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ORIGINAL ARTICLE

The influence of pre-treatment of *Spartium junceum* L. fibres on the structure and mechanical properties of PLA biocomposites

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Abstract Different chemical pre-treatments of *Spartium junceum* L. fibres using alkali (NaOH), nanoclay (MMT) and Citric acid (CA) with the aim of producing biodegradable composite material are discussed. As environmental requirements in processing technologies have been higher in recent years, the Polylactic acid (PLA) is used in this research as a matrix, due to its renewability, biodegradability and biocompatibility. Biocomposites are prepared by reinforcing PLA with randomly oriented, short *Spartium junceum* L. fibres in order to increase material strength. The effects of different pre-treatments of *Spartium junceum* L. fibres on the mechanical properties of final biocomposite material are examined. Fibre tenacity is studied using Vibroscop and Vibrodyn devices. Tensile strength of biocomposite material was measured on the universal electromechanical testing machine Instron 5584. The results indicate that biocomposites reinforced with fibres modified with MMT and CA show upgraded mechanical properties of the final composite material in comparison with the composite materials reinforced with referenced (nontreated) fibres. Infrared spectra of tested fibres and biocomposites were determined with Fourier transform infrared spectroscopy using Attenuated total reflection (FT-IR ATR) sampling technique and the influence of fibre modifications on the fibre/polymer interfacial bonding was investigated. The interface of Spartium/PLA

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composites was observed with scanning electron microscope (SEM) and it was clearly visible that biocomposites reinforced with fibres modified by MMT and CA showed better interaction of fibres and matrix.

1. Introduction

Synthetic fibre reinforced polymer composites have been used for aerospace, defence, marine, automotive, civil infrastructure, etc., for more than 50 years, offering high strength and stiffness, dimensional stability and good thermal properties. Nowadays, due to increased environmental consciousness, the focus of the researchers is shifted to biocomposites, with the application areas remaining the same (Kumar et al., 2010). With the continuous growth for more than 50 years, global plastic production in 2013 was 300 million tonnes (http://www.plasticseurope.org/documents/document/20150227150049-final_plastics_the_facts_2014_2015_260215.pdf). Although the durability of plastics was initially considered as a great advantage, environmental problems caused by the disposal of plastic waste (huge volumes of landfill space around the world, disposal of plastic waste in the marine environment) have arisen (Molinaro et al., 2013; Philp et al., 2013). It led to the conclusion that production of bioplastic, whether it is biobased or biodegradable, would partially solve the problem of its disposal.

The main representative in the group of biodegradable plastic materials is biopolymer based on Polylactic acid (PLA) (Armentano et al., 2013), which is completely degradable. By hydrolysis it can be decomposed to lactic acid, which is subsequently decomposed to water and carbon dioxide by metabolic processes (Oksman et al., 2003). Degradation degree depends on the temperature, size and shape of the polymer, and the proportion of isomers (Oksman et al., 2003; Raquez et al., 2013; Teramoto et al., 2004).

An increasing development of environmental consciousness and thus a significant interest in natural fibres for the production of biocomposites have been initiated in recent years (Li et al., 2011; Mohanty et al., 2005; Pickering et al., 2016; Pickering and Le, 2016; Shalwan and Yousif, 2013). The use of natural fibres as a reinforcement in composite materials has been steadily increasing and has gained a significant interest over past few years (Kim et al., 2014; Ramesh, 2016; Sahari et al., 2013a, 2013b; Sanyang et al., 2015; Vaisanen et al., 2016). Composites reinforced with natural fibres are one of the most commonly used biodegradable materials. They consist of a matrix that can be a biodegradable polymer like PLA, and of reinforcements such as natural fibres, yarns or fabrics. Biopolymers reinforced with biofibres can offer new biocomposites, capable of replacing previously used materials, e.g. glass fibres. One of the most common natural fibres used in biocomposites is bast fibres, such as flax, hemp, jute or *Spartium junceum* L. (Angelini et al., 2013; Caprino et al., 2015; Graupner and Mussig, 2010; Marrot et al., 2014; Mussig and Haag, 2014; Nekkaa et al., 2008; Nekkaa et al., 2009; Pickering and Aruan Efendy, 2016; Sam-Brew and Smith, 2015).

Spartium junceum L. is a native plant used for obtaining fibres of exceptional strength. It grows mostly in the Mediterranean countries, so we can find it at Croatian islands, in particular the Dalmatian ones. Throughout history, *Spartium junceum* L. has had a wide range of applications e.g. perfume and dye production from the flowers, baskets from the stems and textile materials from the fibres (Bischof and Kovačević, 2013). As the fibres still remain the main product, there is a significant value today for their production. The fibres have properties similar to flax fibres and are mostly used in the production of technical textiles (Kovačević et al., 2012). Such fibres could be widely applicable, especially in the automotive industry, in the development of car interiors e.g. carpets, trims on the inside door, cover for the spare wheel (Huda et al., 2008; Partanen and Carus, 2016; Poulikidou et al., 2016; Sindhuphak, 2007).

Production of fibres requires large consumption of water and energy, but production of natural fibres with all of the mentioned above is also a significant time-consuming process. Microwave treatment in textile industry has shown to be fast, uniform and the efficient technique. The microwave energy can easily penetrate inner fibre particle; thus, all the particles can be heated simultaneously, reducing heat transfer problems. Microwave energy has been used in finishing, dying, whitening and thermal treatments of textile materials. The usage of microwave technology in textile industry is still unexplored and open to further improvements. In the work described, microwave technology was used for maceration of *Spartium junceum* L. fibres in order to increase the effectiveness of composite material production (lower use of water and energy) (Büyükakinci, 2012; Mahmoodi et al., 2010).

Furthermore, the application of nanotechnology in biocomposite production has shown promising potential in the development of next generation materials for structural applications (Zhang et al., 2006). In this work we combined PLA as the matrix, *Spartium junceum* L. fibres as the reinforcement and montmorillonite clay (MMT) as the nanofiller in order to investigate mechanical properties of such biocomposites. The increasing use of biocomposites in daily human life provides a better and healthier life for every individual and the steady progress of our eco-system.

2. Experimental

2.1. Materials

Spartium junceum L. fibres were obtained from the *Spartium junceum* L. plant which was harvested in the area of town Šibenik, Croatia (Table 1).

PLA (6201 D) was purchased from Nature Works LLC, USA (Table 2). NaOH pellets (purity $\geqslant$ 97%), Nanoclay (modified with 25–30 wt.% octadecylamine), Citric acid and Sodium Hypophosphite Hydrate (NaH_2PO_2) used for this study were obtained from Sigma-Aldrich Company Ltd., UK.

2.2. Methods

2.2.1. Microwave maceration method

Spartium junceum L. stems were placed into a polytetrafluoroethylene (PTFE) container and into microwave (MW) reso-

Table 1 Physical and mechanical properties of *Spartium junceum* L. fibres.

Density (g/cm^3)	Diameter (μm)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
1.55	45–65	986.46	17.86	6.03

Table 2 Physical Properties data of used PLA polymer. [http://www.natureworksllc.com/~/media/Technical_ Resources/Technical_Data_Sheets/TechnicalDataSheet_6201D_fiber-melt-spinning_pdf.pdf].

Physical properties	PLA Ingeo 6201D
Specific gravity	1.24
Relative viscosity	3.1
Melt index (g/10 min) [210 °C]	15–30
Melt density (g/cm^3) [230 °C]	1.08
Glass transition temperature (°C)	55–60
Crystalline melt temperature (°C)	155–170

nant cavity. Prior to the MW process, fresh stems were immersed in 5% (w/v) NaOH solution (the ratio of stems in (g) to NaOH solution in (mL) was 1:12). After 5 min running at 900 W in the MW the fibres were extracted from the stems. Stems were washed in distilled water and fibres were pulled out. Fibres were washed again in distilled water until neutral pH was reached. After washing, the fibres were air dried.

2.2.2. Fibre pre-treatment

2.2.2.1. Alkali treatment. Fibres were treated with 5% (w/v) NaOH solution, maintaining a fibre/solution ratio of 1:20 (by weight) for 48 h at 25 °C and washed with distilled water repeatedly to avoid any presence of alkali. At the end fibres were neutralized with 1% acetic acid and washed again with distilled water. Alkali treated fibres were dried in the oven at 60 °C for 24 h and stored at ambient temperature in a desiccator.

2.2.2.2. Alkali and nanoclay (MMT) treatment. 5% (w/v) NaOH solution was heated for 15 min at 60 °C. Nanoclay was added inside and the treatment continued for 30 min at the same temperature with the constant mixing, prior to the fibres being immersed. Fibres/nanoclay ratio was 1:1 and fibre/solution ratio was 1:20. Fibres were treated in the solution for 1 h at 60 °C. Finally, fibres were washed with distilled water and dried in the oven at 60 °C for 24 h and stored at ambient temperature in a desiccator.

2.2.2.3. Nanoclay and citric acid (CA) treatment. Solution of 2.2 g Citric acid, 1.1 g NaH_2PO_2, 5 g of nanoclay and 330 mL of water was prepared and treated at 80 °C for 3 h with continuous stirring. After the solution was cooled to the room temperature fibres were immersed and left overnight. After treatment the fibres were washed with distilled water and dried in the oven at 60 °C for 24 h and stored at the ambient temperature in a desiccator.

2.2.3. Composite production

After pre-treatment, the fibres were cut to the length of 2–5 mm. PLA pellets were oven pre-dried at 60 °C for 48 h and then melted in a vacuum oven at 170 °C. 20 wt.% of short fibres was put in an aluminium oval shaped mould, together with melted PLA. The 15 kg weight was placed on the mould (Ø 8.5 cm) and left for 2 h at room temperature. Intermediate composite product was placed between two aluminium sheets protected with release polymer film and preheated in a compression moulding machine at 170 °C. It was left with no load for 5 min and then hot pressed at 170 °C under 1 ton (1000 kg), for 5 min more. The sample was taken out from hot press and left to air cool down under 10 kg weight on the mould.

3. Characterization

3.1. Fibre fineness, strength and elongation

Breaking tenacity, elongation as well as fineness of individual fibres were examined using the Vibroscop and Vibrodyn devices, Lenzing Instruments. Tension, testing speed and gauge length values were 0.015 N, 3 mm/min and 5 mm respectively. Samples were conditioned at the standard temperature (20 ± 2 °C) and relative humidity (65 ± 4%). An average of 150 tests for individual fibres was used in this study.

3.2. Fourier transform infrared (FT-IR) spectra

Infrared spectroscopy (FT-IR) spectra were obtained with a Perkin Elmer Spectrum 100 FT-IR spectrometer using attenuated total-reflection (ATR) method. The analyses were carried out at room temperature and ambient humidity. The solid samples in their original form were placed onto the ATR crystal, ensuring the crystal was completely covered and the pressure was applied. All spectra were registered from 4000 cm^{-1} to 380 cm^{-1}, with a resolution of 4 cm^{-1}. The background was collected at the beginning of the measurement. Each spectrum was collected from an average of 4 scans.

3.3. Composite tensile testing

Tensile tests for polymer/fibre composite materials modified with 3 different pretreatments were carried out using Instron 5584 testing machine at a crosshead speed of 3 mm/min and 20 mm gauge length. Five samples of each category were tested and their average values were reported.

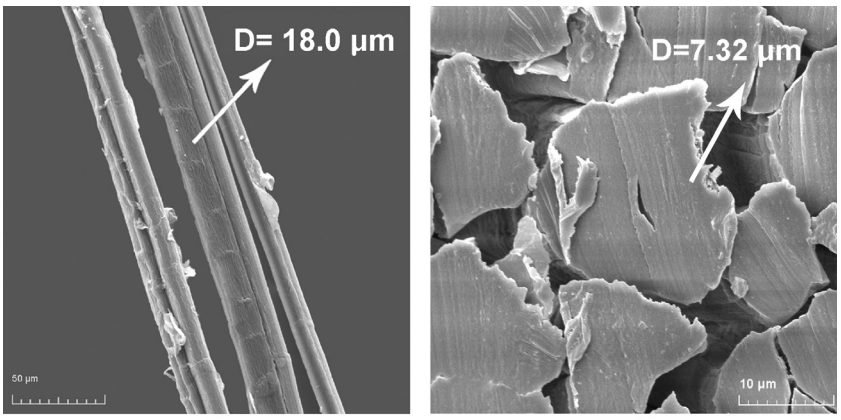
3.4. Scanning Electron Microscopy (SEM) examinations

Polymer/fibre interface and morphological features were studied by using scanning electron microscope (FE-SEM//Mira, Tescan). SEM microscope was operated at 20 kV and various magnification levels due to the need to obtain a good SEM image. Prior to the SEM investigation samples were coated with Au/Pd in order to increase their electrical conductivity.

4. Results and discussion

*4.1. Properties of **Spartium junceum** L. fibres*

Spartium junceum L. (SJL) fibres are produced from the outer part of SJL stem. Its technical fibres come in bundles of elementary fibres held together by pectinous gums. Each elementary fibre can be considered as a network of ultrafine cellulose microfibrils embedded in a matrix of hemicellulose and lignin (Akin, 2010; Kostić et al., 2008). The SJL elementary fibre is about 18.0 μm wide and its cross section indicates the presence of a thick secondary cell wall (7.32 μm), as shown in Fig. 1(a) and (b).



(a) (b)

Figure 1 SEM micrographs of *Spartium junceum* L. fibres (a) longitudinal image of elementary fibre as a part of technical fibre and (b) cross section image of elementary fibre.

The secondary cell wall is of extreme importance because of its influence on fibre properties, while its cellulose-rich fibre structure offers higher tensile strength (His et al., 2001; Zhong and Ye, 2009). Because of the polygonal cross-sectional shape and thick cell wall of its fibres, SJL has the possibility to provide better quality fibres (better light reflection and absorption) (Charlet et al., 2010; His et al., 2001; Khan et al., 2011; Romhany et al., 2003). SJL fibres have fibre nodes and kink bands that appear as horizontal bands in the elementary fibres and bundles and such dislocations are regions where moisture and various chemicals can penetrate and influence fibre properties (Charlet et al., 2010; Khan et al., 2011; Romhany et al., 2003). One of the most important properties is fibre strength. Although it was concluded in our preliminary investigation (Kovačević et al., 2012) that there is no significant difference in the strength of fibres produced by the maceration methods when using water retting or osmotic degumming, our present work shows obvious difference in strength when compared results obtained with those of the MW method of maceration.

Treatment of stems with microwave energy has proven to be an effective method of maceration because it offers shorter time and lower energy consumption, as well as better results regarding fibre tenacity than previously tested maceration methods (Bischof et al., 2014; Katović et al., 2011; Kovačević et al., 2012; Kovačević et al., 2014).

Fig. 2 shows that fibre tenacity after microwave treatment has increased 58.5% and 39.5% in comparison with water retting and the osmotic degumming maceration, respectively. Such results indicate that microwave treatment is an ecological and economical method of maceration, which could be used in the reinforcement production in order to decrease overall costs of composite materials.

4.2. The effect of pre-treatments on fibre strength, fineness and elongation

4.2.1. Fibre strength

In order to improve the properties of the fibre and its composites (tensile strength, fineness, etc.), pre-treatment of fibres was done. Tensile strength results of reference fibres (R), additionally alkali-treated fibres (1), MMT/NaOH-treated fibres (2) and MMT/CA-treated fibres (3) are given in Table 3.

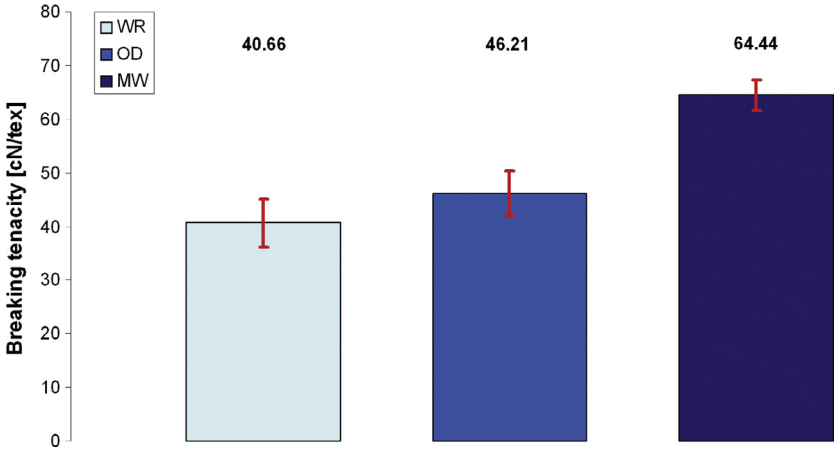


Figure 2 The results of measuring breaking tenacity of *Spartium junceum* L. reference fibres after different maceration methods, where: WR – water retting; OD – osmotic degumming; MW – microwave treatment.

Table 3 Tenacity, fineness and elongation of reference and modified fibres, and data in brackets represent standard deviations.

Sample	Tenacity (cN/tex)	Fineness (dtex)	Elongation (%)
R[a]	64.44 (11.24)	36.75 (11.28)	6.03 (1.14)
1[b]	60.00 (8.28)	35.76 (9.50)	6.70 (1.29)
2[c]	68.84 (9.58)	34.25 (9.33)	8.39 (1.26)
3[d]	67.40 (8.84)	37.19 (9.22)	7.62 (1.44)

[a] The reference fibres.
[b] The fibres treated with NaOH.
[c] The fibres treated with MMT.
[d] The fibres treated with MMT and CA.

ANOVA: Single factor data analysis tool was used to perform analysis of variance during the result processing and to determine whether there are any significant differences between the means of 4 groups of fibres, after the breaking tenacity determination, as given in Table 4. The null hypothesis was that there is no significant difference between the group sample means. According to the *P*-value, a significant difference was established among breaking tenacity of the tested fibres considering the applied pre-treatment method. Since $P \leqslant 0.05$, it could be concluded that there was statistically significant difference with the 95% confidence in the fibre tenacity among at least two group means that are significantly different from each other. To determine which specific groups differed from each other, Tukey's HSD Post hoc test was used (Table 4).

It could be seen that fibres modified with MMT (2 and 3) show statistical insignificant difference in the breaking tenacity values, and more precisely, the pre-treatment method with MMT/CA (3) has not influenced strength of fibres compared to pre-treatment method with MMT/NAOH (2). Tenacity results of samples 2 and 3 indicate improvement in strength while fibres modified additionally with NaOH (1) showed relatively lower strength value, compared with reference fibres (R), which is probably due to the repeated alkali treatment resulting in additional delignification of fibres resulting in weaker or damaged fibre (Li et al., 2007). Alkali solution provided OH^- and Na^+ ions to react with the substances on the fibre, causing partial removal of lignin, pectin, waxes and hemicelluloses, which would be detrimental to fibre strength (Andiç-Çakir et al., 2014). MMT clays consisted of aluminosilicate clay nanolayers which were separated from each other by an interlayer distance, where exchangeable ions existed, causing neutralization of the charge between those layers. MMT-modified fibres (2 and 3) showed improvement in their mechanical properties due to the MMT nanolayered structure and its high aspect ratio (length/thickness) approx. 100–1000 nm (Mohan and Kanny, 2012).

Table 4 ANOVA and Tukey Post hoc Test among the breaking tenacity of the fibres obtained by different pre-treatments.

Groups	Count	Sum	Average	Variance
SUMMARY				
R[a] (cN/tex)	150	9666.25	64.44166667	126.3239
1[b] (cN/tex)	150	9000.32	60.00213333	68.62814
2[c] (cN/tex)	150	10326.24	68.8416	91.84757
3[d] [cN/tex]	150	10109.66	67.39773333	78.15458

Source of variation	*SS*[e]	*df*[f]	*MS*[g]	*F*[h]	*P*-value[i]	*F* crit
ANOVA & TUKEY TEST						
Between Groups	6852.113286	3	2284.037762	25.0337	2.89E−15	3.81462
Within Groups	54378.16885	596	91.23853833			
Total	61230.28213	599				

Groups of fibres	*Q* critical[j]	*Q* statistic[k]	*Q*stat > *Q*crit	Statistical conclusion
R vs. 1	3.6435	5.6924	>	Significant difference
R vs. 2	3.6435	5.6416	>	Significant difference
R vs. 3	3.6435	3.7903	>	Significant difference
1 vs. 2	3.6435	11.334	>	Significant difference
1 vs. 3	3.6435	9.4827	>	Significant difference
2 vs. 3	3.6435	1.8513	<	Insignificant difference

[a] The reference fibres.
[b] The fibres treated with NaOH.
[c] The fibres treated with MMT.
[d] The fibres treated with MMT and CA.
[e] Sum of squares.
[f] Degrees of freedom.
[g] Mean square.
[h] Empirical *F* ratio (MS between groups/MS within groups).
[i] *P*-value (If $P \geqslant 0.05$ there is no statistically significant difference between the arithmetic mean of the samples).
[j] *Q* critical value of the Tukey-Kramer HSD *Q* statistic based on the $k = 4$ treatments and $df = 596$ degrees of freedom for the error term, for significance level $\alpha = 0.05$ in the Studentized Range distribution.
[k] *Q* statistic (Tukey-Kramer HSD *Q*-statistic) – parameter calculated for each pair of columns being compared.

4.2.2. Fibre structural characterization

Fig. 3 shows the IR spectra of *Spartium junceum* L. fibres obtained by different methods of modification (pre-treatments). Bast fibres are usually characterized by several absorption bands: one from 3000 cm^{-1} to 3700 cm^{-1} that represents free OH groups and intra- and inter-molecular hydrogen bonds and two bands at 2844 cm^{-1} and 2900 cm^{-1} which are attributed to the CH and CH_2 groups of pectins, fats and waxes (Kovačević et al., 2012). The broad peak in the range of 3000–3700 cm^{-1} and the peak at 1631 cm^{-1} were due to the

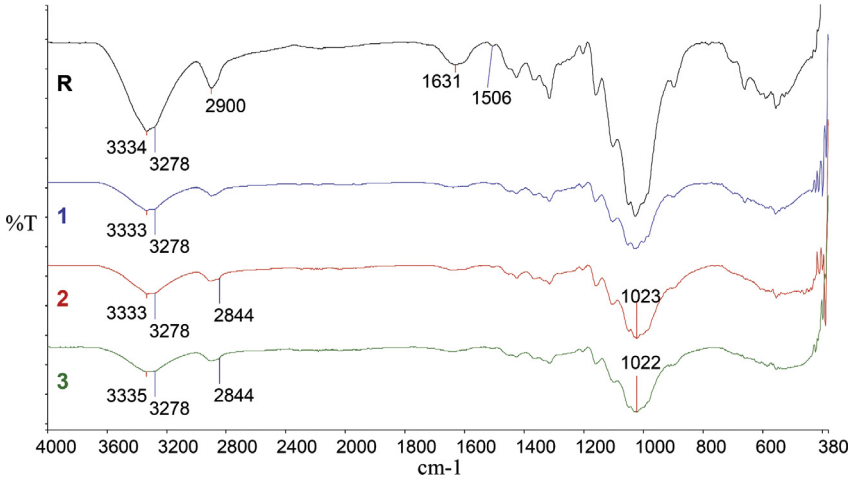


Figure 3 IR spectra of *Spartium junceum* L. fibres, where: R – the reference fibres; 1 – the fibres treated with NaOH; 2 – the fibres treated with MMT; and 3 – the fibres treated with MMT and CA.

Table 5 ANOVA and Tukey Post hoc Test among the fineness of the fibres obtained by different pre-treatments.

Groups	Count	Sum	Average	Variance
SUMMARY				
R[a] (dtex)	150	5512.36	36.74906667	127.1605
1[b] (dtex)	150	5363.29	35.75526667	90.28803
2[c] (dtex)	150	5137.39	34.24926667	86.98075
3[d] (dtex)	150	5579.13	37.1942	84.98998

Source of variation	*SS*[e]	*df*[f]	*MS*[g]	*F*[h]	*P*-value[i]	*F* crit
ANOVA & TUKEY TEST						
Between Groups	766.7242365	3	255.5747455	2.625188	0.049647	2.619853597
Within Groups	58023.47528	596	97.3548243			
Total	58790.19952	599				

Groups of fibres	*Q* critical[j]	*Q* statistic[k]	*Q*stat > *Q*crit	Statistical conclusion
R vs. 1	3.6435	1.2336	<	Insignificant difference
R vs. 2	3.6435	3.1029	<	Insignificant difference
R vs. 3	3.6435	0.5525	<	Insignificant difference
1 vs. 2	3.6435	1.8694	<	Insignificant difference
1 vs. 3	3.6435	1.7861	<	Insignificant difference
2 vs. 3	3.6435	3.6555	>	Significant difference

[a] The reference fibres.
[b] The fibres treated with NaOH.
[c] The fibres treated with MMT.
[d] The fibres treated with MMT and CA.
[e] Sum of squares.
[f] Degrees of freedom.
[g] Mean square.
[h] Empirical *F* ratio (MS between groups/MS within groups).
[i] *P*-value (If $P \geqslant 0.05$ there is no statistically significant difference between the arithmetic mean of the samples).
[j] *Q* critical value of the Tukey-Kramer HSD *Q* statistic based on the $k = 4$ treatments and $df = 596$ degrees of freedom for the error term, for significance level $\alpha = 0.05$ in the Studentized Range distribution.
[k] *Q* statistic (Tukey-Kramer HSD *Q*-statistic) – parameter calculated for each pair of columns being compared.

characteristic axial vibration of the cellulose hydroxyl group. Absorption bands at 2844 and 2900 cm^{-1} could be observed in the spectra of all the fibres, but they were more intensive in the spectra of referenced fibres (R) pointing to the minor amount of pectins, waxes and fats inside other tested fibres.

Lignin is characterized by absorption bands at 1506 cm^{-1} and it could be observed only in the spectra of referenced fibres. The MMT treated fibres (2 and 3) showed broader peaks around 1022 cm^{-1} due to Si—O plane stretching vibrations. In the other treated fibres (1, 2 and 3), the dissolution of lignin phase was clearly observed, due to the absence of their characteristic peak at 1506 cm^{-1}. The hydroxyl group of referenced Spartium fibre (R) at 1631 cm^{-1} (due to cellulose) was less intensive in the treated fibres.

4.2.3. *Fibre fineness*

Fibre fineness is an important factor in determining the stiffness of its final product. The resistance to bending reduces as the fineness of the fibre increases (Morton and Hearle, 2008; Sinclair, 2015; Yan et al., 2016). The most common fineness (measured on the basis of 3 highest values) of the reference fibres (R), NaOH-treated fibres (1), MMT/NaOH-treated fibres (2) and the fibres treated with MMT and CA (3) was in the category from 25 to 40 dtex (57.3% for all the tested (R) fibres), 25 to 40 dtex (58.7% for all the tested (1) fibres), 25 to 40 dtex (61.4% for all the tested (2) fibres) and 30 to 45 dtex (63.3% for all the tested (3) fibres), respectively. Fineness depends not only on the shape but also on the used method of fibre pre-treatment as well (Lanzilao et al., 2016), although, according the Table 5, it can be seen that significant difference in fibre fineness is only between samples 2 and 3.

Fibres obtained by pre-treatment with MMT and CA, as shown in Fig. 4(d), were coarser and their decreased fineness was attributed to the MMT particles, showing better linking to the fibre surface due to CA, which served as a cross linker in comparison with the fibres obtained by the modification with MMT/NaOH (22% of all the tested (2) fibres within the range from 25 to 30 dtex). It was mentioned earlier that dislo-

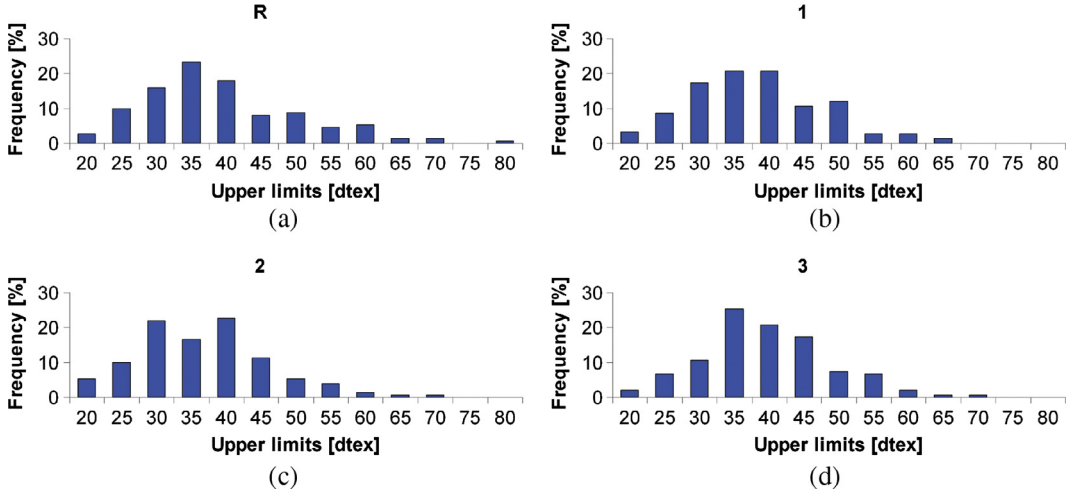


Figure 4 Frequency of fineness for 150 measurements of (a) the reference fibres (R); (b) the NaOH-treated fibres (1); (c) the MMT-treated fibres (2); and (d) the MMT- and CA-treated fibres (3).

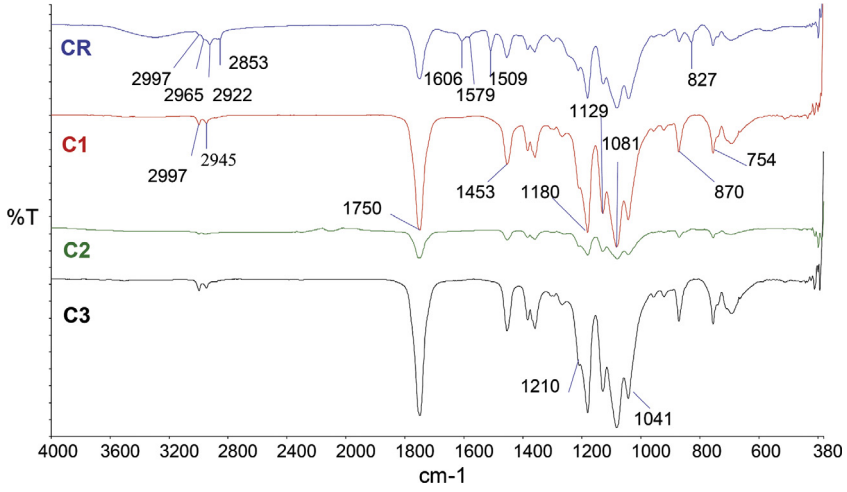


Figure 5 IR spectra of PLA polymer reinforced with *Spartium junceum* L. fibres, where: CR – composite reinforced with reference fibres; C1 – composite reinforced with the fibres treated with NaOH; C2 – composite reinforced with the fibres treated with MMT; C3 – composite reinforced with the fibres treated with MMT and CA.

Table 6 Main infrared transition for PLA.

Wave number (cm^{-1})	Vibration
3000–3600	OH stretching
2997	Asymmetric CH_3 stretching
2945	Symmetric CH_3 stretching
1750	Asymmetric C═O stretching
1300–1500	Symmetric CH, CH_3 deformation
1180	Symmetric C—O—C stretching
1129	Asymmetric CH_3 bending
1081	Asymmetric C—O—C stretching
1041	C—CH_3 stretching
870	C—COO stretching
754	C═O bending

cations in the fibres are regions where moisture and various chemicals could penetrate and influence fibre properties, and as such they represented the weakest link in natural fibres. Therefore, the increase of mechanical properties of composite materials reinforced with MMT/CA fibres could be attributed to the "repair" of dislocations in the fibre (Dai et al., 2013).

4.2.4. Fibre elongation

Elongation at break of the fibres is the elongation of the test specimen produced by the breaking force, expressed as a percentage of the initial gauge length (Li et al., 2007; Reddy and Yang, 2009). Breaking elongation of fibres that underwent modification 2 was higher (8.39%) than the elongation of the

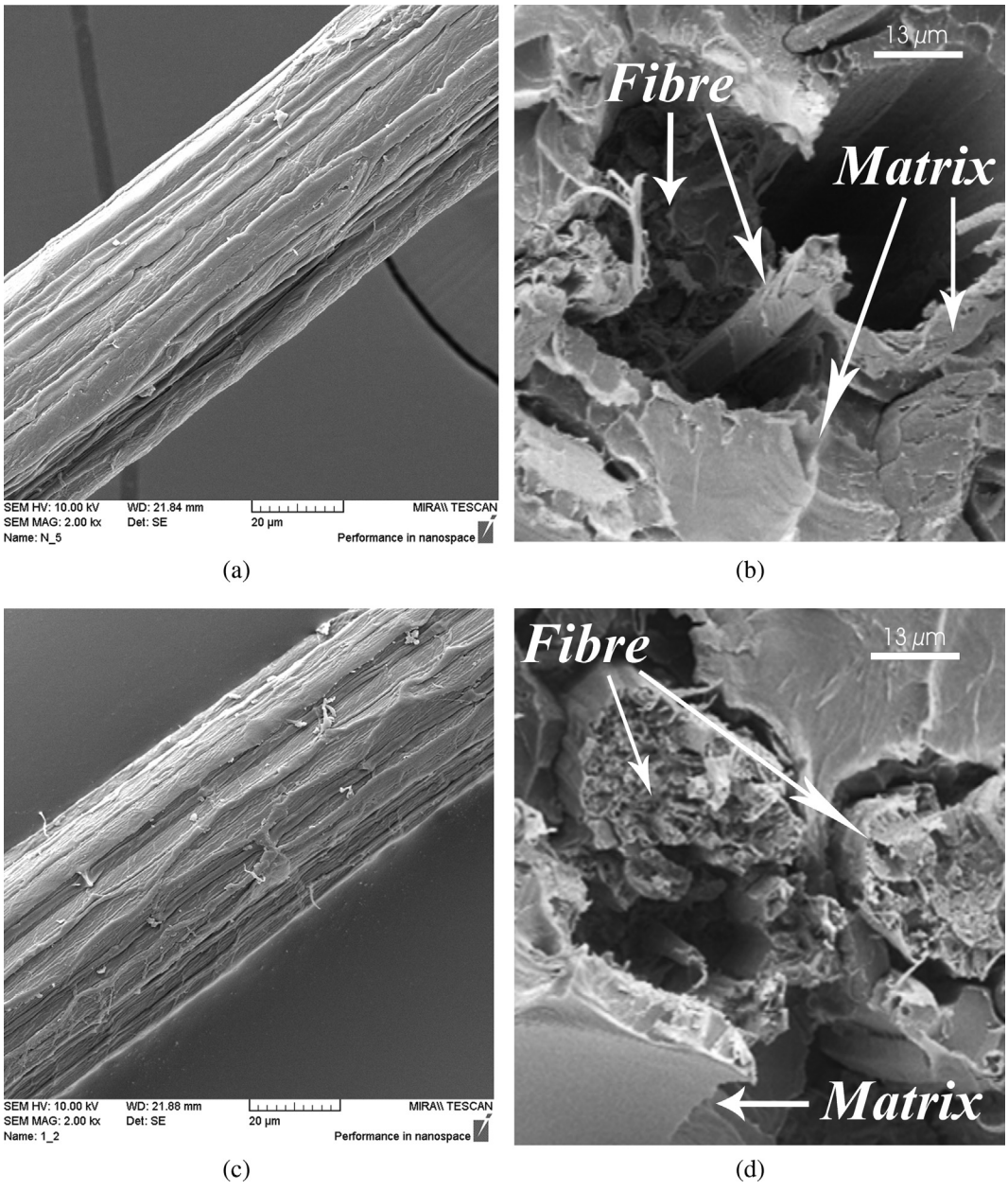


Figure 6 Scanning electron micrographs of the fibre reinforced composites and tensile fracture surface of the composites, where: (a) the reference fibre (R); (b) fractured surface of the CR composite; (c) the NaOH-treated fibre (1); and (d) fractured surface of the C1 composite.

other tested fibres, implying the decreased stiffness and brittleness of the fibres modified only with the MMT. Such property could be explained with interfacial adhesion between the fibre and MMT, where weaker interfacial adhesion resulted in higher elongation at break (Santiago et al., 2011). Therefore, enhancement in mechanical properties of the composite materials reinforced with fibres treated with MMT/NaOH was not expected.

4.3. The effect of pre-treatments on the bonding/interface performance of Spartium/PLA composites

4.3.1. Chemical composition of Spartium/PLA composites

During the analysis of fibres and composites, infrared spectra presented in Figs. 3 and 5 and taking into account the main infrared peaks of pure PLA polymer (Table 6), the chemical composition of biocomposites and the influence of already mentioned modification on the fibre/polymer interfacial bonding, were investigated.

Fig. 5 shows the IR spectra of PLA biocomposites reinforced with *Spartium junceum* L. fibres. The hydroxyl peaks represented between 3000 and 3600 cm^{-1} decreased significantly with the introduction of MMT in the biocomposites (C2 and C3). In the NaOH (C1) and MMT/CA (C3) composites, the hydroxyl peak broadened further and formed a peak at 2945 cm^{-1}. Due to the inter- or the intra-molecular hydroxyl group bonding with polysaccharides, the shifting of frequency to 2945 cm^{-1} (Mohan and Kanny, 2012) occurred. The shifting of peak pertaining to —OH group indicated the participation of hydroxyl group of clay in the crosslinking

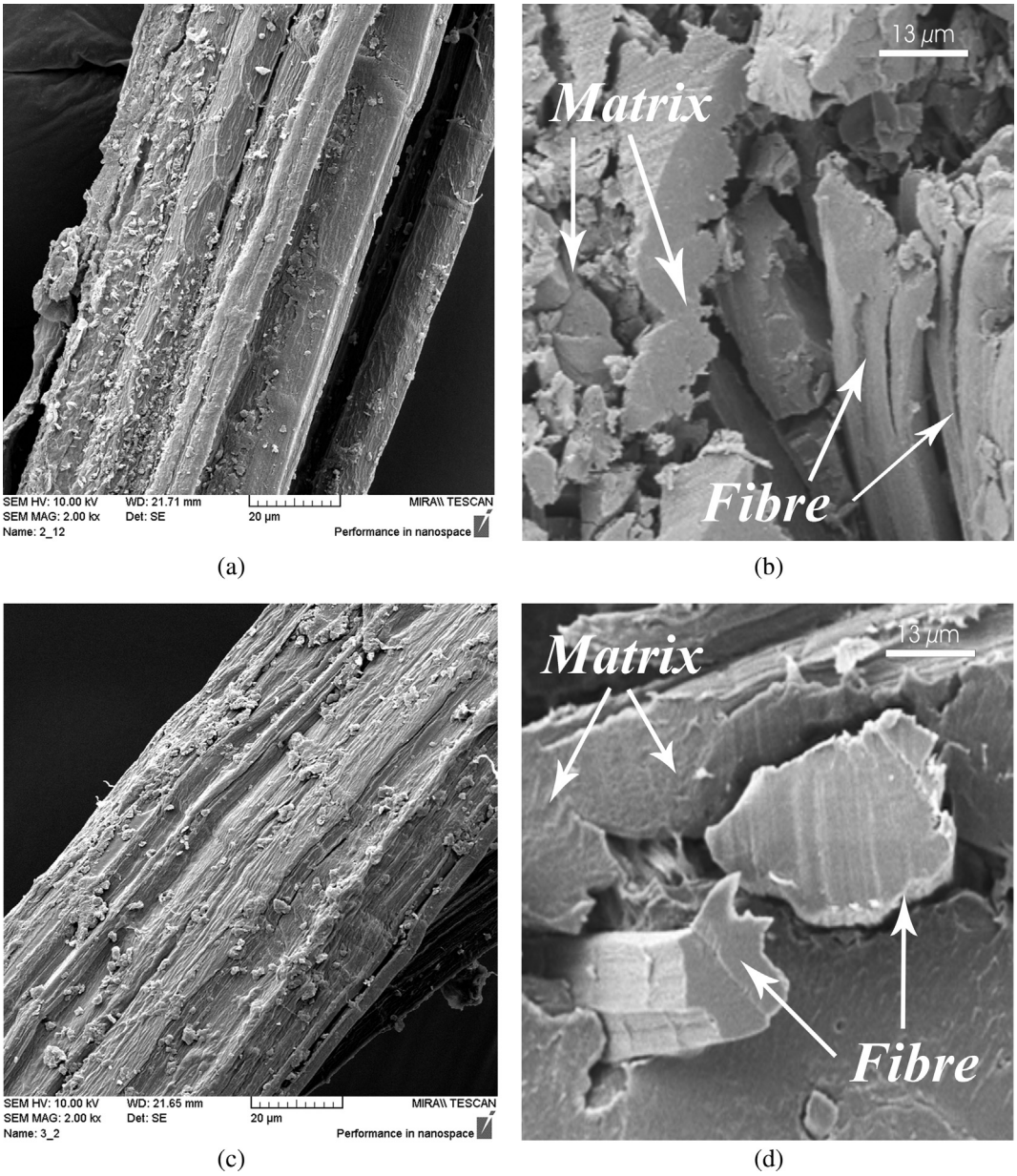


Figure 7 Scanning electron micrographs of the fibre reinforced composites and tensile fracture surface of the composites, where: (a) the fibre treated with MMT (2); (b) fractured surface of the C2 composite; (c) the fibre treated with MMT and CA (3); and (d) fractured surface of the C3 composite.

reaction of fibre and polymer in the C3 composite. The characteristic peak at 1750 cm^{-1} due to the C═O stretching could be observed in all the spectra. The intensity of C═O stretching was found to increase in the crosslinked composite (C3), suggesting the increase of the number of unbounded/free carboxylic end groups in the polymer chain. Moreover, the peak intensity of ─OH bending vibration at 1645 cm^{-1} was also found to decrease, especially in the C3 composite, suggesting the formation of bonds between clay, fibres and polymer. Peaks at 1606 cm^{-1}, 1509 cm^{-1} and 827 cm^{-1} were attributed to the lignin from fibres and they could be observed only in the CR composite reinforced with reference fibres (R). The disappearance of these peaks indicated the delignification of fibres subjected to the modification 1, 2 and 3. Bands visible in the range 1300 –1500 cm^{-1} might be assigned to symmetric and asymmetric vibrations of C─H present in CH_3 of PLA (Iman and Maji, 2012; Molinaro et al., 2013). It was also observed that the C─H bending vibrations at around 1380 cm^{-1} were intensified due to the chemical treatment of *Spartium junceum* L. fibres. The peak at 1180 cm^{-1} was attributed to C─O─C stretching of PLA. The cooling process involved in the composite production seemed to be fast enough to prevent a rearrangement of polymer chain into a crystalline structure. This could explain the shoulder visible at 1210 cm^{-1}. The appearance of the peaks at 1129, 1081 and 1041 cm^{-1} may correspond to C─O stretching vibrations. The peak at around 1080 cm^{-1} was due to the associated hydrogen group. The peaks shown in the range 1030–460 cm^{-1} were the characteristic peaks of oxide bonds of the metals, i.e. Si, Al, Mg, etc. present in the nanoclay. In the spectra of the C2 composite, the intensity of the metal oxide peaks at 1030–460 cm^{-1} was found to be decreased in comparison with the spectra of the C3 composite, indicating lower intensity of the Si─O stretching peaks, which showed that there was no strong interaction among PLA polymer, fibre and clay. Finally, the IR bands detected at 870 cm^{-1} and 754 cm^{-1} could be assigned, respectively, to the amorphous and crystalline phases of PLA (Deka et al., 2012).

4.3.2. The interface of Spartium/PLA composites

Mechanical properties of composites based on natural fibres are strongly influenced by the interface adhesion between the fibres and the polymer matrix, which is related to the chemical composition of the fibre surface and the matrix chemical structure. Good interface causes increment of the stress transmission from the matrix to the fibre and thus enhances the tensile strength of the composite (Li et al., 2009; Oliver-Ortega et al., 2016). There are significant problems of compatibility between the fibre and matrix, i.e. natural fibres tend to be strong polar and hydrophilic materials, while polymers exhibit significant hydrophobicity causing weak interface area between natural fibres and matrices. However, a number of published papers report on possible chemical treatments which might improve the matrix-fibre interfacial adhesion (Alamri et al., 2012; Chen and Yan, 2013; Hossain et al., 2011; Orue et al., 2016).

SEM micrographs of *Spartium junceum* L. reference and modified fibres and fractured surface of its composites without and with clay are presented in Figs. 6(a–d) and 7(a–d), respectively.

The surface of the R fibre (Fig. 6a) was smooth and regular in comparison with the surface of the fibre 1, where roughness at the surface was little bit increased by additional treatment of the technical fibre with NaOH. Fibre matrix debonding and fibre pull-out were more evident in the composite CR than in C1, indicating that the interfacial adhesion between matrix and reference fibre was worse and the fact was supported by lower mechanical properties, in comparison with the C1 mechanical properties (Table 7).

Fig. 7(a) and (c) shows fibres treated with MMT/NaOH and MMT/CA respectively.

Fibre surface roughness was increased with the addition of clay (Fig. 8). However, on adding MMT into the composites (C2), the fractured surface of the composite was found to be very brittle and full fibre/matrix debonding was observed, indicating lower mechanical properties of the C2, in comparison with the other tested composites. The C3 composite showed smoother fractured surface, which might be due to the fact that the combination of the MMT and CA particles increased the

Table 7 Mechanical properties of tested biocomposites.

Sample	Strength (MPa)	Modulus (GPa)	Elongation at break (%)
PLA[a]	17.68 (1.42)	1.40 (0.52)	5.15 (1.06)
CR[b]	41.87 (3.09)	1.65 (0.50)	7.07 (0.86)
C1[c]	42.65 (2.67)	1.89 (0.14)	5.80 (0.69)
C2[d]	19.81 (1.64)	1.17 (0.14)	5.68 (1.26)
C3[e]	46.67 (3.29)	2.60 (0.20)	7.40 (0.53)

[a] Pure PLA polymer.
[b] Biocomposite reinforced with the reference fibres.
[c] Biocomposite reinforced with the NaOH-treated fibres.
[d] Biocomposite reinforced with the MMT-treated fibres.
[e] Biocomposite reinforced with the MMT- and CA-treated fibres.

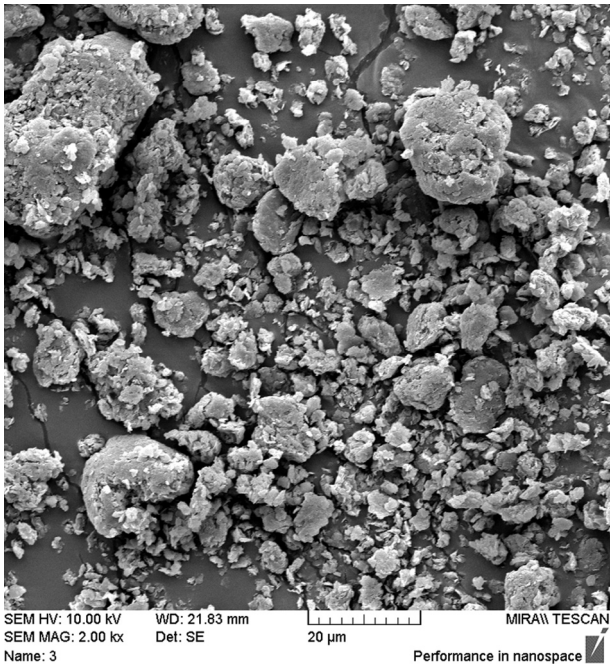


Figure 8 SEM micrograph of pure nanoclay (MMT).

interaction with PLA matrix which resulted in less pulled out fibres from the fractured surface in comparison with the CR, C1 and C2 composites.

4.4. The effect of pre-treatments on the tensile strength of Spartium/PLA composites

Tensile strength of a composite material is influenced by the nature and properties of the matrix and the fibre, reinforcement aspect ratio and its orientation, the fibre content and their dispersion along the matrix as well as the interaction between the matrix and the fibre (interfacial shear strength) which is the most important factor. As already mentioned, the tenacity of the fibres (2) and (3) was practically the same and increased compared to the referenced sample (R). Although fibres showed good results regarding their mechanical properties, some irregularities could be observed in its composite mechanical properties (Figs. 9 and 10, Table 7).

Tensile strength of pure PLA was very low. However, introducing fibres resulted in significant increase in the mechanical properties. Higher strength of 136.8%, 141.2%, 12.0% and 164.0% for the CR, C1, C2 and C3, respectively was recorded, as compared to the pure PLA. Since NaOH treated fibres (1) show decrease in the tenacity in comparison with the (R) fibres because of removal of non-cellulosic compounds and possible creation of the voids in the fibre structure, its composites (C1) have shown increase in strength. The possible reason for that is filling of voids inside the fibre with PLA polymer resulted in improved fibre/PLA adhesion mainly due to mechanical interlocking mechanism (Essabir et al., 2016; Orue et al., 2016;

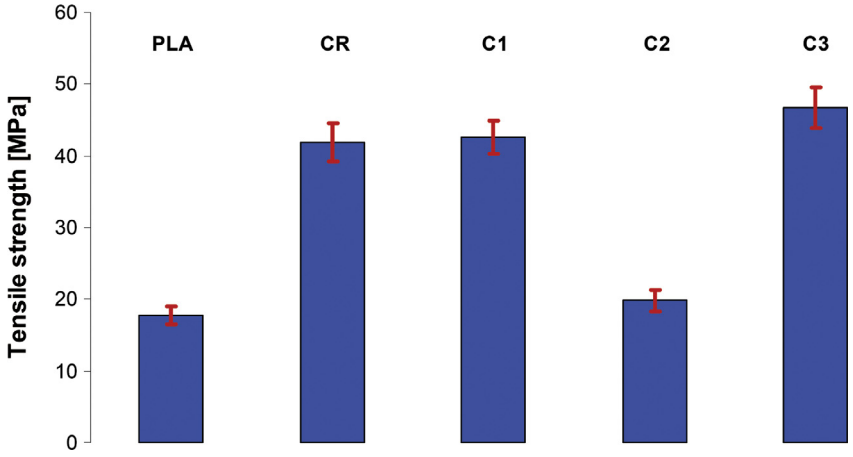


Figure 9 Tensile strength of tested composites where: PLA – pure PLA polymer prepared by the same method as the composites; CR – composite reinforced with the reference fibres; C1 – composite reinforced with the NaOH-treated fibres; C2 – composite reinforced with the MMT-treated fibres; C3 – composites reinforced with the MMT- and CA-treated fibres.

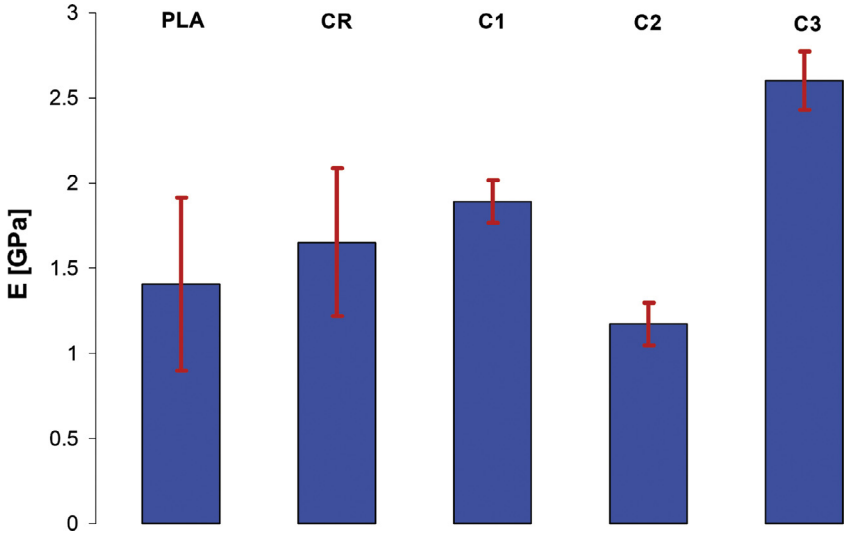


Figure 10 Young modulus of tested composites where: PLA – pure PLA polymer prepared by the same method as the composites; CR – composite reinforced with the reference fibres; C1 – composite reinforced with the NaOH-treated fibres; C2 – composite reinforced with the MMT-treated fibres; C3 – composites reinforced with the MMT- and CA-treated fibres.

Pickering and Le, 2015). Rougher surface of NaOH treated fibres, as well as its ability of rigidly attaching to the matrix, caused improvements in tensile strength and modulus of the C1 Sample over the sample reinforced with the reference fibres – CR (136.8% and 14.5% increase in tensile strength and modulus respectively), which was still lower than the mechanical properties of the MMT/CA modified composite. The sample C3 showed highest strength and modulus values, indicating higher toughness of material. These results indicated that nanoclay adsorbed on the fibre surface contributed to the stiffening of the resulting composite. Increase of the Young's modulus in comparison with the neat PLA was noted in all samples except the sample C2. This increment is a common behaviour when rigid fillers are incorporated into softer polymer matrix. Therefore, the addition of clay particles to a PLA polymer can enhance the stiffness of the composite material since the rigidity of inorganic particles is higher in comparison with polymers or natural fibres (Essabir et al., 2016). The reason for low mechanical properties of the sample C2 could be attributed to the decrease of interface properties and fibre-matrix adhesion due to weak adsorption force between the clay particles and the fibre surface and formation of a greater number of filler to filler bonds (clay-clay or fibre-fibre), which was also visible in larger amount of air voids observed inside the body of the sample (Fig. 11).

Low interaction between matrix and fibre causes the composite's tensile strength to remain similar to the matrix tensile strength possibly due to fibres sliding during testing (Oliver-Ortega et al., 2016; Serrano et al., 2014). Increase of the elongation at break of all composites (CR, C1, C2 and C3) compared to the neat PLA is something unexpected.

In general, polymers have higher elongation at break in comparison with the natural fibres which leads to the increase of brittleness of material made of polymer reinforced fibres. The usual trend between tensile strength and elongation is that one grows while the other decreases.

In this case, when tensile strength and elongation at break both increased, the composite material is tougher and can withstand fracturing if a crack grows so long that the reinforcement cannot support the load (Granda et al., 2016a, 2016b).

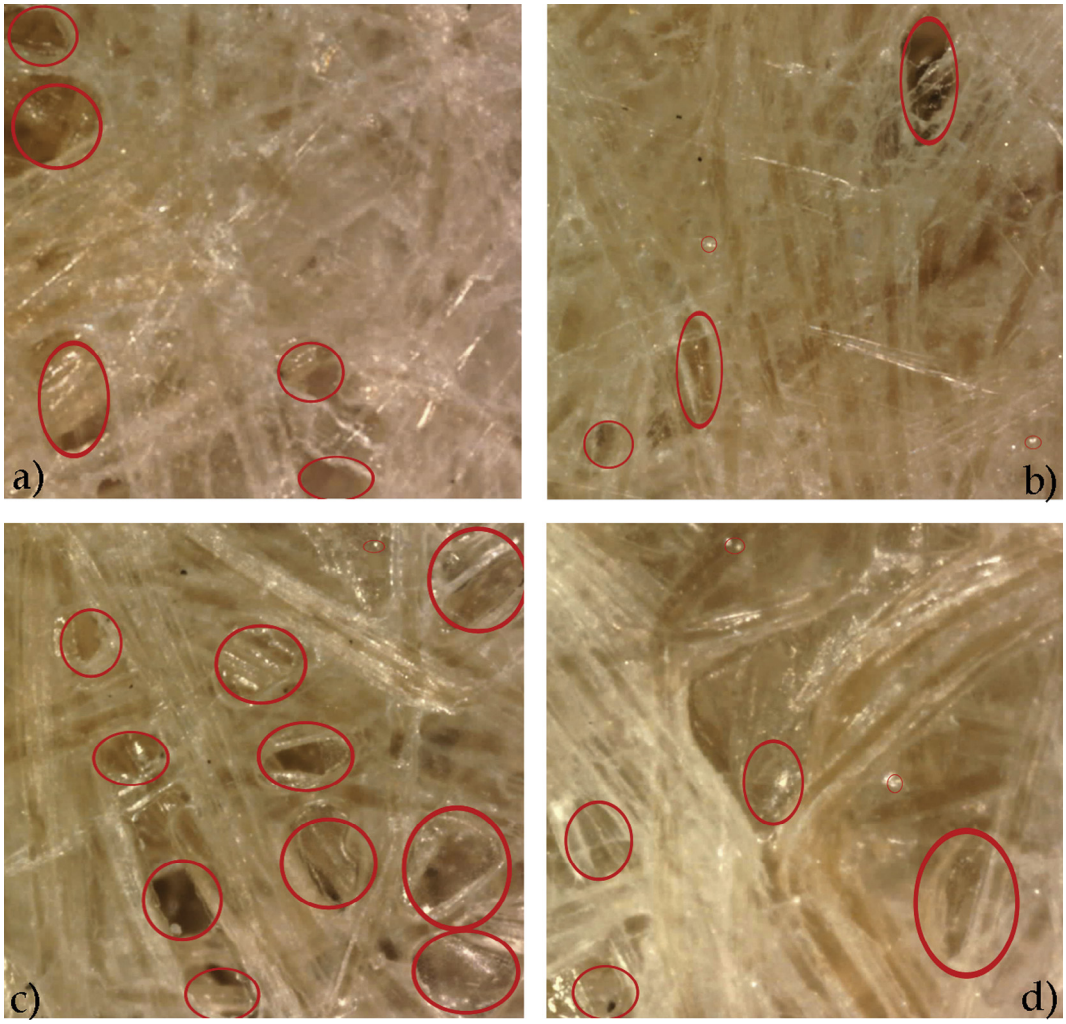


Figure 11 Dino-Lite digital microscope images at 50× magnification presenting voids on the surface of: (a) CR composite; (b) C1 composite; (c) C2 composite; and (d) C3 composite.

5. Conclusion

The aim of this research was to improve mechanical properties of PLA biocomposites reinforced with *Spartium junceum* L. fibres through fibre modification by NaOH, MMT and CA. Development of natural fibres as reinforcement in composite materials is challenging because of the high mechanical properties demanding and the general lack of such properties in natural fibres. Chemical treatment and usage of nanoclay filler increased the compatibility between *Spartium junceum* L. fibre, clay and polymer matrix resulting in higher adhesion and better efficiency for stress transfer.

Tensile strength and modulus of the most promising biocomposites i.e. composite reinforced with MMT and CA treated Spartium fibres (C3) were improved by 164.0% and 85.7% respectively, as compared to the pure PLA sample. Having in mind that CA is well known as eco-friendly crosslinker with a positive impact on the flame retardant properties of cellulose fibres, better thermal properties of C3 composite were expected.

Further improvements of such biocomposites require more investigation on the modification of *Spartium junceum* L. fibres by CA, serving at the same time as an ecological crosslinker in this biosystem, maximizing the affinity between a hydrophilic fibre and a hydrophobic PLA matrix.

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