Industrial Crops and Products, Volume 67, May 2015, Pages 346–354

Improving mechanical properties of novel flax/tannin composites through different chemical treatments

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Abstract

Due to the inherent environmental benefits of using renewable materials, mimosa tannin resin (a natural phenolic resin) reinforced by flax fibres could offer desirable characteristics aiming at reducing carbon footprint of superlight electric vehicles. The non-woven flax mats were chemically treated (alkali, acetylation, silane and enzymatic treatment) to prepare tannin composites through compression moulding (130°C/35min/1.5MPa). The change in fibre morphology was seen in SEM (scanning electronic images). The treatments showed significant improvement in tensile properties, along with enhancement in flexural properties, but little effect on impact resistance. APS treated composites showed highest tensile strength of 60 MPa and modulus of 7.5 GPa. BTCA treatment led to the highest flexural strength of up to 70 MPa. NaOH treatment retained the impact failure force of about 0.5 KN and sustained the saturation energy (4.86 J) compared to untreated composites (4.80 J).

Key words: Flax Bio-composites, tannin, mechanical performances and surface treatments

1 Introduction

To date, crude oil-derived composites (glass/PP, glass/epoxy etc.) have been commercially used to produce lightweight parts, such as doors, panels, chassis pillars etc., for vehicles and other means of transportation (Fan et al., 2011). However, the interest in renewable raw material based composites has been increasing on account of their eco-credentials and the foreseen future scarcity of oil and oil-derived products (Tomas, 2012)(Mohanty et al., 2000). Natural fibres (e.g. bast, leaf and seed) are employed as reinforcement because of their competitive specific properties to synthetic fibres like glass fibres. They also give a nice ‘natural’ look, warmth and grip to composites along with reduced environmental impact. In addition, the use of bio-matrices derived from renewable sources (e.g. soybean oil, pine oil waste, castor oil, cellulose and proteins etc.) to replace synthetic plastics could further develop the ecological and sustainability credentials of the final product (Mohanty et al., 2000).

Among the bast fibres, flax has relatively high tensile strength in the range of 345-1100 MPa due to the high cellulose content and the low microfibril angle. The high tensile strength, high specific strength, low cost and renewability of flax composites become the reasons for its wide use in natural composites (Rosa et al., 2009; Xie et al., 2010). The mechanical properties of flax fibre reinforced polymer composites depend on the nature and orientation of the fibres, the nature of the matrix and the fibre/matrix adhesion (Mishra et al., 2004).

Tannin has lots of phenolic rings with molecular range between 500 to 2000 and is mainly extracted from plants such as wattle, pine, and myrtle. It could be chemically grouped into hydrolysable and condensed tannin. The latter is more stable for resin and composite preparation as the di-substitute hydroxyl groups make the phenolic rings more active to suitable agent like formaldehyde (Pizzi and Mittal, 2003). Theoretically, it can partially or fully substitute phenol to form resins and the associated composites. Barbosa et al. (Barbosa Jr. et al., 2010) reported that the impact strength was found very low for coir/tannin-phenolic composites as a result of poor mechanical properties of coir fibres. Optimised 50_{wt}% sisal fibre content in tannin-phenolic composites was observed by Ramires et al.(Ramires and Frollini, 2012) to present the highest stiffness and impact strength. The 100% use of tannin instead of phenol as matrix was initially investigated by Ndazi and his co-workers (Ndazi et al., 2006) who successfully manufactured composite panel boards from rice husks and mimosa tannins. Pizzi et al. (Pizzi et al., 2009) firstly used flax fibres to produce mimosa tannin based composites. 5% hexamine was applied as hardeners for tannin resins to eliminate formaldehyde emission.

The mechanical performance of natural fibre composites is limited by the poor interface quality between the hydrophilic fibre and the hydrophobic polymer matrix (Zhu et al., 2013b). The hydroxyl groups from its components could be modified for hydrogen bonding with cellulose groups or to introduce new moieties that form effective interlocks within the system (Summerscales et al., 2010). The hydroxyl groups could be modified for hydrogen bonding with cellulose groups or to introduce new moieties that form effective interlocks within the system. Mercerization, acetylation, silane treatment, and other fibre pre-treatments are commonly used for flax modifications to improve the composite performances (Van de Weyenberg et al., 2003). Some example results are summarized in Table 1. Alkali treatment of natural fibres, also called mercerization, is used to produce high-quality fibres (Bledzki et al., 2004). Alkali treatment of flax fibre in 5wt% NaOH for 30 min resulted in a 21.9% and 16.1% improvement of tensile strength and flexural strength of flax/epoxy composites (Yan et al., 2012). Acetylation is a well-known esterification method originally applied to wood cellulose to stabilize the cell walls against moisture, improving dimensional stability and environmental degradation. Tensile and flexural strengths of flax/PP composites were found to increase with increasing degree of acetylation up to

18% and then decreased (Van de Velde and Kiekens, 2001). Proper treatment of fibres with silane can increase the interfacial adhesion to the target polymer matrices and improve the mechanical performances of the composites. The suitable silane modification for fibres in epoxy composites was aminopropyl triethoxy siloxane (APS) and for methacryloxypropyl trimethoxysilane (MPS). 3% APS solution combined with alkali treatment was found to provide better moisture resistance (Singha and Rana, 2012). Enzymes such as laccases or peroxidases are an increasingly interesting option and are often combined with hydrophobic compounds for modification and processing of biomaterials. (Grönqvist et al., 2003). The grafting of lauryl gallate after enzyme treatment showed significant reduction of water penetration for flax composites (Garcia-Ubasart et al., 2011; Garcia-Ubasart et al., 2012).

In the previous work, the effects of production parameters and fibre configurations on properties of flax/tannin composites have been studied by Sauget et al. (Sauget et al., 2013) and Zhu et al. (Zhu et al., 2012; Zhu et al., 2013a), respectively. With respect to the investigation of manufacturing techniques for nonwoven flax/tannin composites, the best mechanical result was obtained by curing at 130°C for 35 min. The 12 unidirectional (UD) flax layers/tannin composites showed very good tensile strength of up to 140 MPa while non-woven flax/tannin composites exhibited good damage resistance as reported by Zhu et al. (Zhu et al., 2013a). The SEM images of the fractured surface suggested that an improvement in flax/tannin adhesion could potentially increase the mechanical properties.

However there is little to no work done on suitable fibre modifications to boost the performance of flax/tannin composites. The current paper reports the research pertaining to the fibre treatments done by authors to fill this gap in the literature. Four treatments, including alkali, acetylation, silane and enzymatic methods, were adopted for non-woven flax mats to prepare flax/tannin composites through compression moulding. The effect of fibre treatments on mechanical properties was obtained through tension testing incorporated with digital image correlation (DIC) method, three point bending tests and low velocity impact tests.

2 Methodology

2.1 Materials

The Retan MD® mimosa tannin (0.4 g/cm^3) mainly extracted from black wattle was purchased from the SCRD, France. The hexamethylenetetramine (hexamine, >99.0%) was purchased from Sigma-Aldrich. The flax fibres used as reinforcement in tannin composites were provided by Ecotechnilin Ltd in the form of non-woven fibre mats with areal weight of 600 g/mm^2 and average thickness of 3 mm. The same fibre mats with different

treatments (NaOH, NaOH-BTCA, NaOH-APS, LD) were supplied by VTT, Finland (Table 2). The NaOH treatment was made by immersing the flax mats into 5 wt% NaOH solution for one hour, washing them two times thoroughly with water and drying in 50°C for 12 h. This NaOH treatment was used as pre-treatment also for butanetetracarboxylic acid (BTCA) and amiopropyltriethoxysilane (APS) treated mats. The BTCA treatment was done by spraying 10 2,5 wt% BTCA-water solution on both mat surfaces to contain 5% of BTCA, followed by heating at 80°C for 20 min and drying at 50°C for overnight (to 24h). APS treatment was done with ethanol (98%): water-solution (80:20) containing 1% APS. Mats were sprayed 'full' on both sides with solutions containing 1% of APS. Then the mats were placed in heat oven at 100 80°C for 4h followed by washing with ethanol-water solution and drying in heat oven in 50°C for overnight. The laccase Doga (LD) treatments were carried out as following steps: a) wetting of the samples with distilled water, b) activation with laccase, c) treatment with DOGA, d) rinsing with water and d) drying.

2.2 Resin preparation

The tannin resins prior to composite manufacturing were prepared using aqueous tannin and 33_{wt}% hexamine/water solution (12:1, w/w). First, the tannin powder was dissolved in water with weight ratio of 5:7 by using a magnetic stirrer. About 0.2_{wt}% de-foaming agent on resin mass was added into water before mixing. Tannin was added in a few steps to minimize the solid precipitation. The stirring was maintained for 20-30 minutes to ensure the complete dissolution and homogenous distribution. After that, the weighted hexamine solution was added, and the temperature was adjusted to 40°C with continuously stirring for 10 minutes. The final tannin resin solution had a solid content of about 41%, combining tannin and hexamine.

2.3 Composite manufacturing

Non-woven flax mats (200*300 mm) were manually impregnated using an impregnation tool pack (from Easycomposite Ltd), including a 100 mg digital scale, laminating brushes and a plastic finned roller designed for chopped strand matting etc. The applied resin was calculated to give a 50_{wt}% fibre ratio in the final composites. Three fibre mats were stacked between two aluminium mould plates (300*300 mm) to form composites by compression moulding. The compression moulding was done by a Jbt 40 Ton Press with the moulding cycle: (1) pre-heating of mould at 130°C; (2) maturation time before applying pressure:15s; (3) 15 ton for 30s and then 9 ton for 34 min. The moulding cycle was determined to get a fibre mass fraction between 50% and 55% while respecting the 2.5mm thickness.

2.4 Characterizations

2.4.1 Scanning electronic microscope

Single fibres were extracted from the treated and untreated flax mats, and then were examined using a XL30 SFEG analytical high resolution scanning electron microscopy (SEM), supplied by FEI.

2.4.2 Quasi-static tensile tests

The flat coupon tensile test (250*25*2.5 mm) was carried out on the Instron 50/100 kN machine according to ASTM D3039 at the cross head speed of 2 mm/min. Aluminium tabs were glued to the samples to avoid stress concentration and premature failure. For accurate micro-scale strain measurement, A Q-400 system from Dyantec Dynamics (digital image correlation –DIC (Zhu et al., 2013a)) was used and the principle strain for the selected area with gauge length of 50 mm was analyzed (see Figure 1).

2.4.3 Quasi-static three-point bending tests

The three point bending tests were performed according to ASTM D7264, on the Instron 50/100kN machine at 1 mm/min rate of loading. The specimen (154*13*2.5 mm) was placed using a standard span to thickness ratio of 32:1. At least four specimens were tested for each composite type.

2.4.4 Low velocity impact testing

The drop-tower tests were performed using an Instrumented Falling Weight Impact Tester, Type 5, according to ASTM D7136. The total input energy was determined by the impactor mass and the nominal impact velocity of 3m/s. Three 100×150 mm specimens were used for every test.

3 Results and discussion

3.1 Fibre morphology analysis

Figure 2 shows the original surface topography of the supplied flax fibres from the untreated and treated flax mats. The neat fibre structure was covered by fibre waxes and fats. Alkalization using NaOH is a very effective procedure to purify the flax fibres, resulting in the removal of wax, the primary cell wall and other additives (Van de Weyenberg et al., 2006). It can be seen from Figure 2(b) that the resulting fibre surfaces became more structured with obvious striations. This is due to the dissolution of lignin, hemicellulose, and waxy materials which increases the inter-fibrillar region and imparts a rough texture to surface. The surface features of fibres are also clearly visible for other two modifications (BTCA and APS). More structure of raw fibre cell wall on the two treatments was exposed on the fibre surface than that of the NaOH-treated flax fibre to increase the

roughness, revealing potential for fibre/matrix adhesion improvement. Another thing noted for LD fibre was the thin layer with many small protrusions, which were considered as the grafted hydrophobic Doga compounds.

3.2 Effect of fibre treatment on quasi-static tension properties

The effects of fibre pre-treatments on tensile properties (e.g tensile strength and tensile modulus) of nonwoven flax/tannin composites are shown in Figure 3. The untreated composites had tensile strength around 41.9 MPa, which is similar to the previous tensile test results of flax/tannin composites reported by Sauget and his co-workers (Sauget et al., 2013). It is clear that every fibre modification had a positive effect on tensile strength at certain level. The tensile strength of pure NaOH treated composites increased by 24.1% (to52.0 MPa) in the comparison with untreated composites. The improvement in the toughness of the fibre surface by alkaline treatment gives rise to the better flax/tannin wettability, interfacial adhesion and consequently the stress transfer. The introduction of silane coupling agent (APS) after NaOH purification enhanced the tensile strength to 58.1 MPa, a 38.6% improvement. When the fibres were impregnated with resins, silane linkages were formed between fibre surface and resin at elevated temperature so as to further improve the interfacial adhesion strength. Based on the results of Young's modulus (Table 3), it can be seen that APS treated composites, which showed the best results in tensile strength, exhibited the highest tensile modulus of 7.5 GPa among all the samples. Similarly, untreated composites had the lowest modulus values of 6.1 GPa.

The advantage of using DIC method not only gave accurate micro-scale strain through full-field analysis, but also reflected precise progress of strain change all through the testing to failure (Laustsen et al., 2014). Figure 4 shows the principle strain distribution from 13s to 40s for flax/tannin composite with different treatment. The principle strain in the area for untreated composites changed from 0.001 and 0.003, which was used to calculate the chord elastic modulus. In the same time-scale of 27s, lower degrees of strain increase was observed for all treated samples, which means that the composite microstructure had a superior strain resistance to untreated ones as a result of less adhesive strength at interface between untreated fibres and tannin resins. It can be seen in the form of less 'yellow' area of treated composite at 40s according to Figure 4. The uneven strain distribution indicated strain localisation, attributed to the inhomogeneous composite with high fibre weight content over 50% as investigated by Ramire et al. (Ramires and Frollini, 2012).

Traditionally for engineering composites, it is assumed that only linear elastic behaviour occurs before the micro-cracks initiation, which causes non-linear transition. However, the plasticity of matrix or fibres could also contribute to the non-linear stress-strain response. For laminates like multi-axis layers with homogenised

properties, Lausten et al. (Laustsen et al., 2014) and Leong et al. (Leong et al., 2013) recently provided an alternative way to simplify the failure analysis to derive failure initiation strength. However, the plasticity of matrix or fibres may also lead to nonlinear behaviour in practical problems. Contributed from elastic (ε_e) and plastic (ε_p) deformation, the strain (ε) could be expressed as:

$$\varepsilon = \frac{\sigma}{E} + a \times \ln\left[1 - \left(\frac{\sigma}{\sigma_0}\right)^m\right]$$

Where ε_e is derived simply using applied stress (σ) and elastic modulus (E); ε_p is a function of three parameters, a (the scale parameter), σ_0 (the horizontal asymptote value) and m (strain-hardening parameter). When the third derivative of a stress-strain curve reaches zero, referring to the peak of 2nd derivative value, the onset of failure strength (S_i) are obtained accordingly.

Due to the quasi-homogeneity of non-woven flax composites, the above theory and calculation could be applied. Curve fitting was based on the RSS (residual of sum of square) method by 1stOpt software. Figure 6 shows the stress-strain curves, together with the failure initiation strength and corresponding parameters for flax/tannin composites with different treatments. This approach takes this effect of damage and plasticity interactions and is based on the numerical differentiation of stress-strain curves with smoothly declining tangent. Non-linear relationships were observed for all composites almost from the beginning of the curves, without any visible transition point. It is apparent that the plasticity of the short fibre mats and the tannin micro-cracks have to be considered. It has to be noted that this prediction method is conservative due to lack of verification, but this value can still present the effect of treatments on the initial failure. The NaOH treated composites had the highest initial failure strength of 24 MPa among the composites. The APS treated composites showed the same initial failure strength of 19 MPa as untreated composites in spite of the significant improvement (36%) in the tensile strength by. The engineering chord modulus differs greatly from predicted modulus, which is based on curve tangent changing significantly in the strain range (0.0015-0.0035) for chord modulus calculation. However, the predicted modulus trend is in line with the trend of engineering modulus (APS>LD>BTCA>NaOH>untreated).

3.3 Effect of fibre treatment on quasi-static flexural properties

The flexural properties (flexural strength and modulus) with static analysis are displayed in Table 3. Flexural stress (σ) is calculated from the load (F), span length (L), specimen wide (w) and thickness (d):

$$\sigma = \frac{3FL}{2wd^2}$$

The flexural strain (ε) is obtained from:

$$\varepsilon = \frac{6\delta d^3}{L^2}$$

Where δ is the mid-span deflection. The flexural strength was determined at the maximum stress.

According to the results, the application of NaOH-BTCA treatment on flax fibres significantly improved the flexural strength by 14.6% and flexural modulus by 6.3% of the untreated flax tannin composites. NaOH and APS treated composites also showed an increase in flexural properties. However, the flexural strength and modulus of LD treated samples was lower by about 18.2% and 11.7% respectively, compared to that of untreated composites. The decrease of fibre strength may be caused by the severe dissolution of hemicellulose as interfibrillar matrix after LD modifications. It has been reported that tensile properties of flax fibre mats were reduced after LD modifications (Zhu et al., 2014). This may account for the reduced the reinforcing effect of flax fibres for flexural properties, although the improved fibre/matrix adhesion sustained the tensile properties. Li and his colleagues (Anonymous 2011) also observed the increase in tensile strength (6.7%) and decrease in flexural modulus (-6.1%) for treated sisal/PLA composites in comparison to the untreated composites. The difference in property trend (tensile and flexural) of alkaline and silane treated henequen fibre/HDPE composites were found by Herrera-Franco (Herrera-Franco and Valadez-González, 2005) as well.

Typical predictions of flexural failure initiation strength by stress-strain curves of flax/tannin composite with each treatment are shown in Table 4. The highest failure initiation stress of 33 MPa was obtained for BTCA treated composites, which also exhibited the best flexural properties. Compared to the untreated composites with 21 MPa as initial failure strength, LD treatments lead to over 50% decrease, showing strong agreement with its reduced flexural strength and modulus. NaOH and APS treated composites showed similar improvement of around 20% in failure initiation strength. The predicted modulus for all composites was relatively close to the chord flexural modulus, indicating good material stiffness under bending condition. The composites showed gradual fall-off in load capacity after their ultimate flexural strength. This is due to that the pulled-out flax fibres bridge the sample to carry the load and slow the crack propagation.

3.4 Effect of treatments on falling-weight impact properties

The low velocity impact tests can simulate the loading issues that the composites are likely to experience in service life. The input energy (L_e) introduced by dart falling action is equal to the energy dissipated by the whole system (L_w) as seen in the energy balance equation below (Belingardi and Vadori, 2002):

$$mgh = L_e = \frac{1}{2}mv^2 = L_w = L_{we} + L_{wi}$$

Where m the dart weight, v the contacting velocity, h the height, g the standard gravity (9.8 m/s^2), Le the input energy equal to kinetic energy ($\frac{1}{2}mv^2$)and gravitational potential energy (mgh), L_{we} is the external energy dissipation, such as friction etc., L_{wi} refers to the internally dissipated energy by material elastic/plastic deformation or fragmentation.

Figure 7 shows the typical load versus displacement curves average-smoothed (Savitzky-Golay method) by Origin software to minimize sample oscillation effect. The load increased with increasing displacement towards the peak force after which visible failure occurred. Then the load capability reduced dramatically to saturation point, followed by a force plateau (around 100 N) with continuous growth of displacement, indicating perforation situation during the impact testing. The other evidence is the velocity-displacement relationship (Figure 8) that the velocity-decrease gradient changed to a lower value after the transition of energy dissipation mainly from L_{wi} by failure to L_{we} by friction. The load-displacement trend of flax/tannin composites is very similar to that of non-woven hemp/polyester composite found by Thakal et al. (Dhakal et al., 2007) who also described the influence of impact load level into four stages. Stage 1 showed sudden load increase without damage, followed by matrix cracking in stage 2. The matrix cracking progress in stage 3 lead to interfacial debonding, and finally, fibre breakage, delamination and perforation occurred in stage 4. Belingardi and Vadori (Belingardi and Vadori, 2002) pointed out that the saturation instant can be defined at the transition time where velocity slope decreases. According to Figure 8, the crack initiation and damage failure until saturation took place in a very small timescale of 4-5 ms. The longest time elapsed to saturation was 5.1 ms for NaOH treated composites while untreated composites had the shortest time of 4.7 ms. This indicated that the saturation time was probably influenced by the flax/tannin interfacial adhesion. The displacement at the saturation point was approximately 1.2-1.3 mm (Figure 7), even less than the composite average thickness of 2.5 mm. Clearly, the cracks propagated very fast through the thickness before the real dart perforation, resulting in total collapse.

The threshold force for visible damage and the associated failure energy are shown in Table 5. The peak force trend (untreated>APS=NaOH>BTCA>LD) did not follow the trend showed by the elastic modulus, which normally is proportional to threshold force (Davies et al., 2006). This is possibly down to the influence of different degree of surface imperfections for each composite type. The force peak of untreated composites (515 N) is only 5 N higher than that of APS and NaOH treated composites (510 N), while LD treated composites (414N) showed 18% force reduction compared to untreated samples. The composite absorbed energy resulting

in crack growth and debonding until the peak force, after which the damage rapidly reduces the load carrying capability (Dhakal et al., 2007).

The 3D time-force energy curves for untreated and treated flax/tannin composites were plotted in Figure 9. The time-force curves were similar to displacement-force curves due to the fact that there was no rebound case allowing force 'fold back'. The XZ projection of the 3D curves reflected the effect of fibre treatment on energy dissipation progress. It can be seen that the energy had a gradient change at the transition time of around 4-5 ms. The energy dissipated by the system before the transition was defined as the impact energy used for crack initiation and propagation. The following energy increment is mainly contributed by the friction between the dart surface and the sample edge in the perforation hole. The total input energy from the dart was about 10.26 J. As seen in Table 5, NaOH treated composites and untreated composites absorbed almost the same energy of 4.86 and 4.80 J, respectively. The impact energy of LD treated composites is the lowest value of 3.68 J (35.9% of the total energy), in line with the lowest flexural properties. The chemical treatments clearly had little effect/improvement on impact energy absorption (low input energy), compared to loading bearing properties (tension and flexural). This indicates that the use of treatments has a detrimental effect on the dynamic impact performances of flax/tannin composites. This impact energy trend could also be observed from the residual velocity in Figure 8 at time of 16 ms. The lower the residual velocity, the higher the energy dissipated by material fragmentation.

4 Conclusions

Mimosa tannin extracted from wattle trees were used with pre-treated flax to prepare flax/tannin composite for potential structural and non-structural applications vehicles. These pre-treatments were found to improve the mechanical properties of flax/tannin composites.. The most significant influence was seen on the tensile properties, where APS treatment resulted in a 36.8% increase in tensile strength, together with a highest tensile modulus of 7.5 GPa. A 14.6% and 6.3 % increase in flexural strength and modulus respectively was observed in BTCA treated composites. The LD treatment reduced the flexural properties due to the decrease in fibre properties. Impact properties of composites were less affected by treatments, however NaOH treatment still slightly increased the saturation energy to 4.86 J. Consequently, for applications under different loading conditions (tension, flexion or dynamic impact), selection of fibre treatments has to be carefully considered for non-woven flax/tannin composites. Considering the overall performance, BTCA treatment seems most promising method to maximise the fibre reinforcement effects. A future research on the environmental

resistance (e.g. water absorption) of flax tannin composites could be conducted to assess the possibility of applications in demanding environments.

Acknowledgment

The authors are thankful for the financial support by the European Commission and the FP7 ECOSHELL Project (Project Reference No. 265838) and would like to acknowledge technical support at Cranfield University.

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Figures

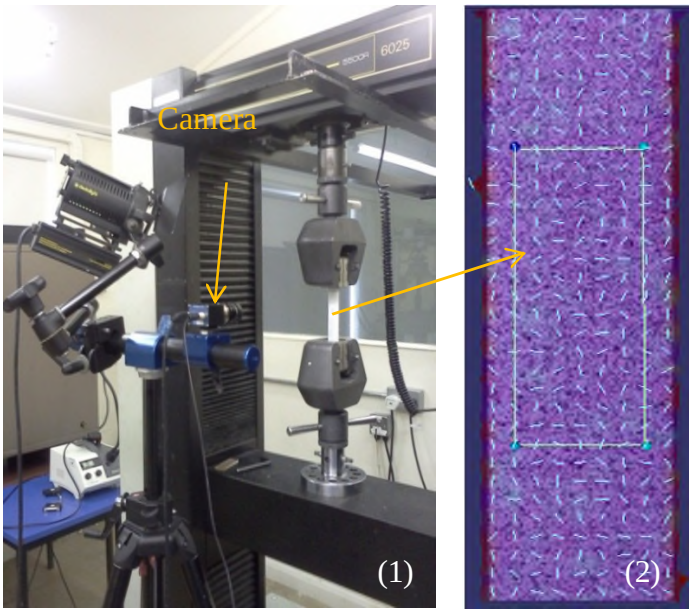

Figure 1. DIC technique for tension (1) DIC set-up (2) evaluated and gauge area

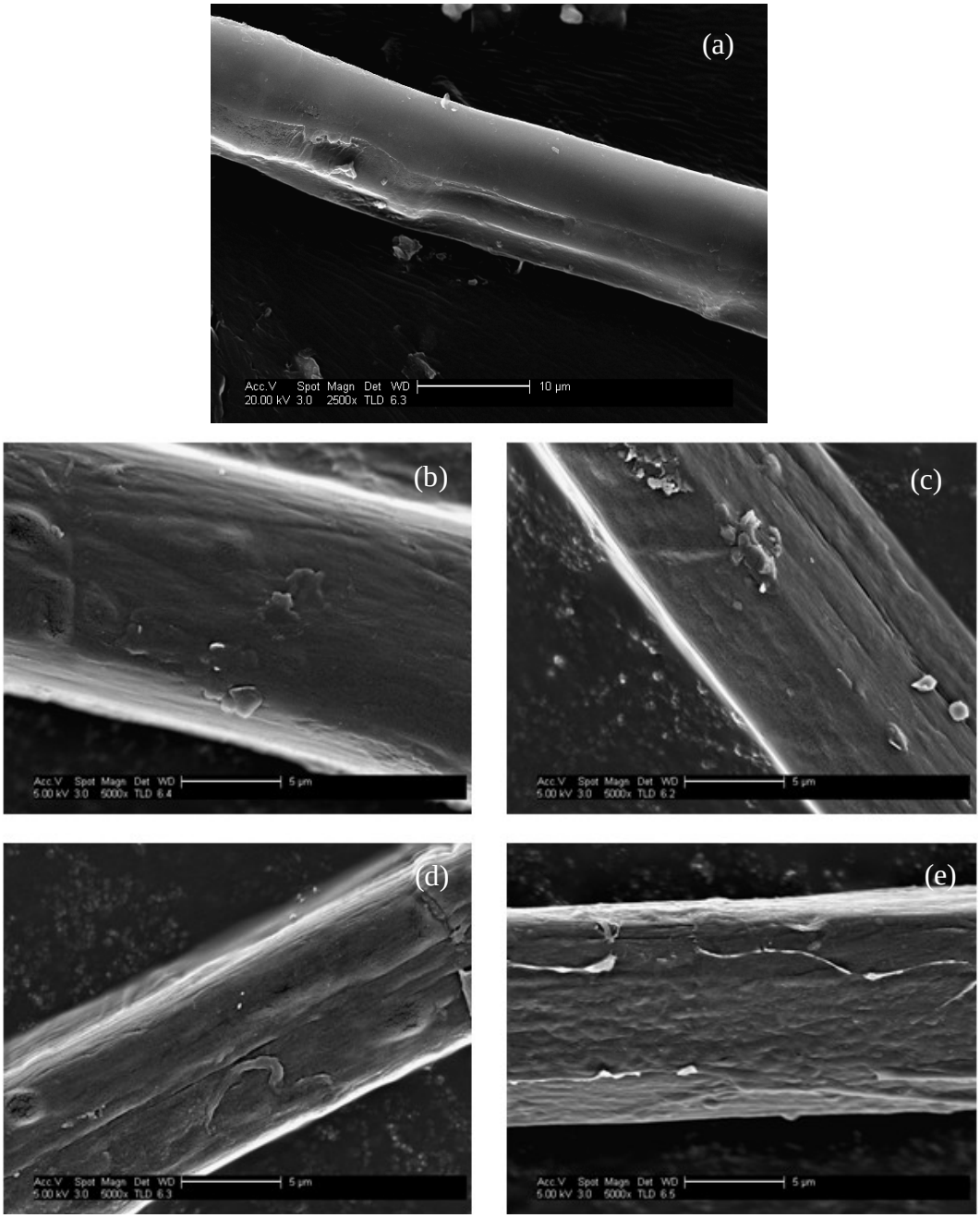

Figure 2. SEM morphologies of flax fibres: (a) untreated; (b) 5% NaOH treated; (c) BTCA treated; (d) APS treated; (e) LG-D treated.

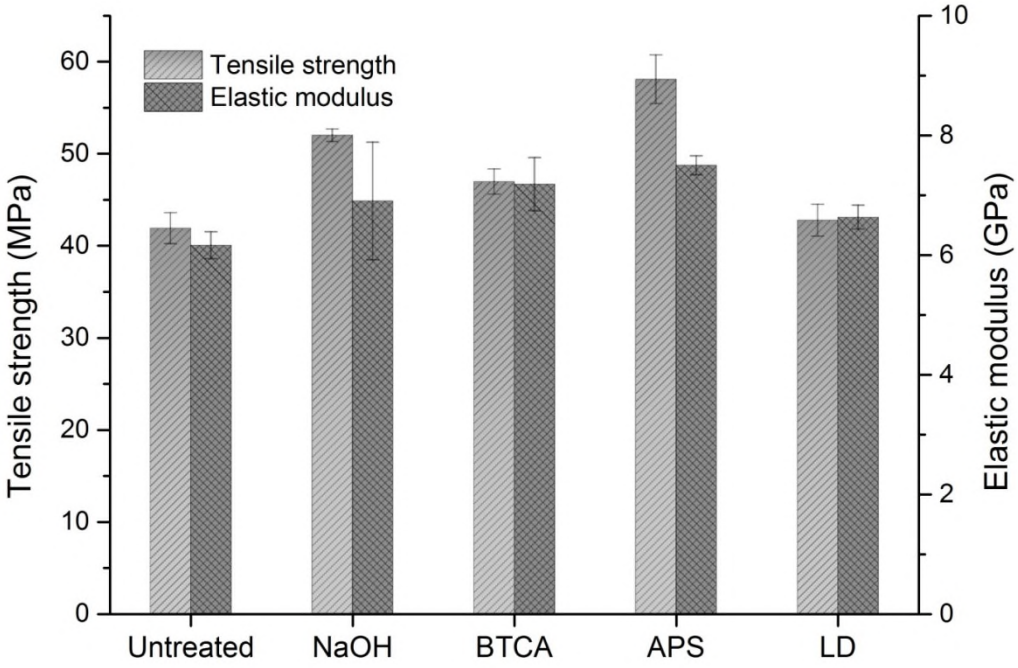

Figure 3. Comparison of tension properties between untreated and treated composites

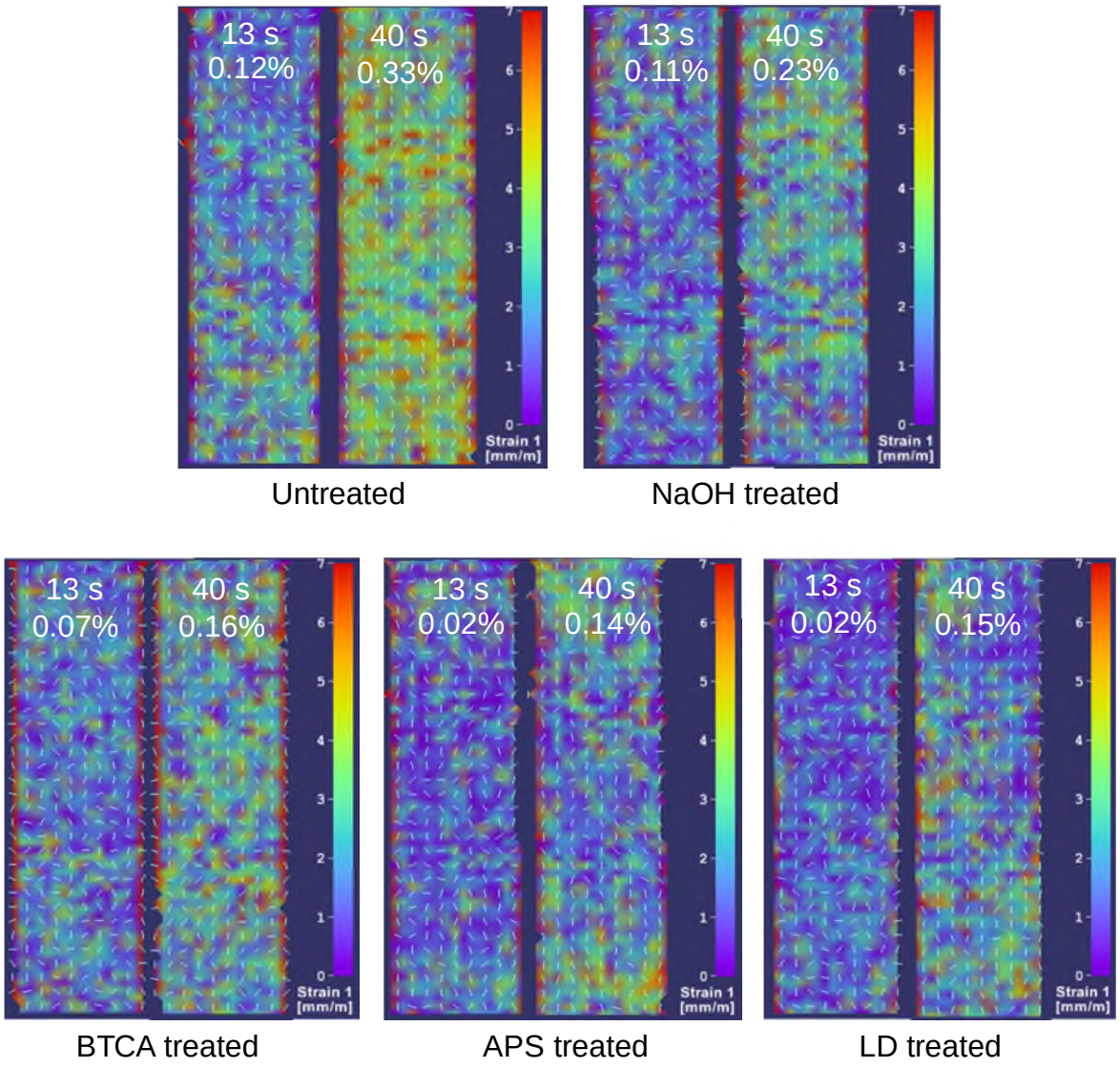

Figure 4. Strain distribution and localisation of flax/tannin composite at 13 and 40 ms.

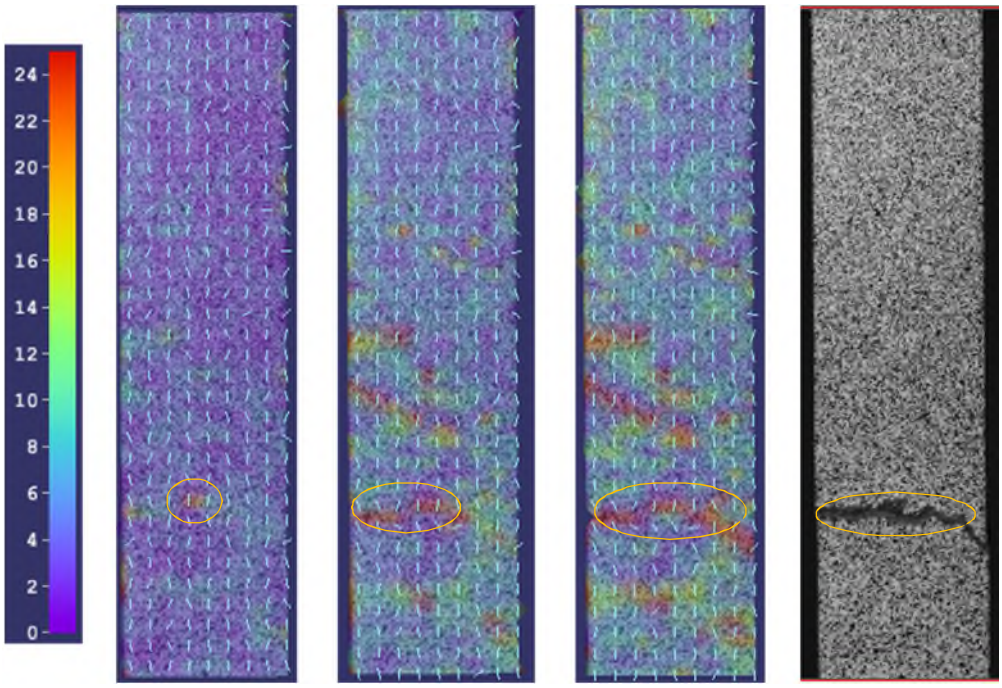

Figure 5. Representative failure progress monitored by strain change for nonwoven flax mat/tannin composites

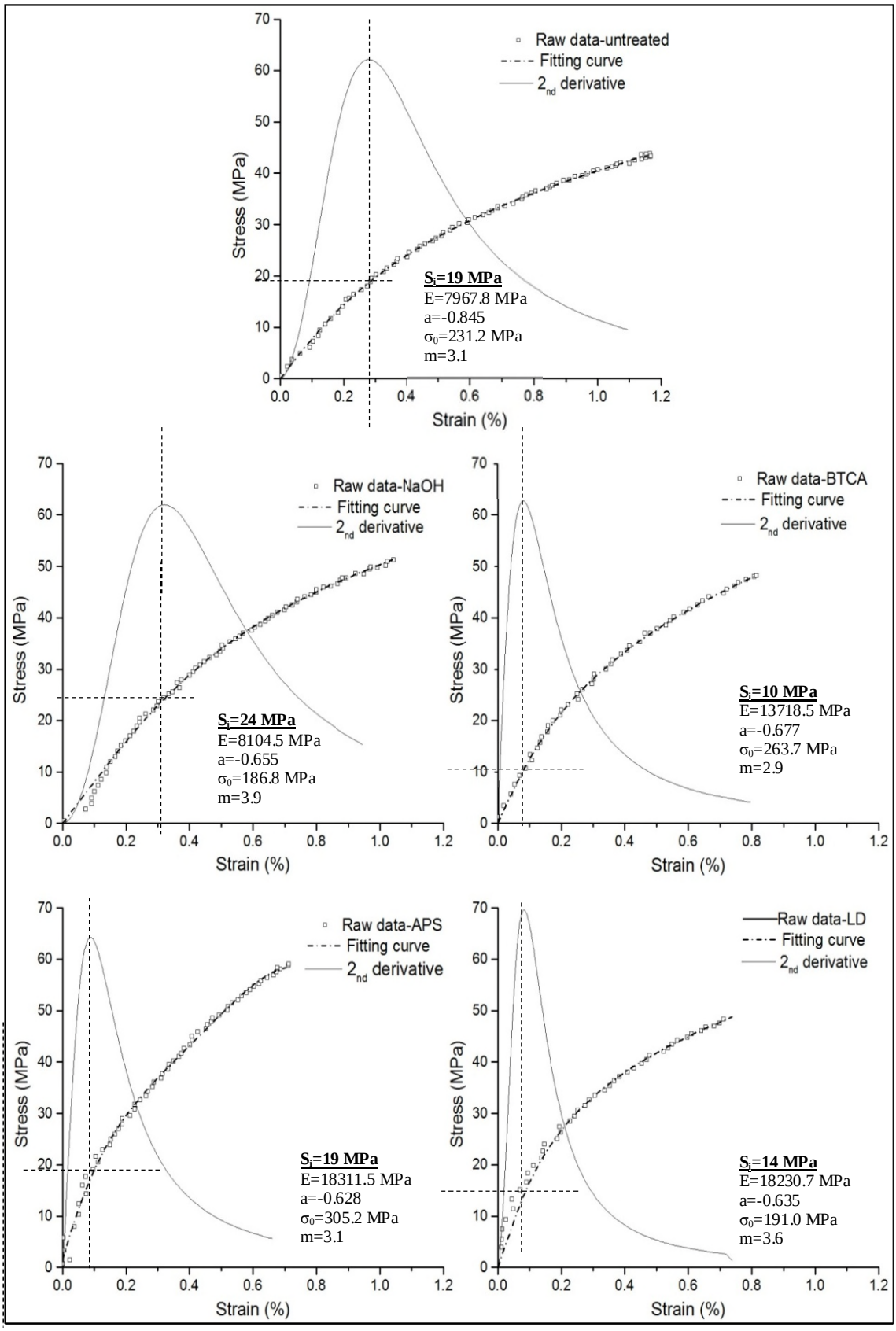

Figure 6. Example of computation of tensile failure initiation for flax/tannin composites.

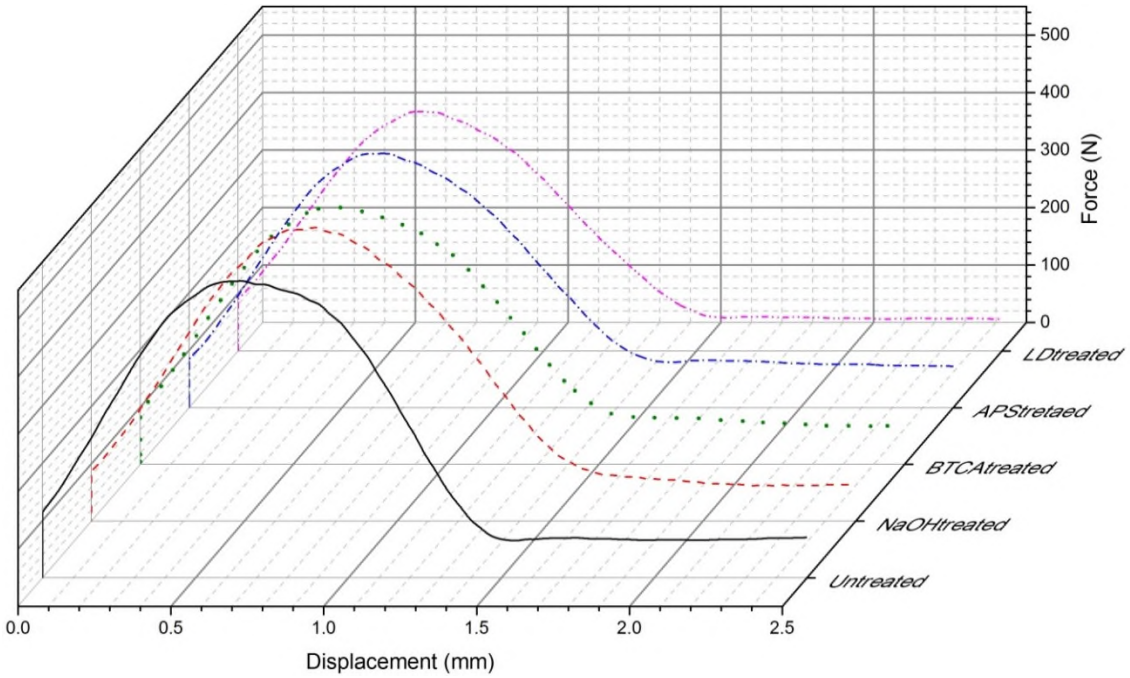

Figure 7. Waterfall description of impact force-displacement for flax/tannin composites

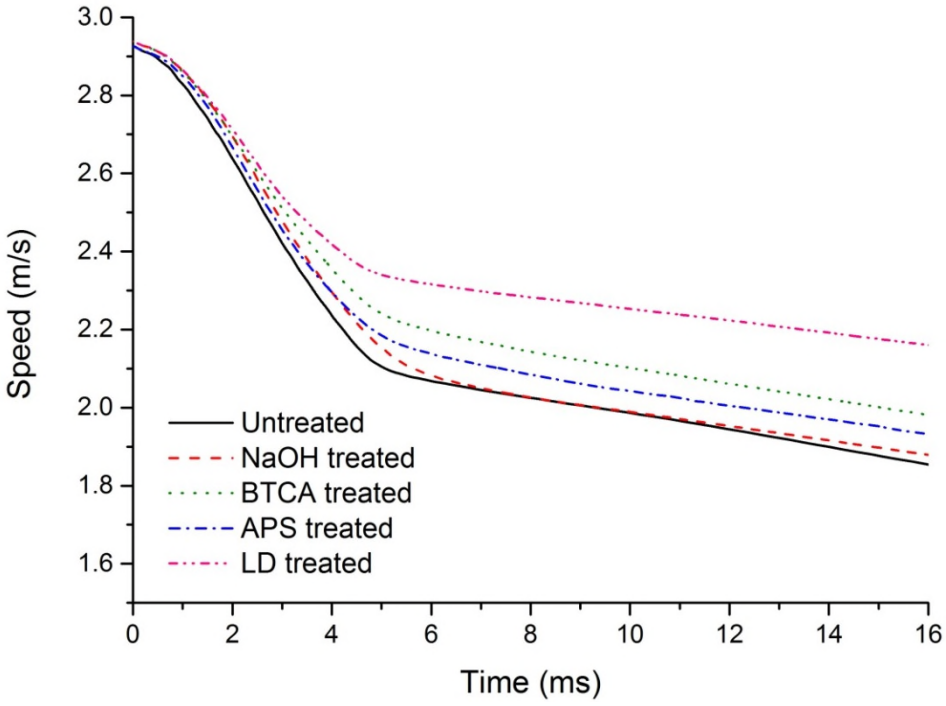

Figure 8. Speed change as a function of time during impact tests

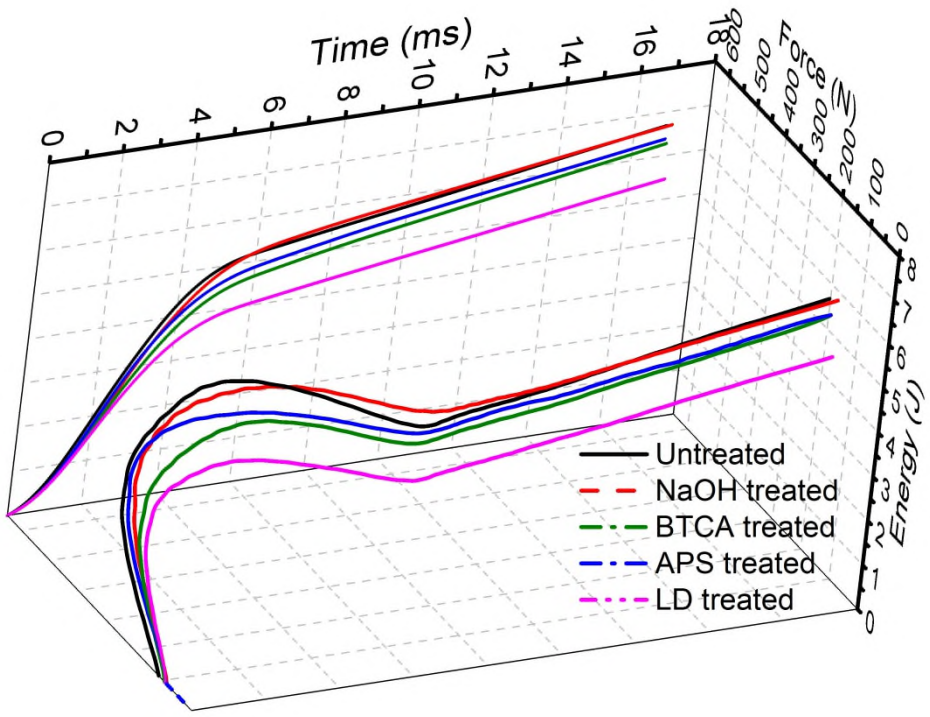

Figure 9. 3D description of time-force-energy for flax/tannin composites

Tables

Table 1. Summarised results of some treatments for flax composites.

Fibre/matrix	Treatment	Conditions	Effect on properties	Ref
Flax/phenolic	Esterification	25wt% MMA, 30min, 210 W	More moisture retardant	(Kaith and Kalia, 2007)
Flax/polyester	Silane treatment	0.05 wt%, 24hRT	Hydric fibre/matrix interface	(Alix et al., 2011)
Flax/epoxy	Alkali treatment	4wt% NaOH,45s	Transvers strength, 30% increment	(Van de Weyenberg et al., 2006)
Flax/epoxy	Alkali treatment	5wt% NaOH,30 min	Tensile strength 21.9%; Flex. Strength 16.1%	(Yan et al., 2012)
Flax/PP	Esterification	MA-PP coupling agent	Interphase compatibility	(Bledzki et al., 2004)
Flax/PP	Esterification	10wt% MA, 25h, 50°C	Highest flexural and tensile strength	(Cantero et al., 2003)

*MMA-methylmethacrylate, MA-maleic-anhydride

Table 2. Untreated and treated fibre used for tannin based composites

Type	Modification	Treatment details
Untreatred	-	-
NaOH	Mercerization	5 wt% NaOH purification
BTCA	Acetylation	Alkali +Butanetetracarboxylic acid
APS	Silane treatment	Alkali +Amiopropyltriethoxysilane
LD	Enzyme treatment	Benzenediol+dodecyl gallate

Table 3. Flexural properties of untreated and treated flax/tannin composites

Material	**Flexural strength (MPa)**			**Flexural modulus (GPa)**			**Failure strain (%)**		
	$\overline{X}$	S	CV (%)	$\overline{X}$	S	CV (%)	$\overline{X}$	S	CV(%)
Untreated	61.27	4.1	6.2	6.12	0.3	5.2	2.49	0.2	9.2
NaOH treated	65.53	4.9	7.3	6.60	0.4	6.4	1.87	0.2	11.8
BTCA treated	71.73	4.8	6.9	6.52	0.6	9.1	2.07	0.2	9.3
APS treated	63.47	4.1	6.8	6.16	0.2	4.0	2.31	0.06	2.4
LD treated	51.88	1.1	2.2	5.48	0.3	6.1	1.82	0.1	5.9

***** $\overline{X}$-average, S-standard deviation. CV-coefficient of variation.

Table 4. Computed 'flexural failure initiation strength' of flax/tannin composites.

Type	**E_{predic} (MPa)**	**a (10^{-2})**	**σ_0 (MPa)**	**m**	**S_i (MPa)**
Untreated	6423.8	-0.72	65.2	2.9	21
NaOH	8027.6	-0.42	68.3	2.7	25
BTCA	8011.1	-0.63	82.5	3.1	33
APS	6797.1	-0.74	70.0	3.2	26
LD	6695.4	-0.46	53.4	2.4	10

Table 5. Impact characteristics of untreated and treated flax/tannin composites.

Sample	Peak force(N)	Failure energy (J)	Impact energy (J)	Saturation (ms)
Untreated	515±33	2.52±0.1	4.80±0.12	4.7±0.1
NaOH	510±23	2.52±0.1	4.86±0.16	5.1±0.2
BTCA	446±22	1.91±0.2	4.31±0.22	4.9±0.1
APS	510±32	2.23±0.2	4.58±0.25	5.0±0.2
LD	416±30	1.64±0.2	3.68±0.15	4.5±0.1