Effects of Surface Modifications on the Mechanical Properties of Flax/β-Polypropylene Composites

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Abstract

In this study, the effect of surface treatment of flax fibers by using vinyltrimethoxy silane (VTMO) and maleic anhydride and maleic anhydride-Polypropylene (MAPP) on the mechanical properties of flax/β-PP composites are investigated. α and β-Polypropylene (β-PP) were used as the matrix for measuring the mechanical properties of flax fiber/Polypropylene matrix. Flax/PP composites composed of double-covered uncommingled yarn (DCUY) were prepared by using a film-stacking technique. The influence of surface treatment on the tensile, flexural, impact and water uptake properties of Flax/PP composites were investigated. The results show that MAPP treatment is a success method for flax/PP composites in terms of superior tensile and impact properties. VTMO treatment shows superior flexural properties and less influence on the impact properties after moisture absorption.

1. Introduction

Research on natural fiber-reinforced composites experiences is a growing interest in academia and industry because of their high environmental friendliness, good mechanical properties, low energy consumption, cost efficiency, and easy incineration at the end of the life cycle, which contrasts with available synthetic opponents [1-9]. Natural fibers such as flax, hemp, sisal, bamboo, and jute are alternatives to the use of glass fibers as reinforcement in polymer composites. Flax is one of the most attractive natural fiber/polymer composite materials because it is a low-density renewable raw material (approximately 1.4 to 1.5 g/cm3) with a highly specific strength and modulus. Furthermore, flax fiber is significantly less abrasive on tooling and moulds compared to glass fiber. Disadvantages of using flax fibers as a composite material include low thermal stability, high moisture uptake, and limited fiber lengths. Another noticeable drawback of these plant fibers are its properties strongly influenced by climate and location. Furthermore, the mechanical properties of flax fibers are affected by manufacturing processes such as retting, scutching, bleaching, and spinning [10-11]. These complex factors influence the final composite properties.

The primary advantages of using polypropylene (PP) as a matrix include their good properties, cost efficiency, and relatively low processing temperature, which is essential because of the

low thermal stability of flax fibers. The major limitations using flax fibers to reinforce such matrices include poor interfacial adhesion between polar hydrophilic fibers and nonpolar hydrophobic matrices, as well as difficulties in mixing because of poor wetting of fibers within the matrix. Weak bonding at the interface between flax fibers and polymer matrices is a common cause of reduced mechanical properties of the composites. Furthermore, flax composites exhibit poor environmental and dimensional stability. Amorphous cellulose and hemicelluloses are primarily responsible for the high water uptake of flax fibers. Therefore, physical or chemical modification of flax fibers is necessary to improve the compatibility and adhesion between fibers and matrices. Various chemical treatments have reported to improve moisture resistance of the flax fibers and to increase their interfacial bonding with polymer matrices [1-3]. Specific alkali pretreatments are commonly used in natural fiber composites to transform cellulose I to cellulose II, increase molecular orientation, and remove impurities, surface roughness, and fiber fibrillation [10, 12-14]. Many studies have selected various chemical treatments such as maleic anhydride and maleic anhydride-PP (MAPP) [3, 15-19], acetic anhydride [20], silane [2-3, 21-24], and styrene [25] to react with the hydroxyl groups on the natural fiber surface.
Isotactic PP is one of the most common polymeric materials for natural fiber-reinforced composites. Commercial-grade PP essentially crystallizes into the most stable α-form with sporadic β-form crystalline structure formation. However, when special crystallization procedures are applied, or specific nucleators are added, the β-form can become a predominant crystalline form [26, 27]. Recently, β-PP has attracted the interest of numerous scholars because it possesses some advantageous mechanical properties, such as high toughness, drawability, and low thermal deformation temperature compared with α-PP. We have reported the surface modifications of flax fiber by MAPP and VTMO on the interfacial bonding of PP resin [28]. However, no study on the mechanical properties of its fiber reinforced β-PP composites has been reported.

This study investigates the effects of the following two chemical treatments on the mechanical properties of flax/β-PP composites: maleic anhydride polypropylene copolymer (termed MAPP), and vinyltrimethoxy silane (termed VTMO). For comparison, the interfacial performances of flax/α-PP composites are also evaluated.

2. Experimental

2.1. Materials

Flax fiber bundles were obtained by retting processes, which involves the biological movement of bacteria in an aqueous medium where pectin and wax were removed. Flax yarns with a linear mass density of 27 tex were purchased from New Fiber Textile Corporation, Taiwan. The α-PP and β-PP draw texture yarns (DTY) with a linear mass density of 50 tex were fabricated by Tri Ocean Textile Corporation, Taiwan. Commercial-grade isotactic PP (2123, Formosa Plastic Corporation, Taiwan) was used as a basic material throughout the study. The material has a melt flow index of 25 g/10 min (2.16 kg, 230 oC) and a density of 0.90 g/cm3. To prepare the β-PP, a specific β-nucleating agent (NAB 83, GCH technology Int., China) and the original α-PP were immixed mechanically and subsequently processed into pellets using a Brabender twin-screw extruder. The nucleating agent was added at 0.15 wt% (i.e., the concentration at which the β-form content reaches the saturation level). The α-PP DTYs showed a higher tenacity than the β-PP DTYs, whereas the elongation was opposite. The NaOH was used for the flax fiber surface pretreatment. VTMO silane (VTMO, Shin-Etsu,

Taiwan), MAPP copolymer (MAPP P613, Dupont), and dicumyl peroxide (DCP, ECHO Chemical, Taiwan) were used as coupling agents.

2.2. Fiber Surface Treatment

The flax surface treatments are detailed in the previous study [28]. The flax fibers were alkalized pretreated first. The flax fibers were then treated by MAPP which was bonded by esterification. VTMO treatment initiated the grafting mechanism by the decomposed dicumyl peroxide radicals. Both treatments are effective for its composites' interfacial adhesive.

2.3. Sample Preparation

Flax and PP yarn designed at a 45/55 volume fraction were used to prepare the double-covered uncommingled yarns (DCUYs; Fig 3a) by using a hollow-spindle spinning machine. The flax yarn was used as the reinforcing core yarn, and PP multifilament yarn was used as the wrapping material, forming linear cowrap spinning yarn preforms. Yarn stability primarily depends on the binding yarn and twist introduced during spinning. The PP filaments served as carriers for the flax yarn during processing and became the polymer matrix in the final composites, facilitating impregnation and preventing damage to the reinforcing flax yarn. To ensure that the distribution of the fiber and thermoplastic resin in the preforms was even and that the fiber content was appropriate (50 wt%), the spinning parameters (hollow spindle twist: 776 T/m and hollow spindle rotational speed: 5554 U/min) were optimized.
DCUY was used as a feed material for the production of plain woven structure preforms in this study. Figure 3a shows the surface of cowrap spinning yarn, the wrapped angle between PP multifilaments and reinforcing flax core yarn axis was demonstrated. By changing the cowrap spinning parameters, different reinforced flax fiber content could be achieved. Then, the cowrap spinning yarns (act as warp and weft yarns) were woven on a rapier weave machine. Table 1 shows the weave density for the plain woven structure. Fig. 3b shows the appearances of the flax/PP perform.
This study presents a modified film-stacking technique used to produce high-quality, impregnated, and void-free (<1%) flax/PP composites. Single laminae were prepared by hot pressing the preform at 180 °C for 1 min at a pressure of 50 kg/cm^2, and then quenching the samples in water. The flax/PP laminates (Fig. 3c) were prepared by stacking four layers of laminae at 200 °C for 3 min at a pressure of 100 kg/cm^2 followed by slow cooling to room temperature (RT) and demolding. The fiber volume fractions of the flax/PP composites were approximately 44%.

2.4 Mechanical Tests

A universal testing machine (AG-100kNX, Shimadzu, Japan) was used to conduct the tensile tests and the three-point bending flexural tests at RT according to the ASTM D638 (type I), D3039, and D790 standards, respectively. The dimensions of the tensile specimens cut from the prepared flax/PP samples were 250 × 25 × 2 mm^3, and an area of 50 × 25 mm^2 was clamped at each end, leaving a gauge length of 150 mm. Aluminum tabs were glued to the ends of the specimens to facilitate gripping, and the grip pressure was hydraulically controlled. The testing crosshead speeds were 5 mm/min for the tensile test. The specimen size for the three-point bending test was 100 × 25.4 × 2 mm^3. A span length of 64 mm ensured that the span-to-depth ratio was 32, and crosshead speeds of 3.4 mm/min were adopted. The Izod impact test was performed at RT according to the ASTM D256 standard by using a pendulum impact tester (CPI, Atlas electric devices, USA) at an impact energy of 5.4 J. The impact

velocity was 3.4 m/s. The dimensions of the Izod impact specimen were 63.5 × 12.7 × 2 mm^3, and the specimens contained a 2.7 mm (± 0.2 mm) deep notch. The reported mechanical properties represent the average value of at least five readings. The damaged specimens were inspected using stereo microscopy (S422L, Microtech, Taipei, Taiwan) and scanning electron microscopy (SEM; S3000, Hitachi, Japan) to characterize their failure modes. Prior to the SEM observations, the samples were mounted on aluminum stubs and sputter coated with a thin layer of gold to prevent electrical charging. SEM micrographs were captured at a 10 kV acceleration voltage at various magnifications.

3. Results and Discussion

3.1. Tensile Properties

The tensile stress-strain curves of the flax/PP composites (Fig. 1) show significant yielding and postyield strain hardening, indicating the reinforcing effects of the flax/PP composites. The yield strength increased significantly was observed in both MAPP and VTMO treated samples, indicating that the surface treatments did improve the interfacial bonding between flax and PP (α-PP and β-PP). Table 1 lists the summarized mechanical properties of the flax/PP composites, namely, the tensile strength, tensile modulus, and elongation. The MAPP treatment yielded the highest tensile strength where VTMO exhibited the highest modulus. By contrast, VTMO shows the lowest elongation (6.0% for α-PP and 2.7% for β-PP) and the MAPP and untreat samples exhibited similar higher values (10.7–12.5%). This low elongation can be attributed to the crosslink caused by VTMO treatment. Compared with the untreat flax/α-PP composites, MAPP treatment exhibited a higher tensile modulus (2.97 GPa) and tensile strength (53.1 MPa), representing increases of 90% and 14%, respectively. Similarly, MAPP treated flax/β-PP composites exhibited a higher tensile modulus (2.65 GPa) and tensile strength (48.8 MPa), representing increases of 60% and 14%, respectively to untreat samples. These results are consistent with those reported by a study of oil palm empty fruit bunch/PP composites with MAPP and silane treated method. Thus, in this study the MAPP is a success treatment method for flax/PP composites. Fig. 2 shows a typical tensile damaged flax/PP sample. No difference was observed in the failure appearance for all treated and untreated flax/PP composites. The samples underwent break-apart failures which involved in yarn fracture, fiber pullout and resin fracture. However, no shear failure and delamination was observed, confirms a superior interfacial adhesion.

3.2 Flexural Properties

Fig. 3 shows the typical flexural stress-strain curves of flax/PP composites prepared using various surface treatments. The flax/PP composites did not collapse within the crosshead limit, indicating that the reinforced woven fabric prevented crack propagation effectively. Stress whitening at the tensile side of the flexural specimen can be observed. The failed specimens (Fig. 4) exhibited no visible failures in the bent flax/PP samples, indicating that their interfacial bonding was high. The flax/β-PP samples treated using VTMO exhibited the optimal flexural properties; furthermore, the VTMO samples (Table 2) yielded the highest flexural modulus and strength of 2.19 GPa and 37.8 MPa, respectively. By contrast, the untreat composites exhibited the lowest flexural modulus (0.59 GPa) and strength (15.5 MPa) values, decreasing 73% and 58%, respectively, compared with the VTMO composites. It is worth to note that MAPP is also an effective method for the flexural properties of the flax/PP composites. Trends similar to those in the tensile properties were observed in the flexural properties of MAPP samples. MAPP treated flax/β-PP composites exhibited a higher flexural

modulus (1.13 GPa) and tensile strength (25.8 MPa), representing increases of 92% and 66%, respectively to untreat samples. The added MAPP used in this study couple bridges the flax fibers and the PP matrices through chemical covalent bond formation and the compatibility improvement, respectively.

3.3 Impact Properties

Table 2 lists the notched Izod impact energy of the flax/PP composites. The impact energy of the flax/PP samples prepared using various surface treatments ranged from 263 to 466 J/m. The VTMO treated flax/PP composites yielded the lowest impact energy and can be attributed to the high crosslink PP structure in the vicinity of flax fiber. The VTMO samples underwent break-apart failures and exhibited the lowest impact energy levels. By contrast, the impacted MAPP composites using α-PP and β-PP did not break-apart, but exhibited tensile and compressive failures on two sides of the impacted specimen. The tensile sides of the MAPP samples exhibited severe fiber pullout and breakage. By contrast, the compressive sides exhibited severe compressive shearing failures accompanied by fiber breakage (kinks and buckles), crushed matrices, and delamination. Compared with the untreat samples, MAPP samples exhibited a higher impact energy in α-PP composites (466 J/m) and β-PP (437 J/m), representing increases of 42% and 19%, respectively.

3.4 Effects of water uptake on the flexural and impact properties of flax/PP composites

Fig. 5 shows the water uptake with immersed time of flax/PP composites in boiling water. The surface treatment did strong reduce the water uptake of the flax/PP composites. It is clear that the water uptake increases with immersion time. The increase in weight is not consistent with respect to the immersion time. At the beginning of the curve, the weight increased sharply, demonstrating the rapid moisture penetration into the composite materials. This phenomenon was attributed to the penetrability of water and capillary action, where it becomes active as the water penetrating into the interface through the voids induced by swelling of the flax fibers. The rate of water absorption slows after 1 day of immersion, and reaching a saturation state gradually. For untreat α-PP and β-PP samples, the water uptake at saturation state is 56 % and 52%, respectively. However, no difference in the water uptake value (35%) for all surface treated samples.

Fig. 6 shows the effect of water uptake on the flexural strength of flax/PP composites. The results show that the flexural strength decreased significantly after absorbed water for all flax/PP samples. Though the flexural strength for MAPP and VTMO samples was higher than the untreat samples, the difference was getting much closer compared with the results of dry samples. Effects of water uptake on the impact energy of flax/PP composites are shown in Fig. 7. Trends similar to those in the flexural properties were observed in the impact properties. The results show that the impact energy decreased significantly after absorbed water. However, the impact energy for VTMO samples show the highest values indicating that the interfacial bonding is effective to hinder the moisture penetration. Besides, soften of the crosslink PP in the vicinity of flax fiber may contribute to the less influence on the impact energy.

4. Summary

This study investigates the effects of MAPP and VTMO treatments on the mechanical properties of flax/β-PP composites. The influence of surface treatment on the tensile, flexural, impact and water uptake properties of Flax/PP composites were investigated. According to the

experimental results, the surface treated flax/PP composites exhibited markedly improved tensile, flexural, and impact properties. In this study, MAPP treatment is a success method for flax/PP composites in terms of superior tensile and impact properties. Because of the MAPP treatment couple bridges the flax fibers and the PP matrices through chemical covalent bond formation and the compatibility improvement, respectively. VTMO treatment shows superior flexural properties. Because of the VTMO treatment caused a crosslink PP structure near the flax fiber which hinder the moisture absorption and thus exhibit less influence on the impact properties.

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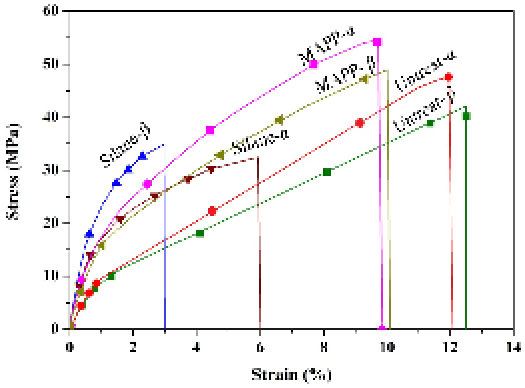

Figure 1. Typical tensile stress-strain curves of flax/PP composites

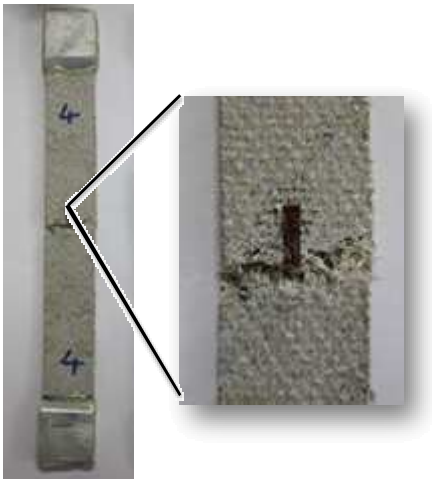

Figure 2. Typical tensile failure of flax/PP composites

Resin	α-PP			β-PP		
Treatment	Untreat	MAPP	VTMO	Untreat	MAPP	VTMO
Strength (MPa)	46.4±2.4	53.1±2.8	31.8±3.7	42.8±0.6	48.8±2.8	34.5±4.0
Strain (%)	12.1±1.1	10.7±1.6	6.0±0.7	12.5±0.9	11.1±0.2	2.7±0.3
modulus (GPa)	1.56±0.23	2.97±0.62	3.01±0.44	1.66±0.22	2.65±0.15	3.97±0.15

Table 1. Tensile properties of flax/PP composites

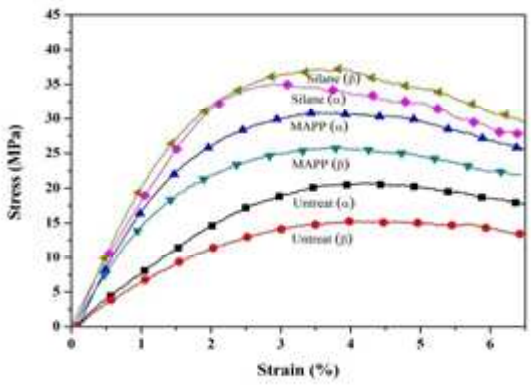

Figure 3. Typical flexural stress-strain curves of flax/PP composites

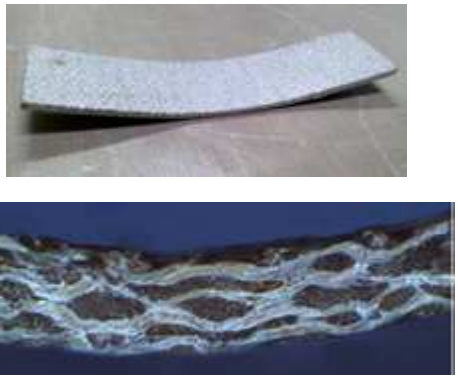

Figure 4. Typical flexural failure of flax/PP composites

Resin	α-PP			β-PP		
Treatment	Untreat	MAPP	VTMO	Untreat	MAPP	VTMO
Strength (MPa)	20.8±1.4	32.1±4.3	34.4±4.0	15.5±1.6	25.8±2.3	37.8±3.1
modulus (GPa)	0.81±0.08	1.73±0.19	1.96±0.23	0.59±0.07	1.13±0.17	2.19±0.13
Impact energy (J/m)	329±21	466±3	263±19	367±18	437±19	265±11

Table 2. Flexural and impact properties of flax/PP composites

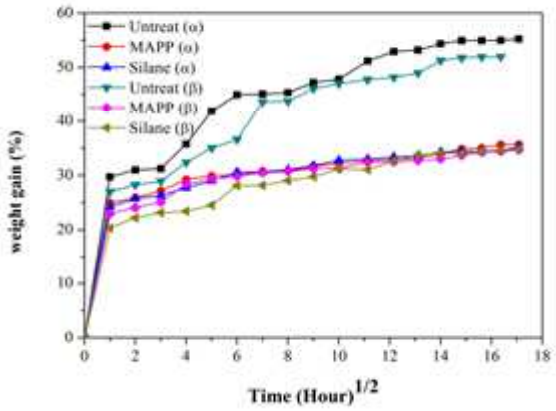

Figure 5. Water uptake of flax/PP composites

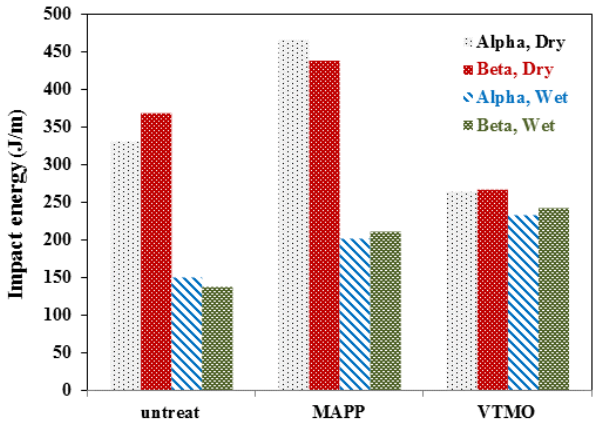

Figure 7. Effects of water uptake on the impact properties of flax/PP composites

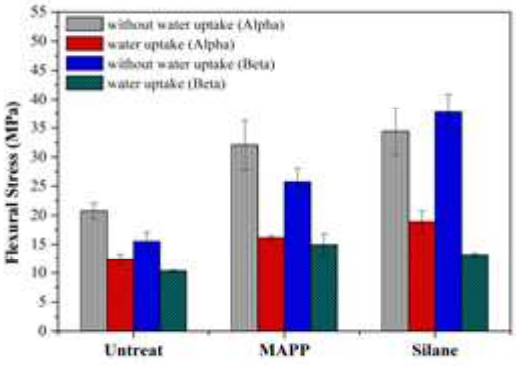

Figure 6. Effects of water uptake on the flexural properties of flax/PP composites