NOVEL RESEARCH ON POLYAMIDE 11 NANOCOMPOSITES REINFORCED BY TITANIA NANOPARTICLE DEPOSITED JUTE FIBRES

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Abstract. The combination of jute fibres and polyamide 11 (PA11) to produce full biocomposites is expectance of scientists due to many benefits of both these materials such as high mechanical performances and environmentally friendly behaviors. Unfortunately, there is scarce published research on these bicomposites uptil now. In order to improve the interfacial interaction and adhesion between jute fibres and PA11 resin matrix, an important key in the fabrication of the composites. In this study, a combination of alkaline treatment and Tetraisopropyl orthotitanate (Tip) modification was employed to modify the surface of jute fibres. The deposition or grafting of TiO_2 nanoparticles was proved by using Fourier transform infrared (FTIR), scanning electron microscopy (SEM) observations and energy dispersive X-ray spectroscopy (EDS/EDX) analysis. The improvement of the interfacial interaction and adhesion between surface modified jute fibres and PA11 resin as well as high performances (mechanical properties, thermal oxidative and water absorption stability) of obtained biocomposites were also clarified.

Keywords: jute fibres, alkaline treatment, polyamide 11, biocomposites, modification, vinyltrimethoxysilane.

Classification numbers: 2.4, 2.9.4, 2.10.3.

1. INTRODUCTION

In recent years, the utilization of natural polymers and plant originated polymers as the replacement of fossil resource originated polymers has been gained a lot of consideration. Jute is one of the most popular used natural fibres because of many outstanding advantages such as non-abrasive; high tensile strength; good heat and sonic insulation; low cost and especially

annual renewable capacity [1]. In addition, due to having low density, jute has high stiffness and specific strength, comparative with some synthesized fibres as well as other natural fibres such as wood, hemp, kenaf, flax, glass, etc. [2]. Owing to these advantages, jute has been employing as reinforcement for various polymers, such as polypropylene, polyethylene, polyvinyl chloride, epoxy, poly (butylene succinate), poly (lactic acid), etc. Therein, using biopolymers as matrix could produce fully biocomposites and maintain the environmental friendliness. These green composites have been receiving more and more attention and are great favorite from scientists in recent years.

Polyamide 11 (PA11) or Nylon 11 is derived from castor oil and is one of the most widely used biopolymers due to owning many benefits such as great mechanical properties and impact strength; durability to chemical agents and UV radiation [3]. Especially, molten temperature of PA11 is the range of 189 to 195 ^{o}C, significantly lower than other polyamides and below the initial decomposition temperature of jute fibres. This could limit the thermal degradation of lignocelluloses during the processing under high temperature. Some natural fibres such as mechanical pulp from pine fibres [4 - 5], flax [6 - 7], beech [8], cellulose nanofibres [9], and bamboo fibres [10 - 11] have been used to reinforce PA11 resin. Unfortunately, there is scarce published research on the combination of PA11 and jute to produce full bicomposites. These materials are expected to have high performances since could combine the individually outstanding advantages of both component polymers. One of the most important keys in the production of jute/polymer composites is the improvement in the interfacial interaction of the compositions. Therein, the surface treatment and modification of jute fibres have been more commonly applied to achieve this aim by using the various agents such as alkaline solution, UV, plasma, corona discharge, etc. Moreover, some recent studies confirmed that the presence of TiO$_2$ particles improved mechanical properties of jute composites. Seshanandan *et al.* indicated that the addition of 6 wt.% TiO$_2$ nanoparticles increased by 24 % in tensile strength, 50 % in flexural strength and 44 % in shear strength of composites [12]. The introduction of TiO$_2$ microparticles also brought a significant improvement. Both tensile strength and tensile modulus of jute/epoxy composites increased by 23.4 % and 54.5 %, respectively with the loading of 7.5 wt.% TiO$_2$ content. In addition, TiO$_2$ particles also exceptionally improved the abrasive wear performance of composites [13]. Pavel *et al.* deposited rutile particles on wood by hydrothermal processing in TiCl$_4$/HCl aqueous solutions at 75 °C and the deposited wood surface became more hydrophobic [14]. Especially, grafting TiO$_2$ nanoparticles on to flax fibres was successfully conducted with the grafting content ranged from 0.89 wt.% to 7.14 wt.%, dependent on the suspension concentration. With the TiO$_2$ nanoparticles content of 2.34 wt.%, tensile strength of the flax fibers and the interfacial shear strength to an epoxy resin were enhanced by 23.1 % and 40.5 %, respectively [15].

This research concentrated on the surface modification of jute by alkali treatment and TiO$_2$ deposition in order to improve the interaction and adhesion between jute fibres and PA11 resin. The influence of this modification on the mechanical property, thermal stability and resistance to water absorption of biocomposites were also clarified.

2. MATERIALS AND CHARACTERIZATIONS

2.1. Materials

Jute fibres were harvested at Nam Thang village, Tien Hai district, Thai Binh province (Viet Nam). The moisture content was about 5 wt.% deduced by the weight loss after 3 hours of

being dried under 105 °C in the oven, while. the cellulose content in jute fibres was determined about 62 wt. %, following the works reported by Ranganagowda *et al.* [16]. Polyamide 11 (PA11) resin, which is named BESNO TL natural, is a commercial product of Arkema Rilsan (Arkema China), melting temperature 189 °C, and density 1.02 g/cm^3. Tetraisopropyl orthotitanate (Tip) was supplied by Aldrich Sigma (Singapore). Other chemicals, consisting of absolute alcohol, sodium hydroxide (NaOH), and hydrochloric acid (HCl) were purchased from Duc Giang Chemical Company, Vietnam.

2.2. Treatment of jute fibres by NaOH solution

Original/untreated jute fibres (u-jute) were combed into the single fibres before being heated at 90 °C for 2 hours in the oven. Then they were immersed into NaOH 5 conc.% solution at 90 °C for 4 hours. Finishing treatment, they were washed repeatedly by distilled water until pH reaching to 7, and then they were continuously immersed into distilled water for 24 hours to completely remove residue NaOH from jute. Next, the treated jute fibres were dried under natural wind, and finally dried in a oven at 90 °C during one day to ensure all the water has been completely removed (constant weight). Finally, treated jute fibres is obtained and denoted as t-jute.

2.3. Depositing nano TiO$_2$ particles onto jute fibres

Tetraisopropyl orthotitanate (Tip) solution was prepared by adding Tip into a beaker containing a certain amount of alcohol. Then, a few drops of HCl acid were added into this solution and mixture was magnetic stirred within 3 hours. Next, 10 - 20 mm lengthened segments of jute fibers, which were pre-dried at 80 °C for 3 hours, were dipped three times in the above solution with 15 seconds for each dipping and then dried at 80 °C to obtain the deposited fibres (Tip-jute). Scheme of the modification process was shown in Figure 1.
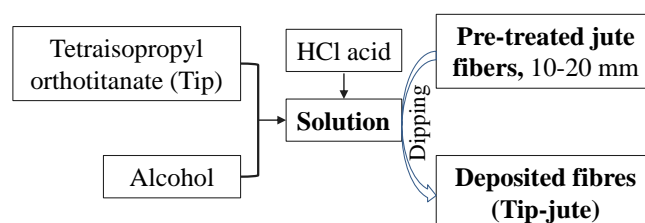

Figure 1. Schematic representation of the jute surface modification.

2.4. Preparation of jute fibres/PA11 composites

The preparation of PA11 and jute/PA11 (20/80) biocomposites was conducted in Haake internal mixer under temperature 205 °C, torque speed 50 rpm and mixing time 7 minutes. To avoid the effect of moisture, PA11 resin and jute fibres were pre-dried at 60 °C in a vacuum oven about 2 hours. Finishing blending process, the molten mixtures were removed from the mixer chamber and quickly pressed into the flat sheets by using 2.0 mm thickened mold and Toyoseiki compressor with temperature preheated at 200 °C and pressure 75 MPa. All the fabricated samples were stored at 25 °C for 24 hours before being subjected to the characterization.

The bicomposites were abbreviated as U, T and TIP, respective to untreated, treated and TiO$_2$ deposited jute fibres used as reinforcing fillers.

2.5. Characterization

Tensile performances (tensile strength, elongation and Young's modulus) of PA11 and biocomposites were measured with ASTM DIN 53503 using Zwick Z2.5 instrument. Each sample was conducted with at least three specimens to get average values.

Izod impact strength measurement was conducted on a 402D-Z2 machine (Test resources, USA) at temperature of 25 °C and the humidity of 40 % according to ASTM D256 standard.

Fourier-transform infrared spectroscopy (FTIR): FTIR spectra of jute and biocomposites were recorded by NEXUS 670 instrument, using the number of scanning 8, resolution 8 cm^{-1}, and scanning from 400 to 4000 cm^{-1}. All the samples were pelletized with KBr before the measurement.

Scanning electron microscopy (SEM): SEM images were taken by JSM- 6510LV instrument. The surface of jute fibres and the tensile fractured composites were covered by silver before capturing.

Energy dispersive X-ray spectroscopy (EDS or EDX) analysis: This measurement was conducted by the combination with JSM- 6510LV instrument, using X-ray energy scattering probe, Oxford Instruments (UK) to determine the distribution and elemental composition of materials. The electron acceleration voltage was applied at 15 kV and the sample surfaces were coated with platinum before testing.

Thermogravimetric analysis (TGA) was conducted at the air atmosphere with using TG209F1 instrument, heating rate 10 °C/min from the ambient temperature to 1,000 °C.

Water uptake was measured following to ASTM D-570 test method at room temperature. The specimens with 2D-dimension 2.0×2.0 cm^2 samples were dried about 1 hour in an oven at 110 °C and sequentially, immersed in a container of distilled water. After each interval, the samples were taken out, gingerly dried with tissue and then weigh to determine the water uptake content as followings:

$$H_F = \frac{(m_u - m_k)}{m_k} \times 100\%$$

where, H_F is water uptake content (wt.%), m_u and m_k are respective to weight of samples after and before water immersion.

3. RESULTS AND DISCUSSION

3.1. FTIR spectra of jute fibres and jute/PA11 composites

The changes in the structure of alkali pre-treated jute before and after the modification with tetraisopropyl orthotitanate (Tip) could be evaluated by FTIR analysis. Figure 2a showed FTIR spectra of alkali-treated jute, Tip-modified jute and Tip. It is seen that the presence of the absorption characteristics appeared at 3438, 1628, 1400 and 1096 cm^{-1}, which were respective to hydrogen bonded hydroxyl groups (-OH); oxygen contained linkages and groups, e.g., C-OH, C-O-C in hemicellulose and cellulose; C-O linkages in acetyl groups of hemicellulose and aromatic rings of lignin. They and C-H bonds existed together in FTIR spectra. As expected, FTIR spectra of Tip-modified jute fibres appeared some new peaks found at 661, 1062 and 1165 cm^{-1},

respective to Ti-O-Ti and Ti-O-C linkages [15, 17]. Besides, the peak at 3438 cm^{-1}, which was assigned to –OH groups, became sharper with the slight decrease in intensity, meaning that a reduction of hydroxyl groups on the fibre surfaces. Wang *et al.* reported that the reason of this reduction is due to the condensation reaction between hydroxyl groups surrounding TiO$_2$ particle surfaces and fibres surfaces [15]. All these results confirmed the formation and grafting TiO$_2$ particles onto the jute fibre surfaces.
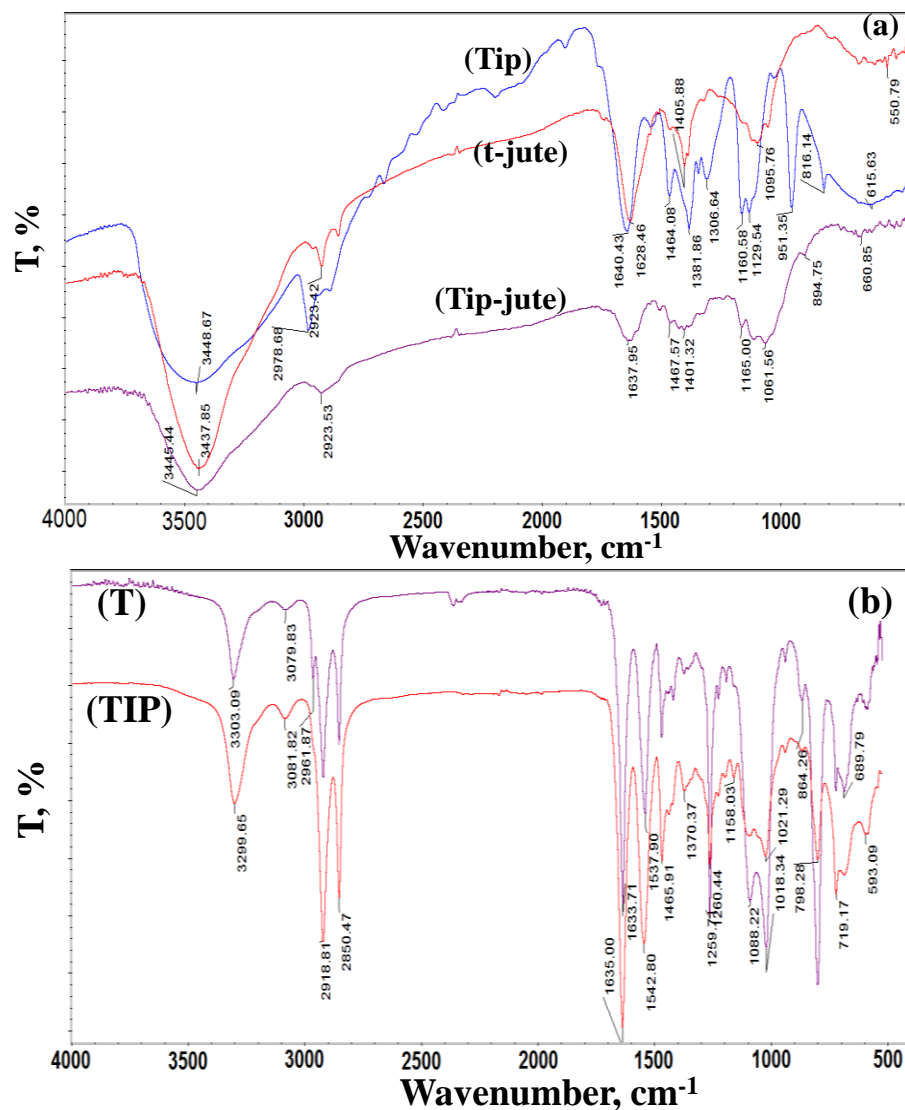

Figure 2. FTIR spectra of (a) alkali-treated jute and (b) TIP modified jute and their composites with PA11.

For biocomposite samples, alkali pre-treated jute/PA11 (T) and Tip-jute/PA11 (TIP) composites, almost the peaks in FTIR spectra of both them had the coincidence in the absorption sites (Figure 2b). The significant difference was the slight shift of some peaks characterizing for the linkages of N-H, C-O and -CONH- at the range of 1020 - 1200 cm^{-1} and 1538 cm^{-1}. It might be due to the interaction between jute fibres and PA11 was enhanced by the increment of hydrogen bonds as TiO$_2$ particles grafted on the fibre surface. Besides, the amide groups of

PA11 could interact with fibres through hydrogen bonds [4]. As results, the interfacial interaction and adhesion of PA11 and jute fibres were enhanced.

3.2. Morphological structure of TiO₂/jute/PA11 nanocomposites

In order to prove the presence of TiO$_2$ particles grafted on jute fiber surface, SEM and EDS analysis was used in this study. Figure 3a and b showed the EDS spectra of untreated and alkali treated jute fibres. It was shown that the intensity of peaks related to the elements presenting in jute; including C, O, N, Al and S; decreased after alkaline treatment. The obtained results on the elemental composition in the fibres also confirmed this decrease. It is explained by the decomposition, dissolution and remove of hemicellulose, lignin and chemical impurities during the treatment by alkaline solution. Therein, aluminum compounds existed as mineral salts in the fibres. After modified with tetraisopropyl orthotitanate (Tip), there was appearance of doublet peaks at 4.5 and 4.8 keV (Figure 3c), which was assigned to Ti element. This confirmed that TiO$_2$ particles were deposited successfully on the fibres. Besides, the decrease of oxygen, which was mentioned above, also caused by the condensation reaction of hydroxyl groups on the surface of both jute fibres and TiO$_2$ particles [15].

The Elemental composition of jute fibres

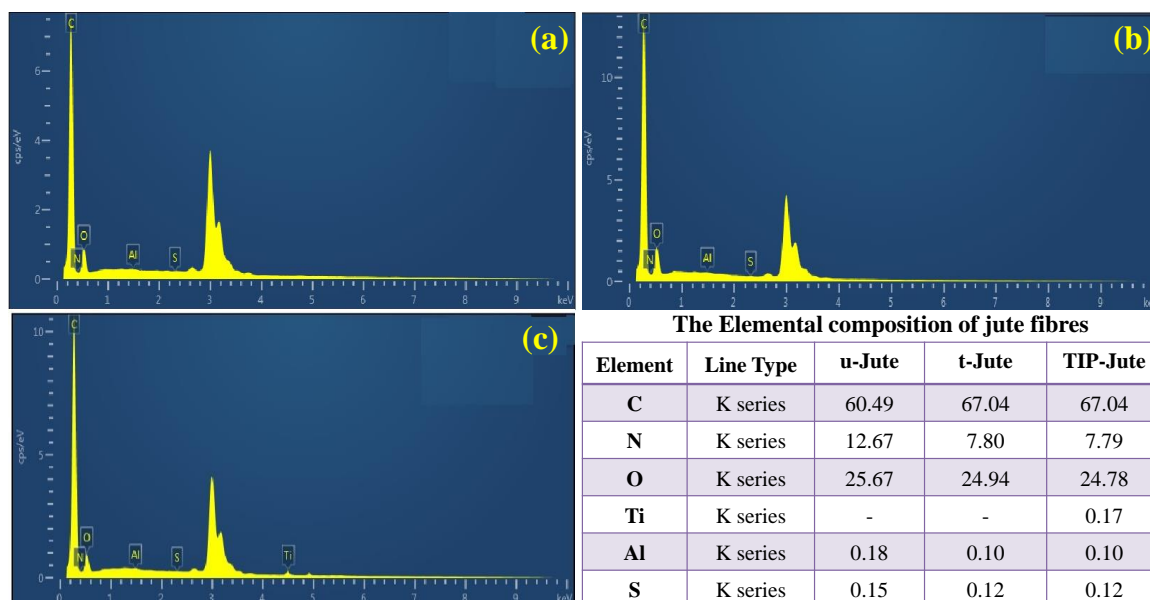| Element	Line Type	u-Jute	t-Jute	TIP-Jute
C	K series	60.49	67.04	67.04
N	K series	12.67	7.80	7.79
O	K series	25.67	24.94	24.78
Ti	K series	-	-	0.17
Al	K series	0.18	0.10	0.10
S	K series	0.15	0.12	0.12

Figure 3. The EDS spectra and elemental composition of (a) untreated jute; (b) alkaline treated jute and (c) Tip-jute fibres

The SEM images of the jute fibres were shown in Figure 4. It was obviously observed that the raw or untreated jute consisted of fibre bundles with an average diameter about 50 - 70 µm. These bundles were cohesive structures formed from some fibres with the estimated diameter of each fibre about 5 - 30 µm (Figure 4a). After alkali treatment, some micro-fibrils with relatively small diameter sizes, only about 7 - 10 µm were separated from the bundles (Figure 4b) due to the destructive of cohesive structures caused by the partially or completely remove of hemicelluloses and lignin, which had the role as the adhesives for the cellulose microfibrills. These removals also generated many grooves longitudinally along the fibres and thus increased the roughness (Figure 4d). After the modification with Tip, there was the appearance of many

tiny particles along the fibre surface (Figure 4e). At the magnification of 10000 times, the diameter of single particle was found about 200 - 300 nm, some particles aggromated together to form the clusters (Figure 4f). These were such TiO_2 particles formed and attached to the fibre surface. The increase of the roughness could enlarge the contact surface area, whereas, the filling of TiO_2 nanoparticles is expected to improve the interaction and reduce the phase separation between fibres and polymer resin. SEM images of tensile fractured surface of PA11 composite reinforced by three kinds of jute (untreated (U), treated (T) and TiO_2 nanoparticles deposited jute (TIP)) confirmed this expect.
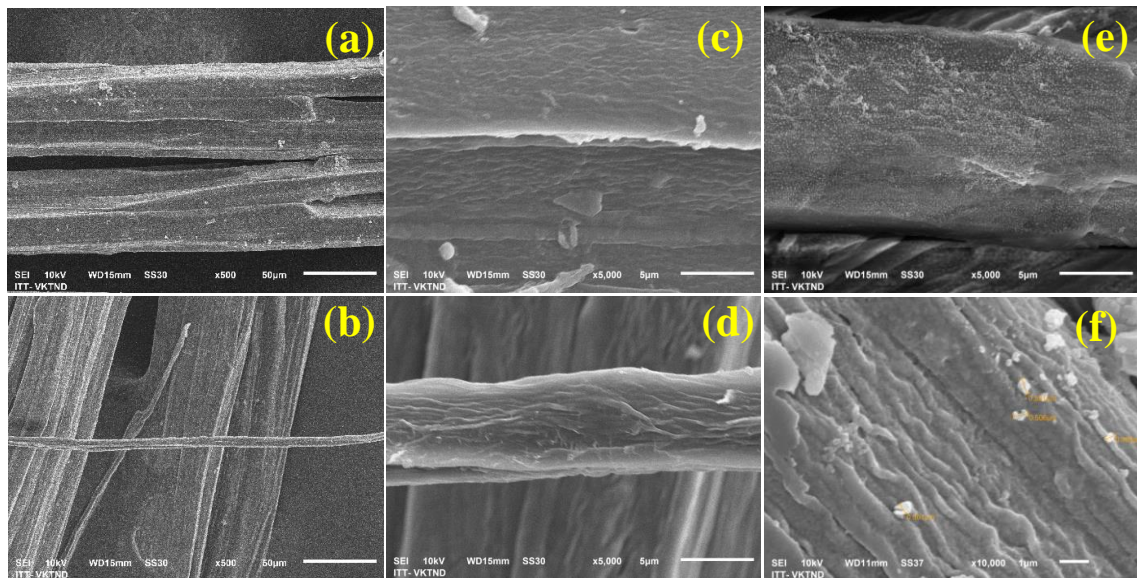

Figure 4. SEM images of (a) untreated jute; (b) alkaline treated jute and (c, d) Tip-jute at the magnification of 5000 times (a, b, c) and 10000 times (d).
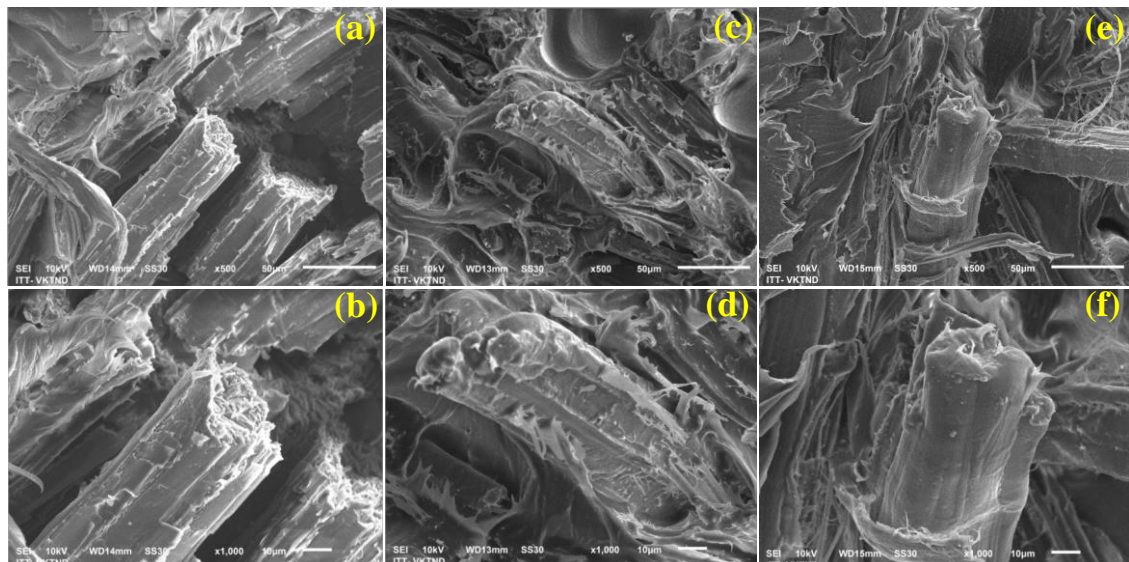

Figure 5. SEM images of tensile fractured surface of PA11 composite reinforced by: (a) untreated jute (U), (b) treated jute (T) and (d) TiO_2 nanoparticles deposited jute (TIP).

Figure 5a and b showed the surface of pulled-out fibres was quite clean almost without trace of PA11 resin. It indicated the indicates a loose bond between untreated jute fibres and PA11 resin matrix. After alkali treatment, the adhesion between the fibres and PA11 resin became more tighter, expressed by the existence of some polymer entangled on the surface of treated jute fibres (Figure 5c and d). The enhancement of this adhesion and the interaction between fibres and PA11 matrix was observed most clearly as the surface of jute fibres was modified with Tip. In this case, there were much traces of PA11 chains still remained on the surface of tensile fractured fibres (Figure 5e and f).

3.3. Thermal stability

Thermal stability is investigated by the weight changes of the materials versus temperature (TGA). As seen that TGA curves of u-jute, t-jute and Tip-jute had similar shape with three distinguished periods of weight loss. Below 120 °C, the weight loss was assigned to amount of moisture absorbed in the fibre. From 230 to 350 °C, the decomposition of hemicellulose and lignin caused the first major weight loss (about 60 wt./%) and final stage at above 350 °C, that related to another major weight loss and was the decomposition of cellulose [18 - 19]. Among three kinds of jute, the TGA curve of t-jute located upper than u-jute, while TGA curve of Tip-jute was the top. This indicated highest thermal stability of Tip-jute as compared with u-jute and t-jute. The TGA characteristics in Table 1 showed the beginning degradation temperature (T_b) of Tip-jute was about 264 °C, increased by 14 °C in comparison to u-jute. This is an interesting result and has great significance in the fabrication of biocomposites from jute fibres with PA11 because this increase could avoid or reduce the decomposition of jute under high temperature processing. The removal of lignin and hemicellulose, strongly hydrophilic components but poor thermal decomposition resistance, was the explanation for the improvement in thermal stability of fibres after alkali-treatment.
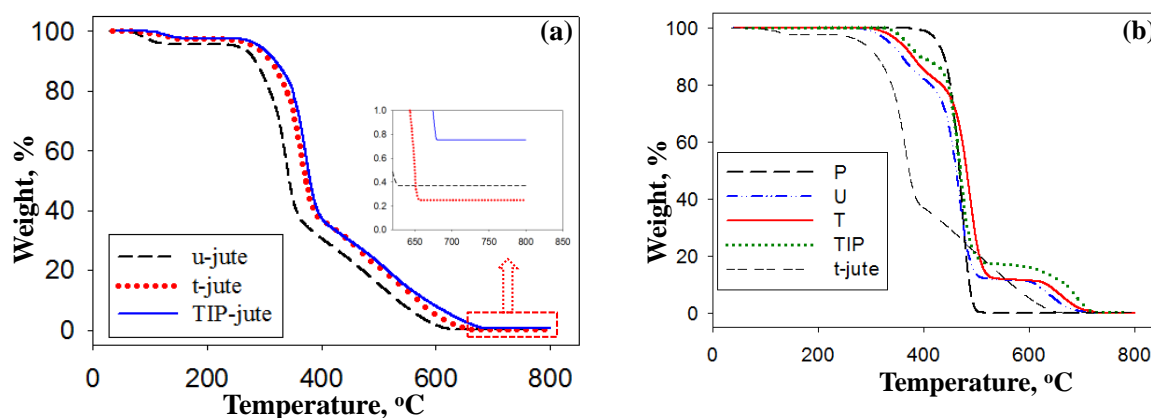

Figure 6. TGA diagrams of PA 11 (P), PA11 composite reinforced by: untreated jute (U), treated jute (T) and TiO_2 nanoparticles deposited jute (TIP).

Whereas, the nano TiO_2 particles grafted on the surface of jute could form a barrier and retard the penetration of oxygen, a dominant factor of thermal oxidation process, hence, improved thermal stability of fibres. Since the separation of lignin and hemicellulose, the absorbed moisture content of t-jute and Tip-jute were respective to 2.3 and 2.1 wt.%, remarkably lower than that of u-jute (5.1 wt%). Above 650 ^{o}C, all organic components in jute were assumed

to have completely decomposed; then the weight of samples hardly unchanged and the resulted product mainly consisted of inorganic compounds such as ash and oxides. The remained weight approached constant values of 0.37, 0.25 and 0.75 wt.% respective to u-jute, t-jute and Tip-jute (see the inserted Figure 5a) and the difference in the residue weight of t-jute and Tip-jute was 0.50 wt.% assigned to TiO_2 content grafted onto the fibres.

For biocomposites, below 450 °C, the TGA diagrams of them located between that of neat PA11 and alkali pre-treated jute (Figure 6b). Thermal decomposition of PA11 had only a stage, but all composite occurred through three stages. From 300 to 420 °C, the decomposition of hemicellulose, lignin and part of PA11 occurred. At the period from 420 to 510 °C, the major weight loss related to the speedily degradation of PA11 residue and partly cellulose. The final stage was found since 520 °C and was thermal decomposition of the cellulose residue. Table 1 showed the T_b of all biocomposites were much higher than treated jute fibres but resily lower than pristine PA11. Obviously, that, blending jute with PA11 shifted T_b of composites to higher temperature. Among three composites, the T_b and the remain weight at same temperature of TIP was highest, followed by T and U biocomposites. It means that thermal oxidative stability of composites sorted in ascending order as follows: U < T < TIP. Once again, these results confirmed that the combination of alkali-treatment and TiO_2 deposition great contributed to the improvement in the interactions and adhesion between two polymeric components (PA11 and jute fibres); therefore, thermal oxidative stability of biocomposites was clearly enhanced.

Table 1. TGA characteristics of neat PA11 and the composites.

Samples	Beginning degradation temperature, T_b (°C)	Weight versus temperature, %			
		400 °C	450 °C	500 °C	600 °C
P	357.5	98.9	80.9	1.0	0
U	264.7	82.1	63.9	13.6	11.0
T	281.8	85.2	76.0	25.4	11.4
TIP	312.4	89.2	77.3	19.9	16.1

3.4. Mechanical properties

Table 2. Tensile performance and Izod impact strength of pristine PA11 and biocomposites.

Samples	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	Izod impact strength (kJ/m^2)
P	31.67 ± 1.4	0.85 ± 0.04	15.4 ± 1.6	8.09
U	23.79 ± 1.0	1.53 ± 0.11	6.5 ± 0.8	3.85
T	28.62 ± 1.2	1.81 ± 0.13	8.4 ± 1.2	4.63
TIP	32.65 ± 1.1	2.27 ± 0.16	7.8 ± 0.9	5.12

The effect of jute fibres on the mechanical properties of jute reinforced-PA11 composites are presented in Table 2. With the addition of jute, tensile strength, Izod impact strength and elongation at break of PA11 were reduced, except tensile strength of TIP sample (32.65 MPa) showing the little higher value in comparison to neat PA11 (31.67 MPa). Interestingly, tensile strength and impact strength of composites increased as the fibres were alkaline treated,

especially combined alkaline treatment and TiO_2 deposition. Tensile strength and impact strength of composites of TIP sample were 37.2 and 33.0 % higher than those of U sample and increased by 14.1 and 10.6 % compared with those of T sample. These results were higher than those reported in Ref. 15 although lower grafted TiO_2 nanoparticle content. Obviously, the role of treatment and modification has been proved in this case. Surprisingly, the Young's modulus of U, T and TIP samples was 1.53; 1.81 and 2.27 GPa, increased by 80 %; 113 %; and 167 % compared with neat PA11, respectively. The fibrous structure of jute fibres, which presents as supporting structure for composites, and the good interaction between jute and PA11 prevented the mobility of the polymer chains, therefore, caused the higher rigidity of composites [20].

3.5. Water uptake

The water absorption is related to the hydrophobic/hydrophilic property and the structure of materials. As seen in Figure 7, the water uptake of PA11 neat (sample P) was lowest, only 1.65 % after 7 days immersed in water. It was due to the existence of hydrogen bonds between amide groups, therefore neat PA11 had a tight structure, which caused difficult for water penetration. For the composites, the presence of jute fibres increased water uptake with the impregnation along and inside fibres. Athough both PA11 and jute fibres are hydrophilic polymers [5], however, water uptake behavior of biocomposites had some difference and depended on the interaction and adhesion between them. For U sample, the low compatibility between untreated jute fibres and PA11 resulted in the defects such as microholes, microcracks in the composite structure, thus, water could easily penetrate into composite, leading to the weight increase of sample. The more defects in samples, the higher water uptake it brings. Water uptake of U sample reached up to 4.87 % after 7 days immersed in water, highest in three biocomposites, whereas, the values were only 2.31 and 2.11 % for T and TIP samples, respectively. This again proved the tight structure due to the higher compatibility and better adhesion of the composite phases limited the water absorption of T and TIP composites.
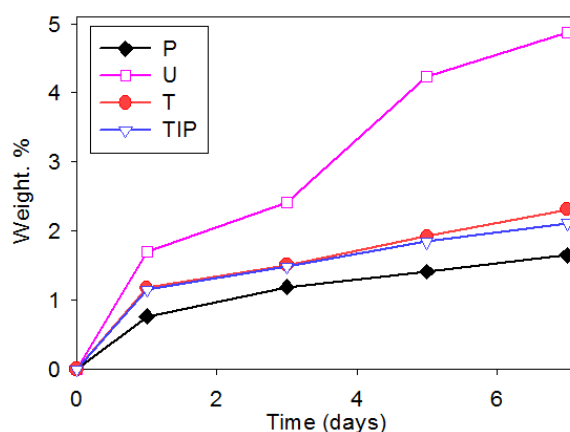

Figure 7. The weight increase of neat PA and composites versus the immersing time in distilled water.

4. CONCLUSIONS

In this work, the surface of jute fibres was modified by the combination of alkaline treatment and Tetraisopropyl orthotitanate (Tip) modification. The obtained results from FTIR

spectra, EDS and SEM analysis proved that TiO_2 nanoparticles were successfully deposited onto the fibre surface with the content of 0.5 wt.% and diameter size about 200 - 300 nm. The presence of TiO_2 nanoparticles on the alkali pretreated jute surface much improved the adhesion and interaction between fibres and PA11 resin, expressed by there were much polymer still attached and entangled on the surface of pulled-out fibres. Thank to this improvement, the hybrid TiO_2-deposited-jute/PA11 nanocomposites (TIP) showed higher mechanical strength with the improvement of 14.1 and 37.2 % in tensile strength; 10.6 and 33.0 % in impact strength in comparison to biocomposites using fibres without alkali treatment (U) and without Tip modification (T), respectively. Thermal oxidative stability and resistance water absorption of obtained biocomposites were also considerably strengthened and arranged in the ascending order: U < T < TIP.

Authorship contribution statement. Do Van Cong (DVC) built scientific idea; DVC, Nguyen Vu Giang (NVG) and Tran Huu Trung presented newpoint of this work and wrote the manuscript. DVC, Do Quang Tham, Nguyen Thi Thai, Mai Van Tien and Nguyen Thi Huong prepared biocomposites and made some analysis and characterization of biocomposites. All authors read and approved the final manuscript.

Declaration of competing interest. There are no conflicts to declare.

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