Enhancement of Spartium junceum L. fibres properties

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Abstract. Properties of lignocellulosic Spartium junceum L. (SJL) fibres were investigated in order to use them as reinforcement in composite material production. The fibres were obtained by microwave maceration process and additionally modified with NaOH, nanoclay and citric acid with the aim to improve their mechanical, thermal and other physical-chemical properties. Tensile and thermal properties of these natural fibres were enhanced by the different modification treatment which is investigated by the Vibrodyn/Vibroskop method and thermogravimetric analysis (TGA), whilst determination of chemical composition and fibre’s surface properties were explored using scanning electron microscope (SEM), electron dispersive spectroscopy (EDS) and electrophoretic analyser. All the results show great improvement of nanoclay/citric acid modified SJL properties.

1. Introduction
The rapidly increasing environmental awareness and growing global waste problem affected the development concepts of sustainability and renewable materials. Due to the need for finding renewable solutions in the development of new materials, the usage of composite materials made of biopolymer matrices and natural fibres that are in the service of reinforcement is increasing significantly.

Considering they are durable, safe and have excellent mechanical properties [1], composite materials reinforced with natural fibers are mostly used in automotive industry [2] in the function of panels, seats, etc. Usage of such materials is favored by the Directive 2000/53/EC of European Union which requires that by 2015th, member countries have to reuse a minimum of 95 % of waste vehicle which ensure that less than 5 % of the waste vehicle would be landfilled [3, 4].

Although, bast fibres have been grown for centuries throughout the world, their production is nowadays much higher in order to meet the demands of global market and to produce recyclable, renewable, ‘green’ products. Some of the most used bast plants are: flax, hemp, kenaf, ramie, jute, etc. Whilst flax and hemp have mostly been used as textile raw material of cellulosic origin in plains, in coastal areas of the Mediterranean wild Spartium junceum L. - SJL has been used as textile raw material since ancient times [5]. Aim of this research was to investigate modified SJL fibres in order to use them as reinforcement in composite materials.
2. Experimental

2.1. Materials
Spartium junceum L. fibers were obtained from the SJL plant which was harvested in the area of town Šibenik, Croatia. NaOH pellets (purity ≥ 97 %), Nanoclay (MMT modified with 25 - 30 wt % octadecylamine), Citric acid (CA) and Sodium Hypophosphate Hydrate (NaH2PO2) used for this study were obtained from Sigma-Aldrich Company Ltd., UK.

2.2. Methods
Methods for determining the content of cellulose, lignin and hemicellulose were conducted in compliance with the regulations previously described in Antonović et al. 2007 [6]. Chemical analysis of modified fibres was conducted with scanning electron microscope (Mira, Tescan) and Quantax EDS (Bruker). Breaking tenacity and fineness of individual fibres were examined using the Vibroskop and Vibrodyn devices (Lenzing Instruments). Pyris I TGA (Perkin Elmer) thermogravimetric analyzer was used for determination of thermal degradation on samples we were investigated. Additional characterization of fibres surface before and after modification was collected by zeta potential determined using the electrokinetic analyzer SurPASS (Anton Paar GmbH) based on the streaming potential method.

3. Results and discussion
Spartium junceum L. fibres were modified by different chemical pre-treatments. Tensile strength results of reference fibres (RF), additionally alkali-treated fibres (1F), MMT/NaOH-treated fibres (2F) and MMT/CA-treated fibres (3F) are given in Table 1. Tenacity results of samples 2F and 3F indicate improvement in strength while fibres modified additionally with NaOH (1F) showed relatively lower strength value, compared with RF sample, which is probably due to the repeated alkali treatment resulting in additional delignification of fibres resulting in weaker or damaged fibre [7].

Table 1. Tenacity, fineness and elongation of reference and modified fibres, data in brackets represent standard deviations.

| Sample  | Tenacity (cN/tex) | Fineness (dtex) | Elongation (%) |
|---------|-------------------|----------------|---------------|
| RF a    | 64.44 (11.24)     | 36.75 (11.28)  | 6.03 (1.14)   |
| 1F b    | 60.00 (8.28)      | 35.76 (9.50)   | 6.70 (1.29)   |
| 2F c    | 68.84 (9.58)      | 34.25 (9.33)   | 8.39 (1.26)   |
| 3F 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

Relative chemical composition of Spartium junceum L. fibres was obtained by using energy dispersive X-ray (EDS) spectroscopy. EDS spectra is acquired by selecting energy requirement in KeV for Kα emission at x-axis and relative abundance on y-axis [8]. EDS analysis has proven the existence of Si and Al (nanoclay) atoms in both samples (2F and 3F) and quantitative analysis shows that sample (2F) has 1.8 % wt. of Si atoms and 0.5 % wt. of Al atoms, while sample (3F) has 11.5 % wt. of Si and 3.2 % wt. of Al atoms, respectively (Figure 1) which might be due to the formation of crosslinking caused by the interaction between the CA and hydroxyl groups of cellulose.

SEM micrographs of Spartium junceum L. reference and modified fibres show that the surface of RF fibre (1a) was smooth and regular in comparison to the surface of fibre R1 (1b) where roughness at the surface was a little bit increased caused by additional treatment of technical fibre with NaOH. Figure 1
c) and d) show fibres treated with MMT and MMT/CA respectively. The roughness of the fibres surface was increased with the addition of nanoclay which is especially visible in the 3F sample.

![Figure 1. EDS spectra and SEM images of a) RF; b) 1F; c) 2F and, d) 3F.](image)

In order to investigate hydrophilic/hydrophobic nature of Spartium junceum L. fibres, their $\zeta$-potential- pH dependence was determined in 1 mM KCl electrolyte solution. Figure 2 shows different $\zeta$-potential plateau values for all the tested fibres regarding their different treatment (modification). Variation of electrokinetic properties within investigated SJL fibres is expected since any treatment of fibres will affect the chemical fibre composition (cellulose, hemicellulose, pectine, lignin, waxes, etc.) and increase the accessibility of dissociable hydroxyl groups [9, 10], therefore causing more negative $\zeta$-plateau value compared to RF. RF and 2F fibres have a small negative $\zeta$-potential plateau values and both of them display a rapid increase of the negative $\zeta$-potential below pH 5. Rapid increment of $\zeta$-potential of 2F goes to more negative values indicating presence of nanoclay particles on the fibre surface, also visible by the scanning electron microscope observations, Figure 1c [7]. Cellulosic fibres have isoelectric point (IEP) values, where $\zeta$-potential=0, at low pH values (around pH 2, extrapolated) and the $\zeta$-plateau values in the alkaline range. Modification of RF fibres additionally with NaOH (1F) resulted in a shift in the IEP to slightly higher pH values (IEP 2.15) but also to slightly increased negative $\zeta$-potential values in the alkaline range. Since all the tested fibres have nearly the same chemical
structure based on cellulose, the IEP is almost identical for all of them (IEP ~2). Samples 1F and 3F show almost no difference in the surface properties depending on the different treatment, indicating their enhanced and ‘open’ structure for the possible treatments. Modification of 3F fibre lead to surface roughening [7] resulting in the more negative ζ-potential.

![Zeta-potential pH dependence graph]

**Figure 2.** ζ-potential- pH dependence of reference and modified Spartium junceum L. fibres.

**Table 2.** Chemical composition of reference and modified Spartium junceum L. fibres.

| Sample | Cellulose [%] | Hemicellulose [%] | Lignin [%] |
|--------|---------------|-------------------|------------|
| RF     | 91.83 ± 0.13  | 2.99 ± 0.33       | 3.42 ± 0.29|
| 1F     | 90.07 ± 0.48  | 5.76 ± 0.68       | 3.30 ± 0.23|
| 2F     | 92.03 ± 0.11  | 4.11 ± 0.23       | 3.20 ± 0.32|
| 3F     | 92.39 ± 0.07  | 2.62 ± 0.18       | 3.98 ± 0.21|

The composition of the fibres obtained under different treatments is reported in Table 2. All the tested fibres show content of cellulose higher than 90 % and content of lignin between 3 and 4 % indicating very well conducted maceration and modification process [7] in comparison to the other results found in the literature [11, 12].

The influence of different treatment on the thermal properties of the Spartium junceum L. fibres was investigated by TGA as shown in Figure 3. Significant weight loss occurred when the temperature is between 290 and 430 °C due to the thermal decomposition of hemicellulose, cellulose and lignin. Decomposition temperature values for RF, 1F, 2F and 3F fibres were 380 °C, 380 °C, 377 °C and 375 °C, respectively.
°C, respectively showing earlier start of decomposition temperature for MMT treated fibres. The analysis of higher temperature (higher than 500 °C) decomposition of fibres showed improved thermal stability for the MMT treated fibres, regarding their residual weight after thermal treatment at 800 °C. The improvement could be attributed to the presence of clays in the treated fibres.

Figure 3. TGA curves of reference and modified Spartium junceum L. fibres.

Conclusion
Spartium junceum L. fibres were modified with NaOH, nanoclay and citric acid with the aim of their usage as reinforcement in the natural fibre reinforced composite materials to improve their mechanical and thermal properties.

Tensile testing results indicate improvement in strength of MMT treated fibres. Thermal stability was also enhanced due to different modification treatment, although better flame retardancy was expected for the MMT treated fibres especially MMT/CA treated fibres regarding their crosslinked structure.

SEM/EDS analysis of modified fibres proved adsorption of nanoclay particles on the surface of MMT modified fibres. Nanoclay skeleton is composed mostly of Silicon, second most is oxygen, third most aluminum and others are: carbon, magnesium, iron and sodium. Morphology of 3F fibres indicates melioration of nanoclay dispersion thus improvement of further surface properties.

ζ-potential measurements together with other characterization methods provide better insight in the surface properties of SJL fibres and enable further manipulation during modification process with the aim of better adhesion between the fibre and the matrix in the composite material.

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