of high performance FRPs has grown steadily in construction of civil infrastructure and has begun to challenge the dominant position of traditional materials. The development and advantages of FRP applications in the building and civil infrastructure have been reviewed thoroughly by Hollaway [2] and [3]. FRPs are finding increasing use for

rehabilitation, seismic retrofitting and upgrading of concrete bridges as ways to extend the service life of existing structures. However, the use of composites are still limited because of their high material and manufacturing costs. With the growing opportunities for composite materials in structural applications, the development of inexpensive composites is of great interests.

Pultrusion is a cost-effective, automatic process for the production of continuous composite parts with constant cross-sectional profiles [4]. Fig. 1 provides a schematic representation of the pultrusion process. During pultrusion, fibers are impregnated with resin by being pulled through a resin bath or a resin injection chamber. The wet fibers then pass through a hot die, where the resin undergoes polymerization. Multiple heating zones are used along the die, depending on the type of resin used. Pultrusion has a number of advantages over other composite manufacturing methods:

- Increased strength because the fibers are aligned in the tension state.
- Highly automatic process with little manual interface, so that it is possible to efficiently produce high fiber volume composites with consistent quality.
- Low cost, typically 80–90% of the cost for pultruded profiles are the raw material costs.

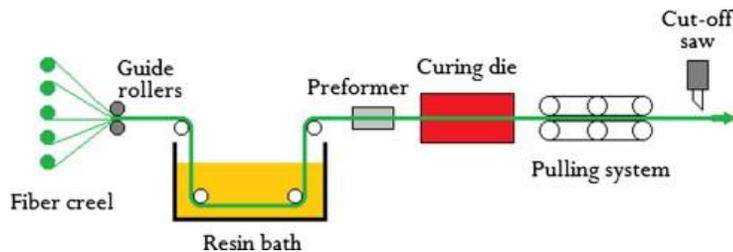


Fig. 1: Schematic diagram of pultrusion

Based on these advantages, pultrusion is the technique of choice for the production of glass fiber reinforced composites when low cost and good mechanical properties are required.

Growing concerns regarding the limited petroleum resources, the volatile price of oil, and the environmental impact of fossil feedstocks have led to an increasing demand for the development of polymeric materials from sustainable resources. Vegetable oils are ideal raw materials for the polymer industry because of their ready availability, structural variety, chemical versatility and relatively low cost. The major components in vegetable oils are triglycerides which contain several reactive sites and functionalities that can be utilized in a variety of synthetic transformations. Over the past ten years, a series of bio-based polymers has been synthesized and developed from vegetable oils using various polymerization methods [5] and [6]. Among them, a copolymer that was prepared from modified linseed oil (Dilulin) and dicyclopentadiene (DCPD) by ring opening metathesis (ROMP) polymerization shows promising mechanical properties [7] and [8]. In addition, the low viscosity of the copolymer and its fast cure kinetics make it a good resin candidate for the pultrusion process. Pultrusion is the most cost-effective

manufacturing method, and combined with low-cost biorenewable resins allows for the production of inexpensive composites for structural applications.

It is well known that the ultimate properties of composite materials depends not only on the properties of the constituent materials (e.g. matrix and fiber reinforcement), but also on the interphase and interface between the matrix and reinforcement [9]. Good interfacial adhesion allows effective stress transfer from the matrix to the reinforcement and increases the ultimate strength of the composite. Surface modification with silane coupling agents [10], [11] and [12] is widely used to improve the interfacial adhesion in glass fiber reinforced polymer composites. Silane coupling agents are difunctional organic compounds which are able to form covalent bonds with both the inorganic reinforcement and the polymer matrix.

In this research, we pultruded Dilulin/DCPD copolymers to produce low-cost, bio-based composites with good mechanical properties. The resin formulation and pultrusion process parameters were optimized based on performance. Surface modification of glass fibers by a monochlorosilane was used to improve the interfacial adhesion of the composites.

## 2. Experimental

### 2.1. Materials

The materials used in this study are listed in [Table 1](#); they include two monomers, a catalyst, lubricant, fillers, and glass fibers. Dilulin and DCPD monomers were mixed at a ratio of 3:7. Then 0.125 wt.% catalyst was added prior to processing. The Grubbs' catalyst was recrystallized by freeze-drying from benzene to allow better dissolution in the resin [13]. Dilulin which is commercially available from Cargill is synthesized from linseed oil and cyclopentadiene using a high temperature, high pressure Diels–Alder reaction. The chemical structure of Dilulin has been studied thoroughly by NMR and FTIR, indicating an average of one norbornene ring pendant group per triglyceride [7] and [13]. The ROMP reaction of Dilulin and dicyclopentadiene is shown in [Fig. 2](#).

Table 1: Materials used in this study.

Material	Parts by weight	Specification	Supplier
Dilulin	30	Dilulin monomer, modified linseed oil	Cargill, MN
DCPD	70	Dicyclopentadiene monomer	Sigma–Aldrich, WI
Catalyst	0.125	2nd Generation Grubbs' catalyst	Sigma–Aldrich, WI
Lubricant	5	Tech Lube SR-150-W2	TECHNICK, NJ
Filler	10	ASP-400p, Kaolin clay	BASF, GA
Glass fiber	N/A	Continuous E-glass, 56 yield	Pella, IA
MCS	N/A	Norbornenylethyltrimethylchlorosilane, silane coupling agent	Gelest, PA

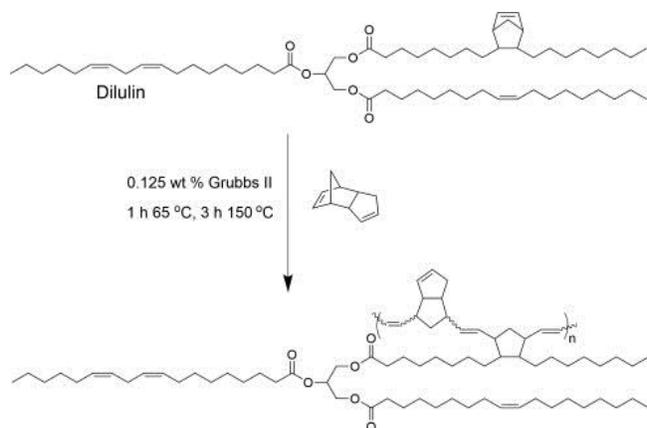


Fig. 2: ROMP reaction of Dilulin and dicyclopentadiene.

## 2.2. Glass fiber surface modification

To improve the interfacial adhesion between the glass fibers and the resin in FRP composites, the glass fibers were modified with a silane coupling agent prior to pultrusion. According to a previous study [14], norbornenylethyldimethylchlorosilane (Monochlorosilane, MCS, see Fig. 3) offered better coupling effects compared to norbornenylethyltrichlorosilane (Trichlorosilane, TCS) because of the reproducible grafting result. Five rovings of glass fibers were cut long enough for one pultrusion running. The fibers were heat-cleaned in a convection oven at 450 °C for 3 h to remove the existing sizing. Silane/alcohol solutions with varied concentrations of MCS were prepared by mixing silane with anhydrous isopropanol alcohol. The solution was warmed to 40 °C for 30 min to promote a reaction between the silane and the alcohol. The heat-cleaned glass fibers were dipped in the silane solution for 3 min and then rinsed with excess isopropanol alcohol. The treated fibers were cured at 120 °C for 10 h to improve silanol condensation reactions on the fiber surfaces.

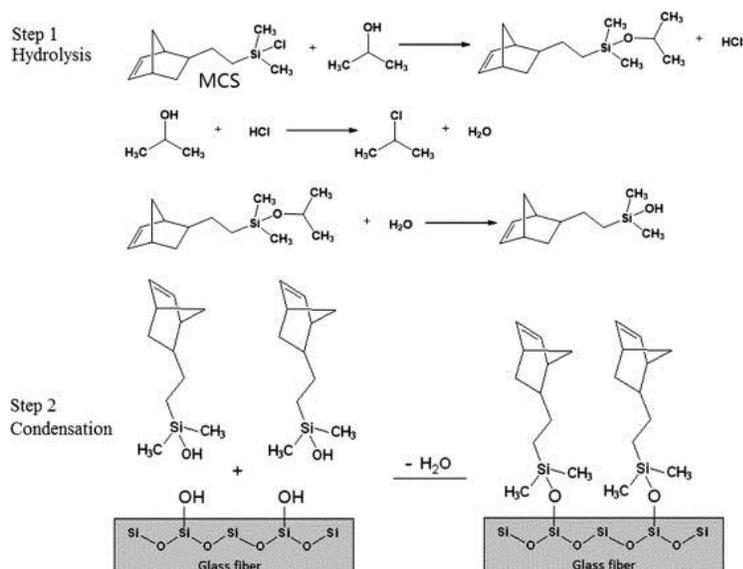


Fig. 3: Two steps of MCS silane reactions: hydrolysis and condensation.

### 2.3. Pultrusion process

A table-top pultrusion machine was designed and built in order to manufacture the composite on a lab-scale. The machine consisted of resin injection block, a pultrusion die with dimensions of 60 mm × 2.5 mm × 1 mm (length × width × thickness), and a puller. The surface of the die was coated with high temperature ultra-slippery PTFE tapes. Although only one heating zone was used in the pultrusion machine, a water circulation system was designed on each end of the die to keep the entrance and the exit of the die cool. The optimized processing temperatures along the die are shown in Fig. 4. Fiber reinforced polymer composites were made with 5 rovings of unidirectional glass fiber, resulting a total fiber content of 50% by volume. The pulling rate was 0.075 m/min and varied slightly throughout the process. The pultruded fiber glass reinforced biopolymer composites are shown in Fig. 5.

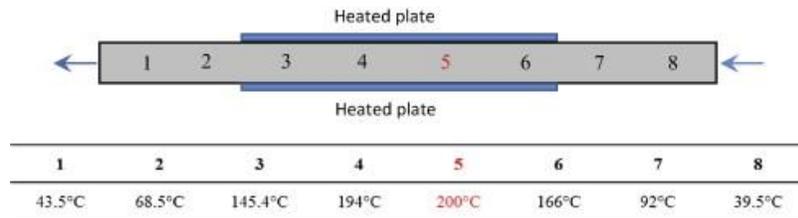


Fig. 4: Temperature distribution along length of the die.



Fig. 5: Pultruded glass fiber/bio-based polymer composites

### 2.4. Characterizations

Surface elemental concentrations of glass fibers treated with varied silane solutions were measured by utilizing X-ray photoelectron spectroscopy (XPS, PHI55000) with an Al K $\alpha$  (1486.6 eV) source. Dynamic mechanical tests of the copolymers were carried out by using a TA Q800 dynamic mechanical analyzer (DMA) in a tension mode. Tests were operated with an oscillation amplitude of 10  $\mu$ m, a preload force of 0.01 N, and a force track of 125%. Samples

were cooled down to  $-20\text{ }^{\circ}\text{C}$  and held isothermally for 2 min, followed by heating up to  $250\text{ }^{\circ}\text{C}$  at a rate of  $3\text{ }^{\circ}\text{C}/\text{min}$ . The glass transition temperature ( $T_g$ ) was determined by the peak of the  $\tan \delta$  curve. Flexural tests were carried out on an Instron 5569 universal testing machine (50 kN load cell and Bluehill software) with a 3-point bending fixture at a crosshead speed of 2 mm/min. Two types of samples were prepared: along fiber direction and transverse to the fiber directions. Flexural strength and modulus were calculated based on at least five samples. The fracture surfaces of the specimens were investigated by a field-emission scanning electron microscope (FE-SEM, FEI Quanta 250) operating at 8 kV in high vacuum to correlate the microstructure and the fracture behavior. The samples were sputtered with 5 nm Iridium film.

### 3. Results and discussion

#### 3.1. XPS

Elemental concentrations for fibers treated with different silane coupling agents are summarized in [Table 2](#). As-received glass fiber had the highest carbon concentration because of the existing sizing on the surface that was applied during fiber manufacturing. Sizing consists of multiple components, including film former, silane, lubricant, and an antistatic agent, which are mostly organic compounds with a large number of carbon atoms in their structure. This high carbon concentration was greatly reduced after heat-cleaning. The small amount of residual carbon may have been caused by contamination. It can be seen in [Table 2](#) that as the concentration of silane solution increased, the concentration of carbon atoms initially increases and then remained at a constant value.

Table 2: Elemental concentrations of differently treated glass fibers.

	C (%)	O (%)	Si (%)
As-received fiber	79.72	19.74	0.53
Heat-cleaned fiber	11.4	69.1	19.5
MCS-0.5%	15.8	65.1	19.2
MCS-1%	17.6	63.9	18.5
MCS-2%	19.5	62.0	18.5
MCS-3%	20.6	61.1	18.3
MCS-4%	19.4	61.5	19.1

The chemical reaction during surface modification is described in [Fig. 3](#). This is a two-step reaction, including hydrolysis and condensation of silane. In the first step, MCS reacts with the alcohol, producing an alkoxysilane and HCl. Mild warming of the solution facilitates the removal of HCl and the completion of the reaction. Then some HCl react with alcohol to produce a small amount of water and alkyl halide. The water causes hydrolysis of alkoxysilane to form silanols. Finally, silanols condense with hydroxyl groups on fiber surface, forming covalent bonds between silane and glass fiber. The coupling effect of monofunctional silane is promising and reproducible, because only one type of grafting is possible [\[15\]](#). The maximum bonding density is limited by the size of the dimethylsilyl group [\[16\]](#). However, the reactions of monofunctional silanes at the solution–solid interface are very slow in the later stages, and long reaction times (several days) are necessary to achieve maximum bonding density [\[17\]](#) and [\[18\]](#).

In our case, the glass fibers were immersed in the silane solution for only 3 min. It can be seen in later section that the interfacial adhesion has been improved greatly with such short time treatment. The XPS measurement revealed that under the treatment conditions used in our investigation, the highest concentration of carbon atoms was 20%. Compared to the results of refluxing reactions used in a previous study [14], we obtained a lower bonding density; however, our approach was time-saving and allowed for the treatment of fibers in large quantities. In a later section it will show that the mechanical properties improved significantly, even with the lowered bonding density.

DMA specimens were cut and tested transverse to the fiber direction. The temperature dependent storage modulus and  $\tan \delta$  are presented in [Fig. 6](#). The storage modulus for all samples showed the typical three-stage behavior: it staid constant in the glassy state and then dropped suddenly in the temperature range between 50 and 100 °C, finally reaching the rubbery plateau. In [Fig. 6](#), the curves between 0 and 50 °C were enlarged to provide more details. The storage moduli at 25 °C and 175 °C are summarized in [Table 3](#). It can be seen that compared to regular fiber composites, the storage modulus of composites made with silane-treated fibers was improved significantly, even when a dilute silane solution was used. The storage modulus at room temperature tripled after silane treatment, indicating that the interfacial interaction between glass fibers and polymer matrix was significantly enhanced. As the concentration of the silane solution increased, the storage modulus increased as well; however, the increase levelled off for concentration above 2 wt.%. It is interesting to note that the storage modulus in the rubbery state (175 °C) did not show the large differences as in the glassy state. The rubbery modulus is related to the cross-link density of polymeric materials. The surface modification with silane coupling agents affected only the interfacial bonding and had little effect on the cross-link density of the bulk polymer.

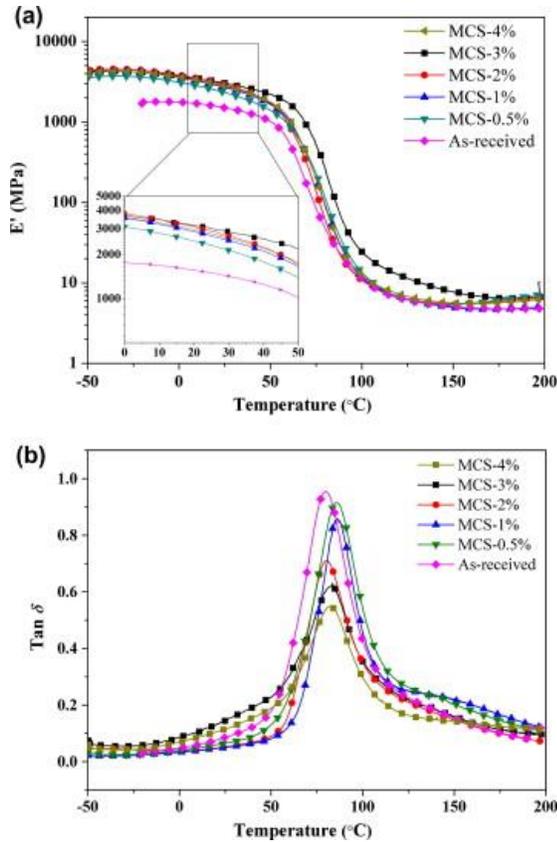


Fig. 6: Temperature dependent storage modulus (a) and  $\tan \delta$  (b).

Table 3: DMA data summary.

	$T_g$ ( $^{\circ}\text{C}$ )	$E'$ (MPa) at 25 $^{\circ}\text{C}$	$E'$ (MPa) at 175 $^{\circ}\text{C}$
As-received	79.5	1491	4.77
MCS-0.5%	85.0	2325	5.37
MCS-1%	86.3	2700	4.94
MCS-2%	84.5	2902	5.49
MCS-3%	88.6	3002	7.77
MCS-4%	86.8	2790	5.6

The glass transition temperatures obtained from the  $\tan \delta$  curves are also listed in Table 3. It can be seen that all samples exhibited a glass transition temperature of approx. 85  $^{\circ}\text{C}$ . The  $\tan \delta$  curves provided not only the glass transition temperatures but also information regarding damping properties which are measured as the magnitude of the  $\tan \delta$  peak. Damping is a sensitive indicator of molecular motions [19]. Under deformation, the fibers usually carry a major part of the stress and allow only small portion of it to strain the interface because of the rigid bonding at the fiber/matrix interface. Therefore, a strong interfacial bond will restrict large-scale movement of more polymer chains, leading to a reduced damping value. Many researchers [20], [21] and [22] confirmed that the magnitude of  $\tan \delta$  is inversely proportional to interfacial adhesion. In Fig. 6b, a gradual decrease in the  $\tan \delta$  value was observed as the silane

concentration increased, suggesting that improved interfacial bonding was obtained after surface modification with silane.

### 3.2. Flexural tests

Flexural tests were carried out with samples cut in both fiber direction and transverse to fiber direction. Flexural strength and the stress–strain curves of samples cut in fiber direction are displayed in Fig. 7. Both flexural strength and flexural modulus increased significantly after surface modification with silane. Composites made with as-received fibers exhibited a flexural strength of only 110 MPa and a flexural modulus of 6 GPa. The flexural strength doubled and the flexural modulus near doubled for treated glass fibers, even when the glass fibers were treated with 1% silane solution for 3 min. During deformation, good interfaces transfer stress from matrix to reinforcement effectively and the strain is restrained by the rigid reinforcement. Therefore, composites with good interfacial bonds require higher forces for the same amount of deformation compared to composites with poor interfacial bonds. Samples made with fibers treated with 3% silane solution showed the highest flexural properties. Further increases in silane concentration did not further improve the flexural properties. Fig. 7b shows typical stress–strain curves obtained by flexural tests. Samples made with as-received, 0.5% silane-treated and 1% silane-treated fibers showed ductile behavior, where stresses change slightly after yielding point. Severe delamination was observed in these samples due to the poor interfacial adhesion. Other composites were seen to fail in semi-brittle manner with less delamination.

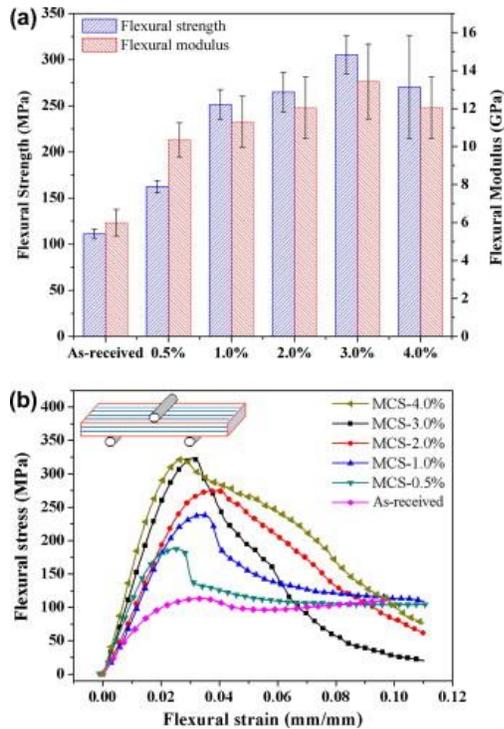


Fig. 7: Flexural tests in fiber direction (a) flexural strength and flexural modulus and (b) typical stress–strain curves for different composites.

Flexural strength and stress–strain curves for samples cut transverse to the fiber direction are presented in Fig. 8. For unidirectional fiber composites, transverse flexural strength and modulus are matrix-sensitive and interface-sensitive. Fig. 8 shows that transverse flexural strength is much lower than flexural strength in fiber direction; however, both show a similar increasing trend. Composites made with 2% and 3% silane-treated fibers show similar transverse flexural strength, while composites made with 4% silane-treated fibers showed reduced flexural strength due to the huge errors. The transverse flexural strength of the composites is lower than the flexural strength of pure polymer, which is around 50 MPa. Because transverse flexural strength of unidirectional fiber reinforced composites is rather sensitive to defects. Any defects, both inside or outside, in sample cause stress concentrations, initiating cracks that will propagate, finally causing failure of the sample. The interface between fibers and matrix in composites is the weakest point, even the interfaces are strengthened by a silane coupling agent.

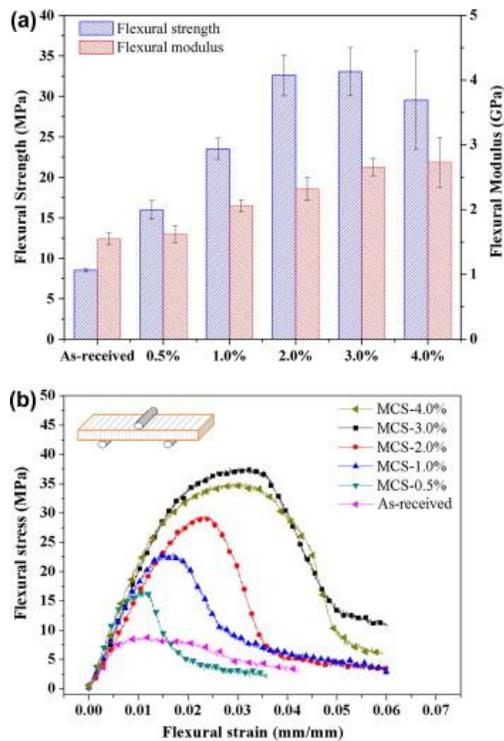


Fig. 8: Flexural tests transverse to fiber direction (a) flexural strength and flexural modulus and (b) typical stress–strain curves for different composites.

### 3.3. SEM

Fig. 9 shows SEM micrographs of the fracture surfaces of fiber reinforced composites. It can be seen that in Fig. 9a, very few resin is adhered on fiber surface after fracture, because no evidence shows that chemical bonding can form between sizing and polymer matrix in composite made with as-received fiber. Fig. 9b shows the fracture surface of composite made with 0.5%-silane-treated fiber. We can see that a few resin is adhered on fiber surfaces and long glass fibers were pulled out from the polymer matrix, both indicating a weak interfacial adhesion exist in this composite. In long fiber reinforced composite with poor interface, the interface usually fails first

under load in the form of debonding, and then the interface cannot transfer load from matrix to fiber reinforcement effectively, finally composite will totally fail when polymer matrix fractures. From flexural test we already know that as the concentration of silane solution increased, the interfacial adhesion was improved gradually. Consistent results were observed in SEM examination. As the silane concentration increased, more and more resin is adhered on fiber surface and less fibers were pulled out after fracture (Fig. 9c–f). Especially in composites made with 3% and 4% silane-treated fibers, glass fibers were still bundled tightly by polymer matrix after fracture which demonstrates that good interfacial adhesion was formed by covalent bonding between fiber and matrix through silane coupling agent. Therefore, load can be transferred to high strength fibers effectively via interface and improve the strength of composite as a result.

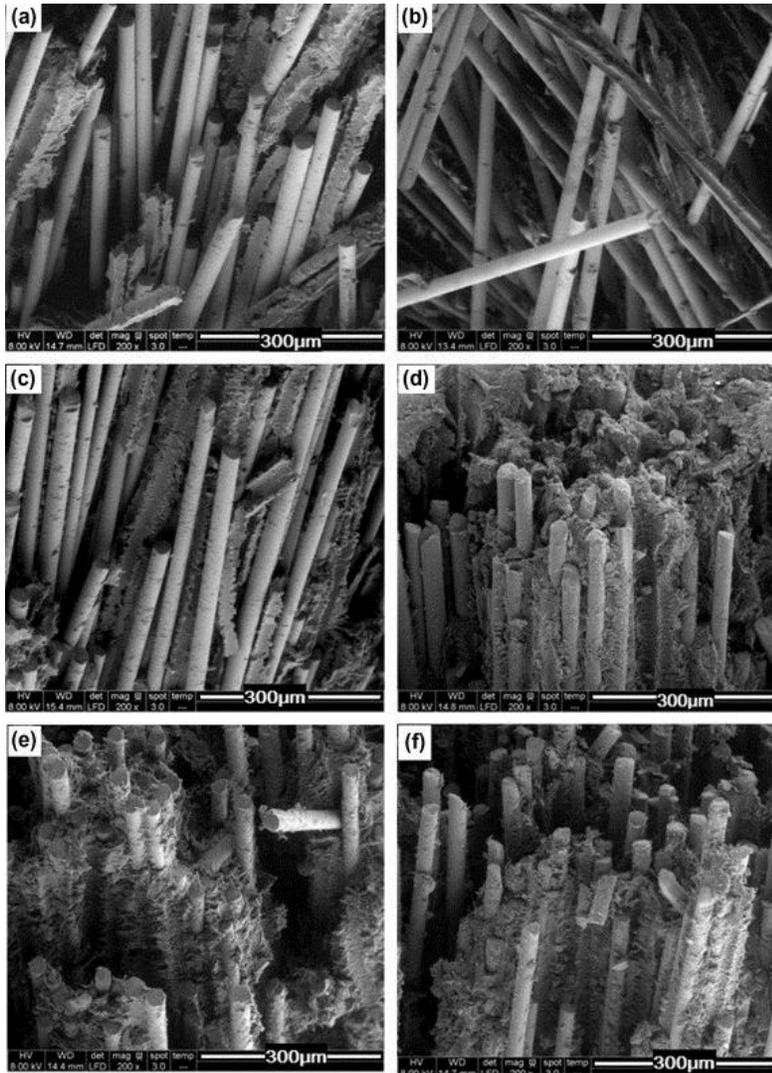


Fig. 9: SEM images of fracture surfaces of different composites (a) As-received fiber; (b) 0.5%-silane-treated fiber; (c) 1% silane-treated fiber; (d) 2% silane-treated fiber; (e) 3% silane-treated fiber; and (f) 4% silane-treated fiber.

#### 4. Conclusions

To improve the interfacial adhesion of pultruded glass fiber/bioresin composites, the glass fibers were treated with silane/alcohol solution in various concentrations. Although the fibers were immersed in silane solution for only 3 min, the interfacial adhesion was enhanced significantly. XPS measurements demonstrated that as the silane concentration increased, the elemental concentration of carbon atom initially increased and reached a maximum level of about 20% with a silane concentration of 2%. DMA tests revealed that the storage modulus was significantly improved after surface modification. The reduced magnitude of the  $\tan \delta$  peak also confirmed that improved interfacial adhesion was obtained. Flexural strength and modulus both in fiber and transverse to fiber direction showed consistent results. DMA and flexure test both indicated that increasing the silane concentration from 3% to 4% did not increase interfacial bonding too much. Therefore, 3% of silane in isopropanol was determined as the optimum concentration for surface modification with a simple dipping method. The morphology of the fracture surfaces of the composites also confirmed our conclusions.

#### Acknowledgements

The authors would like to thank the Consortium for Plant Biotechnology Research (CPBR) for their support of this work. This publication was made possible by USEPA grant EM-83438801. Its contents are solely the responsibility of the grantee and do not necessarily represent the views of the USEPA. Further, USEPA does not endorse the purchase of any commercial products or services mentioned in this publication.

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