

# Surface Modification of Flax Fibers with Isocyanate and Its Effects on Fiber/Epoxy Interfacial Properties

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(Received July 10, 2019; Revised March 12, 2020; Accepted March 18, 2020)

**Abstract:** Natural fiber reinforced polymer composite has been widely used in various industry fields. Natural fiber treatment can effectively improve its mechanical and durability properties, and expands its applications. In the present study, isocyanate was proposed to treat flax fibers in order to reduce the hydrophilic properties of the fibers, and to enhance the bonding of flax fiber to epoxy matrix. The isocyanate treated fabric was evaluated with fourier transform infra-red (FTIR), scanning electron microscopy (SEM) and water uptake. The effects of the fiber treatment on the mechanical properties of flax fabric reinforced epoxy (FFRP) plates were investigated. FTIR and SEM analysis indicated that isocyanate reacts with flax fiber, forming a thin polymer layer on the fiber surface. The water absorption test showed that isocyanate treatment decreased the water uptake of the flax fabric by 4-18 times compared to the control fabric. The flexural and tensile strength of FFRP with isocyanate solution treated fabrics were enhanced more than 20 %, attributed to the improved adhesion of fiber to epoxy. Based on the above results, the treatment method of flax fiber with isocyanate is considered as an effective approach to improve both hydrothermal ageing resistance and mechanical properties of FFRPs.

**Keywords:** Flax fiber, Surface modification, Isocyanate, Interfacial properties

## Introduction

Compared with traditional fiber reinforcements, such as carbon fiber and glass fiber, natural fiber has a plenty of advantages, e.g., lower cost, relatively higher mechanical properties and renewable performance [1-6]. By now, natural fiber reinforced polymer composites has been widely used in a variety field of industry and construction [7,8].

Commonly used natural fiber are cotton, jute, hemp, ramie, flax and so on. Compared with other fibers, flax fiber has advantages of yield and better mechanical properties [5]. Flax fiber can be considered as a kind of composite, with several layers of cell walls. In the cell walls, oriented cellulose microfibrils embedded in hemicelluloses and pectins. As the main part of fiber, cellulose is a kind of polymer whose chains are rich in hydroxyl groups.

The hydroxide radical of natural fiber surface lead to low compatibility with non-polar polymer matrix. Hydrogen bond formed between hydroxide radical of natural fiber, therefore fibers are easily to agglomerate [9,10]. As a result, the stress could not transfer efficiently between the fiber and resin, which lead to poor interfacial properties of composite. Weak interfacial properties cause many problems for applications of natural fiber reinforced polymer [11-13].

Treatments of natural fiber are beneficial to improve the interfacial strength by enhance the roughness of fiber

surface, wettability of resin and fiber or forming chemical bond between fiber and resin [14-16]. The most widely used method is alkali treatment, which could remove the low molecular of natural fiber [17]. Thus enlarge the contact area between fiber and resin. At the same time, this type of treatment also converts the crystalline form of cellulose to cellulose II, which could improve the strength of cellulose. But the concertation and time of treatment both affecting factors of treatment, which limit the effect of surface treatment [10]. Yu *et al.* [18] treated ramie fiber by alkali and silane. The tensile, flexural and impact strength of composites were enhanced significantly. The morphology of fiber surface by scanning electron microscopy (SEM) analysis also shown that the treatment can get achieve better adhesion between fiber and resin. Recent years, many researchers are focusing on grafting nano-particles on fiber surface. Li *et al.* [19] coated CNT onto flax surface by using a “soaking or spraying-drying” process, the result of the experiment showed that ILSS Model interlaminar fracture toughness of laminates was improved significantly. But nanoparticles are easy to agglomerate, expensive and not suitable for large-scale applications [20,21]. Chemical modification could graft polymer onto fiber surface then form covalent bond of fiber and resin. Compare with intermolecular forces, chemical bond is more effective [17, 22].

Many studies has found that treatment of isocyanates is an efficient method [18]. The N=C=O groups of isocyanates are reactive, since the double bonds of molecule and the

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different electronegativity of atom [19]. Siqueira *et al.* [20] grafted the long-chain isocyanate to the cellulosic nanoparticles, the microscopic analysis shows that the effects of chemical modification depends on the specific area, ability of peeling, and solvent dispersion [21]. These factors are also need to be further research even in preparation of FFRP. Gironès *et al.* [22] investigated that stability of blocked isocyanates of cellulose surface during preparation of composites, the results reveal that mechanical properties of composite significantly improved by the surface treatment. Karmarkar *et al.* [23] use the isocyanate as a kind of compatibilizer to improve interfacial adhesion between wood-fibers and polypropylene, tensile strength of composites as prepared increased by almost 45 %, while 85 % increased of flexural properties was studied.

In present study, we used a novel agent by grafting isocyanate to flax surface, composite of flax was manufactured by VARTM (Vacuum Assisted Resin Transfer Molding) method, both micro and macro performance of flax fiber and FFRP was investigated [24]. The mechanism of grafting was revealed that chemical reaction of fiber and isocyanate could enhance the compatibility of fiber and resin. The research in this paper can effectively expand the application scope of natural fiber composites in the field of civil engineering, and provide a theoretical and experimental basis for its applications in other fields.

## Experimental

### Raw Materials

A bi-directional flax fabric woven in warp and weft

directions was provided by Changli Textile Company (Harbin, China). The density of the flax fabric is  $1.5 \text{ g/mm}^2$ . The normalized thickness is 0.16 mm. Room temperature curable epoxy resin (bisphenol-A, (DGEBA)) and curing agent with a weight ratio of 100:34 was provided by Shandong Dagong Composite Materials Co. Ltd., Linyi, China. Isocyanate (Elastocoat CC6226/101) purchased from BASF PU Specialties (Shanghai, China). The type of isocyanate is diphenyl-methane-diisocyanate (MDI).

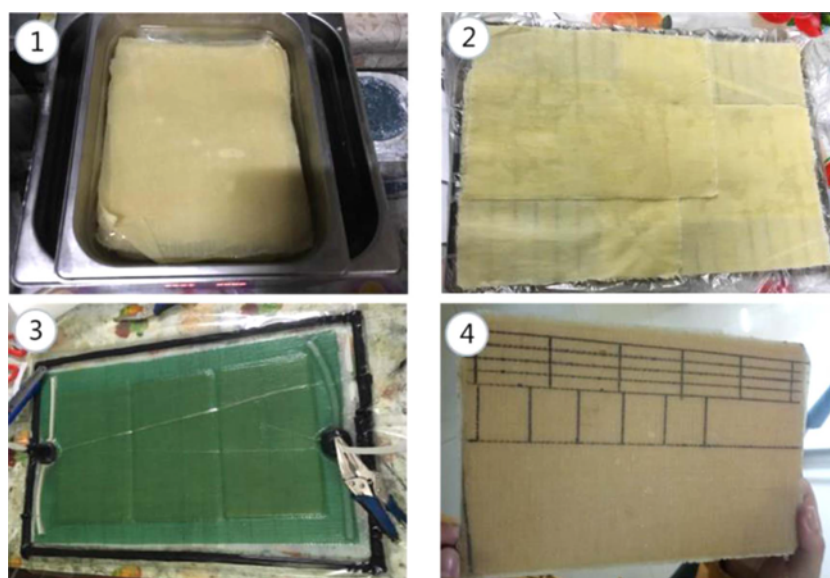
### Flax Fiber Fabric Treatment

In the present study, control flax fabrics were treated with alkali solution, isocyanate acetone solution, as shown in Figure 1. Each treatment was described in details in the following.

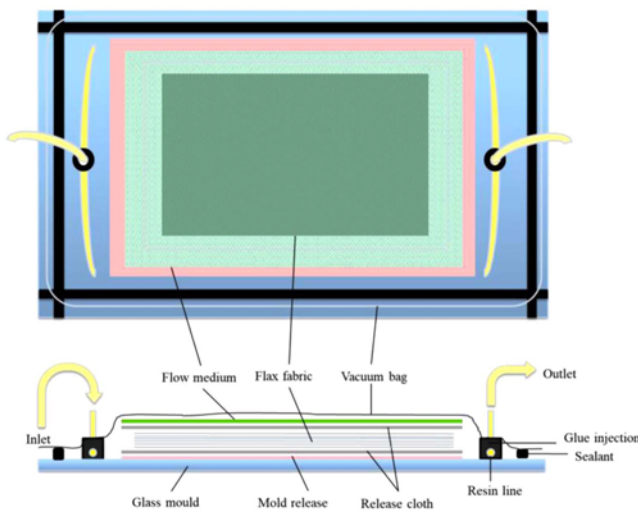
Control treatment: the flax fabric was immersed in distilled water under ultrasonication (Ultrasonic cleaning machine, Model G-060s, 40 Hz, Shenzhen Geneng cleaning equipment manufacturing Co., Ltd., China) for 30 mins. The treated fabric was then dried in an oven at  $110^\circ\text{C}$  for 2 hours, and designated as C.

Alkali treatment: the flax fabric was immersed in 5.0 wt.% NaOH solution under ultrasonication for 15 mins. After that, the fabric was rinsed with pure water until the pH value of the water reached 7. The treated fabric was then dried in an oven at  $110^\circ\text{C}$  for 2 hours, and designated as A.

Isocyanate treatment: the flax fabric was firstly treated by alkaline solution as mentioned above, and then immersed into the isocyanate acetone solution for 30 min. After that, the fabric was dried in an oven at  $110^\circ\text{C}$  for 2 hours, and designated as I.



**Figure 1.** Preparation of flax-epoxy composites. 1) fiber fabric treated in isocyanate solution, 2) treated fabric; 3) VARTM; 4) the fabricated FFRP plate through vacuum assisted resin transfer molding (VARTM), note that the lines indicating the samples to be cut for test).



**Figure 2.** Sketch of VARTM.

### Preparation of FFRP Plate Through VARTM

Flax fiber reinforced epoxy plates were prepared through VARTM process as shown in Figure 2. For each plate, 6 layers flax fabrics were used. The curing cycle for the FFRP plate includes 2 days at room temperature, followed by 2 hours at 110 °C for postcuring. The average thickness of the cured plates ranges from 3.47 to 3.65 mm.

### Water Absorption of Flax Fabric

The flax fabrics were cut to 5 cm×5 cm and expected to a hydrothermal condition (70 °C, 79.5 %RH). The hydrothermal condition was realized using a saturated potassium chloride solution. The fabric was suspended in the box with the saturated solution in an oven at 70 °C as shown in Figure 3.

### Scanning Electron Microscopy (SEM) Analysis

The morphology of flax surface was characterized by SEM and the test voltage was 5 kV. Then the fiber was coated with a layer of gold on the surface by the precision etching and plating instrument (Gatan682, American Gatan company).

### FTIR Analysis

The covalent bond of flax fiber was tested by FTIR analysis (Spectrum 100, Perkin Elmer Instruments, United States) from wavenumbers of 4000  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$ .

### Three-point Bending and Tensile Test of FFRP Plates

For three-point bending test, FFRP samples were cut into 80 mm×12.7 mm×thickness, and the flexural properties were tested according to ASTM D 790 [25]. For each group, 5 samples were tested for each sample, and average results were reported.

For tensile test, the FFRP samples were cut into 250 mm×15 mm×thickness. Tensile test was performed according to ASTM D 3039. 5 samples were repeated for each sample.

## Results and Discussion

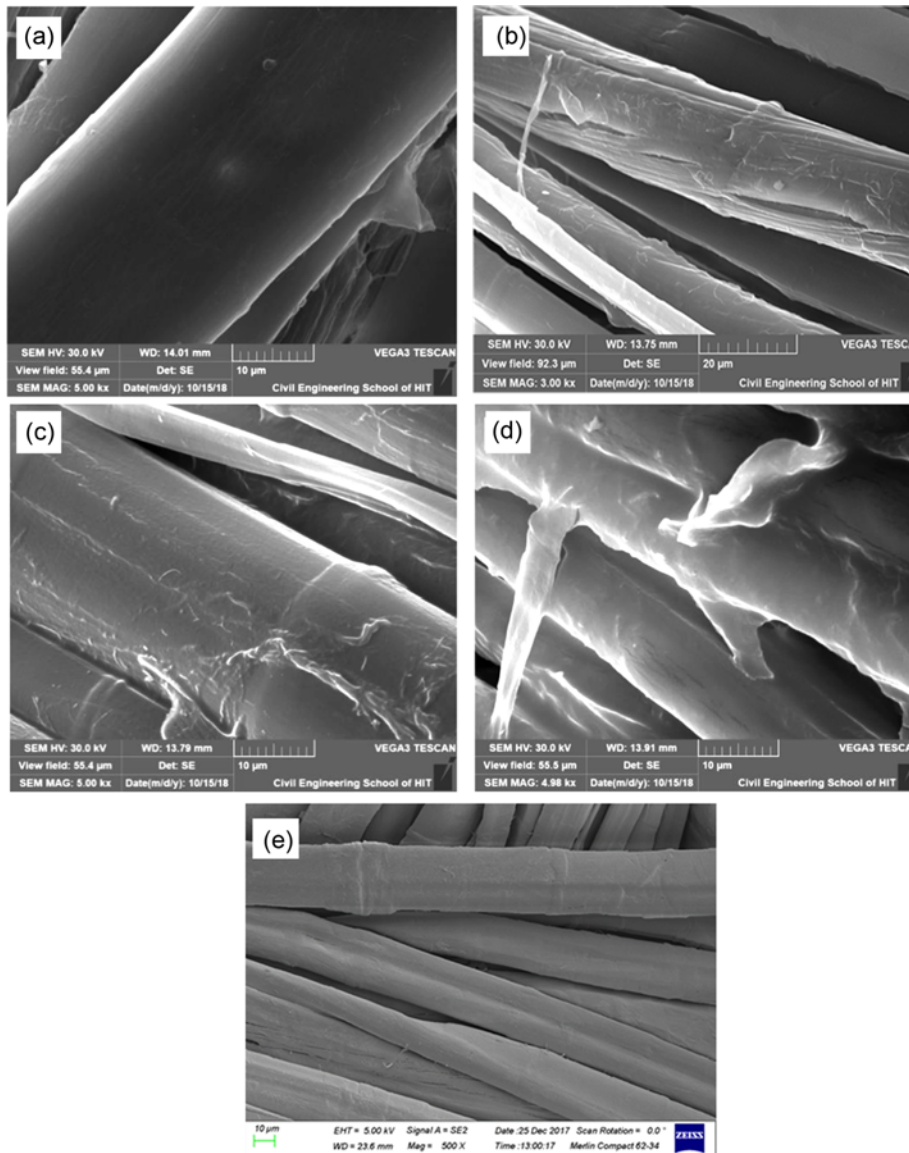
Natural fibers have abundant hydroxyl groups, which bring in many problems, such as high water uptake, and poor resistance to hydrothermal ageing. MDI is believed to react with hydroxyl groups readily to form urethane groups. Accordingly, a method to treat the flax fiber with MDI solvent is proposed in the present paper to improve the bonding between epoxy resin and fibers, and to reduce the hydrophilic properties of the fibers.

SEM photos of treated or untreated flax fibers are shown as following (Figure 4). The surface of control fiber is smooth (Figure 4(a)), as known covered with wax, semi-cellulose, etc. For MDI solution treated fiber, the surfaces are clearly coated with a layer of isocyanate (Figure 4(b-d)). As the concentration of the MDI solution increases, the coating seems to be thicker, indicated by the disappearance of the features of the treated fibers. According to the SEM photos, the coated layer of 4.5 % isocyanate is uniform. As mentioned above, the unsaturated bonds of isocyanate can easily react with -OH group on the flax surface [20,26].

It is worth noting that the surface of flax fiber only treated with alkaline solution becomes much rougher (see in Figure 4(e)) compared to the control fiber or MDI solution treated fibers. This is due to the removal of the low molecules, e.g.,



**Figure 3.** Flax fabric suspended in a box with the predetermined hydrothermal condition.



**Figure 4.** SEM photos of flax fibers (a) control, or treated by (b) 1.5 % MDI solution, (c) 4.5 % MDI solution, (d) 7.5 % MDI solution, and (e) alkaline solution.

wax etc.

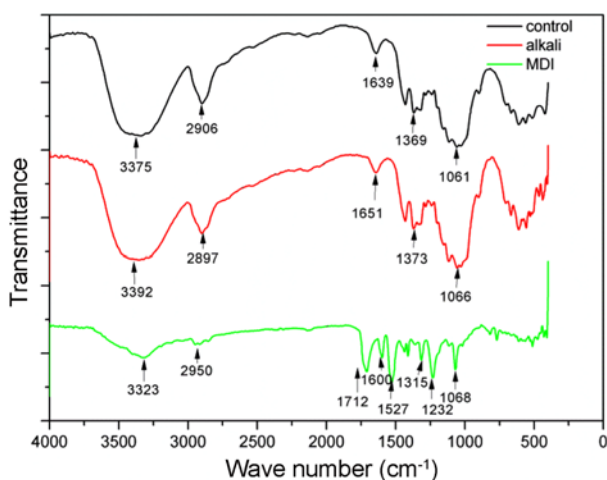
**FTIR Analysis of Flax Fiber**

The FTIR analysis was employed to confirm the covalent bonding result, as shown in Table 1. It shows the peak in the 3570~3050  $\text{cm}^{-1}$  range are responsible for the hydroxyl group stretching of the hydrogen bonding network; at 2910  $\text{cm}^{-1}$  are responsible for the CH group or  $\text{CH}_3$  group;

at 1712  $\text{cm}^{-1}$  are responsible for the  $\text{R-O-C}(=\text{O})-\text{N}$ ; in the 1650-1635  $\text{cm}^{-1}$  range are responsible for the C=O group; at 1600  $\text{cm}^{-1}$  are responsible for the C=N; at 1527  $\text{cm}^{-1}$  are responsible for the  $\text{N}-\text{C}$ ; at 1407  $\text{cm}^{-1}$  are responsible for the

C-OH; at 1234  $\text{cm}^{-1}$  are responsible for the  $\text{C}-\text{O}-\text{C}$ ; at 1068  $\text{cm}^{-1}$  are responsible for the  $\text{CH}_3$ .

The FTIR spectrum of three kinds of flax fiber showed the vibration and stretching bands of cellulose, hemicelluloses and lignin as shown in Figure 5. An obvious reduction can be observed at the 3323  $\text{cm}^{-1}$  band in the FTIR spectra of the 4.5 % MDI treated flax fiber in comparison with the control fiber. The information of reduction revealed that the reaction between OH group on the fiber surface and isocyanate. Meanwhile, new peaks were formed in the FTIR spectra, at 1712, 1600 and 1527, showed that the unreacted and reacted isocyanate on the flax surface. The free -OH on the flax surface was reacted with isocyanate, which lead to the reduction of polarity on fiber surface. Then the adhesion

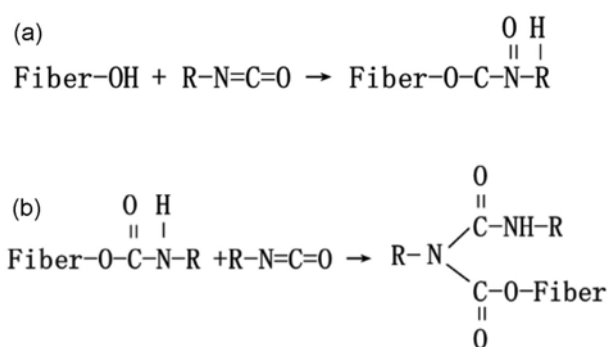


**Figure 5.** FTIR spectrum of three kinds of flax fiber, control fibers, alkaline solution treated fiber, and 4.5 % MDI solution treated fiber.

strength between fiber and resin was improved.

The bonding performance due to the reaction between the isocyanate and OH group of cellulose and lignin [17]. The high polarity and activity of isocyanate lead to its strong reaction of hydroxyl of fiber. Figure 6 shows that the free hydroxyl radical of flax can react with isocyanate to form carbamate. Furthermore, the carbamate can react with isocyanate to form allophanate. The result of FTIR spectra can prove the new covalent bond on the flax surface [26,27].

On the other hand, due to the component of the flax fiber, the cellulose macromolecule have a high degree of crystallinity of three-dimensional regularity and the lignin molecules are amorphous.



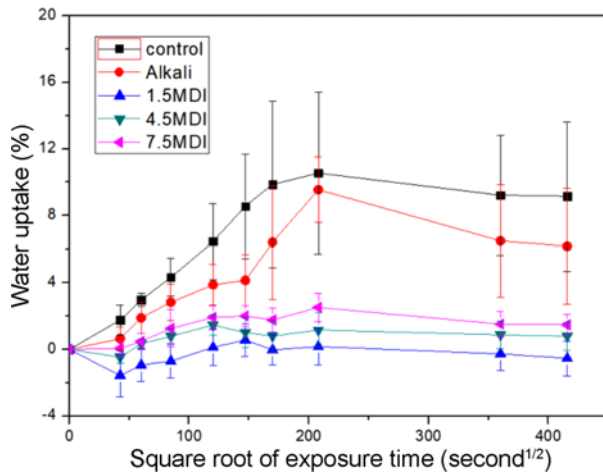
**Figure 6.** (a) possible reactions (a) between isocyanate and fiber (b) carbamate and fiber.

Figure 7 presents water uptake curves of treated and untreated flax fabrics. As shown, The control flax fabric absorbs water very fast and reaches saturation around  $4 \times 10^4$  seconds ( $\sim 11$  hours). The saturation content of water uptake is 10.5 %. Compared with the control flax fabric, alkali treatment only decreases the water uptake slightly. The saturated water uptake of the alkaline treated fabric is about 9.5 %. The less pronounced reduction in water uptake can be attributed to the fact that the alkaline treatment only removes some low molecular substance on fiber surface, rather than changes the chemical structures.

On the other hands, MDI treatment decrease the water uptake significantly. The maximum water uptake of the treated fabric is 0.57 %, 1.47 and 2.57 for MDI content of 1.5 %, 4.5 % and 7.5 %, respectively. The reduction of the water uptake for those three samples is 18, 7.1 and 4.1 times compared to the control flax fabric. The dramatic reduction of the water uptake of the treated fabric is believed coming

**Table 1.** FTIR analysis of flax without and with isocyanate

Wavenumber (cm <sup>-1</sup> ) range of peak			Reference range (cm <sup>-1</sup> )	Bond characteristic
Control	Alkali	MDI		
3375	3392	3324	3570-3050	OH stretching vibration
2906	2897	2910	2960-2875	CH <sub>3</sub> stretching vibration CH stretching vibration
-	-	1712	1740-1690	
1639	1651	-	1650-1635	C=O stretching vibration
-	-	1600	1660-1480	C=N
-	-	1527	1580-1490	
1441	1433	1407	1410-1260	C-OH stretching vibration
-	-	1234	1275-1200	
1061	1066	1068	1380-1370	CH <sub>3</sub>



**Figure 7.** Water uptake curves of flax fabric with different treatment methods.

from the reaction of the -OH groups with MDI. It is worth noting that the higher the MDI concentration used for fiber treatment, leads to relatively more water uptake. This may be due to the polymer coatings formed on the fiber surface with high MDI concentration (see in Figure 4). The coating may absorb water, in addition to the water taken by the fabric

**Mechanical Properties of FFRP Plates**

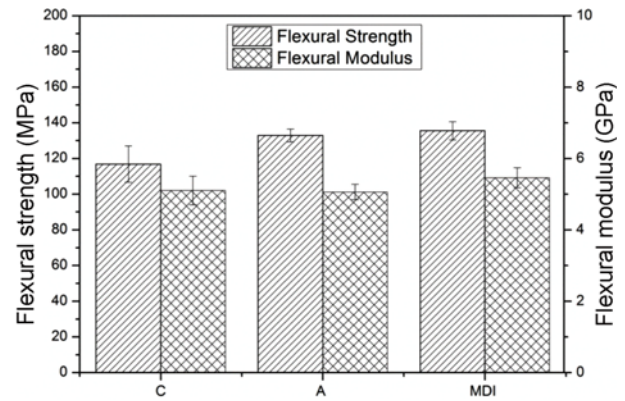
Flexural and tensile properties of FFRP plates were tested and presented below.

Compare with the control composites, the flexural strength of the alkali samples increased by 13.7 % and the flexural modulus decreased by 0.7 %. On the contrary, the flexural strength of 4.5 % MDI solution treated flax fiber - FFRP plate increased by 16.0 %, and the flexural modulus increased by 7.8 %. The improvement of the flexural strength and modulus is readily attributed to the MDI treatment, which is expected to bring in covalent bonds between the flax fiber and epoxy resin.

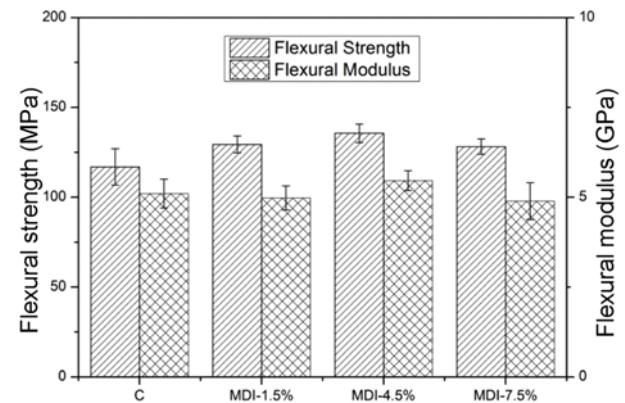
Alkali solution immersion, increasing the roughness of the fibers, and also separating the elementary fibers, benefits the bond between flax fibers and epoxy. As a result, the flexural strength of the FFRP plate with alkaline treated flax fabric is enhanced significantly (Figure 8).

While the reaction of MDI and flax fiber reduces the polarity of the fiber surface, the epoxy is expected diffuse more easily on the surface [23]. The diffusion of the resin is known to play an important role on the interfacial adhesion [12, 28]. As a result, the MDI solution (4.5 %) treated flax fabric - FFRP shows an increase in the flexural properties compared to control one (Figure 8).

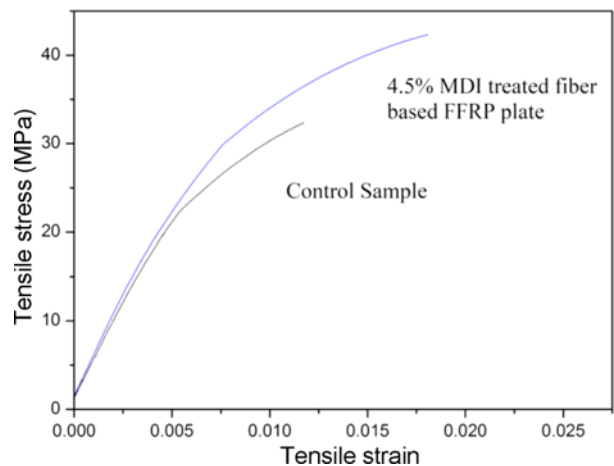
As shown in Figure 9, compare with control samples, FFRP treated with 1.5 %, 4.5 % and 7.5 % MDI solutions, the flexural strength improved 10.7 %, 15.9 % and 9.5 %,



**Figure 8.** Flexural properties of FFRP for different treatment.

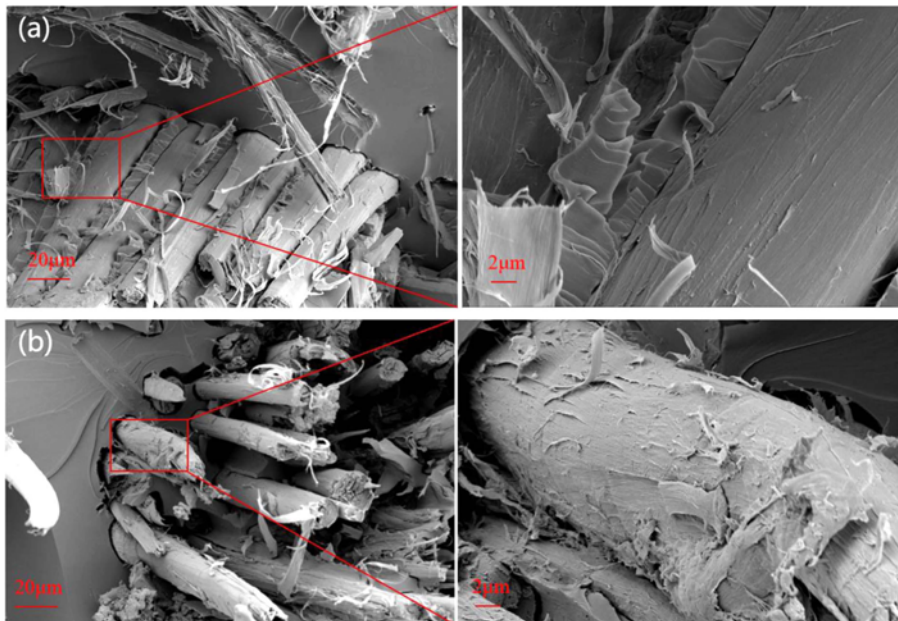


**Figure 9.** Flexural properties of FFRP with various MDI content treated flax fabrics.



**Figure 10.** Tensile stress-strain curves of control FFRP, and 4.5 % MDI treated fiber based FFRP plate.

respectively. On the contrary, the flexural modulus decreased 2.3 %, increased 7.0 % and decreased 3.9 %, respectively. This is due to the reaction mechanism of MDI and resin. With the accumulation of MDI, a weak layer may be formed



**Figure 11.** SEM photos of FFRP after flexural tests (a) control and (b) 4.5 % MDI.

between fiber and resin [3].

Figure 10 shows the tensile strain-stress curves of control FFRP plate, and the plates with 4.5 % MDI treated flax fabrics. As shown, the tensile strain-stress curves of the FFRP plates show non-linear. Such results reported before for both treated and untreated flax fiber reinforced epoxy plates [16]. It is obvious, fiber treatment with optimistic MDI content (indicated by Figure 9) leads to remarkable increase in the tensile strength (~23 %) and elongation at break.

Figure 11 shows SEM photos of the flexural fractography of the FFRP plates. For control sample (Figure 11(a)), elementary fibers are held together, and fiber surface is smooth with few resins attached. On the contrary, after MDI treatment, elementary fibers are well separated for each other, and fiber surfaces are peeled off with more resin attached. Seemly, the treatment with isocyanate solution improves the separation of elementary flax fibers, and also enhances the adhesion of fibers to the epoxy resin. More works are needed to verify the above assumptions.

### Conclusion

In the present paper, flax fabrics were treated with isocyanate and the effects of the treatment of on the water uptake of the fabric and the flexural properties of the flax-epoxy plate were investigated. The following conclusions can be drawn according to the results.

1. A novel flax surface treatment using isocyanate was proposed. With the method, a thin polymer layer is formed on the surface of flax fiber through covalent

bonding.

2. The isocyanate treatment can effectively reduce the water uptake of the flax fabric in hygrothermal environments, because the -OH groups of the flax fabrics reacted with isocyanate forming much less hydrophilic groups.
3. Mechanical properties of FFRP plates with isocyanate treated fabric were improved significantly.

To further enhance the interfacial strength, the analysis of adhesive mechanism of isocyanate grafted fiber and matrix need to be investigated further.

### Acknowledgements

This work is financially supported by Chinese MIIT Special Research Plan on Civil Aircraft with grant No. MJ-2015-H-G-103 and the National Natural Science Foundation of China with Grant No. 51878223.

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