DEVELOPMENT OF ADVANCED POLYLACTIDE NANOBIOCOMPOSITE REINFORCED WITH Spartium junceum L. FIBRES

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Mentori:
Prof. Dr. sc. Sandra Bischof i Prof. Dr. sc. Mizi Fan

Zagreb, 2019.

To my mom & dad

for all the Spartium flowers they have picked, stems they have cut and bundles they have made ☺

*Disertacija je pisana kao skup objavljenih znanstvenih radova popraćen kritičkim preglednim poglavljem (tzv. Skandinavski model) temeljem članka **14. Pravilnika o doktorskim studijima na Sveučilištu u Zagrebu (pročišćen tekst)** od 7. rujna 2016. koji obuhvaća Pravilnik o doktorskim studijima na Sveučilištu u Zagrebu kojega je Senat donio na 11. sjednici održanoj 20. travnja 2010. te Pravilnik o izmjenama i dopunama Pravilnika o doktorskim studijima Sveučilišta u Zagrebu kojega je Senat donio na 10. sjednici održanoj 19. svibnja 2016.*

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Tema doktorskog rada **„Razvoj naprednih nanobiokompozita izrađenih od polilaktidnog polimera ojačanog vlaknima brnistre“** prihvaćena je na 4. redovitoj sjednici u akademskoj godini 2013./2014. Fakultetskog vijeća Sveučilišta u Zagrebu Tekstilno-tehnološkog fakulteta, održanoj 17. ožujka 2014., te odobrena od Senata Sveučilišta u Zagrebu na 10. sjednici Senata održanoj 14. svibnja 2019., u akademskoj godini 2018./2019.

The dissertation was written as a set of published scientific papers accompanied by a critical review chapter (Scandinavian model) based on the article ***14 of the Doctoral studies regulations at University of Zagreb (consolidated text)*** *from 7th September 2016, which includes the Doctoral studies regulations at the University of Zagreb adopted by the Senate at its 11th session, held on 20th April 2010 and the Rulebook on amendments to Doctoral studies regulations at the University of Zagreb, adopted by the Senate at its 10th session, held on 19th May 2016.*

This dissertation was written in English based on the article ***15 of the Doctoral studies regulations at University of Zagreb (consolidated text)*** *from 7th September 2016, which includes the Doctoral studies regulations at University of Zagreb adopted by the Senate at its 11th session, held on 20th April 2010 and the Rulebook on amendments to Doctoral studies regulations at University of Zagreb, adopted by the Senate at its 10th session, held on 19th May 2016.*

The topic of the dissertation **"Development of advanced polylactide nanobiocomposites reinforced with *Spartium junceum* L. fibres"** was accepted at the 4th regular session of the Faculty Council of the University of Zagreb Faculty of Textile Technology, in the academic year 2013/2014, held on 17th March 2014, and approved by the Senate of the University of Zagreb at the 10th Senate session held on 14th May 2019, in the academic year 2018/2019.

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Institutions where research was made:	University of Zagreb Faculty of Textile Technology, Zagreb, Croatia Brunel University, London, UK Institute for Natural Fibres and Medicinal Plants, Poznan, Poland University of Zagreb Faculty of Agriculture, Zagreb, Croatia University of Zagreb Faculty of Forestry, Zagreb, Croatia Croatian Geological Survey, Zagreb, Croatia Institute of Physics, Zagreb, Croatia
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SUMMARY

The main goal of this thesis was to develop biodegradable composite material of sustainable origin for possible usage in automotive industry. Increased demand for usage of sustainable and biodegradable natural materials initiated wider production of biocomposites. For that reason, composite materials made of sustainable polylactide (PLA) polymer and *Spartium junceum* L. (SJL) bast fibres were designed and produced in the course of research for this thesis. Three fibre extraction (maceration) methods were investigated: water retting (WR), osmotic degumming (OD) and alkali retting under the influence of microwave energy (MW). It was proven that long lasting conventional maceration method can be succesfully replaced by ecologically favourable method using microwaves. Tensile strength of MW treated fibres show approximately 60 % higher strength compared to conventional WR and 30 % compared to novel OD method. Functionalization of fibres was carried out using montmorillonite (MMT) nanoclay particles added as a flame retardant nanofiller, and citric acid (CA) as an environmentally friendly crosslinker. Effectiveness of the conducted modifications was examined according to the relevant standardized methods used in current industrial and manufacturing processes (testing of morphological, mechanical, chemical and thermal properties of the final composite material). MMT/CA modified fibres show better thermal stability in comparison to the reference fibre (MWR) which is confirmed with the increase in crystallinity and proved by thermogravimetric analysis by shifting of fibre's onset decomposition temperature to higher value. Fibre/polymer interface was also positively influenced by MMT/CA fibre modification. Therefore, such material has showed higher decomposition temperature at certain weight loss, as well as higher strength and modulus values in comparison to samples without CA. The results indicate formation of crosslinking caused by interactions between the carboxylic acid and –OH groups of cellulose fibre or PLA. Biodegradability of developed composite materials was examined with serine endopeptidase. Concentration of 50 wt% enzyme reveals very positive result of composite degradation. After 5 days of enzymatic treatment, composite material reinforced with MMT/CA modified fibres lost 2.5 % of its initial weight. Additionally, the possibility of residue stem utilization in bioenergy production was investigated. Proximate and ultimate analysis of residues after MW maceration showed increase in content of positive biomass quality indicators. The obtained results confirmed SJL biomass as promising feedstock for solid biofuel production. The significance of the proposed research lies in the application of innovative, sustainable raw materials for the production of new advanced products of wide application.

KEYWORDS: *Spartium junceum* L., PLA, sustainability, green composites, nanoparticles, flame retardant, biodegradation, bioenergy, solid biofuel.

SAŽETAK

Glavni cilj ovog rada bio je razvoj biorazgradivog kompozitnog materijala održivog porijekla koji bi se mogao koristiti u automobilskoj industriji. Naime, upotrebi ovakvih materijala u automobilskoj industriji pogoduje Direktiva 2000/53/EC Europske unije koja traži da zemlje članice do 2015. godine nanovo iskoriste minimalno 95 % otpadnog vozila čime bi se osiguralo da na deponiju završi manje od 5 % otpadnog vozila. Povećana potražnja za korištenjem održivih i biorazgradivih prirodnih materijala, čime se ujedno smanjuje onečišćenje okoliša, potaknula je širu proizvodnju biokompozita. Iz tog razloga su se dizajnirali i proizveli kompozitni materijali izrađeni od održivog polilaktidnog (PLA) polimera i *Spartium junceum* L. (SJL) stabljičnih vlakana koja su se koristila kao ojačalo cijelog sustava. Prirodna vlakna koja se koriste kao ojačala u kompozitnim materijalima su: lan, juta, konoplja, sisal, ramija, kenaf, abaka, kokosova vlakna, vlakna ananasa, šećerne repice, vlakna iz rižine ljuske, itd. Izbor vlakana ovisi o svojstvima koje određeno vlakno posjeduje, ali i o njihovoj dostupnosti. Kompozitni materijal će biti jeftiniji ukoliko su sirovine koje se koriste u njegovoj proizvodnji lokalno dostupne. Oko 30 % ukupnih vlakana koja se koriste u Europskoj autoindustriji se proizvodi u zemljama članicama EU, a 70 % se uvozi iz Istočne Europe i Azije. U gospodarsko nerazvijenijim dijelovima Hrvatske (otoci i Dalmatinsko zaleđe) raste brnistra (*Spartium junceum* L.) – samonikla biljka od koje se dobivaju vlakna izuzetne čvrstoće. Brnistra većinom raste u Mediteranskim zemljama. Kroz povijest je imala široki spektar namjena (izrada mirisa i boja od cvjetova, košara od stabljika, tekstilnih materijala od vlakana). Vlakna su ipak njen najvažniji produkt pa se u današnje vrijeme ponovno javio interes za njihovom proizvodnjom. Istražene su tri metode ekstrakcije vlakana (maceracija): močenje u vodi, osmotsko degumiranje (OD) i močenje u alkalnom mediju pod utjecajem energije mikrovalova (MW). Dokazano je da se tradicionalni način maceracije stabljike SJL (brnistre) močenjem u vodi koji se koristio do sada, može uspješno zamijeniti ekološki povoljnom metodom korištenjem mikrovalova. S obzirom da prirodna vlakna ne pokazuju dobru kompatibilnost s nepolarnim polimernim matricama potrebno je modificirati vlakna ili matricu kako bi se postigla dobra svojstva prijanjanja između vlakna i matrice te kako bi takav kompozitni materijal imao poboljšana svojstva. U ovom radu vlakna brnistre su oplemenjena korištenjem tri metode modifikacije: dodatna obrada s lužinom niske koncentracije (1F), obrada s lužinom i nanoglinom (2F) te obrada s nanoglinom i limunskom kiselinom (3F). Montmorilonitna nanoglina (MMT) se koristila u ulozi usporivača gorenja, a limunska kiselina (CA) kao ekološki pogodno sredstvo za umrežavanje. Kompozitni materijal se izradio metodom kompresijskog prešanja polimera u obliku peleta te kratkih nasumično orijentiranih vlakana brnistre pri

temperaturi od 170 °C. Ispitala su se njegova strukturna, mehanička i termalna svojstva kako bi se utvrdila mogućnost zadovoljavanja minimalnih zahtjeva automobilske industrije. S obzirom na sve veću osviještenost o okolišu i problemima globalnog rasta otpada, te zbog potrebe za pronalaženjem obnovljivih rješenja ispitala se i mogućnost razgradnje ovakvog materijala primjenom enzima endopeptidaze koja pripada skupini proteaza zaslužnih za biorazgradnju PLA. Dodatno, kako je već poznato da proizvodnja prirodnih vlakana za sobom ostavlja popriličnu količinu otpada koji je tijekom procesa maceracije najčešće kemijski tretiran, potrebno je naći rješenje njegove oporabe. Kod ekstrakcije vlakana brnistre metodom močenja u lužini uz korištenje mikrovalne energije količina takvog otpada iznosila je oko 90 % te se stoga istražila i mogućnost upotrebe takvog otpada kao biomase u proizvodnji krutih biogoriva.

Prilikom utvrđivanja optimalne metode ekstrakcije vlakana brnistre napravljeno je močenje u vodi u trajanju od 480 sati pri rasponu temperature od 30,6 °C do 33,0 °C nakon čega je slijedila mehanička obrada uklanjanja drvenastih dijelova močene stabljike kako bi se dobila vlakna. Metoda osmotskog degumiranja rađena je pri 30 °C u trajanju od 672 sata nakon čega je ponovno slijedila mehanička obrada sa svrhom dobivanja vlakana. U trećoj metodi je brnistra močena u 5 % otopini natrijeve lužine i podvrgnuta mikrovalnoj energiji snage 900 W i frekvenciji od 2,45 GHz u trajanju od 10 minuta nakon čega su se vlakna jednostavno izdvojila pod mlazom vode. Kompozitni materijal se izradio postupkom kompresijskog prešanja PLA polimera i vlakana (masenog udjela 20 %) pri temperaturi 170 °C, opterećenju od 3,9 kN/m^2 te vremenskom trajanju od 5 minuta. Prilikom ispitivanja mogućnosti biorazgradnje PLA i kompozitnog materijala korišteno je približno 20 mg uzorka koji se tijekom 5 dana pri temperaturi 37 °C obrađivao u puferskoj otopini različitih koncentracija enzima uz omjer kupelji 1:50. U izradi ovog rada korišten je niz metoda ispitivanja vlakna i kompozitnog materijala. Kemijske komponente neobrađenih i obrađenih vlakana poput celuloze, hemiceluloze, lignina, pepela i ekstrahiranih tvari određene su uvriježenim biotehničkim metodama TAPPI T211 om-02, TAPPI T204 cm-97 i TAPPI T222 om-11. Primjenom vibracijske metode ispitivanja, uz korištenje "Vibroskop" i "Vibrodyn" uređaja (Lenzing Instruments GmbH, Gampern, AT) ispitale su se finoća i vlačna čvrstoća pojedinačnih vlakana brnistre prema normi HRN EN ISO 5079:2003 – Tekstilna vlakna – Određivanje prekidne sile i prekidnog istezanja pojedinačnih vlakana, te HRN EN ISO 1973:2008 - Tekstilna vlakna - Određivanje duljinske mase -- Gravimetrijska metoda i titrajna metoda. Predopterećenje, brzina ispitivanja, te duljina ispitivanog uzorka iznosile su redom 1500 mg, 3 mm/min, odnosno 5 mm. Morfologija vlakana i njihovih kompozita, kao i kemijska analiza određeni su primjenom

skenirajućeg elektronskog mikroskopa FE-SEM (Tescan GmbH, Brno, CZ) pri 20 kV i različitim povećanjima, uz detektor za energijski razlučujuću rendgensku spektrometrijau EDS (Bruker Nano GmbH, Berlin, DE). Prije mikroskopiranja uzorci su se pripremili naslojavanjem u uređaju za "naparivanje" (Quorum Technologies Ltd, Laughton, UK) s tankim slojem Au/Pd kako bi se povećala njihova električna vodljivost neophodna za ovakvo ispitivanje. Kako bi se ispitala efikasnost predobrada prirodnog vlakna iz brnistre, a kasnije i svojstva adhezije vlakno/polimer u kompozitnom materijalu, koristila se infracrvena spektroskopija s Fourierovom transformacijom (FTIR), uz ATR metodu. Svi spektri su snimljeni u području 4000 cm^{-1}-380 cm^{-1}, uz rezoluciju 4 cm^{-1}, te su prikazani kao srednja vrijednost četiri mjerenja. FTIR se dodatno koristio i kao alat za određivanje efekata biorazgradnje uz pomoć određivanja karbonilnog indeksa, pri istim uvjetima kao i za sva prethodna ispitivanja. Određivanje hidrofilnosti vlakna napravljeno je određivanjem zeta potencijala primjenom uređaja za elektrokinetičku analizu SurPASS (Anton Paar GmbH, Graz, AT). Termalne karakteristike vlakana i njihovih kompozita ispitane su korištenjem termogravimetrijske analize i kalorimetrije. TGA analiza (Perkin Elmer Ltd, Beaconsfield, UK) je odrađena pri uvjetima zagrijavanja uzorka od 30 °C do 800 °C s brzinom zagrijavanja 10 °C/min u struji plinovitog dušika brzine protoka 30 ml/min, dok je kalorimetrija sagorijevanja odrađena u skladu s normom ASTM D7309. Vlačna čvrstoća kompozita se ispitala na univerzalnom uređaju za ispitivanje Instron 5584 (Instron GmbH, Darmstadt, DE) pri brzini ispitivanja 3 mm/min i radnoj udaljenosti 20 mm. Biorazgradnja uzorka djelovanjem enzima istražena je određivanjem gubitka mase uzorka pri čemu se koristila analitička vaga uz preciznost očitanja 0.0001 g. Istraživanje mogućnosti upotrebe ostataka brnistre nakon maceracije obuhvatilo je sljedeće metode ispitivanja: određivanje sadržaja vode prema normi HRN EN 18134-2:2015, pepela prema normi HRN EN ISO 18122:2015, koksa prema normi EN 15148:2009, fiksiranog ugljika računskom metodom prema normi EN 15148:2009, te sadržaja hlapive tvari prema HRN EN 18123:2015. Ukupni sadržaj ugljika, vodika, dušika i sumpora proveden je metodom suhog spaljivanja na Vario, Macro CHNS analizatoru (Elementar Analysensysteme GmbH, Langenselbold, DE) prema protokolima za ugljik, vodik i dušik HRN EN 16948:2015 te sumpor HRN EN 15289:2011, dok je sadržaj kisika određen računski. Gornja ogrjevna vrijednost je utvrđena prema HRN EN 14918:2010 normi pomoću adijabatskog kalorimetra IKA C200 (MZ - Analysentechnik GmbH, Mainz, DE). Sadržaj makro elemenata je određen prema HRN EN 16967:2015 normi korištenjem atomskog apsorpcijskog spektroskopa Analyst 400 (Perkin Elmer Ltd, Beaconsfield, UK) s uzorcima prethodno pripremljenim mikrovalnom digestijom prema HRN EN 16968:2015 normi.

Istraživanje u sklopu ovog doktorskog rada započelo je određivanjem najpogodnije metode maceracije u smislu ekološke i ekonomske isplativosti. S obzirom na činjenice koje su učvrstile svoje temelje još u dalekoj prošlosti, vlakna brnistre su se smjestila u skupinu prirodnih stabljičnih vlakana, te su se u ispitivanju koristile metode maceracije karakteristične za dobivanje vlakana lana, a samim time su se i uspoređivala svojstva vlakana iz brnistre i lana kako bi se utvrdila moguća područja njihove primjene. Obrada vlakana u alkalnom mediju niske koncentracije primjenom mikrovalne energije pokazuje najbolje rezultate, i to ne samo u ekološko-ekonomskom smislu već i u kvalitativnom. Čvrstoća, na ovaj način dobivenih vlakana, se povećala za 60 % i 30 % u usporedbi s ostale dvije ispitane metode maceracije – močenje u vodi i osmotsko degumiranje. Vlakna proizvedena pomoću mikrovalne energije su finija od drugih ispitanih vlakana za 10 %, a pokazuju najveće prekidno istezanje od 6,03 %. Repriza ovakvog vlakna se kreće u rasponu od 7 do 8 %. FTIR spektri brnistrinih vlakana nastali različitim metodama maceracije potvrđuju efektivnost mikrovalno potpomognute maceracije što je vidljivo iz odsustva vrpci poput 2850 cm^{-1}, 1730 cm^{-1}, 1537 cm^{-1}, 1239 cm^{-1} koje redom predstavljaju voskove i ulja, pektin i lignin, te iz povećanog intenziteta pikova pri 1000 i 985 cm^{-1} koji ukazuju na bolji razvoj sekundarne stanične stijenke što između ostalog pridonosi i većoj čvrstoći takvih vlakana. Nakon što su se ispitala svojstva vlakana uvidjela se mogućnost njihove primjene u izradi kompozitnih materijala u kojima bi vlakno brnistre imalo ulogu ojačala polimerne matrice. S obzirom da su neki od najvažnijih faktora koji utječu na učinkovitost ovakvih kompozitnih materijala kemijski sastav, struktura, mehanička svojstva njegovih komponenata kao i njihova međusobna interakcija koja je otežana činjenicom da je prirodno vlakno hidrofilnije od polimerne matrice, potrebno je dodatno utjecati na navedena svojstva. Vlakna dobivena maceracijom u lužini su predstavljena kao referentna vlakna (MWR), a modifikacije su uključivale dodatnu obradu s lužinom (1F), obradu s montmorilonitnom nanoglinom i lužinom (2F), te obrada s nanoglinom i limunskom kiselinom (3F). 3F vlakna su pokazala porast u sadržaju celuloze, te smanjen sadržaj hemiceluloze s obzirom na druga modificirana vlakna, a u usporedbi s MWR te su vrijednosti iznosile 0,6 %, odnosno 12,4 %. SEM i EDS analize površine vlakana potvrdile su promjene uslijed modifikacija. SEM slike ukazuju na povećanje hrapavosti koja je posljedica nanosa MMT čestica na površinu vlakana, što je potvrđeno i EDS analizom. FTIR spektar vlakna MWR pokazuje veći intenzitet vrpci (pika) pri 2844 cm^{-1} i 2900 cm^{-1} u odnosu na druga vlakna što ukazuje na dodatno uklanjanje pektina, voskova i masti uslijed kemijskih modifikacija. Također se kod MWR vlakna, za razliku od ostalih, pojavljuje pik pri 1506 cm^{-1} karakterističan za lignin dok su ostali pikovi vezani za lignin neprimjetni ili pokazuju mali intenzitet. Prema

vrijednostima indeksa ukupne kristalnosti (TCI) koji je proporcionalan stupnju kristaliničnosti celuloze, te indeksa lateralne sređenosti (LOI) koji se odnosi na stupanj sređenosti bočnih lanaca celuloze, vlakno 3F pokazuje veću kristaličnost, kao i bolji poredak u odnosu na MWR, i to za 11,2 %, odnosno 19,6 %. Određivanjem zeta potencijala uočeno je da obrada s MMT i CA utječe na smanjenje hidrofilnosti, te su također 3F vlakna pokazala bolju termalnu stabilnost u odnosu na MWR što je vidljivo u pomaku početne temperature razgradnje s 355 °C na 357 °C. Vlakna 2F pokazuju čvrstoću veću za 6,8 % , a vlakna 3F povećanje za 4,6 % u odnosu na MWR. Nižu čvrstoću uzorka 1F najvjerojatnije je uzrokovalo dugotrajnije izlaganje natrijevoj lužini prilikom njegove modifikacije. Ispitivanjem finoće vlakana nakon modificiranja, uzorak 3F je pokazao nešto grublja vlakna te je 63,3 % vlakana iz ove skupine imalo finoću u rasponu 35-45 dtex. Modificirana vlakna su se koristila kao ojačala za PLA matricu te su izrađeni sljedeći kompozitni materijali: kompozit izrađen od MWR vlakana i PLA (CR), kompozit izrađen od 1F vlakana i PLA (C1), kompozit izrađen od 2F vlakana i PLA (C2) te kompozit izrađen od 3F vlakana i PLA (C3). Vrsta provedene modifikacije vlakana utjecala je na čvrstoću kompozitnog materijala. Kompozit ojačan vlaknima 2F pokazuje najnižu čvrstoću uzrokovanu neadekvatnom adhezijom vlakna i polimera. Iako vlakna 1F pokazuju smanjenje čvrstoće uslijed ponovljene obrade s lužinom, kompozit ojačan ovakvim vlaknima pokazuje porast čvrstoće za 115 % u odnosu na C2. Kompozitni materijal ojačan vlaknima 3F pokazuje najveći porast čvrstoće i to za 135 % u odnosu na C2 ukazujući na istovremeni porast žilavosti ovakvih materijala. Razlika u čvrstoći kompozita ojačanih vlaknima 2F i 3F uzrokovana je dodatkom limunske kiseline pri modificiranju vlakana 3F što je potvrđeno i SEM analizom poprečnog presjeka kompozitnog materijala. Uočilo se smanjeno izvlačenje vlakana te njihova bolja adhezija s PLA matricom nego što je to uočeno kod ostalih ispitanih kompozita. FTIR analiza također potvrđuje bolju adheziju kod uzorka C3 što je vidljivo iz jačeg intenziteta pika pri 1750 cm^{-1} značajnog za C=O istezanje te smanjenog intenziteta pika pri 1645 cm^{-1} karakterističnog za –OH vibacije istezanja čime se potvrđuje čvršća povezanost vlakna, polimera i punila. FTIR analiza kod uzorka C2 pokazuje mali intenzitet pikova u području 1030-460 cm^{-1} koje je karakteristično za metalne okside što nam potvrđuje nedovoljno jaku vezu između vlakana brnistre, PLA i nanogline. Prekidno istezanje svih ispitanih kompozita je veće nego što je kod čistog PLA. Uzorak C3 je pokazao najveće prekidno istezanje, čak za 43,7 % veće od čistog PLA što ukazuje na žilaviji materijal koji se može deformirati prije nego dođe do loma.

U sklopu ovog rada se napravilo i matematičko modeliranje sa svrhom predviđanja mehaničkih svojstava kompozitnih materijala, točnije kod predviđanja vlačne čvrstoće i modula elastičnosti. Koristila su se dva najpoznatija modela koja se inače primijenjuju u slučaju

kompozita ojačanih kratkim nasumično orijentiranim vlaknima. Hirschov model je pokazao relativno dobro poklapanje s eksperimentalnim rezultatima – kod određivanja vlačne čvrstoće predviđene vrijednosti su bile za 10 % manje od eksperimentalno određenih vrijednosti vlačne čvrstoće, dok je kod određivanja modula elastičnosti razlika bila veća, tj. predviđene vrijednosti su bile za 20 % veće od eksperimentalnih osim kod uzorka C3 čija je eksperimentalna vrijednost bila za 20 % veća od one predviđene matematičkim modelom. Prilikom ispitivanja termalnih svojstava kompozitnih materijala ojačanih referentnim i modificiranim vlaknima brnistre te korištenjem termogravimetrijske analize definirao se temperaturni raspon od 30 °C - 300 °C u kojem su ispitani materijali pokazali stabilnost. Uzorak C3 koji u svom sastavu ima i nanoglinu i limunsku kiselinu pokazao je puno bolje rezultate od uzorka C2 čiju lošu adheziju s polimerom potvrđuju i sve korištene metode ispitivanja. Određivanje energije aktivacije pokazalo je 41,7 % nižu energiju potrebnu za termalnu razgradnju. Određivanjem temperature staklišta uvidjelo se da dodatak vlakana snižava Tg, a ujedno se snižava i temperatura hladne kristalizacije, te uzorak C3 počinje kristalizirati na nižoj temperaturi od ostalih ispitanih materijala, točnije pri 100 °C. DSC grafički prikaz ponašanja kompozitnih uzoraka uslijed zagrijavanja pokazuje dvostruki pik taljenja koji ukazuje na prisustvo dva različita tipa kristala unutar uzorka, dok čisti PLA pokazuje samo jedan pik taljenja te najveću kristaličnost.

Dodavanje nanogline u sustav utjecalo je na sniženje vrijednosti otpuštene topline, a time i na manju zapaljivost ovakvih materijala. C2 uzorak je otpustio 35 % manje topline u usporedbi s čistim PLA, dok je C3 otpustio 18 % manje topline. Uslijed ispitivanja razgradnje čistog PLA i njegovih kompozitnih materijala djelovanjem enzima različitih koncentracija pri temperaturi od 37 °C uvidjelo se da je nakon 5 dana enzimatske razgradnje najveći gubitak mase materijala nastao korištenjem enzima masene koncentracije 50 %, te je npr. kod uzorka C3 došlo do gubitka mase od 2,5 % u odnosu na početnu težinu materijala prije procesa razgradnje. FTIR ispitivanje uzoraka prije i nakon razgradnje potvrdilo je test ispitivanja gubitka mase.

Naime, za glavne pokazatelje razgradnje uzete su vrpce pri 1750 cm^{-1}-1755 cm^{-1} i 1454 cm^{-1}-1455 cm^{-1} koje predstavljaju karbonilnu, odnosno metilnu skupinu. Pomak ovih vrpci prema višim frekvencijama (višim valnim duljinama) ukazuje na razgradnju uzorka. Također se izračunao karbonilni indeks (C_I) koji je pokazao najvišu vrijednost kod uzoraka koji su bili podvrgnuti 20 wt% i 50 wt% enzima. Prilikom utvrđivanja potencijala ostataka brnistre nakon ekstrakcije vlakana kod korištenja za neposredno izgaranje utvrđen je nizak sadržaj vode (6,5 % - 7,5 %) i pepela (ispod 5 %). Sadržaj fiksiranog ugljika i hlapivih tvari iznosio je 13,2 % i 75 %. Gornja ogrjevna vrijednost, kao najvažniji parametar, iznosila je 17,2-18,8 MJ/kg što ukazuje na kvalitetnu biomasu koja se može upotrijebiti za proizvodnju krutih goriva.

Maceracija vlakana uz obradu s natrijevom lužinom pod djelovanjem mikrovalova može se primijeniti u proizvodnji vlakana brnistre uz značajno smanjenje utroška energije i vremena proizvodnje. Površinska modifikacija vlakana korištenjem lužine i nanočestica uz umrežavanje s ekološki pogodnim sredstvom utjecala je na poboljšanje adhezije vlakna i polimera, te na smanjenje zapaljivosti vlakana brnistre, a ujedno su modificirana vlakna pokazala i najveći sadržaj celuloze. Kompozitni materijal ojačan najuspješnije modificiranim vlaknima pokazuje povećanje čvrstoće i modula elastičnosti za 135 %, odnosno 122 % u odnosu na C2. Prilikom ispitivanja biorazgradnje tijekom 5 dana i pri temperaturi od 37 °C, uzorak C3 je izgubio 2,5 % od svoje početne mase što ukazuje na veliku vjerojatnost razgradnje ovog uzorka unutar 6 mjeseci za minimalno 90 %. Ostaci brnistre nakon proizvodnje vlakana mogu se koristiti kao biomasa u proizvodnji krutih biogoriva. Revitaliziranje proizvodnje vlakana iz brnistre dugoročno može pridonijeti unaprjeđenju nedovoljno razvijenih dijelova Hrvatske kroz primjenu "domaće" obnovljive sirovine u stvaranju proizvoda visoke dodane vrijednosti koji imaju široki način primjene.

KLJUČNE RIJEČI: *Spartium junceum* L., PLA, održivost, zeleni kompoziti, nano čestice, usporivači gorenja, biorazgradnja, bioenergija, kruta biogoriva.

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LIST OF PUBLISHED PAPERS

This work is based on the following scientific papers:

I. Kovačević, Z., Bischof Vukušić, S., Zimniewska, M.: COMPARISON OF SPANISH BROOM (*Spartium junceum* L.) AND FLAX (*Linum usitatissimum*) FIBRE - Textile Research Journal 82 (2012) 17, p. 1786-1798

Abstract:

After a long break, Spanish broom aroused interest as a natural, sustainable and renewable fibre for textile and technical applications. This paper describes the characterization of Spanish broom fibres (*Spartium junceum* L.) in comparison to the flax fibres (*Linum usitatissimum*). Spanish broom fibres were obtained by two different methods of maceration and some of the most significant chemical and physical properties of tested fibres are reported. Scanning electron microscopy has proven to be a useful tool for the determination of morphological characteristics of elementary and technical fibres. Other physical-chemical properties of fibres were determined by infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), fineness and tensile strength methods.

II. Kovačević, Z., Bischof, S., Fan, M.: THE INFLUENCE OF *Spartium junceum* L. FIBRES MODIFIED WITH MONTMORRILONITE NANOCLAY ON THE THERMAL PROPERTIES OF PLA BIOCOMPOSITES - Composites Part B, Engineering 78 (2015) 1, p. 122-130

Abstract:

Biocomposites were prepared by reinforcing polylactic acid (PLA) with randomly oriented, short *Spartium junceum* L. fibres. Prior to the composite production, the fibres were treated with montmorillonite nanoclay (MMT) in order to increase biocomposites resistance to the fire. Characterizations of the biocomposites in the presence and absence of MMT and Citric acid (CA) were performed by Thermogravimetric Analysis (TGA) and Microscale Combustion Calorimetry (MCC). The results indicated that biocomposites reinforced with fibres modified with MMT enhanced some of its thermal properties. Degradation level of residual fibres (char) after the TGA treatment at 800˚C was observed by Scanning Electron Microscope (SEM). The work provided us with the idea of using MMT in the presence of CA as a crosslinker in biocomposites for possible applications.

III. Kovačević, Z., Bischof, S., Vujasinović, E., Fan, M.: THE INFLUENCE OF PRE-TREATMENT OF *Spartium junceum* L. FIBRES ON THE STRUCTURE AND MECHANICAL PROPERTIES OF PLA BIOCOMPOSITES - Arabian Journal of Chemistry 12 (2019), p. 449-463

Abstract:

The thesis discusses 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. As environmental requirements in processing technologies have increased 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 to 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. The research also investigated the influence of fibre modifications on the fibre/polymer interfacial bonding. The interface of *Spartium*/PLA 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.

IV. Kovačević, Z., Bischof, S., Antonović, A.: ENHANCEMENT OF *Spartium junceum* L. FIBRES PROPERTIES - IOP Conference Series-Materials Science and Engineering 254 (2017), article number: 022005

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 of improving 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 surface properties were explored using scanning electron microscope (SEM), electron dispersive spectroscopy (EDS) and elektrokinetic analyser. All the results show great improvement of nanoclay/citric acid modified SJL properties.

V. Kovačević, Z., Bischof, S., Vujasinović, E., Fan, M.: THE POTENTIAL OF NANOCLAY MODIFIED *Spartium junceum* L. FIBRES USED AS REINFORCEMENT IN PLA MATRIX COMPOSITES FOR AUTOMOTIVE APPLICATIONS - International Journal of Nanotechnology 15 (2018) 8/9/10, p. 695-700

Abstract:

Novel bionanocomposite material has been developed using nanoclay modified *Spartium junceum* L. fibres and PLA matrix. Its potential for the automotive industry was examined. *Spartium junceum* L. fibres were previously treated with montmorillonite nanoclay (MMT) and citric acid (CA) in order to enhance bionanocomposite thermal and mechanical properties to comply with the automotive industry requirements. After a macromechanics analysis, a comparison was made between experimental and theoretically modelling results. The evaluated tensile modulus and tensile strength of theoretical Hirsch model were in agreement with those of the tested composites. Tensile strength and modulus of newly developed advanced material were improved by 164 % and 86 % respectively, as compared to the pure PLA matrix.

VI. Kovačević, Z., Grubor, M., Jurišić, V., Matin, A., Krička, T., Bischof, S.: SPANISH BROOM (*SPARTIUM JUNCEUM* L.) – FEEDSTOCK FOR BIOPLASTIC AND BIOENERGY INDUSTRY – The Hollistic Approach to Environment 9 (2019) 3, p. 44-52

Abstract:

Spartium junceum L. (SJL) is a Mediterranean plant of various usage possibilities. Its fibres were known since ancient times but at some point in recent history – more accurately in 1950s their production was abandoned due to the negative economic effect. Another drawback was large time consumption, especially with old traditional method – *Spartium junceum* L. maceration in salt water. Nowadays, due to technology development and ecological awareness it has become much easier to produce Spartium fibres of enhanced quality. One of the fibre extraction methods is the one assisted with microwave oven. The disadvantage of such fibre

production lies in large residue content after obtaining fibres – the loss of approximately 90 % of initial *Spartium junceum* L. weight. The usage of Spartium fibres in the service of reinforcement for biopolymer matrix (PLA) was investigated due to the need for renewable solutions in the development of new materials. Obtained results target further research into the direction of application of Spartium fibres and PLA in the production of green composites. The aim was to prove that developed product can be categorized under the biodegradable group by investigating its degradation properties using serine endopeptidase enzyme. The results show positive degradation effect while using 50 wt% (on weight of material) enzyme concentration over a five-day treatment. Stem residues of *Spartium junceum* L. plant derived from salt water and microwave maceration were investigated for their potential as biomass for biofuel production. Examination of its energy properties consisted of determining the amount of non-combustable and combustable matter content and higher and lower heating values. The results show low moisture content (6.5 % - 7.5 %), ash content was below 5%, higher values of fixed carbon and volatile matter content of 13.2 % and 75 %, respectively. Higher heating value was 17.2-18.8 MJ/kg, indicating that good quality biomass can be used most effectively in solid biofuel production.

1 Table of Contents

ABBREVIATIONS AND SYMBOLS

Å	angstrom unite equal to 10^{-10} m
AC	ash content of SJL residues
ASTM	American Society for Testing and Materials
ATR	attenuated total reflectance
A_{xy}	absorbance
BIO-PA	bio based polyamide
BIO-PBS	bio based polybuthylene succinate
BIO-PE	bio based polyethylene
BIO-PET	bio based polyethylene terephtalate
BIO-PP	bio based polypropylene
BIO-PTT	bio based polytrimethylene terephtalate
C1	composites reinforced with SJL fibres additionally modified with NaOH
C2	composites reinforced with SJL fibres modified with NaOH and nanoclay
C3	composites reinforced with SJL fibres modified with NaOH, nanoclay and CA
CA	citric acid
CEC	cation exchange capacity
CI	crystallinity index
C_I	carbonyl index
CR	composites reinforced with SJL reference fibres
DiCoDe	digestion-compression-decompression
D-PLA	dextrorotatory PLA
DSC	differential scanning calorimetry
DTG	derivative thermogravimetry curve
E_a	activation energy
EBO	European Bioplastics Organization
E^C	tensile modulus of composites

EC	European Commission
EC_e	enzyme commission number
EDS	energy dispersive spectroscopy
E^F	tensile modulus of fibre
EG	ethylene glycol
E^M	tensile modulus of matrix
EU	European Union
fc	compatibility factor for tensile strength prediction
FC	fixed carbon
FDCA	2,5 furandicarboxylic acid
FE-SEM	field emission scanning electron microscope
FR	flame retardant
FTIR	Fourier transform infrared spectroscopy
HBI	hydrogen bond intensity
HHV	high heating value
HRR	heat release rate
IEP	isoelectric point
IR	infrared
ISO	International Organization for Standardization
IUPAC	International Union of a Pure and Applied Chemistry
KNPU	kilo novo protease unit
L	mean fibre length
LbL	layer by layer deposition
Lc	critical fibre length
LDPE	low density polyethylene
LHV	low heating value
LOI	lateral order index
L-PLA	levorotatory PLA

MC	moisture content
MCC	microscale combustion calorimetry
MMT	montmorillonite nanoclay
mo	oven-dry weight of sample
MO_6	octahedral in the crystal structures
Mr	moisture regain
MW	alkali retting under microwave energy
MWR	SJL reference fibres after MW retting
MW_R	SJL residue after MW fibre extraction
M1	weight of sample before oven drying during moisture regain and content determination
m1a	weight of oven-dry sample before ignition for ash content determination
m2a	weight of sample after ignition during ash content determination
m1ex	oven-dry weight of flask during extractive content determination
m2ex	oven-dry weight of extract in flask during extractive content determination
m1l	oven-dry weight of filter paper funnel during lignin content determination
m2l	oven-dry weight of filtered lignin and funnel during lignin content determination
m1c	oven-dry weight of filter paper funnel during cellulose content determination
m2c	oven-dry weight of paper funnel and extracted cellulose during cellulose content determination
NFC	natural fibre composites
NMR	nuclear magnetic resonance
OD	osmotic degumming
PBAT	polybuthylene adipate terephtalate
PEF	polyethylene furanoate
PHA	polyhydroxyalkanoates

PLA	polylactide
PLA 0 %E	material before enzymatic treatment
PLA 100 %E	material after enzymatic treatment with 100 wt.% enzyme
PLA 20 %E	material after enzymatic treatment with 20 wt.% enzyme
PLA 50 %E	material after enzymatic treatment with 50 wt.% enzyme
R	gas constant 8.314 J/Kmol
ROOR	peroxide functional group
SDG	sustainable development goals
SJL	*Spartium junceum* L. (plant and fibre)
SurPASS	electrokinetic analyzer for zeta potential and isoelectric point determination from Anton Paar GmbH, Graz, Austria
SW_R	SJL residue after fibre extraction under salty water
t	temperature in °C
T	temperature in Kelvin
TAPPI	technical association of the pulp and paper industry
Tcc	cold crystallization temperature
TCI	total crystalline index
T_D	decomposition temperature at certain weight loss
Tg	glass transition temperature
TGA	thermogravimetric analysis
THC	total heat of combustion
THR	total heat release
T_i	the initial weight loss temperature
Tm	melting temperature
TO	nanoclay structural unit where the reference plate is formed from a tetrahedral plate T and a octahedral plate O in a ratio 1:1

TOT	nanoclay structural unit where the reference plate is formed from a tetrahedral plate T and a octahedral plate O in a ratio 2:1
TOT:O	nanoclay structural unit where the reference plate is formed of three TOT plates and a isolated octahedral plate O in a ratio 2:1:1
TPS	thermoplastic starch
$T_{shoulder}$	onset degradation temperature
UNGA	United Nations General Assembly
V^F	fibre volume fraction
V^M	matrix volume fraction
VM	volatile matter
w_{ash}	ash content of SJL fibres
w_c	cellulose content
w_{ex}	extractive content
W_F	weight fraction of fibre
w_h	hemicellulose content
W_i	initial weight of sample
w_l	lignin content
W_M	weight fraction of matrix
WR	water retting
W_t	weight of sample at any temperature during determination of activation energy
W_f	final weight of sample during determination of activation energy
W_x	weight at certain time completely dry sample – after enzymatic treatment
X	degree of polymer crystallinity
XRD	X-ray diffraction
Y	rate of weight loss at any temperature during determination of activation energy
YM	Young modulus
βH	parameter for fibre matrix stress transfer

ε	relative complex permittivity
σ^C	composite tensile strength
σ^F	fibre tensile strength
σ^M	matrix tensile strength
η	compatibility factor for tensile modulus prediction
ηo	orientation factor
ηl	length factor
0_R	SJL air dried stem
1F	SJL fibres additionally modified with NaOH
2F	SJL fibres modified with NaOH and nanoclay
3F	SJL fibres modified with NaOH, nanoclay and citric acid
ΔCp	material heat capacity
$\Delta H_{100\%}$	enthalpy of 100 % crystalline polymer
ΔH_{cc}	cold crystallization enthalpy
ΔH_m	enthalpy of fusion
ΔW	material weight loss

LIST OF FIGURES AND TABLES:

1 INTRODUCTION

With continuous growth for more than 50 years, global plastic production reached 350 million tones in 2017 [1]. Since petroleum resources are still extensively used in producing these polymers, it leads to great concerns in terms of economic and environmental sustainability. Utilization of petroleum resources can be alleviated by bioplastic development using biological resources or more precisely annually renewable resources [2]. Although the durability of plastics was initially regarded as a great advantage, environmental problem caused by the disposal of plastic waste (huge volumes of landfill space around the world, disposal of plastic waste in the marine environment) occurred [3, 4]. It was led to the conclusion that production of bioplastic - whether it is biobased or biodegradable, would partially solve the problem about its disposal.

1.1 Biobased polymers

Bioplastics represent a wide spectrum of thermoplastics that are obtained from biological and fossil resources or combination of both. There is a great trend to derive new compounds from biological resources either by industrial biotechnology or by chemical methods. Figure 1 shows all commercially realized pathways from biomass via different building blocks and monomers to biobased polymers.

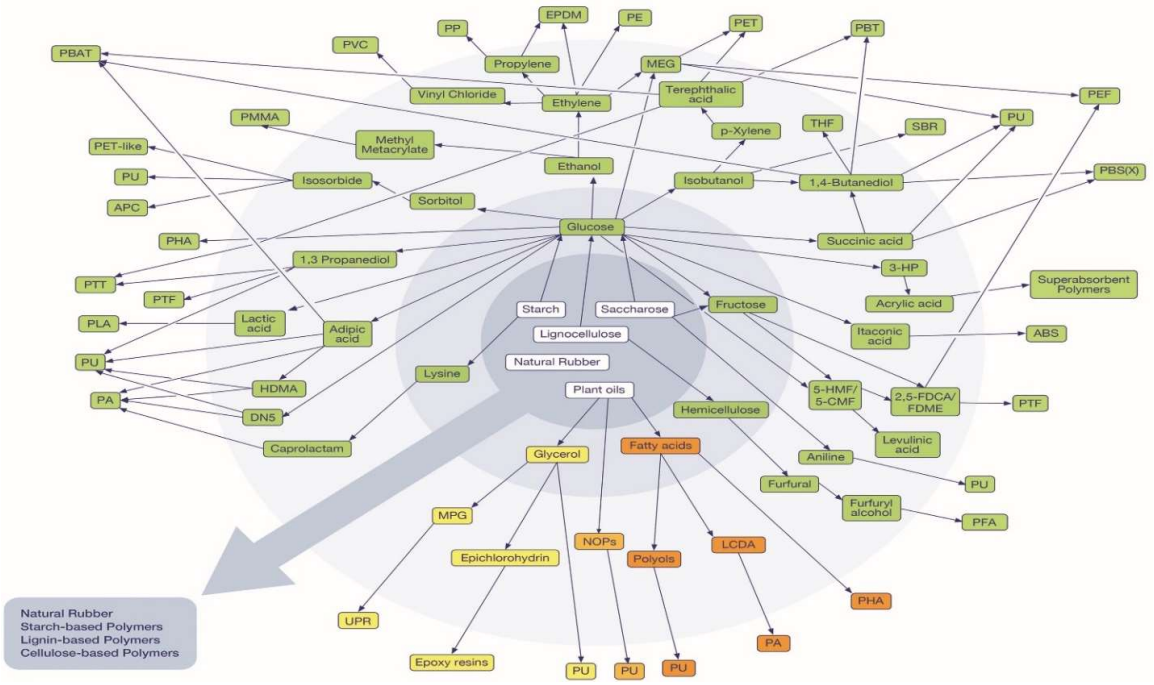

***Figure 1**: Pathways to biobased polymers [5]*

Description of currently used biobased polymers is shown in Table 1.

***Table 1**: Some of the currently used biobased polymers [5-13]*

Biobased polymer	Description
PLA	Renewable, biocompatible and biodegradable polymer. Obtained by ring opening polymerization of lactide or by direct polycondensation of lactic acid. Its thermal stability and impact resistance are inferior to those of conventional polymers used for thermoplastic applications. PLA composites are some approaches that are being used to improve the stiffness, permeability, crystallinity, and thermal stability of PLA. PLA targeted markets include packaging, textiles and biomedical applications.
PHA	Renewable, biocompatible and biodegradable polyesters synthesized by microorganisms from various substrates as carbon sources. They are very sensitive to temperature and shear. Additives, blends and natural fibre reinforced composites are the most obvious ways to overcome these problems.
STARCH	Bioplastic composed of both linear and branched polysaccharides (amylose and amylopectin).Thermoplastic starch (TPS) can be obtained from starch by disrupting its molecular interactions by using plasticizers and by using other complex operations as devolatilization, melt-melt mixing and morphology control. Extreme moisture sensitivity of starch leads to limited practical application. Therefore, blending of TPS with other polymers and additives is desirable.
CELLULOSE	Obtained from wood and cotton or in the pulp form extracted from agricultural byproducts such as bagasse, stalks and cropstraws. Cellulose based materials are used in two forms on an industrial scale - Regenerated cellulose used for fibre and film production and Cellulose esters used in coatings, biomedical uses and other usual plastic applications.
CHITIN & CHITOSAN	They are renewable, biocompatible, biodegradable and non-toxic polymers with excellent adsorption properties. Chitin is natural polysaccharide and is the supporting material in many invertebrate animals such as insects and crustaceans. The deacetylated chitin is known as chitosan. Chitosan has been explored for films and fibres and have generated great interest in biomedical applications.
PROTEINS	Proteineous biomaterial based on the origin proteins can be classified as plant and animal proteins. Water, glycerols, fatty acids and oils are commonly used plasticizers for proteins. Wet and dry processing are used to obtain biomaterials from proteins. Such biomaterials are used in food and pharmaceutical applications, as well as in tissue engineering applications.
BIO-PBS	Obtained by direct polymerization of biobased succinic acid and 1,4-butanediol.
BIO-PTT	Aromatic polyester obtained by polycondensation reaction between biobased 1,3-propanediol with terephthalic acid. It displays very good strength, stiffness, toughness and heat resistance and finds applications in carpets, textiles, films, packaging and automotive and high performance applications.
BIO-PE	Manufactured by polymerization of biobased ethylene. Polyethylene is one of the largely used polymers in the world.
BIO-PP	It can be obtained in similar way as that of PE. Involves production of biobutanol and its dehydration to butylenes and other intermediates step to convert it to propylene.
BIO-PET	Obtained by polyesterification of terephthalic acid with biobased ethylene glycol. PET is one of the widely used polyesters for one time packaging applications.
BIO-PA	PA is synthesized from diamines and dibasic acids. Polyamides are widely used as engineering thermoplastic in automotive, flexible electronics, packaging and electrical applications.
PEF	PEF is generally produced by polycondensation and polytransesterification of EG and FDCA, derivatives of dichloride-FDCA, dimethyl-FDCA, diethyl-FDCA, or bis-(hydroxyethyl)-FDCA. It displays remarkably high gas barrier properties which enables its practical application in the food and beverage industry.
PBAT	Polybutyrate is a biodegradable and compostable biopolymer with similar properties like low density polyethylene (LDPE). PBAT bioplastics is made from fossil resources. Its compounds (starch, PLA) have a biobased carbon content of up to > 30%. Typical application is for the flexible film for packaging, e.g. compostable shopping bags.

As can be seen from the Table 1 bioplastics are widely applied, but still it is necessary to modify their properties combining additives, blends or by manufacturing composite materials made of them.

1.2 PLA

Polylactide (PLA) is thermoplastic aliphatic polyester and currently used in various areas such as biomedical applications, textiles, composite and food packaging. It can be easily spun into fibres and made into films. PLA is one of the most studied polymers of this family because it can be produced via fermentation of renewable resources, like sugar, beets or corn starch [11]. Polylactide derived from renewable resources, e.g. corn, wood residues or other biomass, gain huge interest from scientific community because it could replace many fossil fuel derived polymers but also because of its potentially useful physical and mechanical characteristics. There have been numerous research studies on PLA manufacturing, from polymer processing and modification, to polymer characterization. Studies related to the formation of PLA co-polymers, blends with other polymers or composite materials based on PLA have also been carried out [14-23].

Manufacturers in Europe have been moving towards industrial-scale production of PLA. The biodegradability of PLA is also an advantage because of the growing global problems associated with plastic waste disposal. PLA represents a good candidate to produce biodegradable food packaging because of its good mechanical properties and its processability using most conventional techniques and equipment [5, 24].

The chemistry of PLA involves the processing and polymerization of lactic acid monomer. Lactic acid $HOCH_3CHCOOH$ is a simple chiral molecule which exists as two enantiomers, L- and D-lactic acid (Figure 2), differing in their effect on polarized light [24].

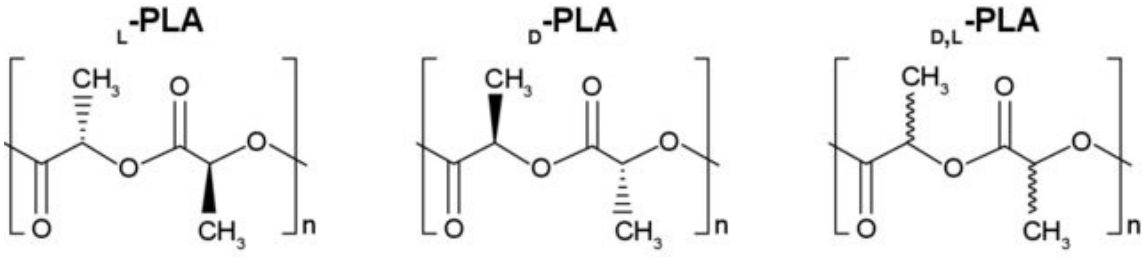

***Figure 2**: Structure of poly(lactic acid) isomers (L-PLA, D-PLA, D,L-PLA) [25]*

Polymerization of lactic acid to PLA can be achieved in three ways [26]:

1. Direct condensation—which involves solvents under high vacuum, forms low molecular weight PLA
2. Two steps polymerization i.e. solid state polymerization forms higher molecular weight PLA but is still limited by the equilibrium reaction of polycondensation due to hydrolysis of ester bonds
3. Ring-opening polymerization induces formation of low molecular weight oligomer which is catalytically depolymerized to form cyclic dimer intermediate (lactide) which is solvent free.

In direct condensation, solvent is used under high vacuum and temperatures for the removal of water produced in the condensation (Figure 3). This approach was used by Carothers and still used by Mitsui Chemicals. The resultant polymer is a low to intermediate molecular weight material, which can be used as is, or coupled with isocyantes, epoxides or peroxide to produce a range of molecular weights. In the solvent-free process, a cyclic intermediate dimer, commonly referred to as lactide, is produced and purified by distillation. Catalytic ring-opening polymerization of the lactide intermediate results in PLA with controlled molecular weight. By controlling residence time and temperatures in combination with catalyst type and concentration, it is possible to control the ratio and sequence of D- and L-lactic acid units in the final polymer [24].

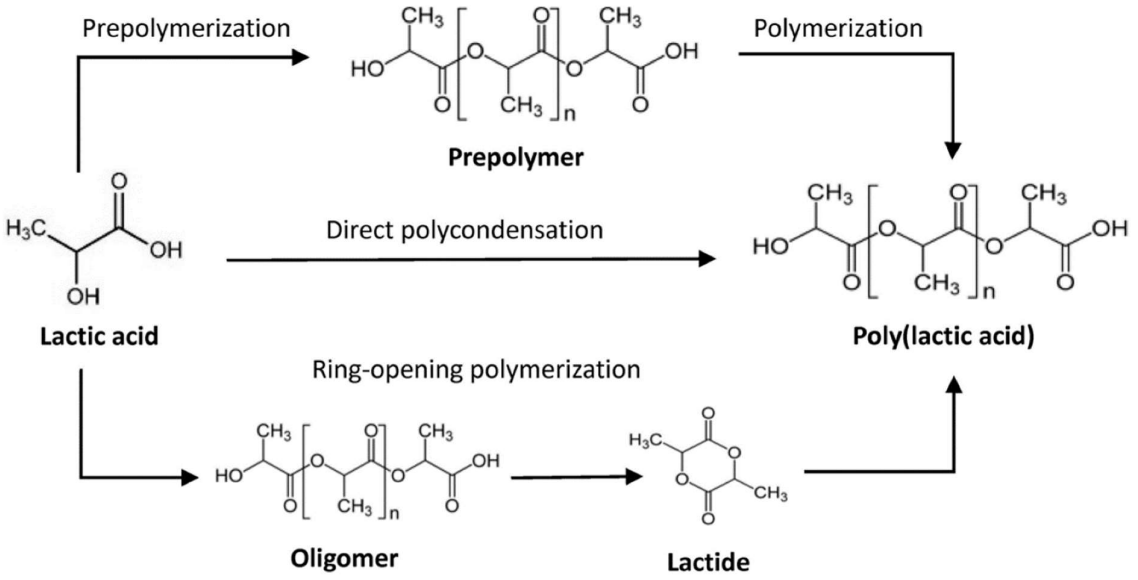

***Figure 3**: Synthesis of polylactic acid [26]*

PLA has several advantages: it is biocompatible and biodegradable, and can be readily broken down thermally by hydrolysis. It is available from renewable agricultural resources. This latter circumstance also helps to improve the farm economy. There is reduction in carbondioxide emissions in comparison with conventional petroleum based commodity plastics because it helps by fixation of significant quantities of carbondioxide. The most important ability of PLA is that one can tailor its physical properties by material modifications. The polymer is relatively hard, with the glass transition temperature in the range 50–70 °C and melting at 140–170 °C [27-31].

1.3 Biocomposite materials

Considering EU legislations like Directive 1999/31/EC, 2008/98/EC, 2000/53/EC, 2009/33/EC, and 2012/19/EU which are mainly about waste problem solving, research on composite materials have received increasing attention [32-35].
Composite materials represent one of the main topics in science and technology of materials, due to their excellent physical, mechanical, chemical and thermal properties reflecting the best properties of its individual constituents [36, 37].

Today's challenge broght to scientists and engineers is to develop the technology needed to make biobased materials revolution a reality. The production of chemicals and materials from biobased resources is expected to be ~25% in 2030. Expectations are that two-thirds of the global chemical industry can eventually be based on renewable resources [37]. Nowadays, the term ''bio'' is extremely important and great number of novel technologies want to incorporate it in their development strategies. One of such technologies is composite material technology which has found as niche in biocomposite production, especially in the fibre-reinforced composite market which is a multibillion-dollar business (Table 2).

***Table 2**: Production of biocomposites in the EU in 2012 and forecast 2020 (in tonnes) [38]*

Biocomposites	Production in 2012	Forecast production in 2020 (without incentives for biobased products)	Forecast production in 2020 (with strong incentives for biobased products)
World production of composites			
Construction, extrusion	190.000 t	400.000 t	450.000 t
Automotive, compression moulding & extrusion/thermoforming	60.000 t	80.000 t	300.000 t
Granulates, injection moulding	15.000 t	100.000 t	> 200.000 t
Natural fibre composites (NFC)			
Automotive, compression moulding	90.000 t	120.000 t	350.000 t
Granulates, injection moulding	2.000 t	10.000 t	> 20.000 t

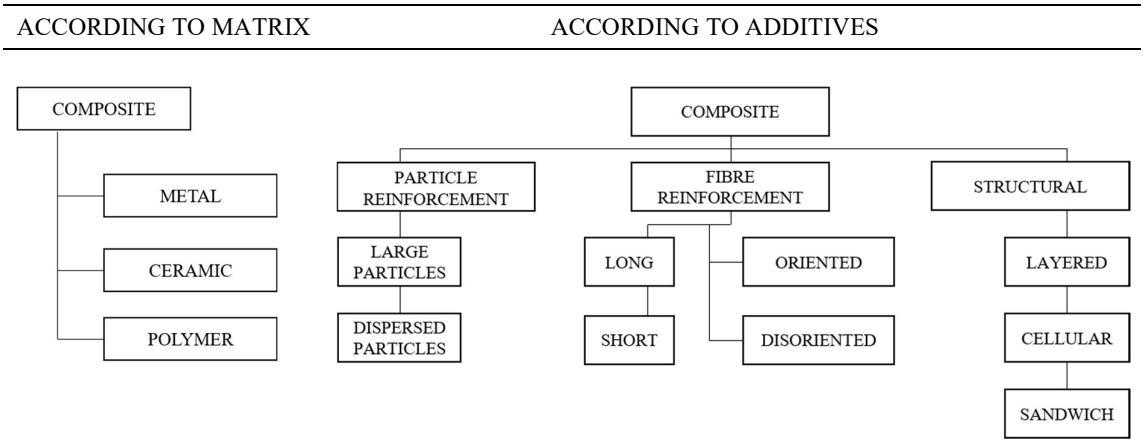

***Figure 4**: Classification of composites according to matrix and additives [39]*

In accordance with the above-mentioned, research and development of composites that are biodegradable and which show structural and functional stability due to storage and use has began [37]. Biocomposites are composites that have natural reinforcements e.g. vegetable fibres in their composition and can be: partial biodegradable with non-biodegradable polymers matrices such as thermoplastic polymers (e.g., polypropylene, polyethylene) and thermoset polymers (e.g., epoxy, polyester) or they can be fully biodegradable with biodegradable polymers matrices such as renewable biopolymer matrices (e.g., soy plastic, starch plastic, cellulosic plastic) and petrobased biodegradable polymer matrices (e.g., aliphatic co-polyester,

polyesteramides). The fully biodegradable ones are 100% biobased materials and show biodegradability and/or compostability properties [6, 37, 40, 41].

Biocomposites made from plant fibres and biopolymers are more environmentally friendly biocomposites and these are called "green" composites (Figure 5) [37, 42].

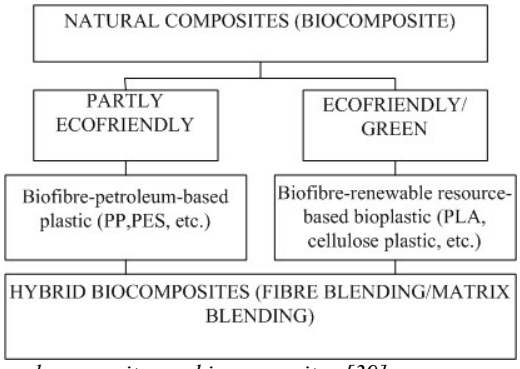

***Figure 5**: Classification of natural composites or biocomposites [39]*

1.3.1 Natural fibre reinforcement

Biopolymers reinforced with biofibres can produce new biocomposite that in many applications replace the composites reinforced with glass fibre and in most cases meet the requirements set by the above mentioned Directives of EU. Natural fibre reinforcements are capable to enhance composite overall properties like mechanical and flame retardant properties, fire resistance as well as water and gas barrier properties [40]. The most commonly used fibres for such applications are natural plant fibres presented in Figure 6 [43].

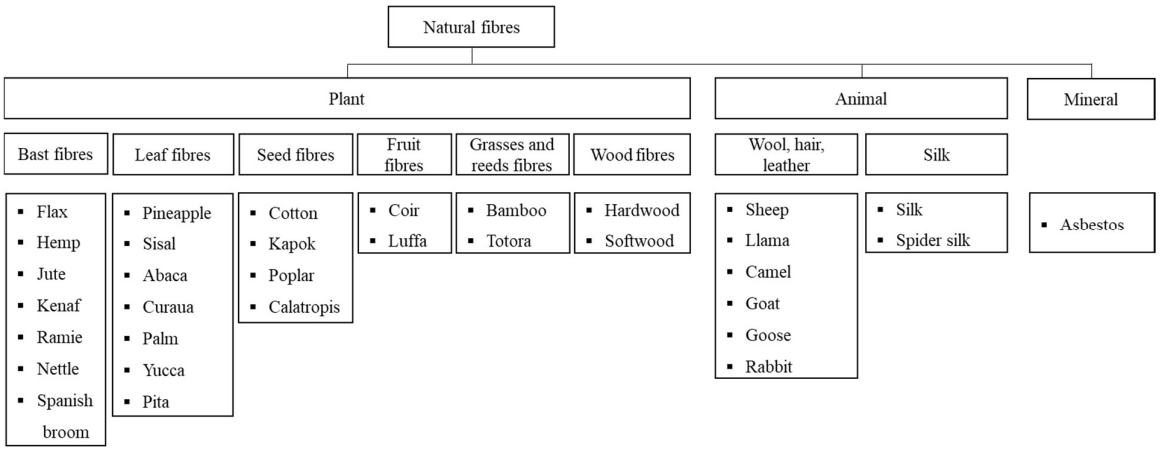

***Figure 6:** Classification of natural fibres [44]*

The interest in the use of plant fibres as reinforcement agents in polymeric composites is growing currently, owing to environmental regulations and ecological concerns of global society.

1.3.2 Bast fibres

Bast fibres are well known as the most promising sustainable and highly commercial available fibres among all natural fibres for the usage as reinforcements in the polymer composite materials. They are abundantly available, fully and easily recyclable, non-toxic, biodegradable, non-abrasive to the molding machinery, easily colored and have lower cost, lower density and lower energy consumption in producing step with respect to synthetic fibres such as glass and carbon fibres [40]. In addition to having lower processing energy requirements they are shatter resistant when compared to synthetic fibres. Additionally, bast fibres have good sound abatement capability, non-brittle fracture on impact, high specific tensile modulus and tensile strength, low thermal expansion coefficient and low mold shrinkage.

1.3.3 Chemical and structural composition

All bast fibres are constituted by cellulose, hemicellulose and lignin combined to some extent as major constituents. In fact, the so-called lignocellulosic fibres have cellulose as the main fraction of the fibres. Cellulose is a linear homopolysaccharide composed of repeating cellobiose units which are joined via β-1,4 glycosidic linkage. Each cellobiose unit is comprised of anhydro-D-glucose subunits, rotated through 180° with successive β-D-glucopyranose units along the cellulose molecular chains with hydroxyl groups in unidirectional parallel orientation when in the structure of elementary fibrils (Figure 7) [45]. There is a large amount of hydroxyl groups in cellulose (three in each repeating unit) and these hydroxyls form hydrogen bonds inside the macromolecule itself and also with hydroxyl groups from the moist air thus imparts hydrophilic properties to the natural fibres. Their moisture content can reach up to 3–13%. Cellulose forms slender rodlike crystalline microfibrils that are embedded in a network of hemicellulose and lignin, i. e., the microfibrils are bonded together through an amorphous and complex lignin/hemicellulose matrix that acts as a cementing material.

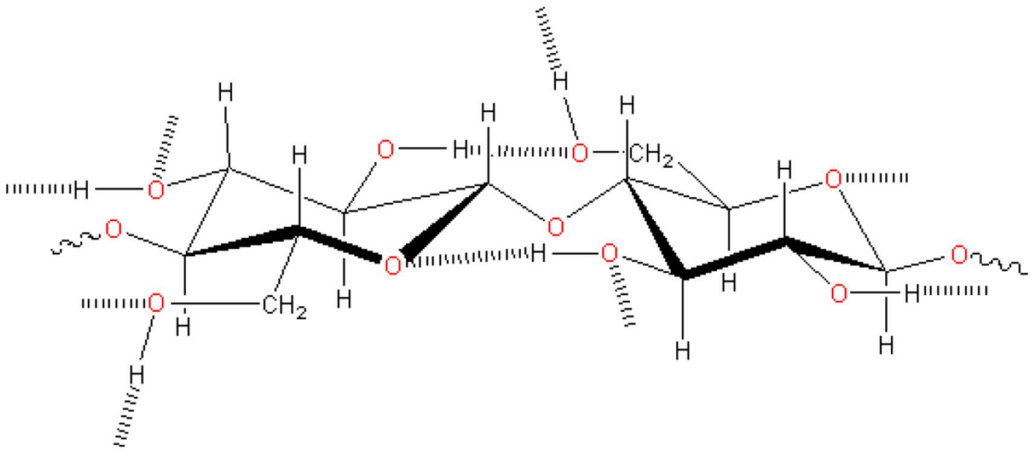

***Figure 7**: Cellulose structure [45]*

Hemicellulose is a polysaccharide with lower molecular weight than cellulose and very hydrophilic (i.e., containing many sites to which water can readily bond). Hemicelluloses are composed of β-1,4-linked D-xylopyranoyl units with side chains of various lengths containing L-arabinose, D-glucuronic acid, or its 4-O-methyl ether, D-galactose, and D-glucose. The main difference between cellulose and hemicellulose is that hemicellulose has much shorter chains and also has branches with short lateral chains consisting of different sugars while cellulose is a linear macromolecule. Both are easily hydrolyzed by acids, but only hemicellulose is soluble in alkali solutions as well as lignin. Lignin is a three-dimensional hydrocarbon polymer with an amorphous structure and a high molecular weight, known as compound which gives rigidity to the plant. Its complex composition presents hydroxyl, methoxyl and carbonyl functional groups [40, 46-48].

Bast fibres are obtained from the outer cell layers of the stems of various plants. The main plants used for the supply of bast fibres are flax, jute, hemp, ramie and kenaf. Regarding the fact that each climatic zone could have its own fibrous crop, the representative of the Mediterranean would surely be *Spartium junceum* L. whose fibres were well known through the history. Like other bast fibres, SJL fibres are comprised of a bundle of tube-like cell walls. Each cell wall contains primary, secondary S1, S2 and S3 layers. The fibres can be much longer than wood fibres with lengths of 20 mm for hemp for example. These types of fibres have a lower lignin content than wood fibres; consequently, the cellulose content is higher. The cellulose in bast fibres also tends to be more crystalline (80–90%) than that of wood fibres (50–70%) [49].

1.3.4 Fibre extraction

The great challenge in producing composites containing bast fibres with controlled features depends on the great variation in properties and characteristics of fibres. The quality of the natural fibres is largely determined by the efficiency of the treatment process and can dramatically influence the properties of the final composites. The overall fibre extraction process, applied to bast fibres, is called retting and consists of the separation of fibre bundles from the cuticularized epidermis and the woody core cells. The role of retting in obtaining high-quality standardized fibres is crucial and research and development are heading toward the industrialization of treatment processes [50]. Retting process is also known as maceration or degumming. The most commonly used extraction methods i.e., water retting and dew retting are based on the microbiological retting. Other methods involve mechanical, physical, chemical, and enzymatic extraction. Enzymatic retting is very promising but not yet practiced on an industrial scale [50-54].

Microbiological retting

Microbiological retting is a traditional and highly widespread retting method. Two different types of microbiological retting are mainly adopted: dew and water retting. Both of them are carried out by pectin enzymes secreted by indigenous microflora.

Dew retting

In dew retting, also called field retting, harvested plants are thinly spread out for 2–10 weeks in fields. During this period, microorganisms, mainly filamentous fungi or aerobic bacteria present in soil and on plants, attack noncellulosic cell types, removing pectins, and hemicelluloses from parenchyma cells and the middle lamellae, without attacking cellulose fibres. In this process, the colonizing fungi possess a high level of pectinase activity and the capacity to penetrate the cuticular surface of the stem: thus, fibre bundles come out separated into smaller bundles and individual fibres. Currently, dew retting is the most used process for the industrial production of bast fibres, mainly flax and jute, because of its low cost. Moreover, often low and inconsistent fibre quality is produced as compared to other methods, such as water retting. Risks of under retting and over retting are also reported: they may cause difficulties in separation or weaken the fibre.

Water retting

In water retting, straws are soaked in freshwater, today in large tanks, while in the past rivers or ponds, even the sea water were used. During this treatment, which last for 7–14 days on most bast fibre crop straws, water penetrates into the central stalk portion, by breaking the outermost layer, and thus provoking an increased absorption of moisture and the development of a pectinolytical bacterial community. The duration of the treatment depends on the water type, temperature and on bacterial inoculum. The first stage of the process consists of the aerobic microorganisms growing, which consume most of the dissolved oxygen, ultimately creating an environment favorable for the growth of anaerobs. Water retting generally produces fibres with a higher quality than those produced by dew retting, but the water retting process impacts the environment due to the consumption and contamination of large amounts of water and energy. With freshwater resources becoming increasingly scarce, an alternative or improvement in water retting will have to be foremost in dealing with water scarcity and pollution reduction. Artificial water retting, employing warm water and bacterial inoculum, has also been used to produce homogeneous and clean high-quality fibres in 3–5 days [50].

Enzymatic retting

A modification of water retting is the enzymatic treatment, also called bioscouring, where degrading enzymes are directly added to tank water or in a bioreactor. This method could be a promising replacement for traditional retting methods in terms of time-saving, ecology friendliness and convenient characteristics. The duration of enzymatic retting ranges from 8 to 24 h. Pectinases are the main enzymes employed for retting, in order to free the fibres from other tissues. Pectinolytic enzymes are a heterogeneous group of related enzymes that hydrolize the pectic substances, mostly present in plants. They are widely distributed in higher plants and microorganisms, since they help in cell wall extention and in softening some plant tissues during maturation and storage. They also help to maintain ecological balance by causing decomposition and recycling of waste plant materials. Enzyme retting via the pectinases is capable of producing consistent high strength renewable fibres with variable fineness values for use in novel resins. For each enzyme, specific conditions are identified for employment in retting, since the activity can change dramatically with pH, temperature and enzyme concentration. Moreover, chelators and surfactants are usually employed in formulations to improve activity. Foulk et al. reported that, with a specific knowledge of the composition of the enzyme mixture, enzyme retting could be used to tailor fibres/fibre bundles with particular

properties, such as strength and fineness, and for specific applications. Strength, which is a major concern in many applications, is preserved by retting with relatively pure pectinase, either pectate lyase, or polygalacturonase. However, a mixed enzyme preparation containing cellulase could be used for advantageous applications where the fibres will be shortened, such as for paper/pulp or injection molding. In fact, it has been found that enzyme formulations like Viscozyme, containing cellulase as a component, can weaken the bast fibres, since the nodes of the fibres are particularly sensitive to the attack by this enzyme [55]. The final application, therefore determines the retting formulation.

Mechanical extraction

The mechanical extraction of fibres consists of various steps:

- a first separation is carried out by breaking, that is the stalks are passed between fluted rollers to crush and break the woody core (shive) into short pieces (hurds);
- the remaining fibres and hurds are subjected to scutching (traditionally performed with boards and hammers), by which the fibre bundles are gripped between rubber belts or chains and carried past revolving drums with projecting bars that beat the fibre bundles, separating the hurds, and broken short fibres (tow) from the remaining long fibres.
- finally, in the hackling (realized in the past by pulling the fibres through a set of pins) thick fibres are divided by passing the long fibres through a series of combs of increasing fineness to clean and align the long fibres and separate the remaining tow and debris.

Interestingly, the modern mills maintain the integrity of the long fibres, by disentangling and aligning the fibres, without destroying length. Another process currently used to mechanically separate the fibres is called decortication and can be performed by hammermilling or rollermilling. In the first case, single or multiple concurrent drums rotating with hammers projecting transversely from the drum surface beat the straw until the separated hurd/shive and fibre particles can pass freely through some meshes placed inside the machine. In the second case, long cylindrical corrugated rollers are assembled in such orientations as to crack the straw stalks while producing minimal damage to the fibre. The two processes differ in the pro and con: if the hammermilling is characterized by higher throughput capability, the rollermilling gives much greater length control, producing even very long fibres and will better preserve the integrity of the fibres, without damages or entanglements. The choice of the preferable

mechanical extraction depends on the type of the fibre, its final application, type of ensuing treatments.

Physical extraction

Among the physical treatments of fibres, the processes using electromagnetic radiation, microwave radiation, high temperature, and/or pressure can be considered. Steam explosion is an autohydrolysis process involving the use of saturated steam at high pressure followed by a sudden decompression, which causes the substantial breakdown of the lignocellulosic structure, the hydrolysis of the hemicellulose fraction, the depolymerization of the lignin components, and the defibrillation. High decompression rates lead to improved fibre freeness but shorter fibre length. During the process, high temperature softens the material and mechanical action during the high-pressure discharge results in fibre separation: the partially depolymerized lignin becomes more or less soluble in various organic solvents, such as alcohols, acetone and alkaline solutions, whereas the cellulose, much more resistant to hydrolysis than pectinic and hemicellulosic polysaccharides, retains its structure. The steam explosion treatment is a fast and well-controlled process, with a low cost and very flexible treatment parameters. It is well adapted for the processing of various fibres, including those not previously retted. It can be carried out downstream, after alkali treatments, bleaching, and sometimes acid hydrolysis in order to completely degrade the hemicellulose and lignin fractions. Usually, steam explosion is combined with an alkaline pre-soaking to favor the cleavage of lignin-hemicelluloses bonds. The reaction results in the increased solubility of the lignin alkaline solvent and in an enhanced water solubilization of hemicellulose.

Recently, a Polish group [56, 57] has developed a new osmotic degumming of flax fibres. The degumming mechanism is based on the diffusive penetration of water inside the stem, where the long bundles of cellulosic fibres are clustered in slivers with polysaccharides, mostly pectins. The pectins, which are highly absorbent, increase their volume several times, which results in a considerable increase of hydrostatic pressure inside the stem and leads to pressing the epidermis. As the peripheral tension is stronger than the longitudinal one, cracks of the epidermis occur lengthwise, without breaking and shortening the fibres. Since the pectins become diluted and solved (together with other bast substances) in water, the technological liquid is subjected to proper filtration, which also serves to recover pectins for further use in the cosmetic industry. This osmotic method produces fibres characterized by good tenacity,

divisibility, and soft touch. It is equally as efficient as the warm water retting method and could be applied to other bast fibres by simply changing the degumming parameters (temperature, flow velocity, and process duration). To specifically modify the surface of fibres in order to improve their compatibility with polymeric matrix, the plasma treatment is an effective physical method, which can be performed at both atmospheric and high pressure under the flow of different types of gas (usually oxygen or argon). Depending on the material to be treated, plasma flow can cause ablation, cross-linking or surface activation. Ablation consists in the removal of organic residues as well as surface layers at a molecular level. Cross-linking occurs as a result of the interaction between two or more radicals leading to the formation of covalent links while surface activation increases the surface energy as a result of the generation of polar groups on the reinforcement surface. Exposure times, pressures, and discharge power are the variables that must be carefully considered to achieve the best results in terms of the surface modification. This kind of treatment is widely used for common natural fibres as flax, cane, coir, and bamboo because, unlike chemical treatments, it is a simple nonpolluting process that can be considered as dry and clean.

Microwave treatment is another phsical treatment for fibre extraction. Microwaves are electromagnetic waves that lie between radio and infrared frequency regions in the elctromagnetic spectrum. Such energy can be used to extract the fibres from the plant by combining thermal and non-thermal effect. Thermal effect was developed when dipole molecules inside the stem try to rotate forcefully in order to orient in the direction of applied electric field thus provide dielectric heating that can be explained by Maxwell's equation. The dielectric property of material influences the conversion of electromagnetic to thermal energy which in turn helps to seperate natural fibres that are bounded together among themselves and to the bark by powerful pectin bonds. The dielectric property of a material is described by the complex relative permittivity (ε*) in (1).

$$\varepsilon^* = \varepsilon' - j\,\varepsilon'' \quad (1)$$

where: $j=\sqrt{-1}$, ε' is real part – dielectric constant that reflect the ability of the material to store electric energy when in an electromagnetic field, ε'' is imaginary part – dielectric loss factor that influence the conversion of electromagnetic energy into thermal energy [58-60].

Non-thermal effect was explained by applying Plack's law – at frequency of a commercial microwave oven the energy carried by microwave photons is approx 1 J/mol while energy needed to break a C-H bond of pectin chain in material is about 413 KJ/mol, but volumetric heating occurs because of conversion of electromagnetic energy to mechanical and heat energy

due to dipole rotation and thus effects the bond breakage [58-62]. The physical treatments are surely not yet completely developed and only few papers describe their use. However, they are characterized by high quickness, easy scalability, and process flexibility, that make this kind of extraction noteworthy of further investigation.

Chemical extraction

With respect to water retting or dew retting, chemical processes are sometimes preferable since they produce fibres characterized by high-constant quality, regardless of weather conditions, usually in shorter times. Numerous chemical treatments can be performed on the fibres depending on their type, the ensuing retting process to be applied, their final applications. The most used chemical process is alkalization, a treatment aimed at removing hemicelluloses: it is usually carried out with sodium hydroxide, added as an aqueous solution at a variable concentration in the range 1–25% by weight. Alkali treatment seems to increase the elongation at break and the surface roughness while improving the ultimate tensile strength, the initial modulus, the electrical properties, and the thermal stability, at the same time it decreases the fibre tensile strength with increasing NaOH concentration, demonstrating that the alkalization could induce damages on fibre. To completely remove the lignins and most hemicelluloses, aqueous ammonia treatments are an interesting alternative to alkali retting. Certainly, chemical treatments are an effective alternative to microbial dew retting which suffers from climatic risks leading to substantial harvest losses. Indeed, chemical retting is not affected by weather variability and can retain the fibre quality. However, difficulties in waste-management and the moderate risk to degrade the fibres currently make such treatments less attractive than in the past.

1.3.5 Fibre modification

Despite all the positive properties of natural fibres already mentioned above, plant fibres have nonuniformity such as in dimensions as in mechanical properties when compared to synthetic fibers. Other drawbacks for the use of plant fibres in biocomposites are: the lower processing temperature (limited to approx. 200°C) due to fibre degradation and/or volatile emissions, the high moisture absorption due to fibre hydrophilic nature and incompatibility with most hydrophobic polymers. These problems are well known and countless research has been developed to reduce them with reasonable success [40].

Because of the low interfacial properties between plant fibre and polymer matrix which often reduce their potential as reinforcing agents due to fibre hydrophilic nature, chemical modifications are considered to optimize the interface of fibres. Chemicals may activate hydroxyl groups or introduce new moieties that can effectively interlock with the matrix. The most common modification treatments are: alkaline, acetylation, benzoylation, peroxide, isocyanate, silane, grafting, coupling agents and nanoparticle treatments [40, 63-69].

Alkaline treatment

Alkaline treatment or mercerization is one of the most used chemical treatments of natural fibre. As a result, the hydrophilic (OH) groups are reduced and the surface roughness of the fibre is increased. This treatment removes a certain amount of lignin, wax and oils covering the external surface of the fibre cell wall, depolymerizes cellulose and exposes the short length crystallites (2). As a result more cellulose molecules are exposed, which improves adhesion between the fibre and matrix. The efficiency of the alkali treatment depends on the type and concentration of the alkaline solution as well as time and temperature of the treatment. Alkali treatment changes the fine structure of native cellulose I to cellulose II.

$$\text{Cell–OH} + \text{NaOH} \rightarrow \text{Cell–O–Na} + + \text{H2O} + [\text{surface impurities}] \qquad (2)$$

Therefore, when the alkaline treated plant fibre is used to reinforce polar polymer composites, in comparison with the composite filled with untreated plant fibre, the enhanced surface roughness and increased reactive sites exposed on the surface would lead to a better mechanical interlocking and adhesion with the matrix, both of which are in charge of the interfacial strength of the composite [40, 63-66].

Nanoparticle treatment

Nanoparticle treatment of natural fibres is a new way to improve the properties of polymer composites. The most used techniques for nanoparticle impragnation are pad-dry-cure method or impregnation process, layer-by-layer (LbL) assembly, plasma treatment, wet chemical etching, hydrothermal treatment, vapor deposition, sol-gel method, application of a synthetic binder or by electroless deposition. Chemical or mechanical binding of nanoparticles to the surface of fibres is done with the aim of improving compatibility between fibres and polymer [70, 71].

Recently, the incorporation of nanoparticles in the finishing fabrics as flame retardant seems to be a valid and interesting approach. The main advantage is that a low amount of them can be employed, although not all the nanoparticles available in the market can be used in the flame retardancy field. It has been corroborated that several key points have to be into consideration in order to obtain better results. Among them shape and size of the nanoparticles are directly related to the treatment conditions, chemical nature, concentration, as well as their distribution as a function of the employed method of treatment [71]. Wetting behavior of a solid surface is controlled by geometric structure as well as chemical composition of the material. Generally, for the conversion of a hydrophilic surface into a superhydrophobic surface, two key parameters are essential: creation of hierarchical surface structures (micro/nano-scale roughness) and low surface energy layer. In such surfaces, microscopic air pockets are trapped beneath the water drops leading to a reduced contact area between the surface and liquid drops and help to create a composite interface which leads to enhanced properties [72] .
Fibres are usually modified with the following nanopartcles: TiO_2, ZnO, Ag, Au, SiO_2, Al_2O_3 [73, 74]. They can exist as nanorods, nanoflowers, nanodiscs, nanospheres, etc. Their geometrical characteristics may affect the properties of the treated fibre [75, 76].

Expansion of nanotechnology in recent years has influenced the scientific, technical and economical competitiveness of renewable resource-based polymers in developing a range of high performance engineering and consumer products. Recently, researchers are investigating the use of nanostructures (cellulose nanostructures, carbon nanotubes, nanoclays etc.) as reinforcements in order to produce a new class of nanobiocomposites. The inherent properties of such nanoparticles are enhancing the thermal, mechanical, dimensional stability and other properties of the composite materials (biodegradability, fire retardancy, etc.) with the added advantages of ecological improvement were effectively utilized to create a new class of materials. Additional advantages like ease to process, low density and recyclability were also provided [77-79].

1.4 Nanobiocomposite materials

New type of composite called nanobiocomposites has emerged and open an opportunity for the use of new, high performance, light weight green nanocomposite materials making them as replacement of conventional non-biodegradable petroleum-based plastic materials [80]. Scientists learn to select suitable matrices (e.g. aliphatic polyesters, polypeptides and proteins,

polysaccharides, and polynucleic acids) and reinforcing fillers of nanometer scale dimensions (e.g. nanotubes, nanofibres, clay nanoparticles, hydroxyapetite and metal nanoparticles, nanocellulose crystals, etc.) and alter their chemistry and structure to suit the target field. Such composite materials are known as nanobiocomposites which are obtained from 100 % biobased material, in which the fillers and the matrix both are obtained from renewable resources [81].
The properties inherent to the biopolymers, that is, biocompatibility and biodegradability, open new prospects for these hybrid materials with special incidence in environmentally friendly materials (green nanocomposites) including food packaging materials and materials used in biomedical fields including drug-delivery, biosensors, cancer diagnosis, and tissue engineering [82]. Research on nanobiocomposites can be regarded as a new interdisciplinary field closely related to significant topics such as automotive industry or construction engineering. The upcoming development of novel nanobiocomposites introducing multifunctionality represents a promising research topic in which the application of nanotechnology to biodegradable polymers may open new possibilities for improving not only the properties but also the same time the cost-price-efficiency. Owing to the nanometer-size particles, these nanocomposites can exhibit markedly improved mechanical, thermal, barrier and physico-chemical properties, when compared with the starting polymers and conventional (microscale) composites. [83, 84].
Most commonly used nanofillers are cellulose based nanofillers, carbon nanotubes and nanoclays.

1.4.1 Nanoclay

These layered silicates are most commonly used nanofillers in the synthesis of nanocomposites due to their availability, versatility and respectability towards the environment and health [85]. Most clays are 2:1 smectite layered silicates, meaning that there are 2 SiO_4 tetrahedral layers sandwiching 1 MO6 octahedral layer, where M is most commonly aluminium or magnesium [86] (Table 3). These layers are approx. 1 nm thick and their tangential dimensions range from 300 Å to a few microns. The variation in the dimensions depends on clay source. The layers also have a very high aspect ratio (length/thickness) and surface area. The Van der Waals gap between these layers (gallery spacing or interlayer) is due to the regular stacking of the layers. The negative charge, generated by isomorphic substitution of Al^{3+} with Mg^{2+} within the layers, is counterbalanced by the presence of hydrated alkaline cations, such as Na or Ca, in the interlayer. Since the forces between layers are weak, it is possible to intercalate small organic molecules between the layers [87, 88].

***Table 3**: Nanoclays identification [91]*

Family		Group	Formula
Phyllosilicates	TO (1:1)	Kaolinite	The reference plate is formed from a tetrahedral plate T and a octahedral plate O. The thickness of the layer is about 0.7 nm. Kaolinite ($Al_4Si_4O_{10}(OH)_8$)
	TOT (2:1)	Smectite (Talc, Mica, Montmorillonite), Sepiolite	Two tetrahedral plates T in both sides of an octahedral plate O form the reference plate. The thickness of the layer is about 1 nm. The group includes many minerals that are major constituents of clays. Montmorillonite ($Na_{0.33}Al_2Si_4O_{10}(OH)2xnH_2O$)
	TOT:O (2:1:1)	Chlorite, Bentonite, Saponite	The reference plate is formed of 3 plates TOT and another isolated O plate. The thickness of the layer is about 1.4 nm. Chlorite di-tri ($Al_2Mg_3Si_4O_{10}(OH)_8$)
Polysilicate	Natural	Kenyaite, Magadiite, Kanemite, Ilerite, Silhydrite, Zeolite	Magadiite ($Na2Si14O29x7H2O$)
	Synthetic	FluoroHectorite, Zeolite	Zeolite ($Na_2Al_2Si_3O_{10}x2H_2O$)
Double lamellar hydroxide	Synthetic	Hydrotalcite	Hydrotalcites ($Mg_6Al_2(OH)_{16})(CO_3^2)x4H_2O$)

Clays provide the characteristic property called cation exchange capacity (CEC). This capacity of cations is described as the quantity of positively charged ions held by the negatively charged surface of clay minerals. In general, most of the clay minerals tend to have a negative charge resulting from the substitution of silica cation by aluminium cation in the clay-sheet structure. This phenomenon (isomorpous substitution) produces the capacity in clay sheets to hold positive charges [89]. The end properties of nanocomposites are influenced by the dispersibility of silicates into their individual layers in the matrix. The dispersibility of layered silicates into individual layers is governed by its own ability for surface modification via ion exchange reactions that can replace interlayer inorganic ions with organic cations. The silicate layers can be miscible only with hydrophilic polymers but can be made miscible with hydrophobic polymers by introducing /exchanging interlayer cations galleries (Na^+, Ca^{2+}, etc.) of layered silicates with organic compounds. Therefore, the organic modification improves both compatibilization between hydrophilic clay and hydrophobic polymer matrix and also increases interlayer spacing [79]. Moreover, organic cations can be used as silicate attached initiators or

mediators for polymerization, thus providing a mechanism for improving interfacial adhesion between matrix and the silicate and a route for effective stress transfer [79, 90].

One of the most common applications of nanoclays is their usage as flame retardant (FR) in order to reduce the flammability of the end-use products.

The existence of cellulose fibres in biobased polymers lead to high flammability of such composite material. Generally, polymers decompose at 300–500 °C in gas and condensed phases, producing combustible gases, liquids, char and smoke with dripping that could be hazardous. The significant release of heat and smoke may also contribute to the fire spread and poor visibility, respectively, thereby causing serious risks to humans and huge loss of property. Furthermore, softening and creep behaviour of fibre reinforcement and polymer matrix under heating can result in buckling and failure of load-bearing composite structures, leading to the loss of structural integrity. Therefore, the vulnerability of composites to fire is a vital issue in determining their acceptance by the stringent standards in public transportation and infrastructural applications. Flame retardant treatments are crucial to overcome the burning deficiency and extend the applicability of natural fibre reinforced composites. Some studies have claimed that the incorporation of flame retardant (FR) or flame retarded fibres can effectively prohibit the burning process (heating, decomposition, ignition, combustion and flame propagation) of natural fibre composites [92].

Therefore, the major interest in the plastics and textiles industries is not the fact that their products burn but how to render them less likely to ignite and, if they are ignited, to burn much less efficiently. Flame retardants act to break this cycle, and thus extinguish the flame or reduce the burning rate by reducing the heat evolved to below that required to sustain combustion and by developing inherently flame retarded polymer systems or in a number of other possible ways.

Following approaches are mostly used in the FR treatments of textile fibres:

1. Usage of inherently flame retarded agents comprising the so-called high-performance fibres
2. Chemical modification of existing textile material
3. Incorporation of flame retardants into fibre structure
4. Making of specific surface treatment

Nanoclays are the most widely utilized nanoparticles, for their low cost, and overall improvement of mechanical, thermal, electrical and optical properties compared with their macro- and micro- counterparts. The research on nanoclay nanocomposites produced thousands

of papers and articles in the last decade and nanoclay have now a variety of commercial applications. The automotive industry was the first one to employ nanoclay in a vast scale, with the production of the step assist for the 2002 GMC Safari and the Chevrolet Astro van, the body side molding of the 2004 Chevrolet Impala, and the cargo bed for the 2005 Hummer H2 SUT. However, nanoclay-hybrids were first developed by Toyota Inc. research laboratories and their development has motivated a number of studies today.

One of the most common applications of biocomposites made from bast fibres such as flax, hemp or *Spartium junceum* L. is in the automotive industry, specifically in the development of car interiors (carpets, trim on the inside door, cover for the spare wheel, airbag, etc.) [93, 94]. The increasing use of biocomposites in the normal human life provides a better and healthier life of every individual, and the steady progress of our eco-system, especially if measures have been taken considering its biodegradation at the end of life of such product.

1.5 Biodegradation

According to the European Bioplastics Organization (EBO), bioplastics are defined as "Plastics based on renewable resources (biobased) or plastics which are biodegradable and/or compostable". Biodegradation is the chemical breakdown of materials by a physiological environment. The term is often used in relation to ecology, waste management, and environmental remediation. Biodegradable polymers may be defined as those that undergo microbially induced chain scission, leading to mineralization, photodegradation, oxidation, and hydrolysis, which can alter a polymer during the degradation process. Biodegradable polymers (those derived from plant sources) begin their lifecycle as renewable resources, usually in the form of starch or cellulose [95].

Further, for a polymer to be categorized as bioplastic, the following four criteria must be fulfilled:

1. Chemical characteristics: At least 50 % of its final composition should be necessarily organic matter.
2. Biodegradation: The developed polymer should degrade by a minimum of 90 % of its weight/volume within 6 months under stimulated composting conditions.
3. Ecotoxicity: Undegradable residuals of biopolymer after biodegradation for 6 months, should not be a potential threat to the growth of plants.

4. Disintegration: The biobased polymer should, at least within a timeframe of 12 weeks, fragment microscopic undetectable components (< 2 mm) under controlled composting conditions [96].

1.5.1 Biodegradation mechanism

For most biodegradable plastics, biodegradation is a single step process, requiring only biological activity, while some of them show two-step degradation profile where heat is responsible for initiating the degradation process.

Biodegradation can take place under oxygen conditions – aerobic biodegradation (3) or within conditions where oxygen isn't available – anaerobic biodegradation (4).

During aerobic biodegradation organic matter is oxidized leading to conversion of carbon (C) to carbon dioxide (CO_2). Oxygen (O_2) is consumed through which carbon of the sample is converted into carbon dioxide and water. Some carbon can remain as residual sample or in metabolites, representing the total residual carbon. Some carbon is used to produce new biomass.

$$C_{sample} + O_2 \rightarrow CO_2 + H_2O + C_{residual} + C_{biomass} \quad (3)$$

In anaerobic biodegradation, no oxygen is consumed. The sample is converted into methane (CH_4) and CO_2, residual sample or metabolites and biomass. Anaerobic conditions are created when oxygen is not present or when oxygen is consumed or depleted more rapidly than it is replaced (mostly by diffusion) [95, 96].

$$C_{sample} \rightarrow CH_4 + CO_2 + C_{residual} + C_{biomass} \quad (4)$$

The primary indicator of biodegradation is CO_2/CH_4 production or O_2 consumption, while other parameters like visual disappearance, weight loss, decrease in molecular weight, etc. present the secondary effects which demonstrate incomplete biodegradation.

Rate and degreee of biodegradation are determined by various factors which can differ from one environment to another. These factors are moisture content, oxygen availability, temperature, type of used microbiology (bacteria, fungi, enzymes), density of microbiology, salt concentration [97].

1.5.2 Enzymatic degradation

Enzymes are named and numbered (EC_e number) according to rules adopted by the Enzyme Commission of the International Union of a Pure and Applied Chemistry (IUPAC). The first number informs on the class of enzymes catalyzing a given chemical reaction [82]:

1. Oxidoreductases
2. Transferases
3. Hydrolases
4. Lyases
5. Isomerases
6. Ligases

Enzymes are catalytic proteins that decrease the level of activation energy of molecules favouring chemical reactions. Some of the most commonly used hydrolases cellulose, starch and cutin degradation are cellulases, amylases and cutinases. Lypases and esterases attack specifically carboxylic linkages while endo-peptidese is characteristic for amide linkages cleavage. Enzymes like endo-peptidase or endo-esterases conduct their catalytic action along the polymer chain but the highest activity is provided at the chain edges.

First, the digestible macromolecules join to form a chain, experiencing a direct enzymatic scission followed by the metabolism of split portions, which leads to the formation of a progressive enzymatic dissimilation of the macromolecule from the chain ends. Oxidative cleavage of the macromolecules may occur instead, leading to the formation of metabolization of the fragments, and thereby the chain fragments become short enough to be converted by microorganisms to H_2O and CO_2 [95].

A very common feature of hydrolases (e.g. depolymerases) is a reaction mechanism that uses three amino-acids residues: aspartate, histidine and serine. Aspartate interacts with the histidine ring to form a hydrogen bond. The ring of histidine is thus oriented to interact with serine. Histidine acts as a base, deprotonating the serine to generate a very nucleophilic alkoxide group (–O). Actually, it is this group that attacks the ester bond (the alkoxide group is a stronger nucleophile than an alcohol group) leading to the formation of an alcohol end group and an acyl-enzyme complex. Subsequently, water attacks the acylenzyme bond to produce a carboxyl end group and the free enzyme. This arrangement of serine, histidine and aspartate is termed as catalytic triad [97].

1.6 Bioenergy

The Sustainable Development Goals (SDGs), adopted by the United Nations General Assembly (UNGA) in 2015, provide a powerful framework for international cooperation to achieve a sustainable future of the planet. The 17 SDGs and their 169 targets, at the heart of "Agenda 2030", define a path to end extreme poverty, fight inequality and injustice, and protect the planets environment. Sustainable energy is central to the success of Agenda 2030. The global goal on energy - SDG 7 - encompasses three key targets: ensure affordable, reliable and universal access to modern energy services; increase substantially the share of renewable energy in the global energy mix; and double the global rate of improvement in energy efficiency. The different targets of the SDG 7 contribute to the achievement of other SDG goals and recently this has been the focus of an increasing number of studies.

A number of alternative combinations of resources, technologies and policies are found capable of attaining these objectives [98].

At present, less than 10% of the chemicals and raw materials offered by the chemical industry are generated from biomass. At the European level, it was proposed that 20% of the overall energy consumption by 2020 should be covered by renewable energy sources and that 10% of the road transport should run on biofuels [99].

Having in mind that in 2030, 90% of energy consumption will be based on fossil resources, the use of biomass for energy can be one way to reduce the everincreasing emissions of carbon dioxide, one of the main gases responsible for global warming and climate changing.

Biomass, a renewable energy source, is biological material derived from living, or recently living organisms, such as wood and herbaceous material. Biomass has a great potential to provide heat and power to industry and to provide feedstocks to make a wide range of chemicals and materials or bioproducts. The chemical composition of biomass depends strongly on its source. Generally, biomass consists of 38% - 50% cellulose, 23 % - 32 % hemicelluloses and 15 % - 25 % lignin.

Biomass for energy uses and chemical production presents the following important advantages:
• It is mainly an indigenous source and therefore reduces dependency on energy imports and increase security supply;
• Like other renewables, it has an enormous potential for job creation predominantly in agriculture, forestry and small- and medium-sized enterprises;
• Technologies for renewable energy of European industry carriers offer promising business opportunities, because world energy consumption is expected to grow;
• In many industries biomass is a by-product of industrial processes, so its utilization solves both a waste and energy problems.

Bioenergy is produced in liquid, solid, or gaseous forms when biomass is treated, using different physical, biochemical, thermochemical and other processes.
Biomass crops (switchgrass, miscanthus), agricultural crop residues, forestry and a wide range of organic materials can be combusted directly or densified into chips, cubes, briquettes, pucks and pellets, for direct combustion to produce heat and power. In general, biomass pellets are used for residential buildings, commercial buildings or greenhouse heating. Because of fluctuations in natural gas and oil prices, some growers in the greenhouse industry are looking for alternative energy sources such as biomass combustion systems as a way of reducing energy costs. Biomass combustion generates heat and produces carbon dioxide, which is being explored for use in the greenhouse to enhance plant growth [100].
The classification of solid biofuels is based on the origin and source. The solid fuels are divided by the following sub-categories [101]:

1. Woody biomass (trees, bushes, and shrubs)
2. Herbaceous biomass (plants that have non-woody stem and which die back at the end of the growing season)
3. Fruit biomass (from parts of a plant which hold the seeds)
4. Blends and mixtures.

2 HYPOTHESES CONFIRMATION

H1. *Spartium junceum* L. fibres and PLA are biodegradable

Hypotheses H1 is confirmed. Natural bast fibres have been chosen due to its biodegradability and it was neccesary to test biodegradability of PLA component so as the final composite. PLA sample showed weight loss of 1.4 %, while the most successful treated sample C3 revealed 2.5 % weight loss during 5 days enzymatic treatment.

H2. Modification of fibres with nanoparticles is achieved for the improved properties of the material

Hypotheses H2 is confirmed. SJL fibres were treated with nanoparticles in two treatments (2F and 3F). Treatment with MMT/CA (3F) improved the strength of C3 material up to 135 % in comparison to C2 composite material.

H3. Newly synthesized environmentally friendly nanoparticles are implemented in the product which is biodegradable

Hypotheses H3 is confirmed. Nanoparticles were synthesized by laser ablation method at Institute of Physics using Si plate. Si is chosen due to its lower environmental impact.

H4. Maceration of fibres using microwaves is developed for the shortening of production time and speed-up of time-to-market

Hypotheses H4 is confirmed. Conventional retting in water requires 20 days of treatment. Novel OD treatment requires 28 days. Developed MW treatment lasts only 10 min which presents significant energy savings.

H5. Utilization of the entire stem of the plant is realized, as well as obtaining biofuels as the end product

Hypotheses H5 is confirmed. Entire stem was used in a way that 10 % was used for fibres production while 90 % was used for biomass. Biomass quality was tested to distinguish possible usage for solid or liquid biofuels. Results showed moisture content below 10 %, ash content below 5%, volatile matter of 75 % and higher heating value of 18 MJ/kg which are parameters that indicate high quality biomass that can be used in solid biofuel production.

3 MATERIALS AND METHODS

3.1 Materials

SJL fibres were obtained from SJL plant, harvested from the area around town Šibenik, Croatia (Figure 8). PLA Ingeo 6201D was purchased from Nature Works LLC, USA with following physical properties: specific gravity is 1.24, relative viscosity is 3.1, melt index is 15-30 g/10 min and melt density is 1.08 g/cm^3. NaOH pellets (purity ≥ 97 %), nanoclay modified with 25-30 wt.% octadecylamine, citric acid, sodium hypophosphite hydrate (NaH_2PO_2) use for this study were obtained from Sigma-Aldrich Inc., UK. The Fluka buffer solutions were used for setting of pH 9.0 (borax/hydrochloric acid). Enzyme Savinase 16 L was obtained from Strem Chemicals, Inc. It is in liquid form with optimum conditions being 30 - 70 °C, pH 8 - 10 and activity of 16 Kilo Novo Protease Unit KNPU (S/g).

***Figure 8**: SJL harvesting locations*

3.2 Fibre extraction

3.2.1 Water retting

SJL samples were placed in a tank with water heated to a temperature of 30.6 °C to 33.0 °C for 20 days (480 h). After retting, the plants were passed through a mechanical process (breaking, scutching), after which fibres were obtained.

3.2.2 Osmotic degumming

SJL samples were placed in a 2000 mL glass gauge filled with warm water and placed in a tank full of water heated to a temperature of 30 °C. One end of the rubber hose was immersed in the glass gauge and the second end was immersed in a small plastic container. This method uses natural physical laws such as water diffusion, osmosis and osmotic pressure. Osmotic degumming of SJL plant lasted 28 days (672 h), after which fibres were obtained by mechanical processes (breaking and scutching).

3.2.3 Alkali retting under microwave energy

The microwave radiation treatment of the fibres was carried out in a microwave oven Tristar MW-2896. Fresh SJL stems were cut into 20 cm length and 50 g of samples were placed into 600 ml of 5 % NaOH solution and treated under microwave irradiation for 10 minutes, 2.45 GHz frequency and using power of 900 W. Since microwaves also influence the efficiency of fibre treatment, the maximum temperature of SJL stems inside the reactor container was determined according to applied microwave energy. Thus initial energy of SJL stem presents amount of microwave power divided by the stem/NaOH solution content – 160 W/g. The SJL stems were than washed in distilled water and fibres were extracted. Fibres were washed again in distilled water to obtain neutral pH and air dried. Such fibres were named *Spartium junceum* L. reference fibres.

3.3 Chemical modification of SJL fibres

3.3.1 Alkali treatment

Fibres were treated with 5 % (w/v) NaOH solution, maintaining a fibre/solution ratio of 1:20 (by weight) for 48 hours 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 hours and stored at ambient temperature in a desiccator.

3.3.2 Alkali and Nanoclay (MMT) treatment

5 % (w/v) NaOH solution was heated for 15 minutes at 60 °C. Nanoclay was added inside and the treatment continued for 30 minutes at the same temperature with the constantly mixing, prior 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 hour at 60 °C. Finally, fibres were washed with distilled water, dried in the oven at 60 °C for 24 hours and stored at ambient temperature in a desiccator.

3.3.3 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 hours with continuous stirring. After the solution was cooled to the room temperature fibres were immersed and left overnight. After this treatment the fibres were washed with distilled water, dried in the oven at 60 °C for 24 hours and stored at the ambient temperature in a desiccator.

3.4 Composite manufacturing

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 were put in an aluminum 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 aluminum sheets protected with release polymer film and preheated in a compression molding machine at 170 °C. It was left with no load for 5 minutes and then hot pressed under 3.9 kN/m^2 at 170 °C, for 5 more minutes. The sample was taken out from hot press and left to air cool down under 10 kg weight on the mold.

3.5 Chemical composition of SJL fibres

The major chemical constituents of SJL fibres were determined according TAPPI test methods. These include: ash, extractives, lignin, cellulose and hemicellulose.

Ash content was determined in accordance with the TAPPI T 211 om-02 [102].

A sample was ignited in a muffle furnace at 525 °C, burnt for 4 hours and ash content (w_{ash}) was calculated according (5):

$$w_{ash} = \left(\frac{m1a - m2a}{mo}\right) \cdot 100, \% \quad (5)$$

where:

$m1a$ – weight of moisture-free sample before ignition, g

$m2a$ – weight of sample after ignition, g

mo – oven-dry weight of sample, g

The determination of *extractive content* was carried out in accordance with the TAPPI T 204 cm-97 [103].

A weight chopped sample was extracted with a mixture of benzene-ethanol ($C_6H_6 – C_2H_5OH$) solvent in a ratio 1:1 for 8 hours in Soxhlet apparatus. The material, extracted in a round bottom flask, was dried in an oven at the temperature of 80 °C to constant weight. The extracted content (w_{ex}) was calculated according (6):

$$w_{ex} = \left(\frac{m2ex - m1ex}{mo}\right) \cdot 100, \% \quad (6)$$

where:

$m1ex$ – oven-dry weight of flask, g

$m2ex$ – oven-dry weight of extract in flask, g

mo – oven-dry weight of sample, g

The *lignin content* was carried out following the TAPPI T 222 om-11 [104].

The extracted sample, prior to being treated in distilled water for four hours, had been pretreated by 72 % sulphuric acid (H_2SO_4) for 2.5 hours. The solid residue lignin was obtained by filtration and drying in an oven at the temperature of 105 °C to constant weight. The Klason lignin content (w_l) was calculated according to (7):

$$w_l = \left(\frac{m2l - m1l}{mo}\right) \cdot 100, \% \quad (7)$$

where:

$m1l$ – oven-dry weight of filter paper, g

$m2l$ – oven-dry weight of filtered lignin + weight of filter paper, g

mo – oven-dry weight of sample, g

Küschner–Hoffer method was used for the determination of *cellulose content* (w_c). The extracted sample was treated in a mixture of nitric acid–ethanol ($HNO_3 – C_2H_5OH$ with a ratio of 1:4) in a hot water bath at the temperature of 100 °C. Solid/liquid ratio was 1:25. Treatment was preformed through four extraction cycles until the sludge became completely bleached. Its

filtration and drying in an oven at the temperature of 105 °C to constant weight provided Küschner–Hoffer cellulose, which was calculated according to (8):

$$w_c=\left(\frac{m1c-m2c}{mo}\right)\cdot 100,\ \% \tag{8}$$

where:

$m1c$ – oven-dry weight of filter paper funnel, g

$m2c$ – oven-dry weight of funnel + extracted cellulose, g

mo – oven-dry weight of sample, g

Hemicellulose content (w_h) was determined by deducting the sum of the ash, extractives, lignin and cellulose content values from the maximum theoretical content of all components (100%). It was calculated according to (9):

$$w_h=100 - (w_{ash}+ w_{ex}+ w_l+ w_c),\ \% \tag{9}$$

3.6 Moisture regain and moisture content

The moisture regain and content of the samples were determined according to ASTM D2495 - 07 using standard conditions for 24 h. Moisture sorption was calculated as a weight percentage of absolute dry material, while moisture content was expressed as a percentage of the samples total weight. Moisture regain (Mr) is defined with the following formula (10):

$$Mr = \frac{M1 - mo}{mo},\% \tag{10}$$

where:

M1– weight of a sample before drying, g

mo – oven-dry weight of sample, g

Moisture content (MC) is defined with the following formula (11):

$$\mathrm{MC} = \frac{M1 - mo}{M1},\% \tag{11}$$

where:

M1– weight of a sample before drying, g

mo – oven-dry weight of sample, g

3.7 Density measurement

Helium gas pycnometer AccuPyc 1330, Micromeritics, USA was used to determine the real density of SJL fibres. Density measurements were carried out using 14-15 g of fibres and 10

runs for each sample at room temperature in a 100 cm^3 cell. Samples were oven dried 24 h prior the test. Calculation was done according to BS EN ISO 1183-3:1999.

3.8 Tensile properties of SJL fibres

Breaking tenacity, elongation and fineness of individual fibres were examined using the Vibroskop 500 and Vibrodyn 500 devices, Lenzing Instruments, Austria. Preload, testing speed and gauge length values were 1500 mg, 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.

3.9 Tensile properties of SJL composites

Tensile tests for composite materials were carried out using Instron 5584 testing machine, Instron, USA 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.

Micromechanical characterisation of composites, predicting its tensile strength and tensile modulus were performed on the basis of mathematical models: Modified rule of mixtures, Hirsch model and Cox-Krenchel model.

The modified rule of mixtures (RoM) was used for composite tensile strength (σ^C) and tensile modulus (E^C) prediction, according the equation (12) and (13).

$$\sigma^C = fc \cdot \sigma^F \cdot V^F + \sigma^M \cdot V^M \quad (12)$$

$$E^C = \eta \cdot E^F \cdot V^F + E^M \cdot V^M \quad (13)$$

Where:

σ^F and σ^M - tensile strength of the fibre and matrix, MPa

V^F and V^M – volume fractions of the fibre and matrix, %

E^F and E^M - tensile modulus of fibre and matrix, GPa

The compatibility factor for tensile strength prediction (fc) is expressed according to Fu and Lauke [105] as (14):

$$fc = \eta o \cdot \eta l \quad (14)$$

The value of orientation factor (ηo) for fibres arranged in planar random fashion is 0.375, while the length & interface factor (ηl) can be obtained using interfacial shear strength (τ) and critical

fibre length (Lc) [106, 107]. The obtained value of the interfacial shear strength, considering the matrix strength, according to Von Misses criterion [106], was 10.21 MPa. Mean fibre length (L) was assumed to be 2.5 mm. The compatibility factor (ŋ) for composites tensile modulus prediction was expressed using Cox-Krenschel model for computing ŋl according to (15) and (16) while ŋo was taken from the literature [105] and is 0.2.

$$ŋl=1-\tanh(\beta L/2)/(\beta L/2) \tag{15}$$

$$\beta = \frac{1}{r}\sqrt{\frac{E^M}{E^F(1-\nu)\mathrm{Ln}\sqrt{\frac{\pi}{4V^F}}}} \tag{16}$$

where:

β - coefficient of stress concentration rate at the ends of the square packing fibres

L - fibre length inside the composite material, mm

r - fibre radius, μm

ν - Poisson's ratio of the matrix, which is assumed to be 0.36 for PLA matrix

The Hirsch model presented in the equations (17) and (18) is a combination of parallel and series models where βH is the parameter that determines the fibre-matrix stress transfer. Its value is 0.1.

$$\sigma^C = \beta H(\sigma^F \cdot V^F + \sigma^M \cdot V^M) + (1-\beta H)\frac{\sigma^M \cdot \sigma^r}{\sigma^M \cdot V^F + \sigma^F \cdot V^M} \tag{17}$$

$$E^C = \beta H(E^F \cdot V^F + E^M \cdot V^M) + (1-\beta H)\frac{E^M \cdot E^F}{E^M \cdot V^F + E^F \cdot V^M} \tag{18}$$

3.10 Scanning electron microscopy SEM

Morphological features of SJL fibres and composites were studied by using scanning electrone microscope FE-SEM//Mira, Tescan, Czech Republic. 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 measurements samples were coated with Au/Pd in order to increase their electrical conductivity.

3.11 Fourier transform infrared spectroscopy FTIR

Untreated and treated SJL fibres were evaluated for their surface chemistry by Spectrum 100 FTIR spectrometer, Perkin Elmer UK using attenuated total reflection method. All spectra were

registered from 4000 cm^{-1} to 380 cm^{-1}, with a resolution of 4 cm-1 and four scans. The background was collected at the beginning of the measurement. Three different measurements for each fibre were evaluated, and the average value was considered. Collected data were analyzed using Spectrum software version 10.4.3.339. The raw spectra were converted from transmittance to absorbance, exposed to auto baseline and auto smooth corrections. The resulting spectra were normalized by the absorbance of the peak at 1158 cm^{-1} or 1129 cm^{-1} which is assigned to C-O-C assymetrical stretching. The intensity values of second derivative peak heights for each sample (used for quantification based on the consistency of signal amplitude after concentration normalization) were used to calculate the three standard crystallinity indexes: total crystallinity index (TCI), lateral order index (LOI), and hydrogen bond intensity (HBI) [108].

The total crystalline index (TCI) is determined by the absorbance ratio from 1370-1372 cm^{-1} (A_{1372}) and 2900 cm^{-1} (A_{2900}) bands according (19) [109]:

$$TCI = A_{1372}/ A_{2900} \quad (19)$$

The lateral order index (LOI) is determined by the absorbance ratio from 1425 cm^{-1} (A_{1425}) and 895 cm^{-1} (A_{895}) bands as follows (20):

$$LOI = A_{1425}/ A_{895} \quad (20)$$

The hydrogen bond intensity (HBI) is determined by the absorbance ratio from 3300 cm^{-1} (A_{3335}) and 1315 cm^{-1} (A_{1315}) bands as follows (21):

$$HBI = A_{3300}/ A_{1315} \quad (21)$$

TCI corresponds to the C-H stretching and LOI corresponds to a CH_2 bending vibrations. Care was taken to ensure all samples remained dry during sample preparation and FTIR analysis.

The carbonyl index was calculated by the ratio of the peak intensity between the carbonyl and methyl group at 1750 -1756 cm^{-1} and 1454 cm^{-1} to 1455 cm^{-1}, respectively according to (22):

$$C_I = A_{1755}/ A_{1455} \quad (22)$$

3.12 Zeta potential

Surface properties of the fabrics were characterized by zeta potential calculated from streaming potential. Fabrics were placed in the adjustable gap cell of an SurPASS instrument from Anton Paar GmbH, Austria. Streaming potential of the fabrics was measured varying the pH of an electrolyte solution (1 mmol/l KCl).

3.13 Thermogravimetric analysis TGA

Thermal degradation of the investigated samples was analyzed by thermogravimetric analyzer Pyris 1 TGA, Perkin Elmer, UK. Samples were heated from 30 °C to 800 °C with the heating rate of 10 °C/min in a nitrogen flow of 30 mL/min.

Thermogravimetric data have been also used to determine kinetic parameters of SJL composites using different kinetic models. The energy of activation was calculated employing the integral method of Broido model. The equation used for the calculation of activation energy (E_a) is (23 and 24):

$$\ln\ln\left(\frac{1}{Y}\right)=\left(\frac{-E_a}{R}\right)\cdot\left(\frac{1}{T}\right)+\text{const.} \tag{23}$$

$$Y=\frac{(W_t-W_f)}{(W_i-W_f)} \tag{24}$$

Where:

W_t – weight of sample at any temperature t, g

W_f – final weight, g

W_i – initial weight, g

R – gas constant 8.314 $JK^{-1}mol^{-1}$

T – temperature, K

By plotting lnln (1/Y) against 1/T at constant heating rate, E_a/R was obtained from the slope of the line.

3.14 Differential scanning calorimetry DSC

Glass transition temperature (Tg), melting temperature (Tm) and cold crystallization temperature (Tcc) were investigated by differential scanning calorimetry (DSC) using Perkin Elmer DSC 8000 instrument. DSC measurements were carried out on samples weighting

approx. 5 mg. Samples were analyzed in three replicates using a heating/cooling rate of 10 °C/min under nitrogen atmosphere. For heating–cooling-heating measurements, the following thermal procedure was used: first heating from 25 °C to 250 °C, held for 5 minutes to remove the thermal history, cooling from 250 °C to 25 °C and held again for 5 min. The degree of polymer crystallinity (X) of the samples was calculated by the heat of fusion for the tested samples and a reference sample with 100 % crystallinity using the following relation (25):

$$X = \frac{\Delta Hm - \Delta Hcc}{\Delta H100\%} \cdot 100 \ , \% \qquad (25)$$

where:

ΔHm – enthalpy of fusion, J/g

ΔHcc – cold crystallization enthalpy, J/g

ΔH100% – enthalpy of fusion for 100 % crystalline PLA which is 93.1 J/g

3.15 Microscale combustion calorimetry MCC

The heat of combustion of the gases evolved during controlled heating of the SJL composite samples was investigated on MCC-2, Govmark, US. Measurement was performed in three replicates according to ASTM D7309.

3.16 Biodegradability

The weights of the oven dried samples were measured prior to immersing them in separate vials containing approx. 1 mL of buffer (pH 9) and Savinase enzyme. The buffer solution was prepared in a 25 mL flask by adding $2.66 \cdot 10^{-5}$ mol/mL $CaCl_2$, 5 mL 1 % Triton solution and 100, 250 and 500 mg respectively of Savinase enzyme, while pH 9 buffer was added to the 25 mL mark on the volumetric flask. Since measurements were made on the basis of 5 parallel tests, every single test vial was filled up with 1 mL of buffer/enzyme solution containing 4, 10 and 20 mg of Savinase and approx. 20 mg of investigated composite material. The enzymatic degradation was performed in the laboratory oven operated at 37 °C for 5 days.

The percentage weight loss after enzymatic degradation ($\Delta m_{24,72,120}$) was measured according to equation (26).

$$\Delta m_{24,72,120} = (W_i - W_{24,72,120})/W_i * 100 \quad (26)$$

where:

W_i - initial weight of completely dry sample measured after oven drying at 105±5 °C, g

$W_{24,72,120}$ - weight of completely dry sample after enzymatic degradation within a certain time period (24 h, 72 h and 120 h), g

3.17 Determination of biofuel quality

Residue samples after fibre extraction were grounded in a laboratory grinder IKA Analysentechnik GmbH, Germany. Three replicates of each sample were measured in order to provide reproducibility of the analysis. The biomass samples were analysed according to the following standard methods: moisture content HRN EN 18134-2:2015, ash content HRN EN ISO 18122:2015, coke content and volatile matter HRN EN 15148:2009 and fixed carbon by difference. Carbon (C), Hydrogen (H), Nitrogen (N) and Sulphur (S) were determined by the method of dry combustion in a Vario Macro CHNS analyser, Elementar Analysensysteme GmbH, Germany according to the standard methods HRN EN 15104:2011 and HRN EN 15289:2011. Oxygen content was calculated by difference according to the following formula (27):

$$O = 100 - C(\%\ db) - H(\%\ db) - N(\%\ db) - S(\%\ db) - ash\ (\%\ db),\ \%\ db \quad (27)$$

where:

db - stands for dry basis

Heating value was determined according to the HRN EN 14918:2010 standard method by using an oxygen bomb calorimeter IKA C200, Analysentechnik GmbH, Germany.

4 DISCUSSION

4.1 Fibre quality

The last 10 years have witnessed a huge interest for composite materials reinforced through natural fibres. The most commonly used fibres include cotton, pineapple, bamboo, followed by flax, hemp, sisal and jute. Considering the number of scientific research articles on natural fibres in composites (Figure 9), it can be seen that flax fibre is the most frequently used reinforcement fibre in the composite material production in the group of bast fibres (flax, hemp, jute, ramie, etc.).

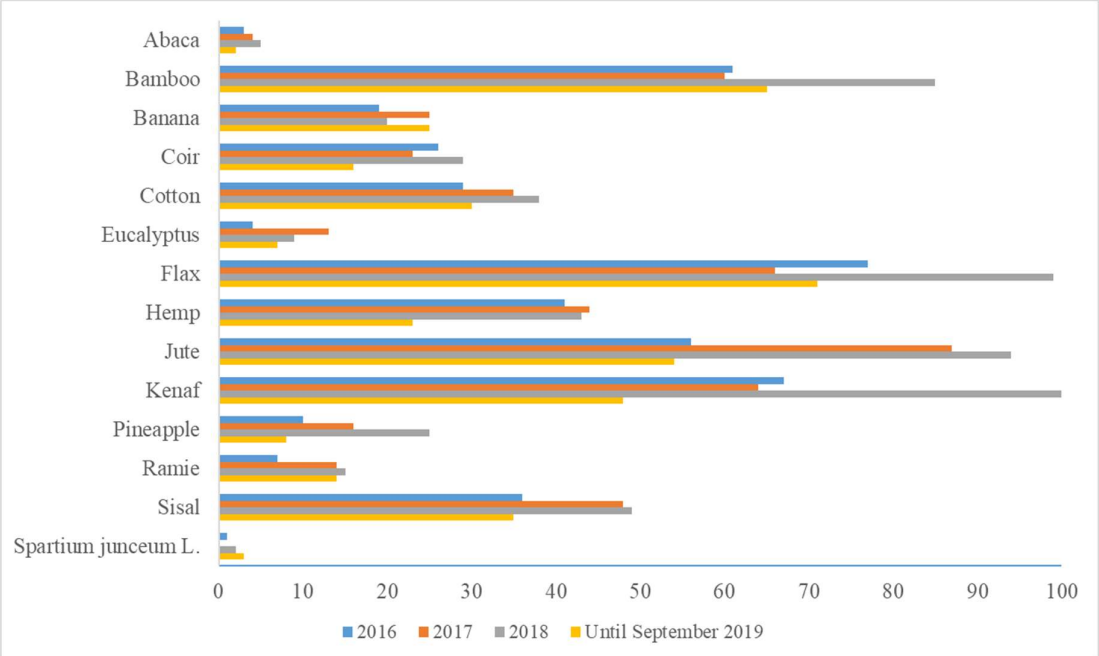

Figure 9: *Number of recent research articles about natural fibres in composites. Cross-reference search criteria within WoS (by search term: "fibre name" composite and by title or keyword: "fibre name" composite)*

Since SJL fibres also belong to the group of bast fibres, the purpose of this research was to answer the question whether the quality of SJL fibres is comparable to flax fibres. This part of research was conducted in cooperation with our partnering institution Institute of Natural Fibers and Medicinal Plants (INFMP), Poznan, Poland, during the research secondment in duration of 2 months.

Bast fibres are obtained from the outer layer (inner bark of the phloem) of bast surrounding the plant stem (Figure 6 in [109] and Figure 10 from this thesis). The fibres are usually very long (as long as stem) and relatively strong [51, 110].

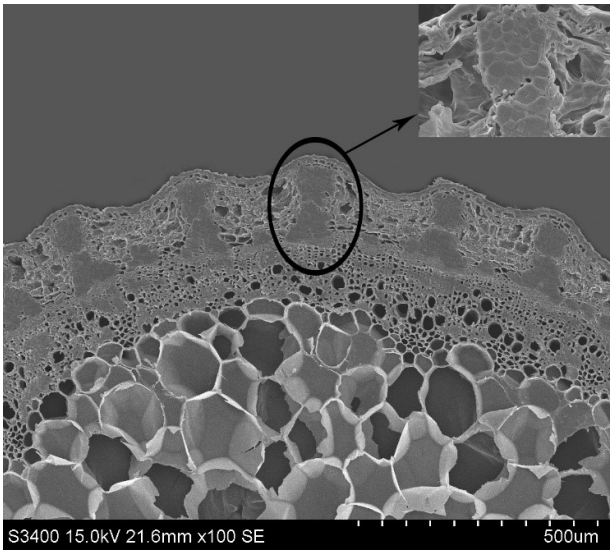

***Figure 10**: SEM micrograph of cross section of SJL stem with fibres visible in the outer layer of bast (Hitachi S-3400N, Institute of Natural Fibers and Medicinal Plants, Poland)*

Key parameters for the determination of fibre quality are strength, fineness, length and length uniformity, method of fibre extraction, moisture content, color grade, climate factors throughout the season and soil quality [111]. Some of them were investigated in this research:

4.1.1 Fibre extraction process

There are many extraction techniques such as manual (hand decortication), mechanical (mechanical decortication and crushing), chemical (acid, alkali, enzymes), biological (running water, sea and distilled water retting, dew retting), physical (steam explosion, ultrasound oscillation, osmotic degumming) or their combinations (DiCoDe process, microwave process) [56, 112-115]. The manual extraction method yields good quality fibres, but it is a difficult and time-cosuming process. The common aim was to determine extraction techniques that are economically feasible but withhold chemical and physical properties of natural material such as length, fineness, breaking tenacity, purity, optimal efficiency and homogeneity [112].

This thesis investigates three extraction methods: biological/mechanical (water retting with mechanical decortication - WR), physical/mechanical (osmotic degumming with mechanical decortication - OD) and physical/chemical (alkali retting under microwave energy - MW) method.

Fibre fineness is one of the intrinsic fibre properties. Fibre fineness is directly connected with fibre width and since the cross sectional shape of fibres varies, "dtex" unit has been accepted as a SI unit of fibre fineness [116, 117]. In Table 4 it can be seen that MW extracted SJL fibres

show increase in fineness comparing to other two types of fibre treatment (WR and OD) which leads to less stiffness.

***Table 4**: Prime quality parameters of SJL fibres extracted by various treatments*

	Breaking tenacity (cN/tex)	Fineness (dtex)	Elongation (%)
WR	40.66 ± 1.85	41.17 ± 1.74	3.48 ± 0.14
OD	46.21 ± 1.94	40.97 ± 1.46	5.01 ± 0.19
MW	64.44 ± 1.80	36.75 ± 1.81	6.03 ± 0.18

where WR is water retting extraction method; OD is osmotic degumming method and MW is alkali retting under microwave energy. Results are presented as mean value within 95 % confidence interval.

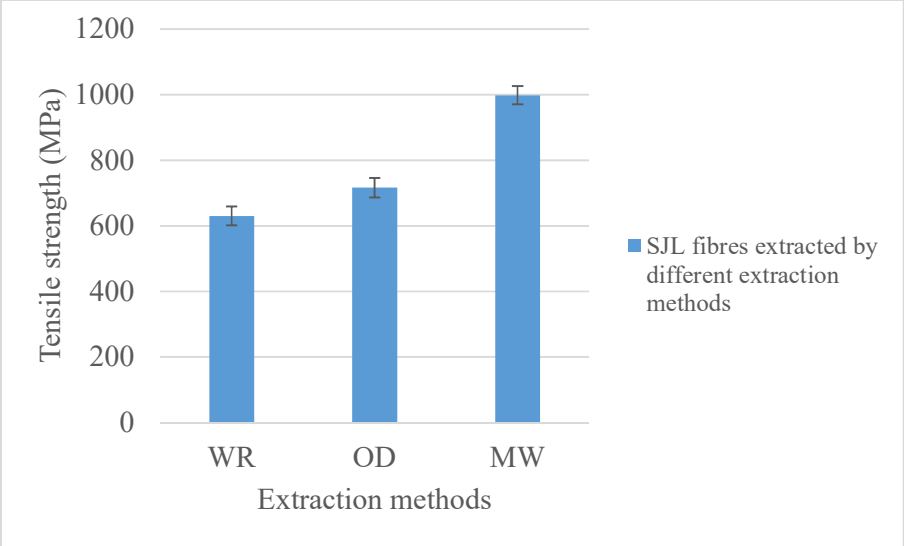

***Figure 11**: Tensile strength (MPa) for Spartium junceum L. fibres extracted by different methods (where WR is water retting extraction method; OD is osmotic degumming method and MW is alkali retting under microwave energy) calculated using fibre cross section area which is approximated to circle shape [118]*

Since the bundle of fine fibres has more accessible surface area than the same volume of the coarser fibres, its targeted chemical modification leads to more promising results [120, 121]. Fibre fineness depends on the structural characteristics of the secondary cell wall which mainly consist of cellulose, but there is also a minor amount of xylan and lignin [111]. Lignin content from the secondary cell wall, altough in low quantity, is able to affect fibre fineness in a way that coarser fibres show higher lignin content [122, 123, 124]. Fibre fineness can also reflect the degree of fibre separation during the extraction method.

Fibre biological fineness is influenced by genetics, but also affected by environment and fibre processing techniques [121, 123]. The highest elongation at break (6.03 %) and breaking

tenacity (64.44 cN/tex) values were determined for MW extracted SJL fibres, implying the increased toughness of the SJL fibres obtained by MW treatment (Figure 11).

4.1.2 Moisture regain

Natural textile fibres are hygroscopic and they absorb or release moisture, depending on the humidity of the surrounding air and the moisture loss. Gain occurs at every stage from the initial processing of fibres until the end product [125]. Change in moisture content has a direct impact on the fibres properties i.e. handle, comfort, weight, strength, abrasion resistance, colour stability, etc. Moisture content of various textile fibres is presented in Table 5.

***Table 5**: Moisture regain of various textile fibres [125]*

Material	Moisture regain at 65 % RH and 20 °C (%)
Cotton	7-8
Mercerised cotton	Up to 12
Hemp	8
Flax	7
Jute	12
Viscose	12-14
Silk	10
Wool	14-18
Polyamide	4.1
Polyester	0.4
Acrylic	1-2
Modacrylic	0.5-1
Polylactic acid	0.4-0.6
Para-aramid (Kevlar, Twaron)	Low modulus 7
	High modulus 1.2
Meta-aramid (Nomex)	5
Polyethylene	0
Polypropylene	0
Glass	0

Low moisture regain or low hygroscopic values of fibres affect the processing of fibres (fibres become more brittle and subjected to damage during processing, increase of static electricity, poor results of dyeing and finishing). Man-made fibres have low moisture regain which causes end users to feel uncomfortable wearing such products, but a majority of people agree that cotton is highly comfortable with its 7-8 % of moisture regain [126, 127]. The moisture regain of SJL fibres obtained from various treatments was investigated under 65 % of relative humidity at 22°C. It ranges between 7.14 and 7.76 % as presented in Figure 12. Fibres processed under MW treatment have higher moisture regain, which is due to the more succesful pectin, lignin and wax removal. The presence of lignin decreases moisture absorption, since lignin is hydrophobic and its layers in the inner middle lamella hinder the penetration of moisture into the cellulosic cell wall. Thus, the moisture sorption appearance in bast fibres is more complex than in the case of cotton fibres [128]. SJL fibres are composed mainly from cellulose and hemicellulose. Hemicellulose possess free hydroxyl groups important for the absorption of water that penetrates inside the amorphous regions of fibre in the form of water vapour or liquid state water. Thus, absorption of water is proportional to the extent of noncrystalline, less oriented regions assuming that tested fibres have constant number of free hydroxyl groups. Therefore, changes in moisture sorption of fibres influences changes in chemical composition, crystalinity and changes in pore structure [128].

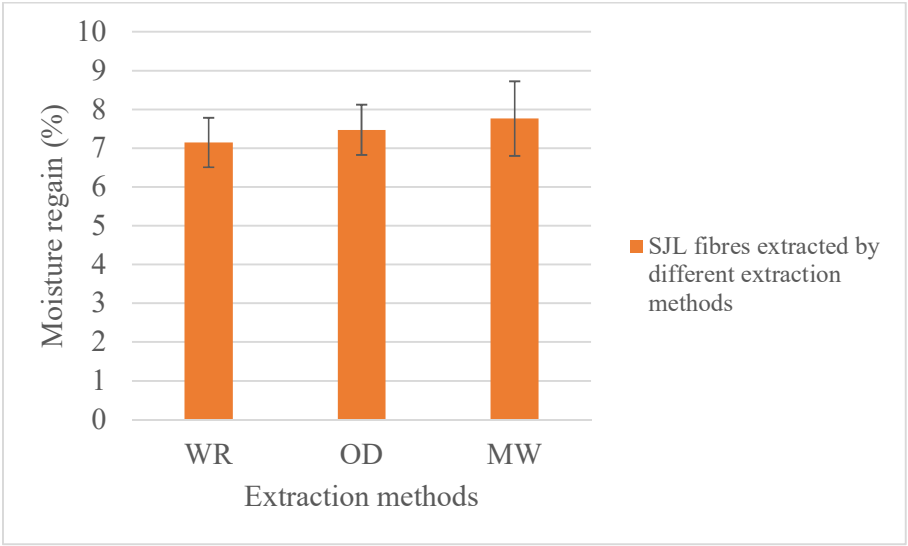

Figure 12: *Moisture regain of Spartium junceum L. fibres extracted by different methods where WR is water retting extraction method; OD is osmotic degumming method and MW is alkali retting under microwave energy*

4.1.3 FT-IR spectra

The ATR-FTIR spectra of *Spartium junceum* L. fibres extracted by different methods of maceration are shown in Figure 14.

Bast fibres are multicellular and present a complex structure made of biopolymers composing the core structure of the cell walls. As the main component, cellulose macromolecules crystallize in microfibrils which are oriented along the fibre axis with a helix angle around 5 ° to 10° and embedded in a matrix of non-cellulosic components such as hemicellulose, lignin, pectins and proteins (Figure 13). Cellulose and noncellulose content affects strength and break extensions of natural fibres. Cell walls are made of an outer layer, the primary wall (P) and concentric inner layers forming the secondary walls (sublayers - S1 and S2), in which various biopolymers are distributed and organised, thus forming a multi-component and tri-dimensional fibrillar structure. These individual fibre cells (elementary fibres) are usually assembled in fibre bundles (technical fibres), within the stems of plants. The elementary fibres are small and short, but in bundles they provide the reinforcement to stems [129, 130].

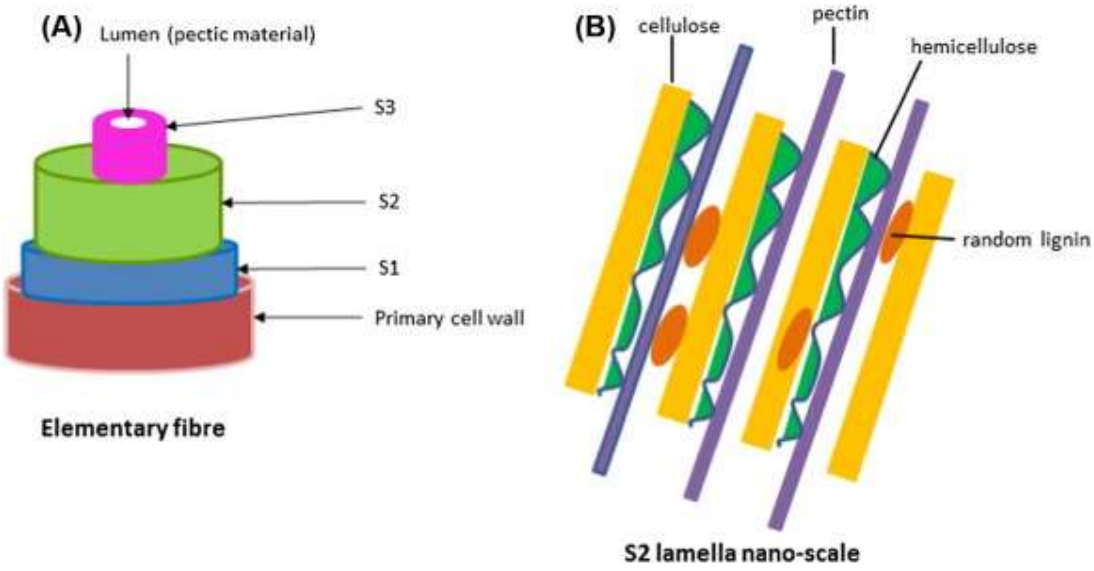

Figure 13: *(A) Layers forming elementary fibre; (B) Arrangement of the different components of the S2 cell wall [131]*

Table 6: *Main Infrared (IR) transitions of Spartium junceum L. fibres [108, 132-136]*

Wavenumber (cm^{-1})	Vibration	Sources
3200-3400	OH stretching	Cellulose, Hemicellulose
2917-2919, 2850	C-H symmetrical stretching	Cellulose, Hemicellulose
1730	C=O stretching vibration	Pectin, Waxes
1635	OH bending of absorbed water	Water
1537	aromatic skeletal vibrations and C=O stretch	Lignin
1510-1515	C=C aromatic symmetrical stretching	Lignin
1456	C-H and C-O deformations, bending or stretching vibrations in lignin and carbohydrates	Cellulose, Hemicellulose, Lignin
1426	HCH and OCH in-plane bending vibration	Cellulose
1368	In-the -plane CH bending	Cellulose, Hemicellulose
1335	C-H vibrations, O-H in plane bending and S ring stretching	Cellulose, Hemicellulose, Lignin
1316	CH_2 rocking vibration	Cellulose
1239	C=O and G ring stretching	Lignin
1204	C-O-C symmetric stretching	Cellulose, Hemicellulose
1158	C-O-C asymmetrical stretching	Cellulose, Hemicellulose
1105	C-O-C glycosidic ether	Cellulose
1051,1030,1000	C-C, C-OH, C-H ring and side group vibrations	Cellulose, Hemicellulose
985	C-O valence vibrations	Cellulose
895	COC, CCO and CCH deformation and stretching	Cellulose
836	Out of plane aromatic CH	Lignin
795-797	-CH- twisting (out of plane) of the aromatic ring	Lignin
781	Deformation vibrations of C-H bonds in associated to aromatic rings	Lignin

Band assignations of SJL fibres are summarized in Table 6. FTIR absorption spectra indicated structural differences between SJL fibres treated by different extraction methods, which are presented in Figure 14. Usually, FTIR spectra are divided into 4 regions: 4000 cm^{-1} -2500 cm^{-1} characterized with X-H single bonds i.e. C-H, O-H, etc.; 2500 cm^{-1} – 2000 cm^{-1} characterized with triple bonds, i.e. C≡C; 2000 cm^{-1} – 1500 cm^{-1} characterized with double bonds i.e. C=C and fingerprint area from 1500 cm^{-1} – 400 cm^{-1} characterized with single bonds, i.e. C-C bond. A large absorption band detected within range of 3200-3400 cm^{-1} is attributed to the –OH group while bands at 2918 cm^{-1} and 2850 cm^{-1} are attributed to CH_2 and CH groups of cellulose, hemicellulose, pectin, fats and waxes [116, 137, 138]. Furthermore, disappearing of the peak at 2850 cm^{-1} in the MW extracted SJL fibre indicates that the treatment was successful in removing lipophilic components such as waxes and oils, compared to the other two maceration

treatments (WR and OD). Band at 1730 cm^{-1} is characteristic for the free –COOH groups of polygalacturonic acid, which is the main constituent of pectins. Pectins are situated in the middle lamella and their role is to act as a "glue" that connects the macrofibrils and ensure the cohesion of fibre bundles [138]. Absence of this peak in MW treated SJL fibres indicates successful removing of pectins which is also confirmed with fineness testing (Table 4). The absorption band at 1635 cm^{-1} corresponds to adsorbed water and derived from hydrogen bonding in the amorphous region of the cellulose macromolecules [139]. In MW extracted SJL fibres this peak is broader and has lower intensity than the other two spectra, which is due to the removal of the hemicellulose after MW treatment and leads to an increase in the internal organization of the cellulose chains (a closer packing of the cellulose chains), allowing the establishment of highly crystalline regions, which improve the fibres strength and its properties (Table 4) [117]. The absorption bands at 1537 cm^{-1}, 1513 cm^{-1}, 1239 cm^{-1}, 836 cm^{-1} and 800-780 cm^{-1} correspond to stretch vibrations of C=O and C=C linkages of aromatic ring, CO stretch of the acetyl group and out of plane CH deformations of aromatic ring present in lignin, respectively [140, 141]. Absence of band at 1537 cm^{-1} and low intensity of band at 1513 cm^{-1} indicates effective lignin removal in MW extracted SJL fibres [142]. The peak at 1239 cm^{-1} is a CO stretch of the acetyl group of lignin and CO linkage in guaiacyl aromatic methoxyl groups. Therefore, its dissapearance in MW extracted SJL fibres also confirms the elimination of lignin. Peak at 1158 cm^{-1} presents C-O-C asymmetrical stretching of Pyranose ring in cellulose and hemicellulose [143]. The absorption band at around 1420-1430 cm^{-1} is associated with the crystalline structure of the cellulose, while the band at 895 cm^{-1} is allocated to the amorphous structure of the cellulose [144]. The absorption bands at 1105, 1051 and 1030 cm^{-1} are assigned to COC glycosidic ether, CO stretching vibrations of acetyl xylan and CO stretching vibrations of the polysaccharide components, mainly cellulose. Peaks at 1000 and 985 cm^{-1} (CO and ring stretching deformations in cellulose) are visible only as shoulders in the spectra of WR and OD extracted fibres pointing to more developed secondary cell wall of MW extracted SJL fibres, which makes a major contribution to the mechanical strength of such fibres [139].

FTIR analysis was successfully used to characterize the efficiency of applied extraction methods.

Chemical modifications can be used to finalize the separation process and improve fibre quality. [116].

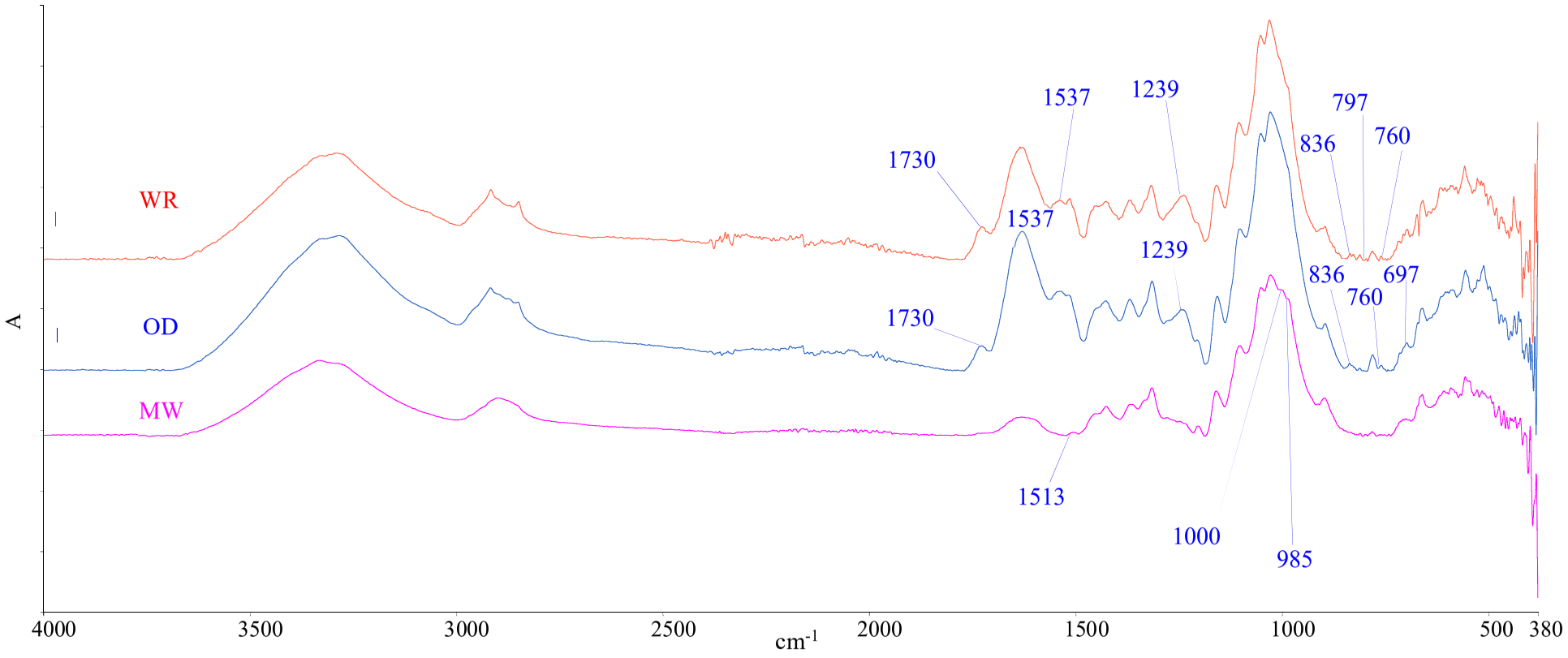

***Figure 14**: FTIR spectra of Spartium junceum L. fibres extracted by different methods where WR is water retting extraction method; OD is osmotic degumming method and MW is alkali retting under microwave energy*

4.2 Fibre functionalization

As presented in the previous chapter, SJL fibres extracted by MW method have better quality than fibres extracted by WR or OD method, while in this chapter, the emphasis will be placed on their modification in order to meet the requirements of current attractive sectors, i.e. construction and automotive industry.

Hydrophilicity of natural fibres presents the biggest problem in the adhesion of fibre with polymer matrix. Therefore, it is necessary to modify the fibre or polymer to enhance the properties of the final material [145]. Surface treatment reduces the hydrophilicity of the fibres by lowering the number of hydroxyl groups in the fibres. This leads to the improvement of adhesion between fibres and polymers. Some of the most common fibre surface chemical modifications are [65-69, 77, 78]:

1. Alkali treatment (removes impurities from the fibre surface and breaks the hydrogen bonds within the structure which increases the surface roughness)
2. Coupling agents treatment (contain the chemical groups that can react with both the fibre and the polymer, thus leading to compound cross linking by covalent bonding)
3. Acetylation (reaction of hydroxyl and acetyl functional groups called esterification which causes the reduction of cellulosic fibres hygroscopic nature)
4. Graft copolymerization (usage of various functional groups: metyl groups, isocyanates, triazine, organosilanes, etc.)
5. Enzyme treatment (removes impurities from the fibre surface which results in better adhesion between fibre and polymer matrix)
6. Nanoparticle treatment (chemical or mechanical binding of nanoparticles to the surface of fibres with the aim of improving compatibility between fibres and polymer).

Spartium junceum L. fibres were modified with comercial and newly synthesized nanoparticles with precisely targeted properties aiming at flame retardant protection of the material.

Structural, thermal, mechanical and physio-chemical properties of fibres modified with alkali (NaOH) and commercial nanoclay were investigated and presented throughout four published papers [146-149], while thermal properties of SJL fibres modified with newly synthesized nanoparticles were analyzed but have not been published yet.

After the MW extraction method, SJL fibres (MWR) were additionally modified with NaOH (1F) and with nanoclay (2F and 3F). One of the inherent drawbacks of natural plant fibres is their variability of properties. The variability of the physical and mechanical properties mainly originates from the variation in their chemical structure and composition, such as cellulose content, degree of polymerization, orientation of molecular chains, crystallinity, etc. These parameters are highly dependent on the growth conditions of the plant and also on the fibre extraction methods. Therefore, natural fibres extracted from plants or grown in different locations and weather conditions present huge variability in their properties [150].

4.2.1 Structural properties

Structural properties were investigated by means of chemical composition assessment SEM and EDS analysis.

Plant fibres are made of highly complex organic matrix which consists of three main components: cellulose, hemicellulose and lignin and of small quantities of ash and extractives (Table 7). Quantity of these constituents was determined by isolating, purifying and quantifying the components by weight [49].

***Table** 7: Chemical composition of SJL reference and modified fibres*

	Cellulose [%]	Hemicellulose [%]	Lignin [%]	Ash [%]	Extractives [%]
MWR	91.826 ± 0.325	2.994 ± 0.795	3.419 ± 0.700	0.030 ± 0.001	1.731 ± 0.204
1F	90.066 ± 1.152	5.756 ± 1.626	3.303 ± 0.564	0.045 ± 0.029	0.829 ± 0.073
2F	92.026 ± 0.258	4.112 ± 0.541	3.202 ± 0.778	0.023 ± 0.013	0.637 ± 0.046
3F	92.385 ± 0.161	2.620 ± 0.433	3.979 ± 0.508	0.003 ± 0.002	1.010 ± 0.063

Where MWR is reference SJL fibre extracted by alkali retting under microwave energy, 1F is SJL fibre additionally modified with alkali, 2F is SJL fibre modified with alkali and nanoclay, 3F is SJL fibre modified with nanoclay and citric acid. Results are presented as mean value within 95 % confidence interval.

Among these four fibre modifications, cellulose content was in the range from 90.07 % to 92.39 %. The highest cellulose content was observed in SJL fibres modified with nanoclay and citric acid, pointing to stronger fibres of improved quality from the chemical composition point of view. The ash content of all tested fibres is low, indicating the absence of various chemicals of metallic or mineral matters and suggesting good quality of products consisting of such fibres [151]. The removal of the hemicellulose after alkali treatment removed the inner limitations and the fibrils became more capable of rearranging themselves in a compact manner. This leads

to a closer packing of cellulose chains, which have improved the fibre strength and its tensile properties [117]. Higher content of hemicelluloses in fibres 1F and 2F indicates higher moisture absorption and faster thermal degradation, because hemicellulose and lignin remain dispersed in the interfibrillar region separating the cellulose chains from oneanother which affects the formation of more amorphous phase. Lignin is an undesired polymer but all modified fibres show lignin content in the range of 3 to 4 % which makes the fibre strength increase and difficult to break. On the other hand, hydrophobic lignins act as a cementing agent and increase the stiffness of the cellulose/hemicellulose composite. Extractives are plant components of lipophilics and hydrophilics and their presence in fibres increases the consumption of chemicals in the production process and reduces yield [152].

Results of SEM and EDS analyses were presented in [149] and show surface morphological characteristics, as well as relative chemical composition of SJL modified fibres.

Surface of reference fibre MWR was smooth and regular, while fibres 1F, 2F and 3F show increased roughness caused by additional treatment of technical SJL fibre with alkali and nanoparticles, respectively. Alkaline processing dissolves lignin phase in which cleavage reaction of various bonds between the units of lignin macromolecules occurs [153]. This treatment breaks down the fibre bundles to release the individual – elementary fibres with a higher aspect ratio and a rougher topography that increases fibre matrix adhesion, if such fibres are used as reinforcement in composite materials.

EDS analysis has proven the presence of Si and Al atoms in nanoclay modified samples (2F and 3F) with an increase in Si and Al content in the fibre treated with nanoclay and citric acid (3F) which might be due to the formation of crosslinking caused by the interaction between the citric acid and hydroxyl groups of cellulose [154].

4.2.2 Physico-chemical properties

IR spectra of SJL fibres obtained by different modification methods were presented in a paper published in Arabian Journal of Chemistry [147]. The differencies among modified fibres (1F, 2F and 3F) are mainly in peak intensities of absorption bands. Absorption bands at 2844 and 2900 cm^{-1} could be observed in the spectra of all fibres, but with higher intensity in the spectra of referenced fibres (MWR) pointing to the minor amount of pectins, waxes and fats inside other tested fibres. Nanoclay modified fibres (2F and 3F) showed broader peaks around 1040 cm^{-1} due to Si-O plane stretching, while the absence or lower intensity of lignin characteristics peak at 1506 cm^{-1} for fibres 1F, while 2F and 3F indicate succesful delignification and a well-

conducted maceration process. Chemical treatments of bast fibres are known to change the cellulose content, as well as the degree of crystallinity. The rigidity of cellulose fibres increases and their flexibility decreases with increase of the ratio of crystalline to amorphous regions. While the increase of crystallinity causes greater strength, decrease of crystallinity caused increased elongation, higher water intake since amorphous regions can absorb more water [155], and more sites available for chemical reactions. A parameter called crystallinity index (CI) has been used to present relative amount of crystalline or amorphous regions in cellulose. The CI has been determined by XRD, solid state NMR, IR spectroscopy, Raman spectroscopy, etc. FTIR spectroscopy turned out to be the simplest method and in good correlation with the more detailed XRD method [156]. The crystalline characteristics of modified fibre structure were investigated in each FTIR spectra by comparing the peak of the functional group in crystalline region with a peak of other functional group in amorphous region.

Table 8 presents the values of different crystallinity ratios (TCI, LOI, and HBI) for SJL reference and modified fibres. Usually, elevated TCI and LOI values indicate the highest degree of crystallinity and a more ordered cellulose structure, while lowest TCI and LOI values designate the amorphous structure of cellulose [108]. Reference fibres showed the lowest TCI index of 0.77 % pointing to higher crystallinity of modified fibres. Within modified SJL fibres, there was no significant difference regarding TCI index, which is visible from standard error of mean presented in Table 8. LOI method is correlated to overall degree of order in cellulose [157]. All of the tested fibres showed similar LOI values indicating no significant difference in order in cellulose structure, although HBI value of sample 3 was significantly higher than in other samples. Hydrogen bond intensity of cellulose is closely related to the crystal system and the degree of intermolecular crystallinity, therefore it is assumed that cellulose chains of sample 3 are highly organized and arranged in crystalline structure [158].

Table 8: *Main FTIR crystallinity indices for reference and modified SJL fibres*

Sample	TCI [%]	LOI [%]	HBI [%]
MWR	0.77 ± 0.007	0.69 ± 0.08	2.07 ± 0.20
1F	0.97 ± 0.05	0.65 ± 0.03	2.04 ± 0.04
2F	1.00 ± 0.07	0.63 ± 0.02	2.14 ± 0.12
3F	0.90 ± 0.02	0.60 ± 0.01	2.42 ± 0.06

Where MWR is reference SJL fibre extracted by alkali retting under microwave energy, 1F is SJL fibre additionally modified with alkali, 2F is SJL fibre modified with alkali and nanoclay, 3F is SJL fibre modified with nanoclay and citric acid, TCI is the total crystalline indeks, LOI is the lateral order indeks, HBI is the hydrogen bond intensity. Results are presented as mean value within 95 % confidence interval.

Changes in the surface chemistry of SJL modified fibres were determined by ζ-potential mesurement as a function of pH in the range of 2 < pH < 10 by adding 1mM of KCl solution. The measured ζ-potential of SJL fibres changes towards more negative values in the higher acidic range. The isoelectric point (IEP) was found to be almost identical for all tested fibres (IEP ~ 2), indicating very similar chemical constitution of surface functional groups. Samples 1F and 3F show IEP shifted to slightly higher pH values (IEP 2.15) and ζ-plateau values were more negative, indicating their less hydrophyllic surface in comparison to the (R) and (2) sample, thus making them more suitable for polymer matrix adhesion process. All these modification processes result in the removal of non-cellulose components from the natural fibre surfaces, thus increasing the accessibility of surface functional groups which can be used in further chemical modification steps to increase the compatibility of natural fibres to non-polar polymers [159, 160].

4.2.3 Thermal properties of SJL fibres

Thermal properties of fibres were influenced by adding NaOH and nanoclay into the fibre structure. Results from TGA analysis were presented in the paper published in Autex 2017 Book of Proceedings [149]. Water loss is observed at approx. 100 °C for all tested fibres and the significant weight loss occured in the temperature range 290-430 °C due to the thermal decomposition of hemicellulose, cellulose and lignin. Thermal decomposition of carbohydrates is a complex process which comprises of dehydration, depolymerization, fragmentation, rearrangement, repolymerization, condenzation and carbonization [161]. According to the literature [161, 162], degradation of hemicellulose occurs in the range 190-350 °C, followed by cellulose depolymerization visible in the temparature range below 400 °C and pyrolysis of lignin that takes place in the range below 800 °C. Hemicellulose has random and branched, relatively amorphous structure of lower molecular weight and is more readily decomposed compared to cellulose. Thermal stability of SJL fibres was influenced by cellulose content and its crystallinity. Lignin is thoroughly cross-linked and has very high molecular weight and thermal stability, and it is therefore difficult to decompose [108]. As can be seen in detail of Figure 15, sample 2F show a more significant weight loss, at around 250-260 °C, which might be due to higher volatility of its structural components. Mainly it is composed of cellulose, but according to Table 7 it also has approx. 4 % hemicellulose which is followed by more rapid degradation process, where degradation of one component may accelerate the degradation of the other fibre components [108].

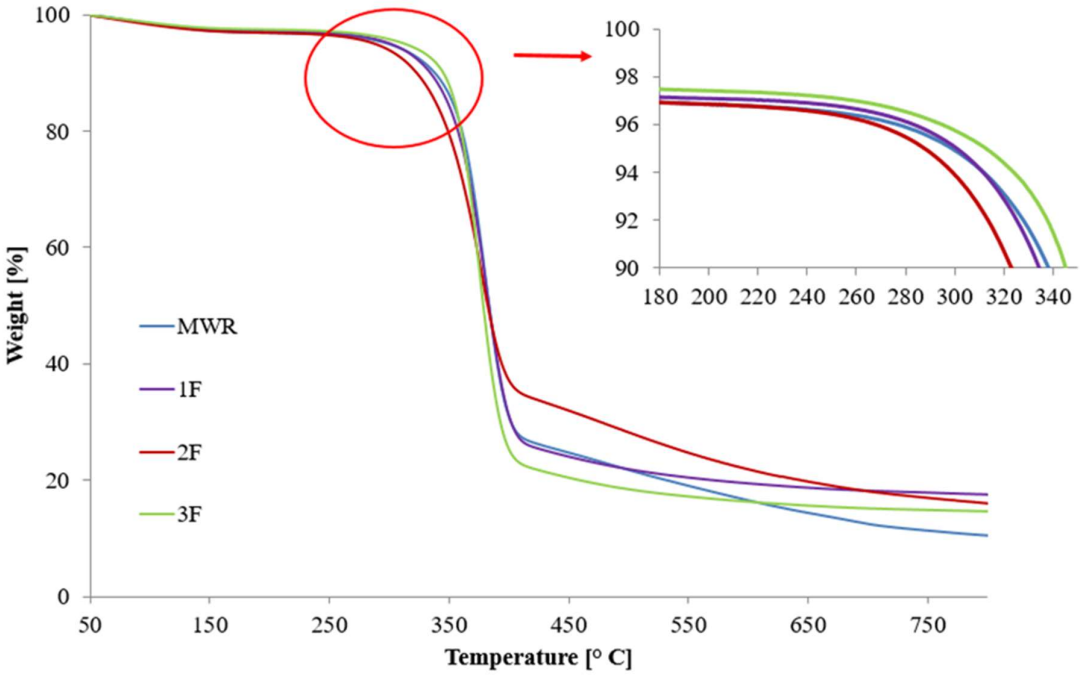

***Figure 15**: TGA analysis of SJL fibres*

Table 9 presents several characteristic temperatures within thermal degradation process. The initial weight loss temperature, T_i, presents the temperature at which the sample loses 3% of its weight. $T_{shoulder}$ is the onset temperature described as the initial stage of the degradation process. Comparing T_i and $T_{shoulder}$ values of modified fibres, it is noticeable that sample 3F shows higher thermal stability than others, although its final decomposition temperature is lower comparing to other samples. Modified fibres showed higher residue content at 800 °C than reference SJL fibre which is due to more inorganic content inside the modified fibres (additional modification with NaOH for sample 1F and nanoclay modification for sample 2F and sample 3F). This feature might be explained by the highest lignin content in sample 3F compared to other tested samples and the higher crystallinity of this fibre, as presented in Table 8. Crystalline regions of cellulose improve the thermal stability of lignocellulosic fibres causing shifting of thermal decomposition of natural fibres to higher temperatures with an increase in the cellulose crystallinity [108, 155]. In addition, the higher value of hydrogen bond intensity of sample 3F indicates a more closed packaging cellulose structure that makes the heat transfer difficult, because the cellulose crystallinity domains act as barriers for the heat transfer, which possibly increases the fibre thermal stability.

It seems to be difficult to distinguish and model the thermal decomposition behavior of each specific component in lignocellulosic fibre, due to the complexity of the growth of the fibres, which causes variance in component contents, crystal structure and chemical composition within fibres of natural origin [163, 164].

***Table 9**: Thermal properties of SJL fibres*

Sample	T_i (°C) 3 wt% loss	$T_{shoulder}$ (°C)	DTG peak (°C)	Residue at 800 °C (%)
MWR	171	355	381	10.40
1F	230	355	381	17.56
2F	169	343	377	15.98
3F	260	357	375	14.64

Where MWR is reference SJL fibre extracted by alkali retting under microwave energy, 1F is SJL fibre additionally modified with alkali, 2F is SJL fibre modified with alkali and nanoclay, 3F is SJL fibremodified with nanoclay and citric acid

4.2.4 Mechanical properties of SJL fibres

Investigation of mechanical properties of SJL reference and modified fibres was published in the Arabian Journal of Chemistry [147]. Breaking tenacity, elongation, as well as linear density of individual fibres were examined by vibration method.

***Table 10**: Fibre strength and Young modulus of SJL fibres*

Sample	Fibre Density	Fibre Strength		Young Modulus	
	g/cm^3	cN/tex	MPa	cN/dtex	GPa
MWR	1.55 ± 0.0026	64.44 ± 1.80	998.85 ± 27.97	114.45 ± 4.22	17.87 ± 0.66
1F	1.55 ± 0.0019	60.00 ± 1.33	930.04 ± 20.62	118.71 ± 4.19	18.53 ± 0.65
2F	1.55 ± 0.0027	68.84 ± 1.54	1067.04 ± 23.85	116.65 ± 4.30	18.21 ± 0.67
3F	1.55 ± 0.0028	67.40 ± 1.42	1044.67 ± 22.00	114.82 ± 3.95	17.93 ± 0.61

Where MWR is reference SJL fibre extracted by alkali retting under microwave energy, 1F is SJL fibre additionally modified with alkali, 2F is SJL fibre modified with alkali and nanoclay, 3F is SJL fibremodified with nanoclay and citric acid. Results are presented as mean value within 95 % confidence interval.

From the published results and according to the new and summarised Table 10, it can be concluded that fibre strength is increased by nanoclay modification due to the MMT nanolayered structure. Alumino-silicate clay nanolayers possess high aspect ratio

(length/thickness) approx. 100-1000 nm which causes improved mechanical properties of 2F and 3F fibres [154, 165]. There is no significant difference in strength between sample 2F and sample 3F, indicating that CA usage in sample 3F affects only the interface adhesion with polymer in fibre-reinforced composite and has no influence on the SJL fibre strength. This phenomenon will be explained in more detail in the next chapter.

Sample 1F reveals lower strength value in comparison to other fibres which is due to the repeated alkali treatment of fibres resulting with weaker or in some cases damaged fibre, confirming the hypothesis that higher alkali concentration influences fibre strength [166, 167]. It is visible from Table 10 that Young modulus of modified fibres is slightly higher than modulus of MWR, but with no significant difference between sample MWR and sample 3F. Lower modulus indicates softer fibres with higher cohesion forces [168]. Fibre diameter is inversely proportional to fibre strength since smaller fibre diameters smooth the way for stress transfer from fibre to matrix. However, the main indicators of mechanical properties lie in biochemical differences rather than morphological ones [169]. Basically, tensile strength and Young modulus of bast fibres increase with increasing cellulose content of the fibres while increase in the hemicellulose content leads to reduced strength since hemicellulose is amorphous in nature and nonhomogeneus in properties [170]. Usually, fibre strength is inversely proportional to fibre elongation, so fibres with a decrease in strength have an increase in elongation [155]. Despite this, as can be seen in Table 3 in our paper [147], MMT modified SJL fibres showed increase in both tensile strength and elongation at break, pointing to strong and tough fibre which can be used for wide-range industrial purposes, where a combination of lightness, strength and toughess is required.

An example of SJL fibre fineness distribution is presented in Figure 4 in our paper [147]. There is no significant difference in fineness of tested fibres, except in the case of fibres modified with nanoclay. Sample 3F is slightly coarser, showing 63.3 % of fibres in the range of 30-45 dtex. Its decreased fineness was assigned to the MMT particles which were efficiently bonded to the fibre surface due to the CA crosslinking ability. Fineness of fibres is an important factor in determining their stiffness. The distribution of 150 fibres shows high variability among the SJL fibres. High variability of natural fibre properties is a challenge when developing composite products based on bast fibres.

4.3 Biocomposites – mechanical and thermal properties induced by interface phenomena

The contemporary challenge to scientists and engineers is to develop the technology which will revolutionalize biobased materials. Expectations are that two-thirds of the global chemical industry would be based on renewable resources [37]. Nowadays, the term ‘’bio’’ is a hot topic and a great number of novel technologies is incorporating it within their development strategies. One of the examples is the composite material technology, which has found a niche in biocomposite production, especially in the fibre-reinforced composite market, which is a multibillion-dollar business [171].

This chapter will discuss the results of mechanical and thermal properties of PLA composite material reinforced with SJL fibres, which were investigated and presented in three published papers [146-148].

4.3.1 Mechanical properties of composite materials

Tensile properties of natural fibre reinforced materials are mainly improved by adding fibres to a polymer matrix, since natural fibres show higher strength and stiffness values in comparison to matrix polymers. Therefore, the properties of composites are influenced by the hydrophilic and hydrophobic nature of fibre and polymer matrix, fibre content or amount of filler in matrix, fibre aspect ratio and its orientation, uniformity of its dispersion along the matrix, manufacturing techniques and process parameters. One of the most important parameters that influence tensile properties of composite materials is the interfacial adhesion between the matrix and the fibres [106]. Good interface causes increment of the stress transmission from the matrix to the fibre and thus enhances the tensile strength of the composite material [172]. Several chemical modifications are employed to improve the interfacial matrix-fibre bonding in natural fibre reinforced polymers, which is caused by poor compatibility between polar and hydrophilic fibres and hydrophobic polymer, resulting in the enhancement of tensile properties of the composites [173-177].

As already mentioned in chapter 3, the tenacity values of Sample 2F and Sample 3F were enhanced compared to Sample MWR, but some irregularities could be observed in its composite mechanical properties. Tensile strengths for CR, C1 and C3 fibre reinforced composites were increased compared to the sample C2. Its increment in strength was increased by more than 100 %, which denoted an inappropriate interface of C2 composite. Even though sample 1F showed a decrease in strength caused by more concentrated alkali treatment, its composites have shown the increase in strength of 115 % compared to C2. This phenomenon is probably induced by

filling of voids inside the fibre with melted polymer, leading to the improvement of fibre/PLA adhesion mainly due to mechanical interlocking mechanisms [174, 178]. Sample C3 showed the highest strength and modulus values, indicating higher material stiffness, while SEM analysis revealed its smoother fractured surface in comparison to other samples, indicating better interfacial adhesion between the reinforcement and the matrix. These results indicated significant influence of nanoclay modification on the composite material's strength. Only in case nanoclay particles are coupled with citric acid, the interconnection of all composite phases (matrix-fibre-nanofiller) is enhanced. The result is a decrease of fibres pulled out from the fractured surface in comparison to CR, C1 and C2 samples. Such enhanced interface quality of sample C3 was proved by FTIR analysis. The intensity of the peak at 1750 cm^{-1}, significative to C=O stretching, is higher than in other tested samples and suggests the increase of the number of free carboxylic end groups in the polymer chain due to citric acid crosslinking. The intensity of peak presenting –OH bending vibration at 1645 cm^{-1} decreased, suggesting the formation of new bonds between clay, fibres and polymer [179, 180]. Regarding the Young's modulus, it is noticeable from the Figures 9 and 10 of our paper published in the Arabian Journal of Chemistry, that sample C2 has low mechanical properties. This material can be elastically deformed more easily than other tested composites. This could be attributed to the decrease of interface properties and fibre-matrix adhesion due to weak adsorption forces between the clay particles and the fibre surface, followed by the formation of a higher number of filler to filler bonds (clay-clay or fibre-fibre) [181, 182]. In the FTIR spectra of Sample C2, the intensity of the metal oxide peaks at 1030-460 cm^{-1} was found to be decreased in comparison to the sample C3, indicating lower intensity of Si-O stretching peaks, and low interaction among PLA polymer, fibre and clay. The creation of voids, microcraks and other similar discontinuities inside the interphase (Figure 11 [147]) does not primarily separate material phases (matrix-fibre-nanofiller), but decreases the capability of transmitting and sustaining loadings, and reduces structural stiffness. Sample 2F (reinforcement in the sample C2) has the smallest diameter of all tested fibres [148] and thus the higher aspect ratio which might cause the so called twisting phenomenon [93], and influence the modulus and fibre/matrix adhesion. In general, increase of composite material stiffness is related to increase of its modulus. If the rigidity of reinforced components (fibres or fillers) is higher than matrix rigidity and if the fibre content increases up to an optimal value, the stiffness grows higher [173].

Figure 1, presented in [148], shows stress-strain curves of composite materials and confirms that pure PLA material breaks at a lower strain than others, indicating its brittle nature. In general, synthetic polymer materials show higher elongation at break than natural fibres, which

leads to the increase of composite material's brittleness. In our case, tested composite materials show higher values of elongation at break, indicating tougher material which can withstand fracturing if a crack grows so long that the reinforcement cannot support the load from the matrix [183].

Usually, composite materials aim to obtain better structural or functional properties compared to their individual composite components/phases. However, in the case when fibres are shorter than the critical length and randomly oriented, the resulting composite does not necessarily display enhanced properties [93]. This is the reason why the prediction of properties and product design is so difficult. Table 1 and Figure 2 from our paper [148] explain applied micromechanical models, experimental and predicted values for composite material's tensile strength and modulus. Properties such as tensile strength of the fibre (σ^F) and matrix (σ^M), volume fractions of the fibre (V^F) and matrix (V^M) and tensile modulus of fibre (E^F) and matrix (E^M) are the fundamental quantities used to predict composite properties. In this research, two mathematical models were investigated – Modified rule of mixtures with incorporated Cox-Krenchel equations and the Hirsch model. Those models are most commonly used in the case of composites reinforced with short and randomly oriented fibres [105, 107, 184].

Table 11: *Experimental and predicted tensile modulus values according Hirsch model*

Fibre/ Composite	W_F	V^F	W_M	YM matrix (GPa)	YM fibres (GPa)	Exp YM composite (GPa)	Predicted YM composite (GPa)
MWR/CR	0.2	0.1667	PLA/0.8	1.40	17.868	1.65	2.01
1F/C1	0.2	0.1660	PLA/0.8	1.40	18.533	1.89	2.03
2F/C2	0.2	0.1665	PLA/0.8	1.40	18.212	1.17	2.02
3F/C3	0.2	0.1665	PLA/0.8	1.40	17.926	2.60	2.02

Where W_F is weight fraction of fibres, V^F is volume fraction of fibres, W_M is weight fraction of matrix and YM is Young moduli, PLA is neat polylactide, and CR, C1, C2, C3 are composites made of PLA matrix and MWR, 1F, 2F and 3F fibres, respectively.

After micromechanical modelling, it can be assumed that the Hirsch model offers relatively good correlation between experimental and predicted results, especially for tensile strength. Predicted tensile strength values were about 10 % lower in comparison to experimental values, except for sample C2, where predicted values are 113.5 % higher than experimental ones. Predicted tensile modulus values (presented in Table 11) were about 20 % higher for sample

CR and sample C1. Sample C2 shows 70 % higher tensile modulus value regarding its poor adhesion with matrix. On the contrary, sample C3 shows 20 % lower values than predicted in comparison to other composites. If developed composite material will be used for structural applications, a higher safety margin is required when natural fibres are used as the reinforcement of polymer based structures [150]. Estimation of final product's mechanical properties is an important starting point of the new material design. Our future work will include the establishment of more accurate design criteria using predictive models.

4.3.2 Thermal properties of composite materials

Three major thermoanalytical techniques (TGA, DSC and MCC) were used to investigate the thermal properties of SJL composite materials. Fibres' chemical modification can improve both mechanical and thermal properties of composite materials. Modification of SJL fibres with the aim of providing fire protection was conducted with MMT used in the role of flame retardant nanofiller and CA in the role of environmentally friendly crosslinking agent.

Thermal degradation curves of PLA and SJL composites were showed in Figure 5 of the paper published in Composite B Part B: Engineering [146]. All samples show thermal stability in the temperature range 30 °C to 300 °C. When samples are exposed to temperature higher than 300 °C, only MMT treated fibres could improve thermal stability regarding their residual weight after thermal treatment at 800 °C. Among all the tested materials (PLA, CR, C1, C2 and C3) the neat PLA has shown the highest initial decomposition temperature of 354 °C. Other materials are reinforced with natural fibres, which influence the start of decomposition and shift it to lower temperatures. TGA results revealed poor adhesion between polymer and fibre in sample C2, since all the measured temperatures up to the decomposition temperature were lower than in the other samples. One of the possible explanations for this phenomenon is the uneven nanodispersion of clay particles within SJL fibre surface or the creation of its clusters ranging from over 5 μm down to submicrometer scale and the increase of the number of air voids inside the body of material (Figure 4 in [146]). Sample C3 showed higher decomposition temperature at certain weight loss T_D in comparison to sample C2, indicating formation of crosslinking caused by interaction between the CA and –OH groups of fibre cellulose or PLA polymer. Only samples C2 and C3 have formed the composite chars by pyrolysis at 800 °C and SEM analysis of these chars offered a clear view of the possible nanoclay effect, where the migration of nanofiller from the inner part of the technical fibre to its surface could be observed, thus inhibiting access to oxygen and preventing combustion process from being sustained.

Additionally, the energy of activation was determined for the main decomposition stage of PLA matrix and SJL composites. Sample C2 has the lowest thermal stability (156.59 kJ/mol) compared to other tested materials. For most natural fibres, activation energy of 160-170 kJ/mol was obtained throughout the composite processing temperature range [185], indicating fast decomposition of cellulose from reinforcing fibres in sample C2. In Figure 7 of the same paper [146], it is shown that the fitted lines are nearly parallel and show similar trend, except for C2 sample, indicating changed reaction mechanism. This change is probably caused by poor interface properties and insufficient wetting of SJL fibres with PLA matrix and therefore induced accelerated decomposition process of the main fibre structural components [186].

Glass transition temperature (Tg), melting temperature (Tm) and cold crystallization temperature (Tcc) were investigated by differential scanning calorimetry. During the second heating, the neat PLA and its composites show 3 distinct peaks (Tg, Tcc and double melting) presented in summarized Table 12. It can be observed that Tg, Tcc and Tm peaks shift towards lower temperatures with the addition of SJL fibres. Samples with a low degree of crystallinity, where polymer chain's ends can move more easily, show lower Tg values, characteristic for flexible materials [176]. Tg values were found to decrease in correlation with fibre modification process according to the order: PLA>CR>C1>C2. Sample C3 shows no glass transition temperature within the tested temperature interval. This could occur due to heavily crosslinked structures within the composite material or more likely due to very ununiform linkage density distribution that leads to hardly detactable Tg [187]. Reduction in Tg values with the addition of SJL fibres is an indication of the plasticizer effect. The result is the increase of polymer chain mobility in the interphase zone presented in the Table 7 of our published paper [147] through noticeable increase in elongation at break. The glass transition is a complex phenomenon related to many factors such as chain flexibility, molecular weight, branching, crosslinking, and intermolecular interaction [188, 189].

***Table 12**: DSC analysis of PLA and SJL composite materials*

Sample	Tg [°C]	ΔCp [J/g°C]	T_{cc1} [°C]	ΔH_{cc1} [J/g]	T_{m1} [°C]	T_{m2} [°C]	ΔH_m [J/g]	X [%]
PLA	58.06	0.63	110.31	0.62	/	165.21	43.34	46.71
	(0.52)	(0.08)	(0.67)	(0.48)		(0.16)	(3.07)	(3.12)
CR	51.26	0.33	107.24	17.59	156.11	163.90	27.03	10.15
	(1.38)	(0.08)	(0.43)	(0.34)	(0.21)	(0.47)	(0.89)	(1.32)
C1	49.61	0.37	108.50	29.40	155.60	162.00	34.58	5.57
	(1.20)	(0.00)	(0.27)	(1.64)	(0.84)	(0.46)	(1.04)	(1.68)
C2	49.50	0.38	110.18	8.85	145.22	155.00	14.25	5.81
	(0.51)	(0.04)	(0.48)	(0.60)	(0.48)	(0.17)	(0.77)	(1.40)
C3	none	none	100.53	9.40	150.87	158.53	23.06	14.69
			(0.90)	(1.77)	(3.23)	(2.70)	(2.61)	(4.65)

Where Tg is glass transition temperature, Cp is heat capacity, T_{cc} is temperature of cold crystallization, ΔH_{cc} is cold crystallization enthalpy, T_m is melting temperature, ΔH_m enthalpy of fusion, X is degree of polymer crystallinity, PLA is neat polylactide polymer, and CR, C1, C2, C3 are composites made of PLA and MWR, 1F, 2F and 3F fibres, respectively. Data in brackets represent standard deviations

Crystallization at lower temperatures during the heating cycle was influenced by SJL fibres, which act as nucleating agents that naturally lower the surface free energy barrier for nucleation [187, 188]. Sample C3 shows the lowest temperature of cold crystallization (Figure 16), indicating that the fibres modified with MMT/CA are better nucleating agents for PLA crystallization due to the heating cycle. This early crystallization can be explained by the formation of stronger hydrogen and covalent bonds between fibres and matrix and the presence of a transcrystalline zone form at the fibre-matrix interface [190, 191]. In general, the nucleation stage and the crystal growth are more complicated for the polymeric composites due to the possibility that fillers (fibres or nanoparticles) act as nucleating agents.

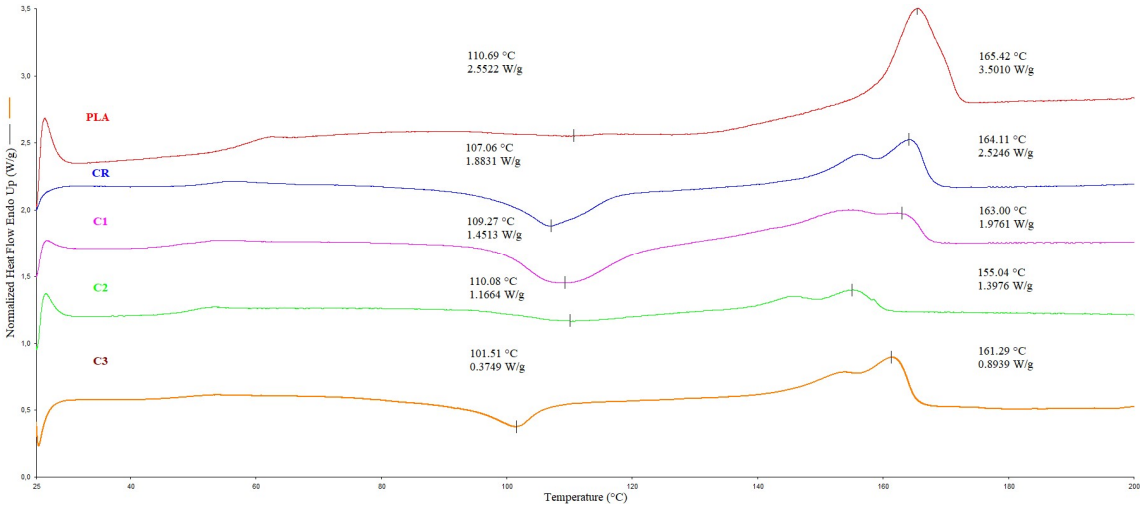

***Figure 16:** DSC curve for neat PLA and its composites, Where PLA is neat polylactide polymer, and CR, C1, C2, C3 are composites made of PLA and MWR, 1F, 2F and 3F fibres, respectively.*

Fillers can increase the crystallization or limit the normal crystal growth in certain areas, such as the interphase between fillers and polymer matrix [188], depending on the interfacial adhesion.

Beg et al. (2013) investigated the properties of natural fibre/PLA biocomposites. Among various testing methods, interfacial adhesion between chemically modified natural fibres and PLA was also explained by DSC. They found that neat PLA shows only one melting peak while its composites show double melting behaviour, confirming the presence of two different types of crystal. Both crystals have the same structure but with one exception – the less perfect crystal has a smaller lamella thickness [190]. Higher Tm is attributed to the creation of more perfect crystals which would usually melt at higher temperatures than the less perfect crystals [188-190]. It can be confirmed that Sample C3 gives the best results among other tested samples regarding their fibre modification and the usage of CA as a coupling agent, which allows better adhesion of matrix and fibre and therefore better interface properties.

Flammability properties of tested composites revealed that nanoclay treated SJL fibres, which serve as an reinforcement in the sample C2 and C3, affect the occurrence of lower heat release values (W/g) indicating much higher flammability of CR and C1 samples. The heat release rate plots of all samples are presented in Figure 8 of our paper [146] and the corresponding combustion data are summarized in Table 13, within this chapter. It could be observed that materials reinforced with SJL fibres show lower peak heat release rate (HRR) and total heat release (THR) in comparison to the neat PLA. The formation of residue in Sample C2 after exposure to 750 °C affects the creation of a thermal barrier [192, 193] which decreases the heat release of the nanoclay treated samples.

***Table 13**: MCC data of PLA and SJL composite materials*

Samples	HRR (W/g)	THR (kJ/g)	THC, gas (kJ/g)	Yield of pyr. residue (g/g)
PLA	475.133±22.633	17.133±0.131	17.330±0.161	0.011±0.003
CR	388.400±24.894	14.433±0.653	15.160±0.436	0.048±0.035
C1	395.567±10.329	14.800±0.408	15.562±0.385	0.049±0.014
C2	280.926±16.735	13.833±0.663	14.581±1.212	0.074±0.006
C3	341.437±6.637	14.800±0.299	15.447±0.172	0.042±0.009

Where PLA is neat polylactide polymer, and CR, C1, C2, C3 are composites made of PLA matrix and MWR, 1F, 2F and 3F fibres, respectively. HRR is heat release rate, THR is total heat release and THC is total heat capacity. Results are presented as mean value within 95 % confidence interval.

4.4 Biodegradability

Due to the rise of ecological awareness, more and more members of the scientific community are involved in the research of biodegradable polymers which turn out to be a suitable replacement for nondegradable polymers [9, 194-196]. Biodegradability means the complete degradation of polymer in the presence of microorganisms [197]. PLA is a linear aliphatic thermoplastic polyester that can be made from completely renewable resources such as sugar, corn, potato, cane, beet, etc. and has adoptable degradability. Industrial production of PLA polymer is based on the ring opening polymerization of lactide monomer formed from lactide acid, which is produced by fermentation of renewable agricultural resources [198]. Through hydrolysis, it can be decomposed to lactide acid, which is subsequently decomposed to water and carbon dioxide by metabolic processes [199]. Degradation degree depends on the temperature, size and shape of the polymer and the proportion of isomers [198-200].

Due to the need for renewable solutions for the development of new materials, the usage of composite materials made of biopolymer matrices reinforced with natural fibres is increasing significantly. These materials are relatively cheap, have specific properties contributing to the neutralization of CO_2, and are biodegradable. Although PLA is biodegradable, the basic comprehension of its enzymatic degradation related to its blending with another biodegradable polymer still requires better understanding [201].

The factors investigated through enzymatic degradation of PLA were: stereochemistry, melting temperatures, crystallinity, crystal structure, glass transition temperature, molecular weight and molecular weight distribution.

So far, scientists have found [202-204] that:

- The degradation rates of PLA decreases with an increase in crystallinity
- Enzymatic hydrolysis of completely crystallized PLA films with restricted amorphous regions mainly took place through the chains in the constrained amorphous regions of the spherulites
- In crystalline PLA films, the degradation of the free amorphous region was faster than that of the restricted regions
- Proteinase K preferentially degraded (L)-PLA over (D)-PLA.

Our results dealing with PLA and its composites biodegradability are published in The Hollistic Approach to Environment Journal and disscussed in this chapter.

Materials used in this experiment were composites made of PLA, SJL fibres and nanofillers. They were subjected to enzymatic degradation. The weights of the samples after enzymatic degradation in duration of three and five days are presented in Table 14.

***Table 14**: Moisture content and weight loss percentage of PLA and its composites after enzymatic degradation, data in brackets represent standard deviations*

Sample	Enzyme (%)	Δm_{72} (%)	Δm_{120} (%)	Moisture content (%)*
PLA	20	0.464 (0.064)	0.793 (0.247)	0.660 (0.135)
	50	0.820 (0.466)	1.433 (0.851)	
	100	0.180 (0.031)	0.516 (0.057)	
CR	20	0.993(0.403)	1.368 (0.206)	1.520 (0.189)
	50	0.849 (0.425)	1.462 (0.105)	
	100	1.278 (0.421)	1.248 (0.444)	
C1	20	0.078 (0.042)	0.416 (0.004)	1.580 (0.393)
	50	1.333 (0.170)	1.498 (0.150)	
	100	0.800 (0.277)	0.667 (0.197)	
C2	20	9.362 (0.183)	23.518 (1.374)	1.604 (0.059)
	50	22.230 (4.997)	42.943 (3.488)	
	100	42.435 (21.168)	67.660 (31.679)	
C3	20	1.171 (0.402)	1.445 (0.242)	0.791 (0.127)
	50	1.120 (0.059)	2.517 (0.872)	
	100	0.705 (0.117)	1.399 (0.250)	

Where PLA is neat polylactide polymer, and CR, C1, C2, C3 are composites made of PLA and MWR, 1F, 2F and 3F fibres, respectively. Data in brackets represent standard deviations. *Moisture content is defined as the percentage of water present in a material of total weight of the material determined in a standard atmosphere – under a relative humidity of 65 ± 2 % and a temperature of 20 ± 2 °C.

Weight loss is the result of a hydrolytic cleavage of ester bond [205, 206, 207]. According to the weight loss measurements, it could be concluded that fibre reinforcements increased the degradation rate over that of neat PLA. The highest weight loss of PLA, CR, C1 and C3 samples after 5-day enzymatic treatment was observed when using the 50 wt.% enzyme and the results were 1.43 %, 1.46 %, 1.50 % and 2.52 % respectively, while sample C2 showed the highest weight loss of 67.66 % when using the 100 wt.% enzyme. The effect on the biodegradation rate of composites depends on the biodegradability of the other involved components and the nature of their miscibility [200]. Study of Singh et al. [208] showed that the incorporation of MMT

into PLA increased the biodegradation depending on the organic modifier used in the clays. It is most likely that degradation depends on the presence of excess –OH groups in the MMT [207, 208]. Those groups may accelerate the hydrolytic decomposition responsible for higher biodegradation of C2 and C3 samples. Along with that, higher biodegradation of C2 is caused by poor compatibility of PLA matrix and 2F fibre. Additionally, moisture content has a noticable influence on biodegradation. Sample C2 shows weaker mechanical properties in comparison to other composites; therefore, sample C3 seems to be the most successful for biodegradation.

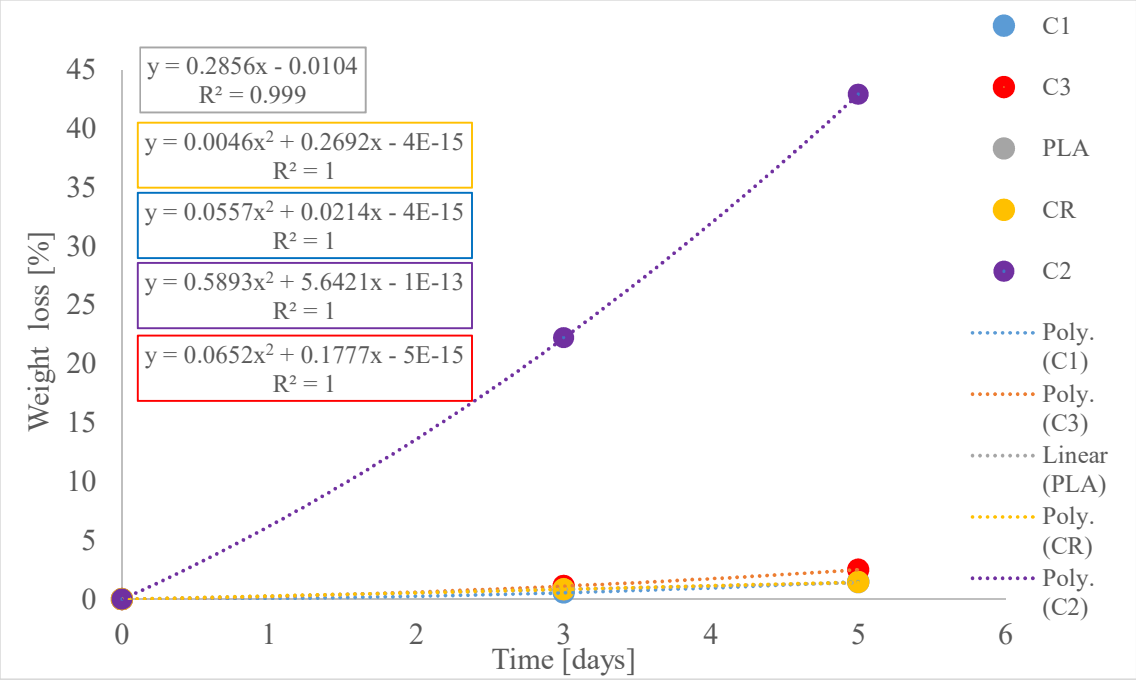

Figure 17: *Linearity and polynomial regression of weight loss/time function for neat PLA and its composites when using 50 % of enzyme Sagvinase 16 L, Where PLA is neat polylactide polymer, and CR, C1, C2, C3 are composites made of PLA and MWR, 1F, 2F and 3F fibres, respectively.*

Figure 17 shows the linearity of PLA sample and polynomial regression of other tested samples regarding their weight loss/time function. All tested samples indicate a direct proportionality in data regarding trendline and R squared. According to prediction results, composite materials CR, C1, C2 and C3 will degrade by minimum of 90 % weight loss within 6 months of biodegradation treatment, more accurately within 114, 40, 8 and 36 days, respectively. PLA showed linear proportionality and it will degrade by minimum of 90 % weight loss within 315 days.

FTIR spectra of samples before and after the enzymatic degradation are presented in Figures 18-22. FTIR spectra of PLA show narrow peak at 1753.5 $cm^{-1,}$ which corresponds to C=O stretching. Peaks at 1180 cm^{-1}, 1129 cm^{-1} and 1082 cm^{-1} are attributed to C-O-C stretching.

Peaks at 957 cm^{-1} and 921 cm^{-1} are attributed to –CH bending and α crystals of polymer, respectively. Its descending intensity presumably corresponds to the presence of an amorphous region. The spectra of enzyme treated PLA spectra show a slight shift in the band characteristic for C=O group to higher wavenumber – from 1753 cm^{-1} to 1755 cm^{-1}, which confirms PLA degradation [208]. Peaks at 2997 cm^{-1} and 2881 cm^{-1} present the asymmetric and symmetric stretching band of –CH from $–CH_3$ groups of the side chains while their bending vibrations could be observed at 1454 cm^{-1}. Peak at 1454 cm^{-1} has also been shifted to higher frequencies, which represents degradation of the sample due to the change in chemical structure during biodegradation. The peak at 2946 cm^{-1} was attributed to the stretching of –CH groups from the main chain of PLA polymer, while its bending vibrations appeared at 1359 cm^{-1} and 1383 cm^{-1}. Splitting peak characterized with two wavenumbers at 1293 cm^{-1} and 1304 cm^{-1} presents the semi crystalline state of PLA [209]. Peaks at 870 cm^{-1} and 755 cm^{-1} are attributed to the rocking vibrations of CH_2 from the amorphous and crystalline phase. The similar behaviour was observed in other tested samples. Figure 19 represents FTIR spectra of composite (CR) made of PLA polymer and reference (fibres without additional modification) SJL fibres before and after the enzymatic degradation. Broad peak at 3304 cm^{-1}, which is characteristic for the – OH groups of cellulose, is visible in the spectra of material before degradation indicating presence of fibres on the sample surface, which might be due to inappropriate wetting of fibres with polymer. Peak at 1505 cm^{-1} (exhibits aromatic ring vibration of lignin from the natural fibres) is visible in the spectra of CR sample before enzymatic degradation and after a 5-day treatment with 20 % enzyme concentration. Degradation of samples was confirmed by shifting peaks from approx. 1754 cm^{-1} to 1756 cm^{-1}. A similar behaviour was observed in other tested samples; therefore ranges from 1750 cm^{-1} to 1755 cm^{-1} and from 1454 cm^{-1} to 1455 cm^{-1}, which were the area of interest. In Figure 9, sample C1 show carbonyl peak shifting from 1753 cm^{-1} to 1755 cm^{-1} and methyl band shifting from 1454 cm^{-1} to 1455 cm^{-1}, confirming PLA degradation. Figures 21 and 22 show FTIR spectra of composites reinforced with MMT treated fibres before and after enzymatic degradation. Higher biodegradation rate of sample C2 is primarily due to its poor fibre/matrix interface and unsatisfactory mechanical properties, while for sample C3, this is due to crosslinking of MMT with polymer and fibre which may lead to an increase of amorphous region, thus increasing the chance for faster degradation rate, since hydrolysis of PLA starts at the amorphous region [210].

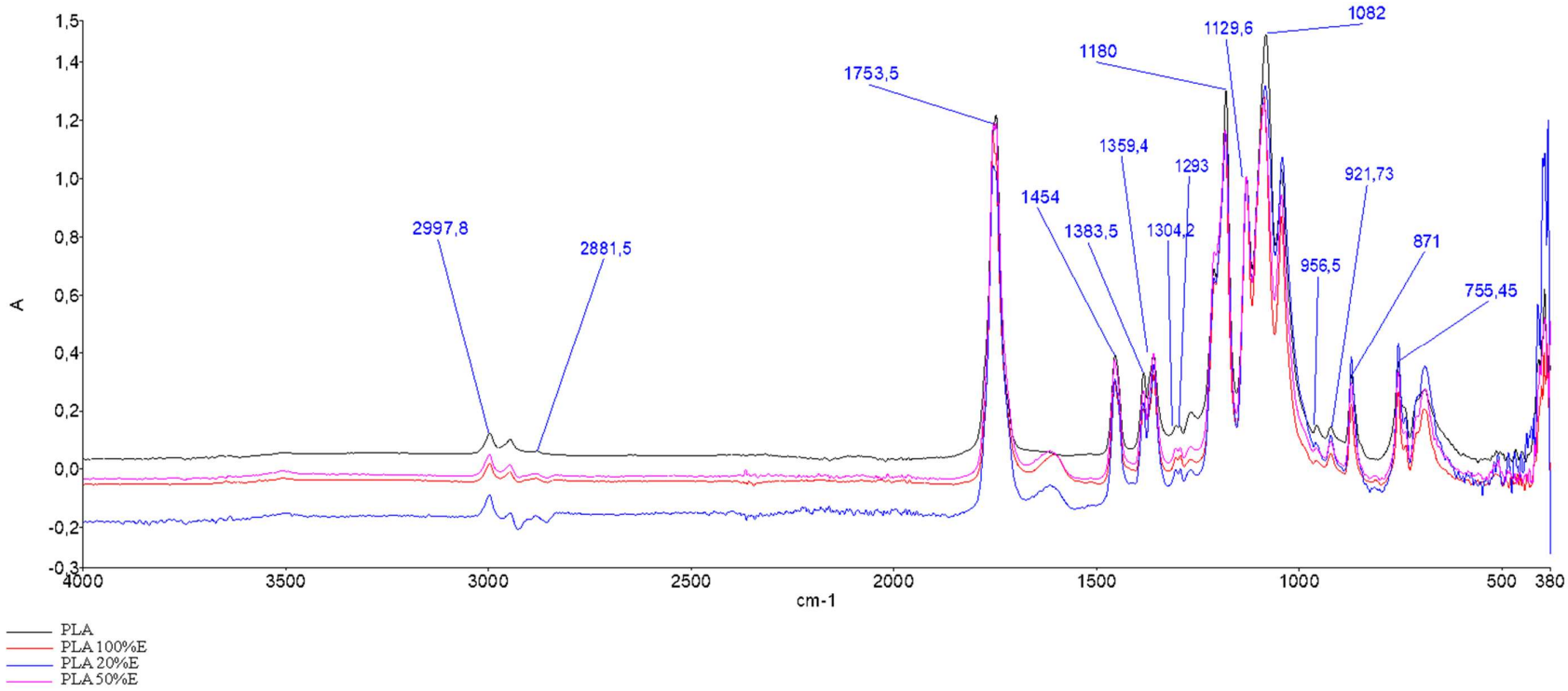

***Figure 18**: FTIR spectra of neat PLA before and after enzymatic degradation with 20 wt.%, 50 wt.% and 100 wt.% Savinase 16 L enzyme during 5-day treatment*

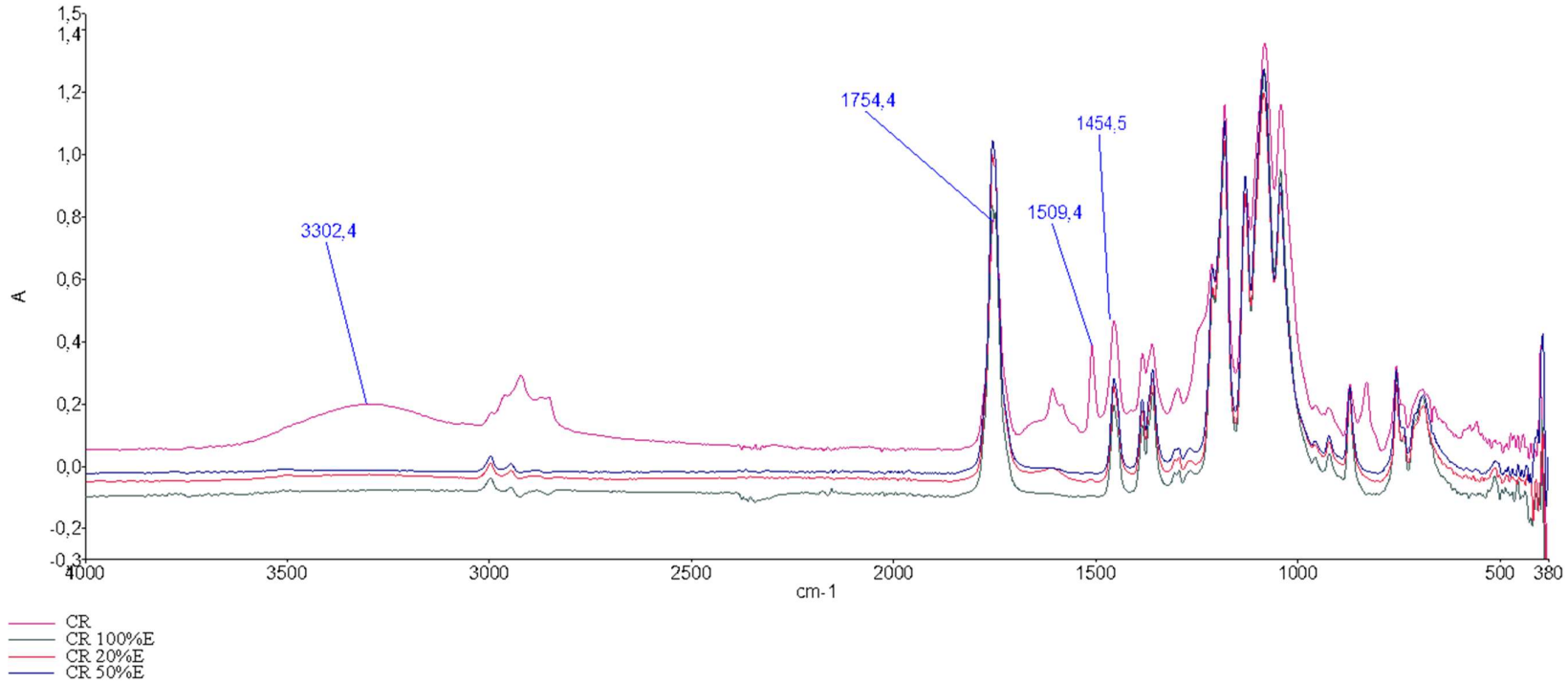

Figure 19: *FTIR spectra of CR composite before and after enzymatic degradation with 20 wt.%, 50 wt.% and 100 wt.% Savinase 16 L enzyme during 5-day treatment*

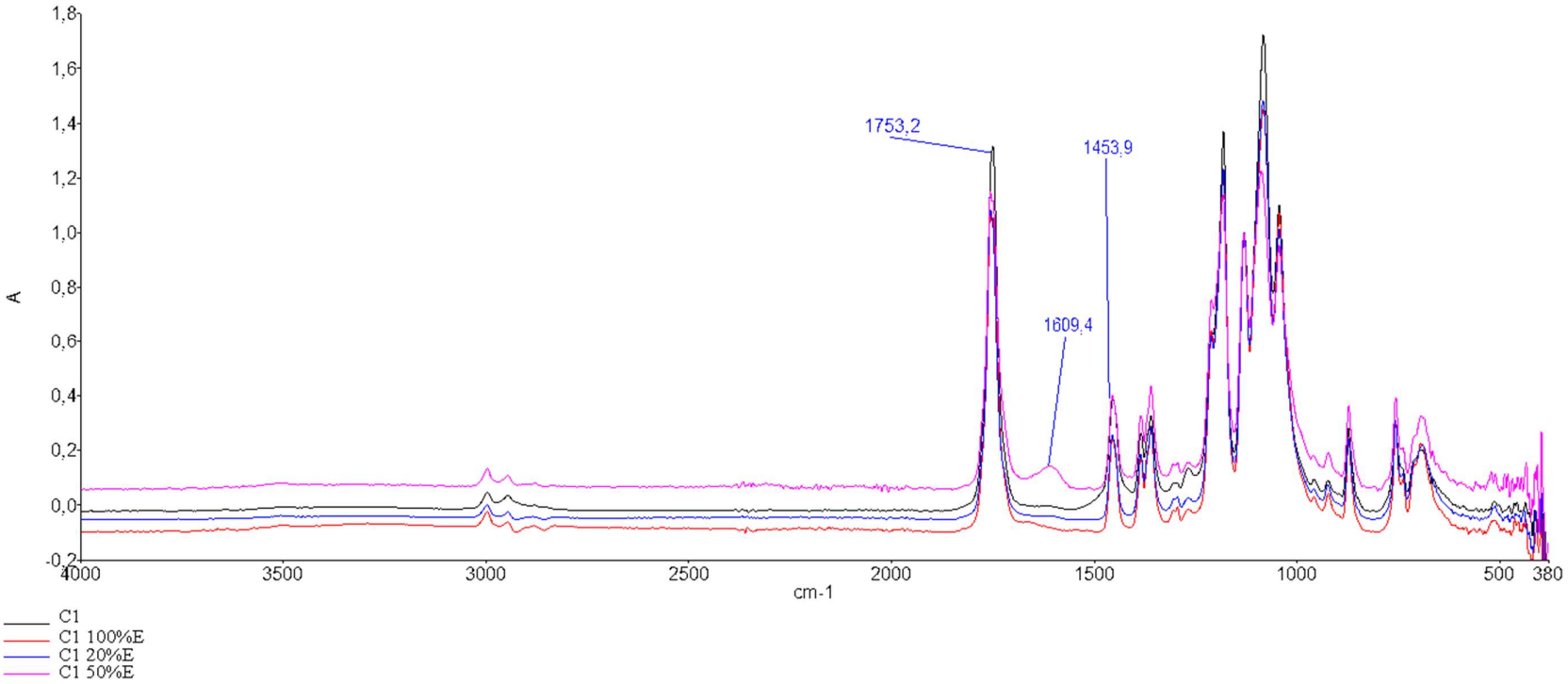

Figure 20: *FTIR spectra of C1 composite before and after enzymatic degradation with 20 wt.%, 50 wt.% and 100 wt.% Savinase 16 L enzyme during 5-day treatment*

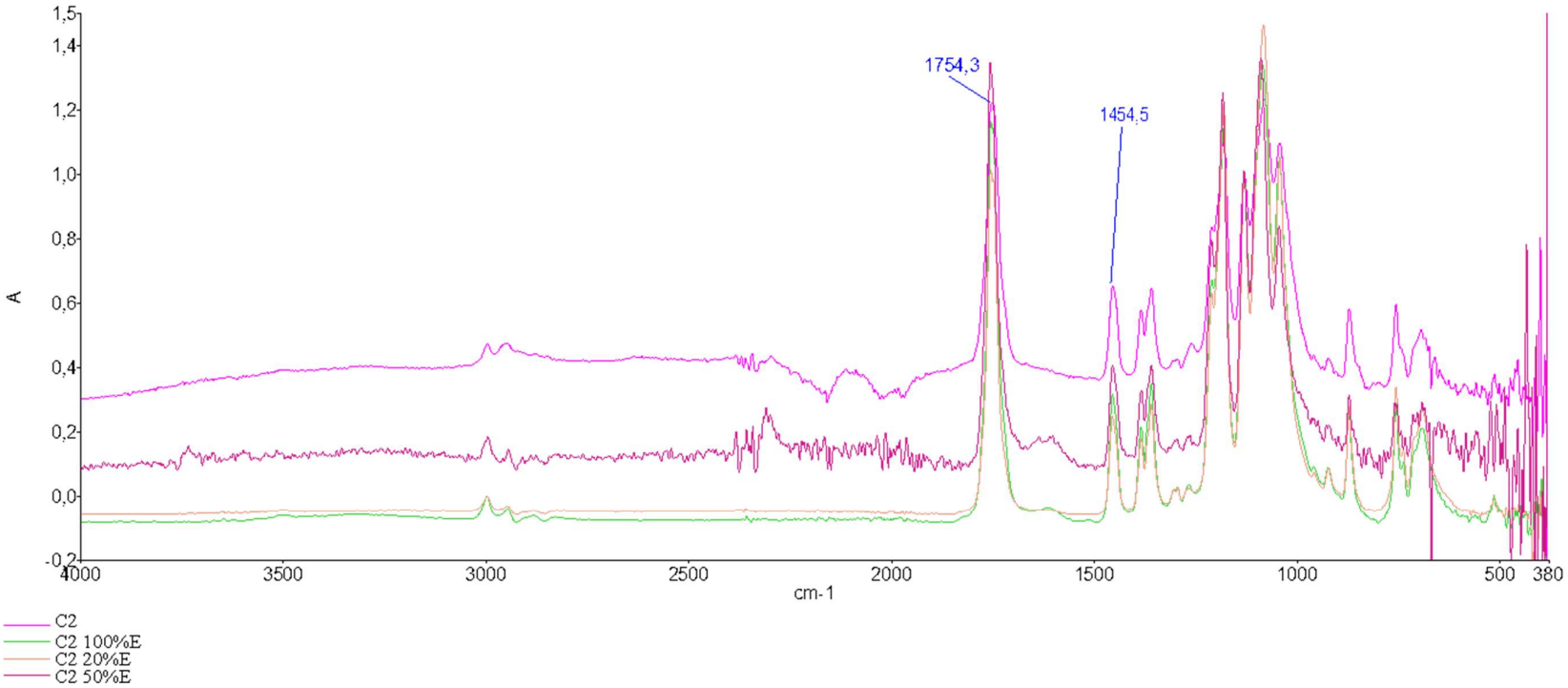

***Figure 21**: FTIR spectra of C2 composite before and after enzymatic degradation with 20 wt.%, 50 wt.% and 100 wt.% Savinase 16 L enzyme during 5-day treatment*

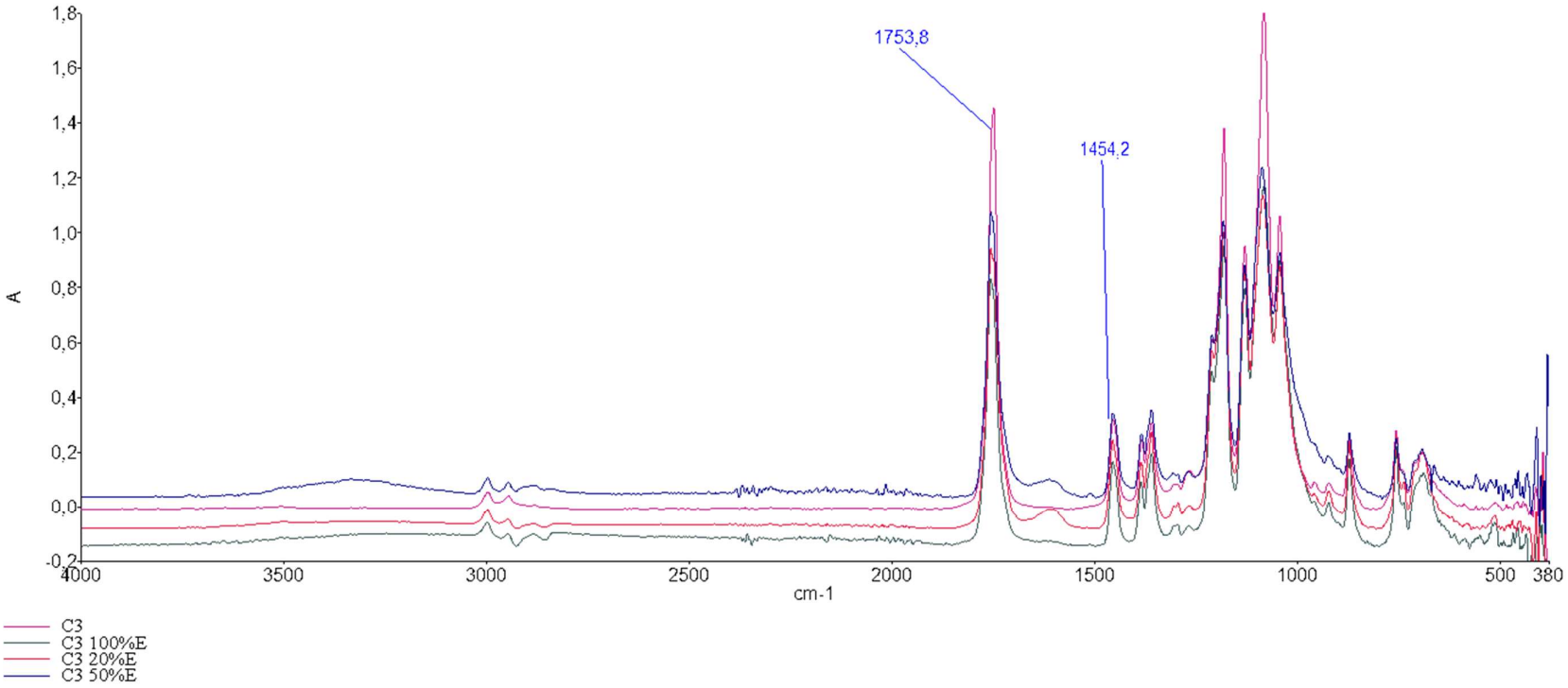

Figure 22: *FTIR spectra of C3 composite before and after enzymatic degradation with 20 wt.%, 50 wt.% and 100 wt.% Savinase 16 L enzyme during 5-day treatment*

Degradation of C2 and C3 is also confirmed by carbonyl shifting from 1752 cm^{-1} to 1756 cm^{-1} and 1753 cm-1 to 1755 cm-1, and methyl peak shifting from 1454 cm^{-1} to 1455 cm^{-1} for both of samples. Additionally, biodegradation in the PLA biocomposites was evaluated by the carbonyl index (C_I). It is expressed with the absorbance intensity ratio between the carbonyl and methyl group [211] and presented in Table 15.

Table 125: *Carbonyl index of PLA and its composites before and after enzymatic degradation with enzyme Savinase 16 L under following conditions: pH 9, 37 °C and during 5-day treatment*

Sample	Wave number cm^{-1} (Carbonyl group)	Wave number cm^{-1} (Methyl group)	C_I
PLA	1753.51	1454.64	3.37
PLA 20%E	1755.00	1454.82	2.75
PLA 50%E	1755.24	1455.41	2.99
PLA 100%E	1755.88	1455.63	3.42
CR	1754.80	1455.39	1.87
CR 20%E	1755.69	1455.46	3.38
CR 50%E	1755.56	1455.45	3.46
CR 100%E	1755.87	1455.58	3.12
C1	1753.30	1454.26	3.31
C1 20%E	1755.65	1455.49	3.52
C1 50%E	1755.70	1455.44	3.37
C1 100%E	1755.54	1455.46	2.91
C2	1752.42	1454.68	3.50
C2 20%E	1755.70	1455.49	3.84
C2 50%E	1756.57	1455.55	3.20
C2 100%E	1755.14	1455.37	4.58
C3	1753.90	1454.49	3.16
C3 20%E	1755.83	1455.40	3.03
C3 50%E	1755.69	1454.74	3.40
C3 100%E	1755.79	1455.41	3.14

Where PLA is neat polylactide polymer, and CR, C1, C2, C3 are composites made of PLA and MWR, 1F, 2F and 3F fibres, respectively; 20%E, 50%E and 100%E is label for material treated with 20 %, 50 % and 100 % of Savinase 16 L enzyme, respectively; C_I is carbonyl index.

The increase in the C_I is attributed to an increase in terminal carboxyl end groups due to enzymatic degradation [212-214]. The best results of weight loss were obtained with the 50 wt.% enzyme, which is also partially confirmed with C_I. Sample C3 showed the highest value of carbonyl index when treated with the 50 wt.% enzyme. The decrease in the C_I of neat PLA confirms utilization of oxidized polymer by microorganisms [215].

Biodegradation reaction depends on the physicochemical properties of the tested material such as molecular weight, chemical composition, crystallinity and surface area, but also on the enzyme properties like its activity, stability, local concentration, amino acid composition and 3-d conformation. Another important condition for satisfying rate of biodegradation is to maintain coresponding and optimal pH and temperature values, since they influence both the properties of the tested material and the enzyme [97, 216].

4.5 Biofuels

Since the most important role of *Spartium junceum* L. crop is its utilization for the bast fibre production, a huge disadvantage is the organic residue left after the fibre extraction, that represents almost 90 wt% of initial stem weight from which fibres were extracted. Nowadays, we are witnessing the rise of biomass energy industry since the European Commission has set a long-term goal to develop a competitive, resource-efficient and low carbon economy by 2050 [217].

Stem residues of SJL plant derived from salty water and microwave maceration were investigated for their potential as raw material for second-generation biofuel production. Examination of its energy properties consisted of determining proximate and ultimate properties of the biomass. The results show low moisture content (6.5 % - 7.5 %), ash content below 5 % and higher values of fixed carbon and volatile matter content of 13.2 % and 75 %, respectively. Higher heating values that were determined (17.2-18.8 MJ/kg, indicate high quality biomass that can be used most effectively in solid biofuel production.

Katović et al. investigated the properties of SJL fibres and their associated residues after various extraction methods – traditional sea water retting and microwave assisted alkali retting [218]. The authors compared chemical composition content of SJL stem before and after the fibre extraction and found that chemical composition of residue after extraction depends on the chosen extraction method. Microwave-assisted alkali treated residues have shown increase in cellulose and lignin content compared to sea water retted residues for approximately 5 % and

14 %. Considering such increase in lignin content and the fact that after MW extraction approx. 90 % of SJL residue remains unused, we realized the need for further investigation of possible usage of SJL residues as feedstock in bioenergy production.

All the samples show significant difference in the non-combustible matter content, except fixed carbon values, which show that the content is not affected by the type of the applied method of fibre extraction. Fixed carbon (FC) represents covalently bonded carbon, whereas higher content of bonded carbon correlates with the higher quality of biomass [219].

Moisture content (MC) is important for the purpose of raw material storage [220]. Residues after microwave-assisted extraction show no significant difference in moisture content compared to samples prior to fibre extraction. It is usually advised to keep the moisture content in biomass within the limits of 10-15 %, since higher moisture content can cause endothermic reaction [221, 222].

Ash is an undesirable component of biomass, considering its catalytic influence on thermal decomposition. Higher ash amount points to higher carbon and gas concentrations. Melting point of biomass ash is low, so during thermal process, melted ash produces slagging, which prevents energy transfer and lowers combustion efficiency [219]. The obtained ash content (AC) of residues after different fibre extraction methods shows no significant difference. Its content is approx. 4.5 %, which is within the expected limits, since SJL belongs to herbaceous and agricultural biomass group that commonly reveals higher ash content than wood biomass, because of different chemical composition and higher mineral share, such as potassium, calcium, magnesium or phosphorus, which are ash-forming elements [23].

The most commonly found macro-elements in biomass are calcium, potassium, magnesium and sodium. Table 16 presents content of such macro elements in SJL residues after fibre extraction. Residues after microwave fibre extraction (MW_R) show lower content of calcium, potassium and magnesium, but higher sodium content compared to SJL residues after fibre extraction in salty water (SW_R). Sample 0_R presents SJL stem before the fibre extraction. Ca and Mg usually increase the ash melting point, while K decreases it. Therefore, the fuel is of better quality if it has a lower proportion of K and Na. Sample MW_R shows the lowest content of potassium and highest Ca/K ratio, which is an indicator of lower slag occurrence, compared to other tested samples. The majority of macro element content values of MW_R sample are in accordance with or slightly vary from the CEN/TS 14961:2005 specification for fuel quality classes. Significant increase in sodium content is due to the exposure of SJL stems to NaCl from salty water and NaOH from alkali and microwave treatment.

Table 16: *Macro elements content in SJL residues after fibre extraction*

Sample	Macro element [g/kg]			
	Ca	K	Mg	Na
0_R	3.6 ± 0.07	13.7 ± 0.15	0.5 ± 0.03	0.2 ± 0.005
SW_R	3.3 ± 0.06	0.7 ± 0.005	2.8 ± 0.04	8.7 ± 0.13
MW_R	3.2 ± 0.04	0.3 ± 0.01	0.5 ± 0.19	9.9 ± 0.06

Where 0_R is SJL stem before fibre extraction, MW_R is SJL residues after microwave fibre extraction, SW_R is SJL residues after fibre extraction in salty water. Results are presented as mean value within 95 % confidence interval.

Coke content is considered a positive property of biomass, since an increase in coke content for residues after the microwave-assisted extraction process can be observed. The proximate analysis of two different biomass samples derived from different extraction methods shows that volatile matter (VM) content is reduced while fixed carbon (FC) increased, pointing to lower concentrations of light hydrocarbons like CO, CO_2, H_2, moisture and tars in the samples which underwent microwave assisted extraction of fibres [220-222].

By increasing carbon and hydrogen content, higher heating value (HHV) also increases because C and H oxidized during combustion by exothermic reactions (formation of CO_2 and H_2O) [223]. The highest heating values were obtained for residues after microwave-assisted fibre extraction, with HHV of 18.16 MJ/kg and related lower heating value (LHV) of 16.69 MJ/kg.

Based on the obtained results of moisture, ash, fixed carbon, coke, volatile matter, nitrogen, sulphur, carbon, hydrogen and oxygen content, as well as the obtained heating values, it can be concluded that the residues after fibre extraction can be further utilized as raw material for solid biofuel production in order to achieve more efficient and sustainable production.

5 CONCLUSION

This thesis gives an insight into research of possible usage of *Spartium junceum* L. plant as a raw material for fibre production and its application as reinforcement in the composite material manufacturing. This thesis has examined the effects of surface functionalization of SJL fibres on the properties of natural fibre reinforced PLA composites, including thermal and mechanical behavior, biodegradability and agro-waste utilization.

- The results of the present work confirm that the extraction process aided by microwave energy can be successfully used to produce fibres, with properties suitable for textile and composite applications inter alia automotive applications. Additionaly, the fibre production time was significantly shortened and the energy consumption was notably lower.
- The surface of SJL fibres was modified by alkali and nanoparticle treatment with the addition of environmentally friendly crosslinkers in order to enhance fibre/polymer interface and to achieve better flame retardancy. The highest cellulose content was observed in SJL fibres modified with nanoclay and citric acid (3F) leading to the production of stronger fibres of improved quality.
- Composite materials reinforced with fibres of optimum quality show tensile strength and modulus improvement by 135 % and 122 %, respectively, as compared to the sample C2. The experimental values of composite tensile strength were compared to the values predicted by the Hirsch model and offer a relatively good correlation, since predicted tensile strength values were about 10 % lower in comparison to experimental ones.
- Biodegradability examination indicates significant biodegradation over 5-day test and 37 °C temperature. Sample C3 show weight loss of 2.5 % after 5-day test with the 50 wt.% enzyme, pointing to high probability of sample degradation by a minimum of 90 % of its weight/volume within period of 35 days.
- SJL residues after fibre extraction proved to be good quality biomass for solid biofuel production based on the obtained results of moisture, ash, fixed carbon, coke, volatile matter, nitrogen, sulphur, carbon, hydrogen and oxygen content, as well as the obtained heating values, in order to achieve more efficient and sustainable production.
- Poverty reduction through the revitalization of SJL fibres would be a tangible outcome of the production of feedstock and the development of bioproducts.

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7 ANNEX

7.1 Comparison of Spanish Broom (*Spartium junceum* L.) and flax (*Linum usitatissimum*) fibre - Textile Research Journal 82 (2012) 17, p. 1786-1798 – *reused with permission from publisher*

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Comparison of Spanish broom (*Spartium junceum* L.) and flax (*Linum usitatissimum*) fibre

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Abstract

After a long break, Spanish broom gained interest as a natural, sustainable and renewable fibre for textile and technical applications. This paper describes the characterization of Spanish broom fibres (*Spartium junceum* L.) in comparison to the flax fibres (*Linum usitatissimum*). Spanish broom fibres were obtained by two different methods of maceration and some of the most significant chemical and physical properties of tested fibres are reported. Scanning electron microscopy has proven to be a useful tool for the determination of morphological characteristics of elementary and technical fibres. Other physical-chemical properties of fibres were determined by infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), fineness and tensile strength methods.

Keywords

Flax fibres, FT-IR, morphological analysis, SEM, Spanish broom fibres, *Spartium junceum* L., TGA

Introduction

The rapidly increasing environmental awareness and growing global waste problem affected the development concepts of sustainability and renewable materials. Over the last ten years, the real revolution in bast fibre production technology started. Although, bast fibres have been grown for centuries throughout the world, their production is much higher nowadays in order to meet the demands of the global market and to produce recyclable, renewable, 'green' products. Some of the most used bast plants are: flax, hemp, kenaf, ramie, jute, etc.[1,2] Whilst flax and hemp have mostly been used as textile raw material of cellulosic origin in the plains,[3] in coastal areas of the Mediterranean, wild Spanish broom (Figure 1) has been used as the textile raw material since ancient times.[4–6]

The habitat of Spanish broom is the Mediterranean area of south Europe, south-west Asia and north-west Africa.[7,8] It grows in coastal areas with rugged soil and clean air, and as such it is not exposed to pesticides like the cotton is. It is a shrub-like plant from the family of legumes and the only species in the genus *Spartium*. Spanish broom grows 1–1.5 m tall and the only old examples grow into smaller trees of 4–5 m tall and 15–20 cm thick. Spanish broom produces intensively yellow flowers between May and July, and its legumes mature between August and October. Its roots are deep and it binds the soil quite well. As a legume plant, it uses symbiosis to bind atmospheric nitrogen in the roots' lumps, thickening and enriching the soil.[9]

A production of Spanish broom fibres already existed in Mediterranean countries, but because of high production costs, caused by the conventional maceration method, it has been abandoned now – except in Italy and Romania. Since the general production of Spanish broom fibres is negligible nowadays, accurate statistical data of the theoretical amount of Spanish broom fibres are not available.[10]

The fibre yield of wild Spanish broom plant is approximately 5% according to our experiments while

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Figure 1. Spanish broom (*Spartium junceum* L.).

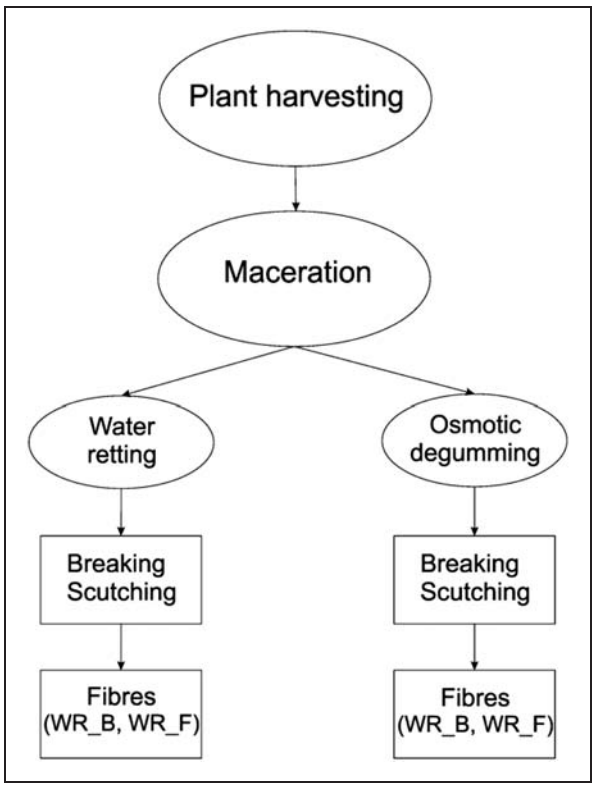

Figure 2. Fibre processing scheme: WR_B – Spanish broom fibres (B) obtained by water retting maceration method (WR); WR_F – flax fibres (F) obtained by water retting maceration method (WR); OD_B – Spanish broom fibres (B) obtained by osmotic degumming maceration method (OD); OD_F – flax fibres (F) obtained by osmotic degumming maceration method (OD).

the fibre yield of the cultivated flax plant is 20–25%. In general, fibre yield depends on the pretreatment process known as maceration or degumming, as well as on the plant cultivar and plant maturity.

Maceration of natural fibres can be easily described as the separation of fibre from the woody part of the plant and the removal of its non-cellulosic components such as pectin, hemicellulose, lignin, waxes and fats.[13–15]

Some maceration methods e.g. DeCoDe process[9,14] have shown better results in fibre yield, but in this paper the most common maceration method of water retting was used, as well as osmotic degumming of the flax.

With maceration, it is possible to obtain fibres of very good quality, which were used for the ropes, baskets, mats, etc., in ancient times. Today these fibres are increasingly used in biocomposite materials, especially for the automotive industry.[16] The most recent papers of our research group[6–9,15] try to draw the attention to this promising area of application. The purpose of this research is to answer the question of whether the quality of Spanish broom is comparable to flax.

Experimental

Materials

Polish flax cultivar Modran (collected in Poland) and Spanish broom (picked in the area of town Šibenik, Croatia) were used in the study. The extraction of fibres was conducted at the INFMP (Institute for Natural Fibres and Medicinal Plants, Poland). Prior to the testing, fibres were obtained from the plant through a maceration process (Figure 2).[17] Two maceration methods were applied: water retting and osmotic degumming.

In this study, technical fibres were characterized, except within the SEM analysis where both the elementary and technical fibres were used.

Methods

Water retting. Samples were placed in a tank with water heated to a temperature of 30.6–33°C. The Spanish broom was retted in a tank for 20 days (480 h) and flax for 3 days (72 h). After retting, the plants were passed through a mechanical process (breaking, scutching), after which fibres were obtained.

Osmotic degumming. Samples (Spanish broom and flax) were placed in a 2000 mL glass gauge filled with warm

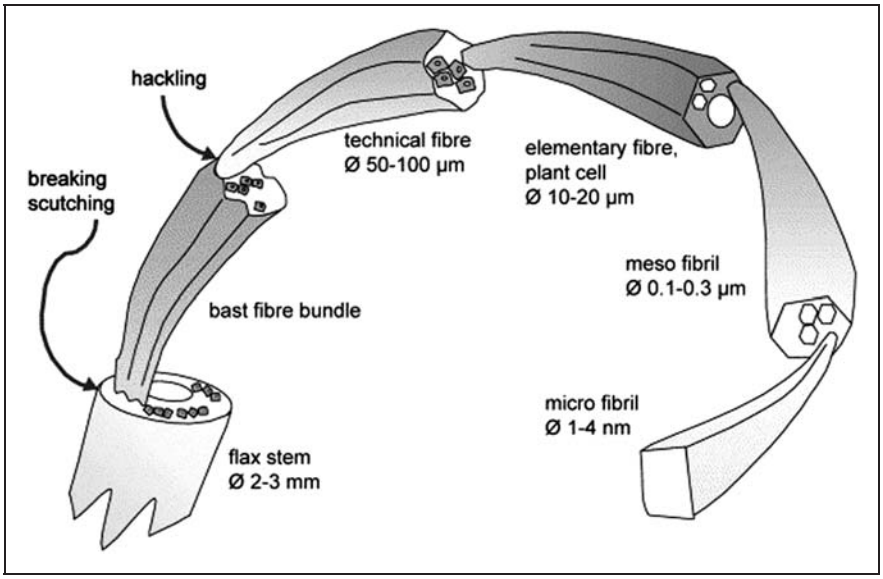

Figure 3. Architecture of bast fibres: from stem to the fibrils.

water and placed in a tank full of water heated to a temperature of 30°C. One end of the rubber hose was immersed in the glass gauge and the second end was immersed in a small plastic container. This method of maceration uses natural physical laws such as water diffusion, osmosis and osmotic pressure.[17,18] Osmotic degumming of the Spanish broom plant lasted 28 days (672 h) and for flax 3 days (72 h), after which fibres were obtained by mechanical processes (breaking and scutching).

Physical properties

SEM and optical microscopy. Surface morphological analysis of the Spanish broom fibres was carried out using a field emission scanning electron microscope, Mira, Tescan. Samples were previously coated with gold/palladium in a sputter coater.

Cross-sectional optical micrographs of both plants with a magnification of 20× were conducted with Nikon Elipse E 400 microscope.

Fineness, strength and elongation. Breaking tenacity and fineness of individual fibres were examined using the Vibroscope 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 ± 2%). An average of 250 tests for fibres was used in the study.

Moisture regain. The moisture regain of the fibres was determined according to ASTM standard method 2654 using standard conditions for 24 h. Moisture sorption was calculated as a weight percentage of absolute dry material.

Fourier transform infrared (FT-IR) spectra. Infrared spectroscopy (FT-IR) spectra were obtained with a Perkin Elmer Spectrum 100 FT-IR spectrometer using ATR (attenuated total-reflection) method. All spectra were registered from 4000 cm^{-1} to 380 cm^{-1}, with a resolution of 4 cm^{-1} and 100 scans. The background was collected at the beginning of the measurement. In order to normalize the infrared spectra obtained, we used the 1314 cm^{-1} band, assigned to CH_2 rocking vibrations.

Thermal analysis

Thermogravimetry (TG). A Perkin Elmer Pyris 1 thermogravimetric analyzer was used for determination of thermal degradation on Spanish broom fibres. The samples were crushed into small pieces before testing. The weights ranged from 7 mg to 10 mg. The samples were heated from 30°C to 800°C at the heating rate of 10°C/min in a nitrogen flow of 30 mL/min. Two parallel probes for each sample were made to achieve more accurate results.

Results and discussion

Maceration methods

Spanish broom fibres need more time for the maceration treatment. The main cause lies in the tougher stem of Spanish broom compared to the flax.

The main issue that has to be solved is to find a better and quicker maceration process. Preliminary experiments have already been performed.[9]

SEM and optical microscopy

Scanning electron micrograph. Spanish broom and flax fibres are technical fibres, both consisting of a number of elementary fibres held together by pectinous gums.

A schematic structure of the flax and Spanish broom fibres, from stem to microfibril, is given in Figure 3.[19] Technical fibres are isolated from the stem by the maceration process and by mechanical decortication (breaking, scutching, etc.).

The width of the elementary fibre of Spanish broom, as shown in Figure 4(a), is similar to the width of flax elementary fibre, shown in Figure 4(b).

The cross-section of both fibres indicates the presence of a thick secondary cell wall (e.g. 7.32 μm for Spanish broom and 5.41 μm for flax), as shown in Figure 5.

The secondary cell wall is of extreme importance because of its influence on the fibre properties while its cellulose-rich fibre structure influences higher tensile strength.[20,21]

Each elementary fibre can be considered as a network of ultrafine cellulose fibrils embedded in a matrix of hemicelluloses and lignin.[22] Both of the fibres have fibre nodes and kink bands that appear as horizontal bands in the elementary fibres and bundles, by which they are easily recognized. These dislocations are regions where moisture and various chemicals can penetrate and influence fibre properties. They also represent weak points in the fibres which can be seen after breaking tests.[22–24] The surface of tested fibres is

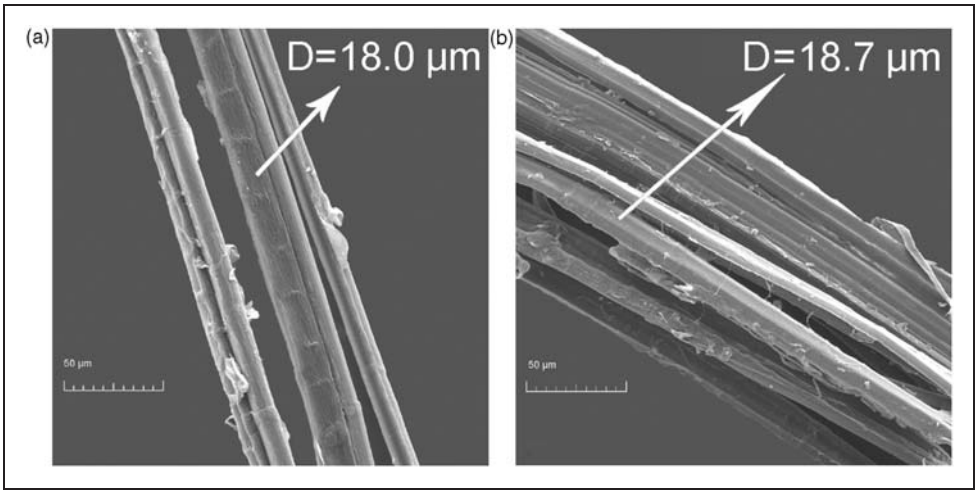

Figure 4. Longitudinal SEM image of (a) Spanish broom fibre, (b) flax – elementary fibre as part of the technical fibre.

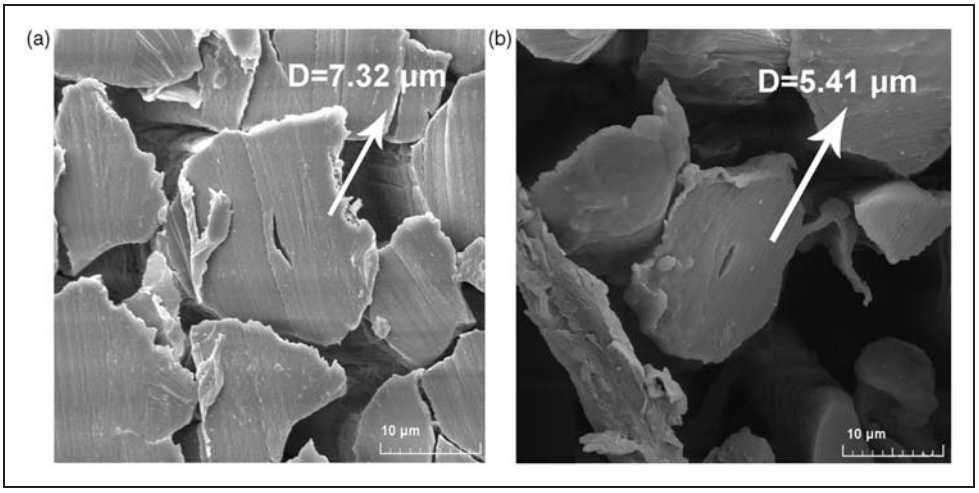

Figure 5. Cross-section SEM image of (a) Spanish broom, (b) flax – elementary fibre.

slightly irregular, which is caused by the maceration method. In general, addition of NaOH is recommended during the maceration process, enabling more suitable fibre surface of samples used for the SEM analysis.

Optical micrograph. Bast fibres are produced in the outer regions of the stem. The fibres exist in bundles of elementary fibres in a ring encircling the core tissues. About 40–70 bundles are in cross-sections of Spanish broom stems, while 20–50 bundles are in cross-sections of flax stems, with 10–40 elementary fibres per cross-section of single bundle for both plants. Oval-shaped bundles in flax stems indicate high quality fibre (Figure 6(b); 2), while the Spanish broom plant has irregularly shaped bundles that indicate poor quality (Figure 6(a); 2).

Despite of that, Spanish broom has a polygonal cross-sectional shape of elementary fibres, as well as thick cell walls (Figure 5.) and the possibility to provide better quality fibres (better light reflection and absorption).[20,23–25]

Fineness, strength and elongation

Figures 6 and 7 represent the graphical review of chi-square test which is non-parametrical method for data analyzing. Deviation of the normal distribution can be assessed by the mentioned analyzing method. This test was applied for fineness measurements.[23,24,28,29]

The technical fibres obtained by osmotic degumming behave in a normal distribution, as shown in Figures 7(a) and 7(b), which means that empirical values are pretty similar to theoretical values ($p \geq 0.05$; the p-value is the number that represents the probability of obtaining a test statistic). The most common fineness of the Spanish broom technical fibres is in the category from 40 dtex to 45 dtex (18% of

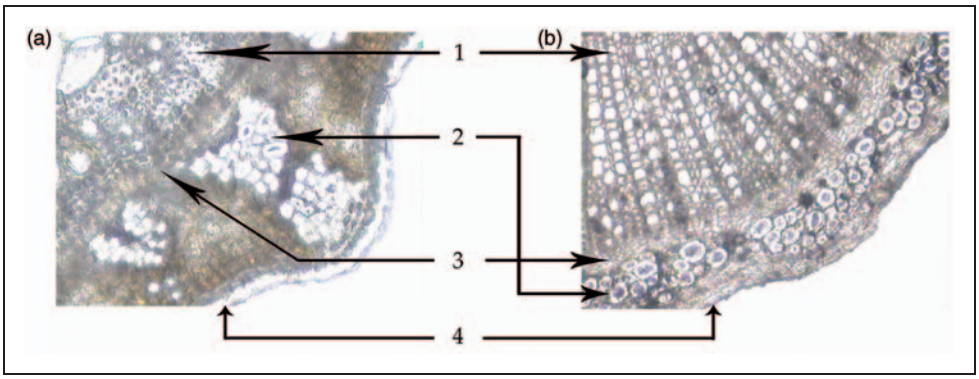

Figure 6. Cross-section of Spanish broom (a) and flax (b) plant: 1, xylem; 2, sclerenchyma (bast fibres); 3, phloem; 4, epidermis.

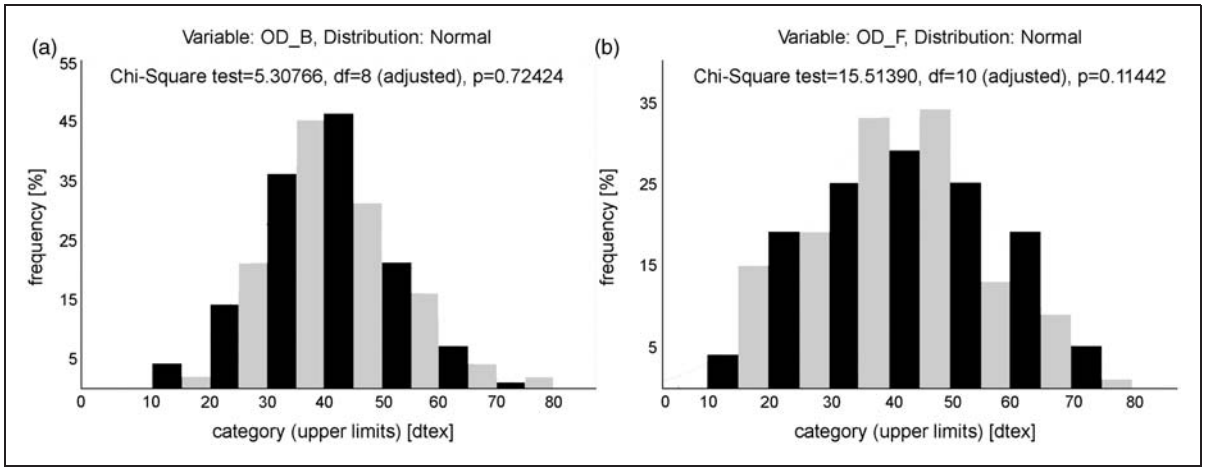

Figure 7. Frequency of fineness in 250 measurements of (a) Spanish broom fibres (B) obtained by osmotic degumming (OD), (b) flax fibres (F) obtained by osmotic degumming (OD).

all fibres) while for the flax fibres that category is from 45 dtex to 50 dtex (14%).

Technical fibre fineness depends on the shape and length of elementary fibres, their number in the fibre bundle to be measured and the processing method.[29] Our results clearly support this statement. Upon the treatment of osmotic degumming the mean results of Spanish broom and flax fibres fineness are within the range 40.97 dtex (Spanish broom) to 41.83 dtex (flax) causing higher quality in comparison to water retting.

Technical fibres obtained by water retting as shown in Figures 8(a) and 8(b) are coarser. The most common fineness is in the category from 30 dtex to 35 dtex (16%) for Spanish broom and 35 dtex to 40 dtex (12%) for flax fibres. The average value for fineness is 41.17 dtex for Spanish broom and 47.83 dtex for flax fibres. The decreased fineness value of the fibre after osmotic degumming is attributed to the cellulose molecules in the fibre that are loosely held after lignin removal.

The stress-strain curves for the Spanish broom and flax fibres are shown in Figures 9 and 10. Elongation at break of the fibres is the elongation of a test specimen produced by the breaking force, expressed as a percentage of the initial gauge length.[23,29,30] Breaking elongation of the Spanish broom fibres obtained by the osmotic degumming method of maceration (5.0%) is

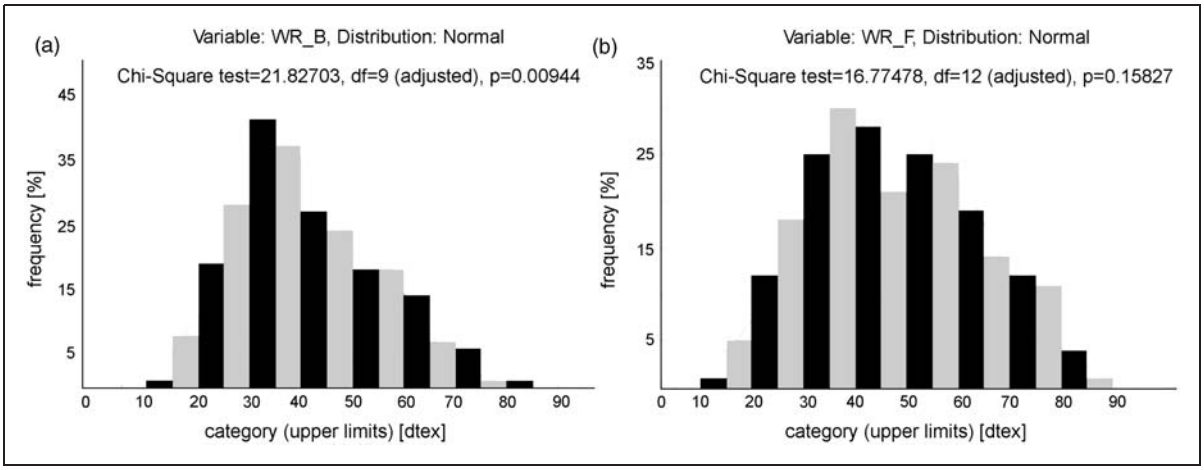

Figure 8. Frequency of fineness in 250 measurements of (a) Spanish broom fibres (B) obtained by water retting (WR), (b) flax fibres (F) obtained by water retting (WR).

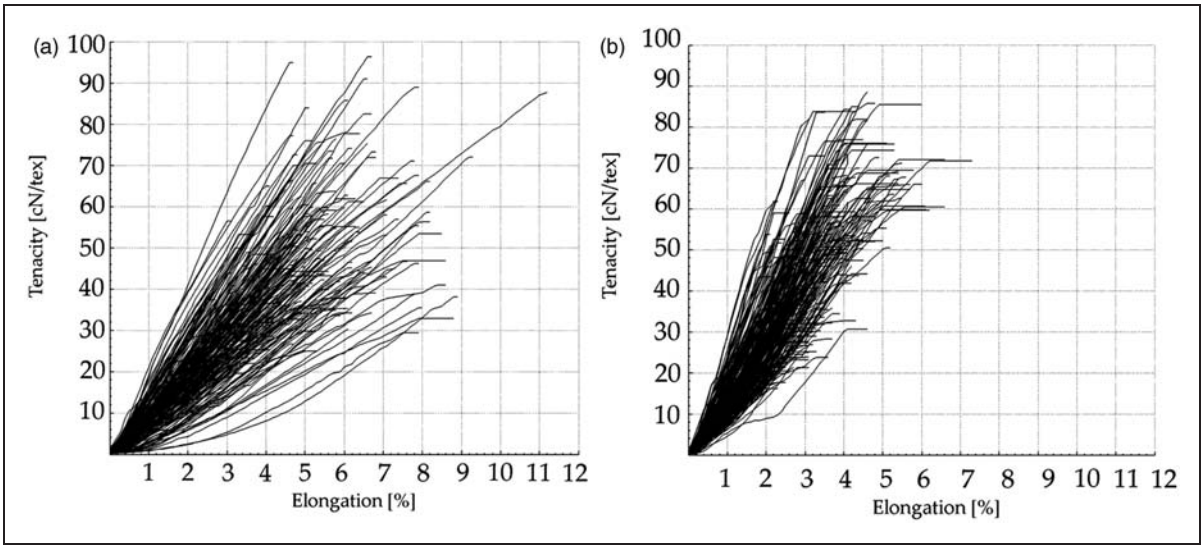

Figure 9. Stress-strain curves for (a) Spanish broom fibres (B) obtained by osmotic degumming (OD), (b) flax fibres (F) obtained by osmotic degumming (OD).

higher than elongation of the other tested fibres, implying the decreased toughness of the Spanish broom fibres is obtained by osmotic degumming. The mean value for the breaking elongation of the fibres varied among tested fibres from 3.6% to 5.0% in the osmotic degumming method of maceration, and 3.5% to 3.6% in the water retting method of maceration. Flax fibres exhibited better uniformity of breaking elongation as shown in Figures 9(b) and 10(b), which is also evident from variation coefficient. Flax fibres show a coefficient of 28.14% after the water retting and 30.01% after the osmotic degumming while Spanish broom has a coefficient of variation of 31.01% and 32.75%, respectively. One of the reasons causing the higher coefficient of variation of Spanish broom fibres compared to flax, is the choice of the conventional maceration method.[9]

Factorial analysis ANOVA was used during the result processing after the breaking tenacity determination as given in Table 1.[23,24,28,29] According to the *p*-value, a significant difference is established between the breaking tenacity of the tested fibres considering the type of plant and applied method of maceration.

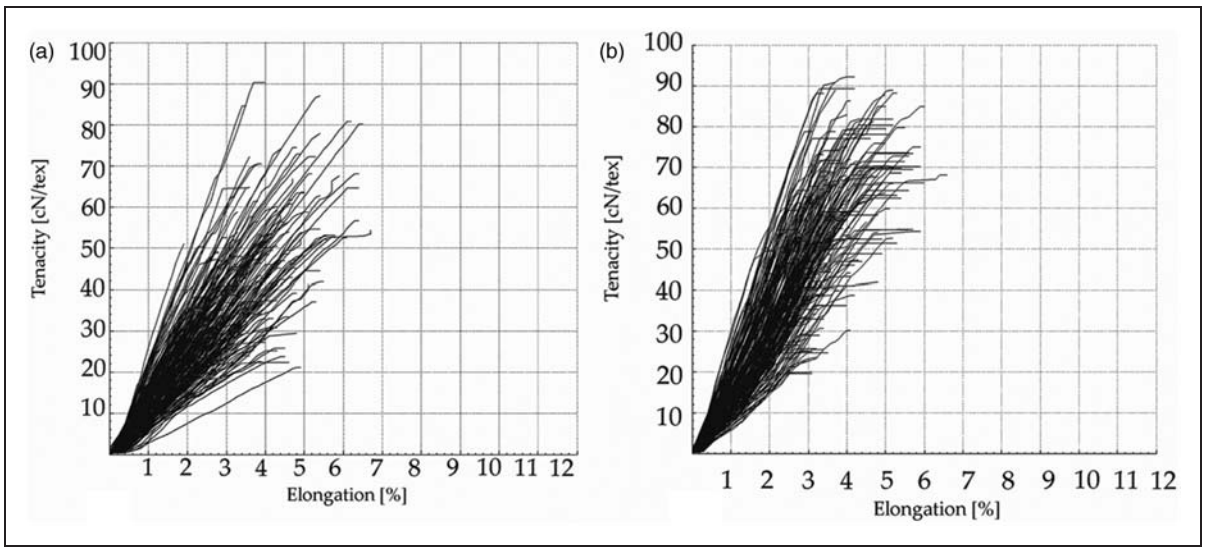

Figure 10. Stress-strain curves for (a) Spanish broom fibres (B) obtained by water retting (WR), (b) flax fibres (F) obtained by water retting (WR).

Table 1. ANOVA test of significance for Spanish broom and flax fibres tenacity

Effect	Univariate tests of significance for tenacity (cN/tex) sigma-restricted parameterization				
	Effective hypothesis decomposition				
	SS[d]	Df[e]	MS[f]	F[g]	P[h]
Intercept	2225691	1	2225691	8254.684	0.000000
WR_OD[a]	47	1	47	0.175	**0.675867**
Plant[b]	13987	1	13987	51.874	0.000000
WR_OD*Plant[c]	6551	1	6551	24.297	0.000001
Error	268549	996	270		

[a]Maceration methods (WR-water retting; OD-osmotic degumming).
[b]Plant (Spanish broom or flax).
[c]Maceration method and plant species together.
[d]Sum of squares.
[e]Degrees of freedom.
[f]Mean square.
[g]Empirical F ratio (MS between groups/MS within groups).
[h]*P*-value (If $p \geq 0.05$ there is no statistically significant difference between the arithmetic mean of the samples).

Since $p \geq 0.05$ it can be concluded that the maceration method has no significant influence on tenacity as shown in Figure 11.

Figure 11 shows that there are no significant differences in the tenacity of selected fibres. Error bars in the graph refer to relative standard deviation (coefficient of variation). Coefficient of variation is within the usual range of the natural fibres. Osmotic degumming created slightly better results in the case of the Spanish broom (B) treatment in comparison with the water retting (WR) method.

Moisture regain

Bast fibre water interaction can be explained as a competition of hydrogen-bond formation between hydroxyl groups of the polymer (mainly cellulose) and between the polymer and a water molecule or a water cluster. The water penetrates inside the fibre in the form of vapour or water in liquid state. It breaks the secondary interactions between cellulose macromolecules and is adsorbed into the fibre by hydrogen bonds, which causes a swelling of the fibres.[31–33] Free hydroxyl groups at the fibre amorphous regions and at crystallites' surfaces are responsible for the moisture sorption. The sorption of water vapour starts with the formation of a monolayer, where one molecule of water is bonded to each accessible hydroxyl group and continues with the formation of a multilayer of progressively increasing thickness. Therefore, moisture sorption values yield information on the extent of areas accessible to water vapour within a fibre. Changes in moisture sorption of fibres reflect changes in chemical composition, crystallinity and in pore structure.[34]

The moisture regains of the tested fibres were in the range 7.14% to 7.82% as given in Table 2. Flax fibres have a little higher moisture regain which is probably due to the difference in the composition of the fibres. The osmotic degumming method of maceration increased the moisture sorption of tested fibres which is due to the lignin removal.

FT-IR spectra

Figures 12(a) and 12(b) show the IR spectra of Spanish broom and flax fibre obtained by different methods of maceration.

Bast fibres are usually characterized by several absorption bands (Table 3): one from 3000 cm^{-1} to 3700 cm^{-1} that represents free OH groups and intra- and intermolecular hydrogen bonds, and two narrower bands at 2850 cm^{-1} and 2917 cm^{-1}–2919 cm^{-1} which

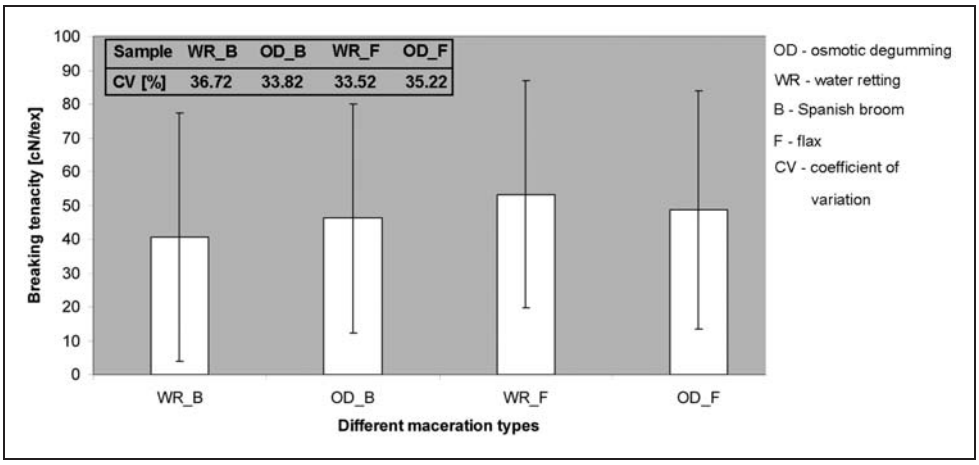

Figure 11. Mean value of breaking tenacity for different maceration types.

Table 2. Moisture regain of tested fibres under 65% of relative humidity

	OD_B	OD_F	WR_B	WR_F
Sample description	Spanish broom fibres obtained by osmotic degumming	Flax fibres obtained by osmotic degumming	Spanish broom fibres obtained by water retting	Flax fibres obtained by water retting
Moisture regain (%)	7.47	7.82	7.14	7.63

are attributed to the CH_2 and CH groups of pectin, fats and waxes.[35,36,37]

Pectins are characterized by several bands: 1731 cm^{-1}–1734 cm^{-1} is characteristic of the free COOH groups of polygalacturonic acid, and those at 1426 cm^{-1} and 1615 cm^{-1} are of symmetrical and asymmetrical oscillations of ionized carboxyl groups respectively.[30,38,39]

Absorption bands at 1731 cm^{-1}–1734 cm^{-1}, 2917 cm^{-1}–2919 cm^{-1} and 2850 cm^{-1} can be observed

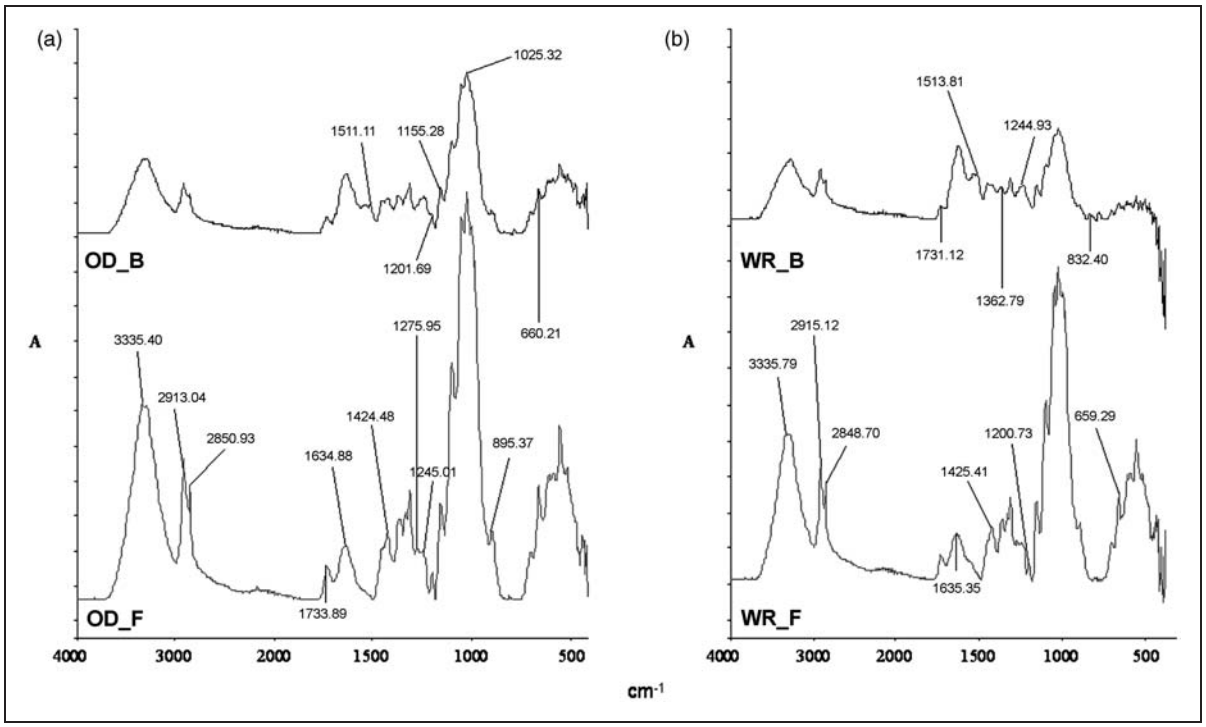

Figure 12. (a) FT-IR spectra of Spanish broom (B) and flax (F) fibres obtained by osmotic degumming (OD), (b) FT-IR spectra of Spanish broom (B) and flax (F) fibres obtained by water retting (WR).

Table 3. Main infrared transition for Spanish broom and flax fibres

Wavenumber (cm^{-1})	Vibration	Sources
3200–3400	OH stretching	Cellulose, hemicellulose
2917–2919, 2850	C–H symmetrical stretching	Cellulose, hemicellulose
1731–1734	C = O stretching vibration	Pectin, waxes
1635	OH bending of absorbed water	Water
1515	C = C aromatic symmetrical stretching	Lignin
1426	HCH and OCH in-plane bending vibration	Cellulose
1368	In-the -plane CH bending	Cellulose, hemicellulose
1313	CH_2 rocking vibration	Cellulose
1241–1245	C = O and G ring stretching	Lignin
1202	C–O–C symmetric stretching	Cellulose, hemicellulose
1155	C–O–C asymmetrical stretching	Cellulose, hemicellulose
1047,1025,1000	C–C, C–OH, C–H ring and side group vibrations	Cellulose, hemicellulose
895	COC, CCO and CCH deformation and stretching	Cellulose
660	C–OH out-of-plane bending	Cellulose

Table 4. Index of crystallinity for tested fibres

	OD_B	OD_F	WR_B	WR_F
Sample description	Spanish broom fibres obtained by osmotic degumming	Flax fibres obtained by osmotic degumming	Spanish broom fibres obtained by water retting	Flax fibres obtained by water retting
Index of crystallinity (I_c)	0.77	0.57	0.68	0.52

in the spectra of all fibres, but they are less intensive in the Spanish broom spectra pointing to the minor amount of pectins, fats or waxes. It should be noted that CH_2 and CH groups of the fats and waxes could also contribute to the same bands.

According to the literature,[37] lignin is characterized by absorption bands at $1600\,cm^{-1}$, $1515\,cm^{-1}$, $1241\,cm^{-1}$–$1245\,cm^{-1}$ and $820\,cm^{-1}$–$850\,cm^{-1}$. Peaks at $1515\,cm^{-1}$ and $1241\,cm^{-1}$–$1245\,cm^{-1}$ can be seen in the spectra of the Spanish broom and only as the shoulder in the spectra of flax. In the area of $1600\,cm^{-1}$, no clear band was observed, nor at $820\,cm^{-1}$–$850\,cm^{-1}$, which suggests that there is still a certain amount of fats and pectins in the fibres. Removing fats and pectins leads to the decrease in intensity of peaks at $2850\,cm^{-1}$ and $2917\,cm^{-1}$–$2919\,cm^{-1}$ and probably to a more symmetrical band at $2917\,cm^{-1}$–$2919\,cm^{-1}$, which is related to cellulose.

In this case it was impossible to remove all pectins because they are present not only in the wall of elementary fibres, but also in the interfibre bands, so consequently a more intensive treatment of fibres is required to obtain total pectin removal.

IR spectroscopy is very helpful in the determination of the index of crystallinity (I_c) of cellulose.[25,36,37] The index is determined as a ratio of intensities of absorption bands at $1368\,cm^{-1}$ and $2917\,cm^{-1}$.

$$I_c = I_{1368}/I_{2917} \quad (1)$$

Table 4. presents the index of crystallinity for tested fibres that were calculated using IR spectra and equation 1.

According to the data presented in Table 4. the crystallinity index of fibres is decreased after the water retting maceration method which indicates that the cellulose crystals are better oriented after osmotic degumming.[36,37,40,41] Results clearly indicate that the cellulose crystals are better oriented in Spanish broom fibres.

The percentage of crystallinity of Spanish broom and flax fibres is also influenced by the moisture in the sample, and fibres with higher moisture contents, as given in Table 2, have been reported to have a lower percentage of crystallinity. The lower percentage of crystallinity of the tested fibres is caused by the lower amounts of lignin and hemicellulose.

TG analysis

Thermogravimetry is one of the most widely used techniques to monitor the composition and structural dependence on the thermal degradation of natural cellulose fibre. Lignocellulosic fibres are constituted by three main components: hemicellulose (20–40%), cellulose (40–60%) and lignin (10–25%), and known as a very complex structure. These components are not thermally stable and tend to degrade at an early stage of heating. Further processing of a composite requires thermal stability information for materials selection and process operation.[42,43]

The thermogravimetric analyses of fibres show distinct processes of weight loss occurring at different temperatures.[44] The first process of weight loss of the Spanish broom and flax fibres is attributed to the thermal degradation of pectin, lignin and hemicellulose. The next weight loss is associated to decomposition of the α-cellulose present in the fibres. The thermogravimetric analysis (TG) of the fibres in nitrogen atmosphere is shown in Figure 13. The TG measurement gives information about the composition and thermal stability of fibres.[40] The curves can be divided into three different regions. For the temperature below 200°C (i.e. the first stage), the slight decay of the weight is attributed to water loss in the form of absorbed moisture.[45] In this stage, the weight loss of the tested material is less than 10%. The onset of degradation temperatures for tested fibres for the second stage of degradation in N_2 were around 200°C. This implies that the fibres are quite stable up to 200°C, in nitrogen. When the temperature is between 200°C and 400°C (the second stage), a significant loss of weight is observed, stemming from the thermal decomposition of hemicellulose, cellulose and lignin. In this stage, the weight of the tested materials has been reduced from 65% to 85%. When the temperature is higher than 400°C (third stage), the weight loss is not as significant as the previous period (ca. 12%), mainly as a consequence of thermal decomposition of other heavy components.[46] In this stage, it can be seen that fibres after water retting still show a certain percentage of residue (~10%) due to charring at 800°C, while fibres obtained by the osmotic degumming method of

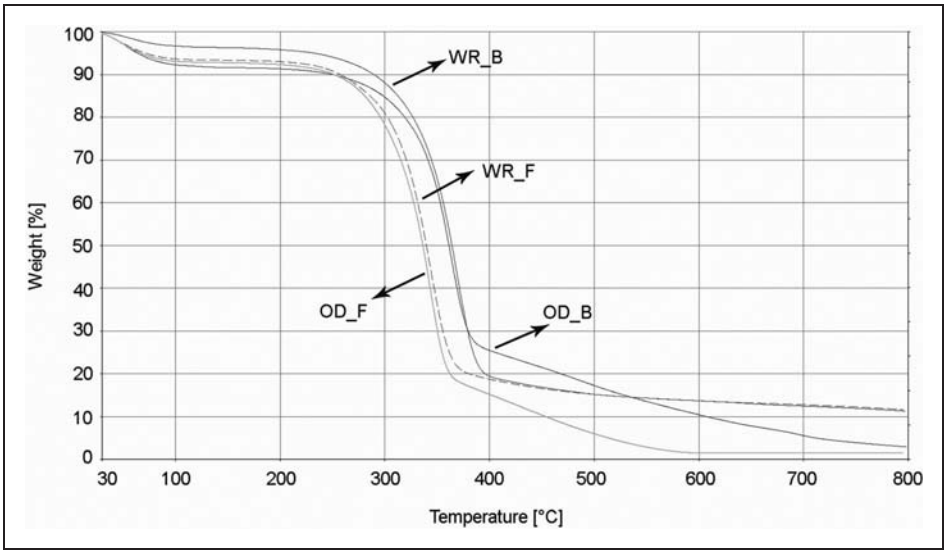

Figure 13. TGA curves of tested fibres.

maceration show less than 5% of residue at the same temperature.

Conclusions

Many well known lignocellulosic fibres such as flax, jute, ramie, sisal, hemp, coir have been studied and well documented, but there are a few vegetable fibres which still remain unutilized and are going as weed species. One of them is Spanish broom fibre.

The main goal of this paper was to answer the question of whether the quality of Spanish broom is comparable to flax. After we have tested the most important properties of two selected technical fibres we made several conclusions:

- Surface morphological properties of elementary fibres, which are part of technical fibres are very similar. Both fibres have dislocations and surface irregularities, which are the consequence of maceration methods.
- Polygonal cross-sectional shape of elementary fibres, as well as the thick cell wall, provides good quality of technical fibres.
- Spanish broom technical fibres are finer than flax fibres, especially the ones obtained by osmotic degumming.
- Elongation of both fibres is very similar with the exception of Spanish broom fibres obtained by osmotic degumming. These fibres show higher elongation than the others and accordingly suggests a decreased rigidity of the same fibres.
- Flax fibres obtained by water retting show higher tensile strength than the others, but it is not significantly different in comparison to other fibres. It is clear that Spanish broom fibres after osmotic degumming treatment show better results of breaking tenacity than after the water retting. Their tenacity is still very similar to the flax fibre tenacity.
- Spanish broom fibres have lower moisture regain than flax fibres and after osmotic degumming, both fibres show higher moisture regain than after water retting maceration.
- FT-IR spectra of tested fibres demonstrated that Spanish broom has lower amount of pectins and waxes, but higher amount of lignin, than flax fibres. The crystallinity index of cellulose showed better crystal orientation in Spanish broom fibres obtained by osmotic degumming method of maceration. It is important to note that the crystallinity index is used to indicate the order of crystallinity rather than the absolute crystallinity of crystalline regions.
- TG analysis shows better thermal stability of Spanish broom fibres compared to the flax fibres. Decomposition of Spanish broom starts at 300°C, in comparison to flax fibres when decomposition starts already at 250°C. This confirms the better suitability of Spanish broom for the production of composite materials and the possibility of applying for larger scope of thermoplastic materials.

The overall conclusion is that fibres obtained from Spanish broom have comparable properties to the flax fibres and they could be suitable for usage in technical textiles, especially for the production of polymeric composite materials. Further work should be focused on the development of processing and spinning technology of Spanish broom fibres for ensuring diversity of their application.

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The influence of *Spartium junceum* L. fibres modified with montmorrilonite nanoclay on the thermal properties of PLA biocomposites

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ABSTRACT

Biocomposites were prepared by reinforcing polylactic acid (PLA) with randomly oriented, short *Spartium junceum* L. fibres. Prior to the composite production, the fibres were treated with montmorillonite nanoclay (MMT) in order to increase biocomposites resistance to the fire. Characterizations of the biocomposites in the presence and absence of MMT and Citric acid (CA) were performed by Thermogravimetric Analysis (TGA) and Microscale Combustion Calorimetry (MCC). The results indicated that biocomposites reinforced with fibres modified with MMT enhanced some of its thermal properties. Degradation level of residual fibres (char) after the TGA treatment at 800 °C was observed by Scanning Electron Microscope (SEM). The work provided us with the idea of using MMT in the presence of CA as a crosslinker in biocomposites for possible applications.

1. Introduction

The use of natural fibre reinforced composites has spread recently due to their numerous advantages, like easy processing, low cost, contribution to the improvement of final material properties, its biodegradability and renewability [1]. The plant fibres used as a reinforcing agent rapidly improves mechanical, thermal and other properties of the composite [2,3]. They are used in different outdoor and indoor applications, like decking, fencing, docks, landscaping, building and construction and automobile industry as well [4].

One of the most common natural fibres used in biocomposites are bast fibres, such as flax, hemp, jute or *Spartium junceum* L. *S. 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 and inland Dalmatia. Throughout history, *S. junceum* L. has had a wide range of applications (perfume and dye production from the flowers, baskets from the stems and textile materials from the fibres) [5]. As the fibres still remain main product, new applications have added significant value today to their production. The fibres belong to the group of bast fibres, with properties similar to flax fibres and are mostly used in the production of technical textiles [6]. The fibres cover a wide range of applications, especially in the automotive industry, specifically in the development of car interiors (carpets, trims on the inside door, cover for the spare wheel, etc.) [7]. Transportation vehicles contain different type of products based on plastic, textiles or foams in order to improve fuel efficiency, reduce vehicle weight or enhance shock-absorbing properties [8].

Since the application of natural fibre-reinforced polymer composites generally has a fire risk scenario in the background, it is necessary to provide some kind of fire protection for such composites, so that the fibre/polymeric material does not contribute to the additional flame spread or damage. Therefore, flame retardants are incorporated into the composite system, as they help to reduce considerably fire risk in transport. Flame retardants act both by reducing the likelihood of a fire starting and by slowing the development of the fire, reducing smoke and heat release, thereby giving passengers more time to escape [9,10].

Furthermore, the application of nanotechnology in biocomposite production has exhibited promising potential in the development of next generation material for structural applications [11]. Polymer-layered silicate nanocomposites containing small amounts of inorganic nano phase, have exhibited superior properties like modulus, strength, thermal stability and flammability resistance, as

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compared to those of pure polymers. The unique properties are due to the nanometric size effect. Among all the potential nanocomposite technologies, montmorrilonite clay is most commonly used layered silicate for the preparation of nanocomposites [12,13].

In the work presented here, we combined PLA as a matrix, *S. junceum* L. fibres as a reinforcement and montmorrilonite clay (MMT) as a nanofiller, with the aim of investigating thermal properties of such biocomposites.

2. Experimental

2.1. Materials and methods

Materials and modification treatments used are presented in Fig. 1.

3. Characterization

Methods and devices for material characterization used are presented in Table 1.

3.1. Theoretical background

The first set of experiment regarding thermogravimetry was used to evaluate thermal decomposition temperature of pure PLA and *S. junceum* L. reinforced composites. The percent weight loss and derivative weight loss were plotted against temperature, in order to evaluate the onset and maximum degradation temperatures of the pure PLA and its biocomposites respectively.

The second set of experiments was aimed at establishing the activation energies of the thermal degradation of PLA and its composites. Many studies of thermogravimetric data have been used until now to determine kinetic parameters using different kinetic models, such as Ozawa, Flynn and Wall, Friedman, Coats-Redfern, Kissinger, Broido, Horowitz and Metzger, etc. [14–17]. In our work, the energy of activation was calculated employing the integral method of Broido model [16,18]. The equation used for the calculation of activation energy (E_a) is:

$$\ln \ln\left(\frac{1}{Y}\right) = \left(\frac{-E_a}{R}\right)\cdot\left(\frac{1}{T}\right) + \text{const.} \quad (1)$$

$$Y = \frac{\left(W_t - W_f\right)}{\left(W_i - W_f\right)} \quad (2)$$

where: W_t – weight anytime t; W_f – final weight; W_i – initial weight: R – gas constant 8.314 JK^{-1} mol^{-1}; T – temperature in K.

By plotting lnln (1/Y) against 1/T at constant heating rate, E_a/R was obtained from the slope of the line.

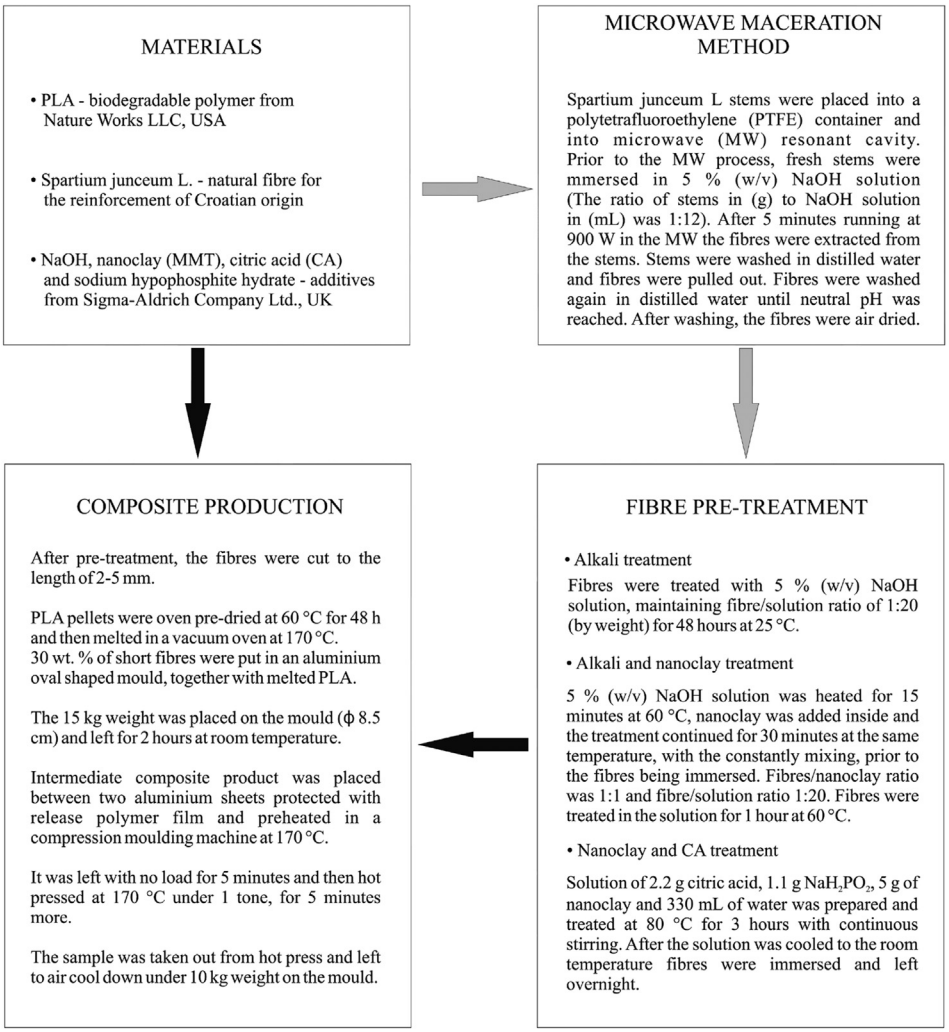

Fig. 1. Applied materials and modification treatments.

Table 1
Methods and devices for material characterization.

Characterization methods/device	Samples/technique	Purpose
Morphology and structure/FE-SEM Mira (Tescan)	• SEM microscope was operated at 20 kV and at various magnification levels • samples were coated with Au/Pd in order to increase their electrical conductivity	• Testing fibres and composite samples in order to investigate their structure and morphology
Thermogravimetry/Pyris 1 (Perkin Elmer)	• samples were heated from 30 °C to 800 °C at the heating rate of 10 °C/min in a nitrogen flow of 30 mL/min • two parallel probes for each sample were made	• Testing composite samples in order to evaluate their thermal decomposition temperature and to establish the activation energies of thermal degradation
Microscale combustion calorimetry/MCC-2 (Govmark)	• measurement was performed in three replicates according to ASTM D7309	• Testing composite samples in order to investigate the heat of combustion of the gases evolved during controlled heating of the samples

4. Results and discussion

4.1. S. junceum L. fibre properties

S. junceum L. (SJL) fibres belong to the group of bast fibres produced in the outer part of SJL stem. Its technical fibres come in bundles of a number of elementary fibres held together by pectinous gums. Each elementary fibre can be considered as a network of ultrafine cellulose fibrils embedded in a matrix of hemicellulose and lignin [5,6,19]. 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). The secondary cell wall is of extreme importance,

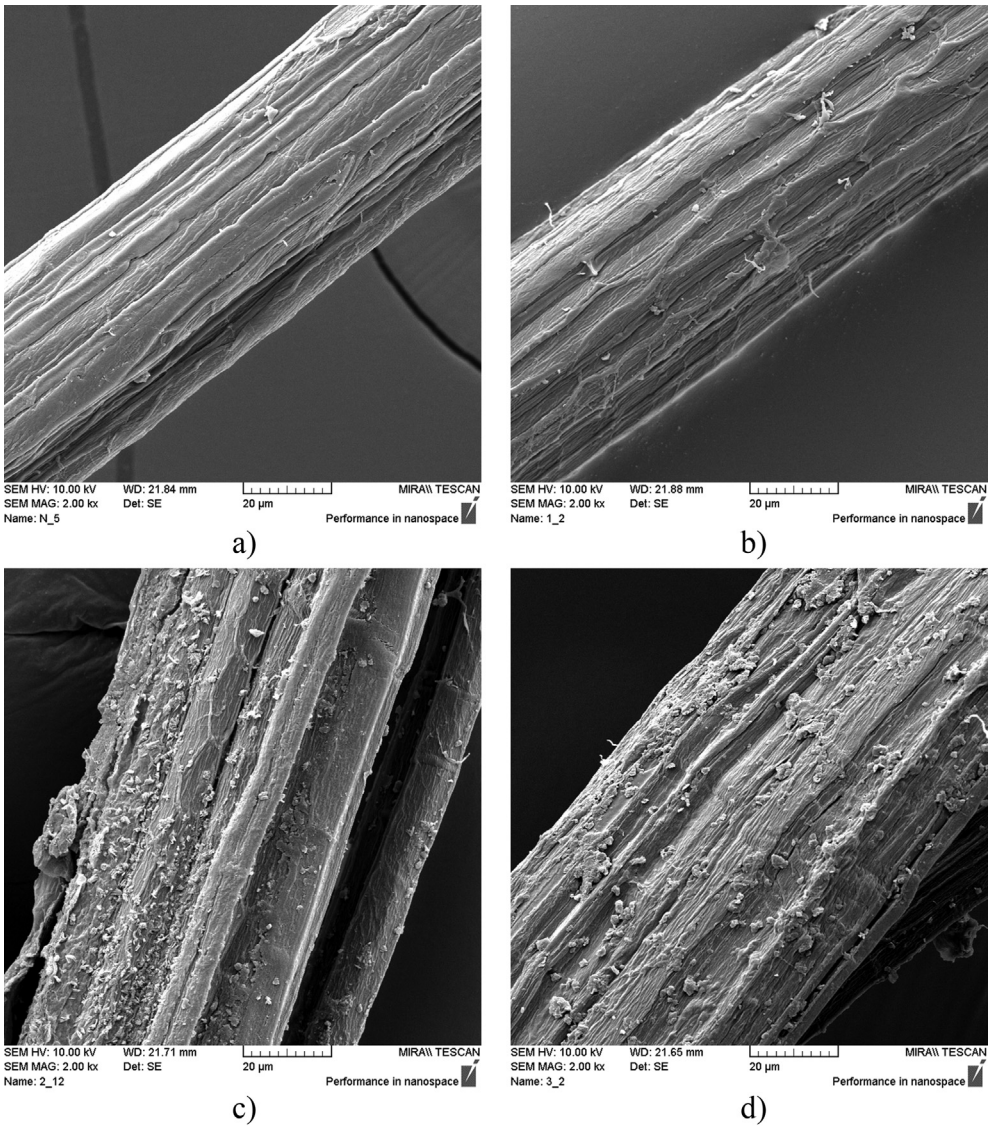

Fig. 2. Scanning electron micrographs of the fibre reinforced composites, where: a) the reference fibre (R); b) the NaOH-treated fibre (1); c) the fibre treated with MMT (2); d) the fibre treated with MMT and CA (3).

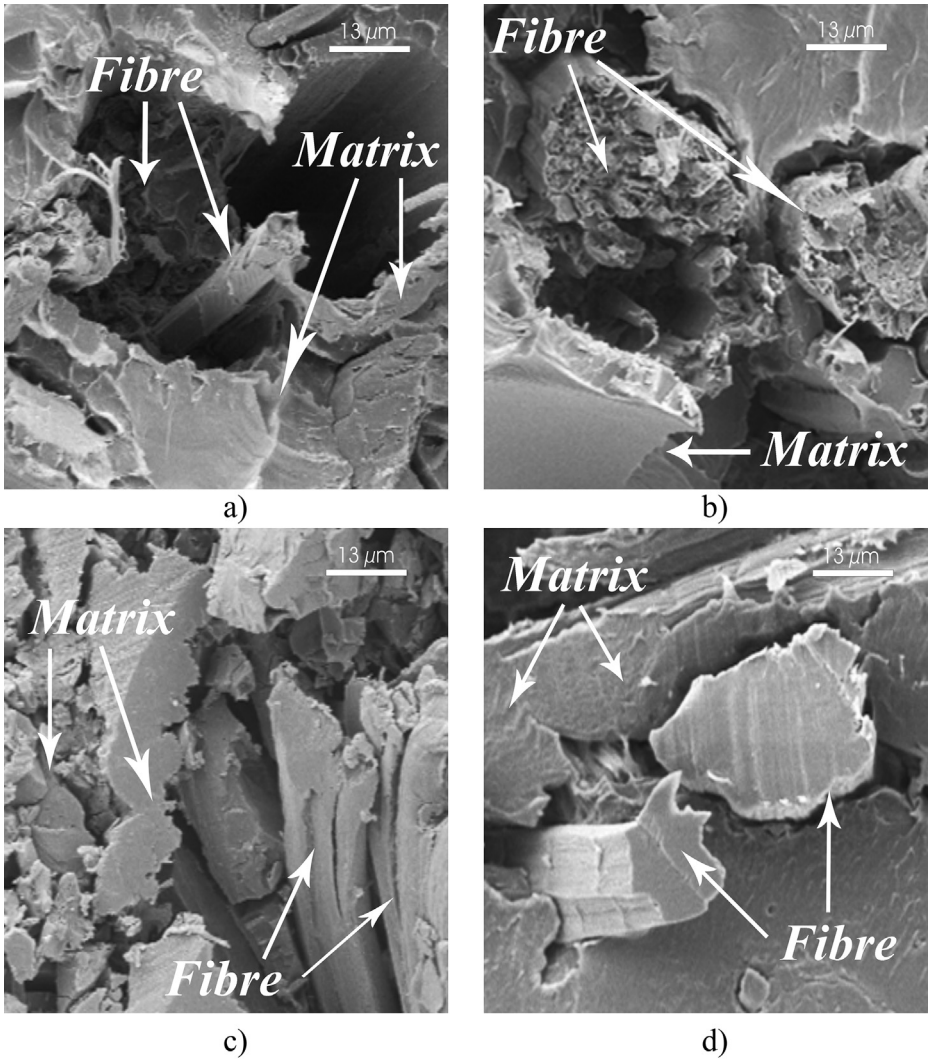

Fig. 3. Scanning electron micrographs of tensile fracture surface of the composites, where: a) fractured surface of the CR composite; b) fractured surface of the C1 composite; c) fractured surface of the C2 composite; d) fractured surface of the C3 composite.

because of its influence on fibre properties while its cellulose-rich fibre structure offers higher tensile strength [20,21]. Because of the polygonal cross-sectional shape and thick cell wall of its fibres, SJL provides better quality fibres (better light reflection and absorption) [20,22–24]. 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 the fibre and influence its properties [22–24]. Adding NaOH and nanoclay into fibre structure, the improvement of thermal properties can be influenced. Alkaline treatment dissolves lignin phase, suggesting increment of crystalline phase and enhancement of fibre hydrophobicity, as the tendency of water molecules held by lignin and hemicelluloses are reduced. A chemical treatment of bast fibres with NaOH leads to fibrillation and thereby increases the effective surface area contact to the matrix, if such fibres are used as reinforcement in composite materials. Due to the increase in the effective surface contact area, there is a possibility for improvement in the composite properties [25–28]. The increase in thermal stability of the fibres modified with nanoclay is attributed to the hindered diffusion of volatile decomposition products within it, or it can be due to physico-chemical adsorption of the volatile degradation products on the silicate surface. The volatilization of the degraded products originated by C–C bond scission in the composites is delayed by winding path provided by the silicate layers [12].

In general, the implementation of flame retardant filler (MMT) into flammable materials, such as natural fibre reinforced composites, improves fire behaviour of the sample. Nanoclays are the most commonly used flame retardant fillers. MMT clays consist of alumino-silicate clay nanolayers which are separated from each

Table 2
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.

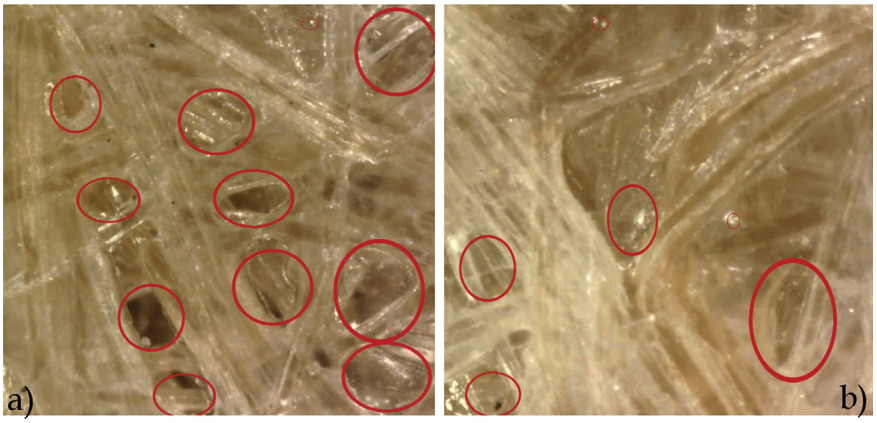

Fig. 4. Dino-Lite digital microscope images at 50× magnification presenting voids on the surface of: a) C2 composite; b) C3 composite.

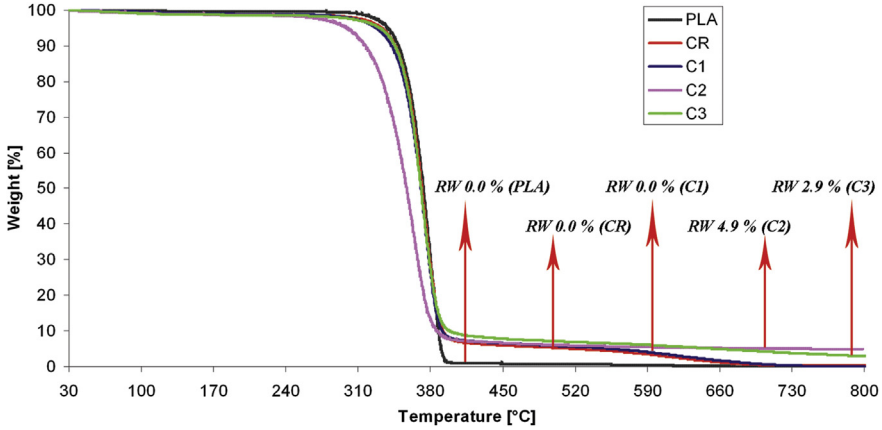

Fig. 5. TGA curves of pure PLA and *Spartium junceum* L. reinforced composites.

other by an interlayer distance, where exchangeable ions exist, causing neutralization of the charge between these layers. The particle size is the main factor which influences its efficiency, due to the large surface area of the nanoparticle. The increase in mechanical properties can be an indication of nanodispersion, which leads to more homogeneity between the fibre and the clay, thus inhibiting access to oxygen and preventing combustion process from being sustained. Nanocomposite is a new product able to create high flame retardancy while simultaneously withstanding high loads [29–31].

Table 3
Thermal properties of PLA and its biocomposites.

	PLA[a]	CR[b]	C1[c]	C2[d]	C3[e]
T_i [°C]	354.1	352.4	350.9	328.0	350.5
T_m [°C]	379.0	374.5	374.8	364.8	372.0
T_{D20} [°C]	358.3	357.2	355.0	333.2	356.3
T_{D40} [°C]	368.8	368.2	366.5	350.2	367.0
T_{D60} [°C]	376.5	375.6	374.8	361.9	374.6
T_{D80} [°C]	383.2	384.2	383.1	373.4	384.0
RW [%] at 800 °C	0.0	0.0	0.0	4.9	2.9

[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.

4.2. Nanoclay pre-treatment and its influence on the bonding interface of Spartium and PLA composites

Nowadays, fibre modifications provide a new way to overcome the possible limitations in composite production. Modifications are used to enhance the compatibility between the hydrophilic fibre and hydrophobic matrix in a natural fibre reinforced composite. Properties of composites based on natural fibres are strongly influenced by the interface adhesion between the fibres and the polymer matrix.

The bond interface between the fibre and its surrounding matrix is an important factor because it determines thermal properties of natural fibre reinforced composites. However, a number of published papers report on possible chemical treatments which might improve the matrix-fibre interfacial adhesion [32–36].

SEM micrographs of *S. junceum* L. reference and modified fibres and fractured surface of its composites without clay and with it are presented in Fig. 2a–d) and Fig. 3a–d) respectively. The surface of the R fibre (2 a) was smooth and regular in comparison to the surface of the fibre 1 (2 b), where roughness at the surface was a little bit increased by additional treatment of the technical fibre with NaOH. Fig. 2c and d show fibres treated with MMT and MMT/CA respectively. The results from scanning electron micrographs indicated that in Fig. 2c nanoclay existed in clusters ranging from over 2 μm down to submicrometer scale, while in Fig. 2d the clusters ranging from over 5 down to submicrometer scale

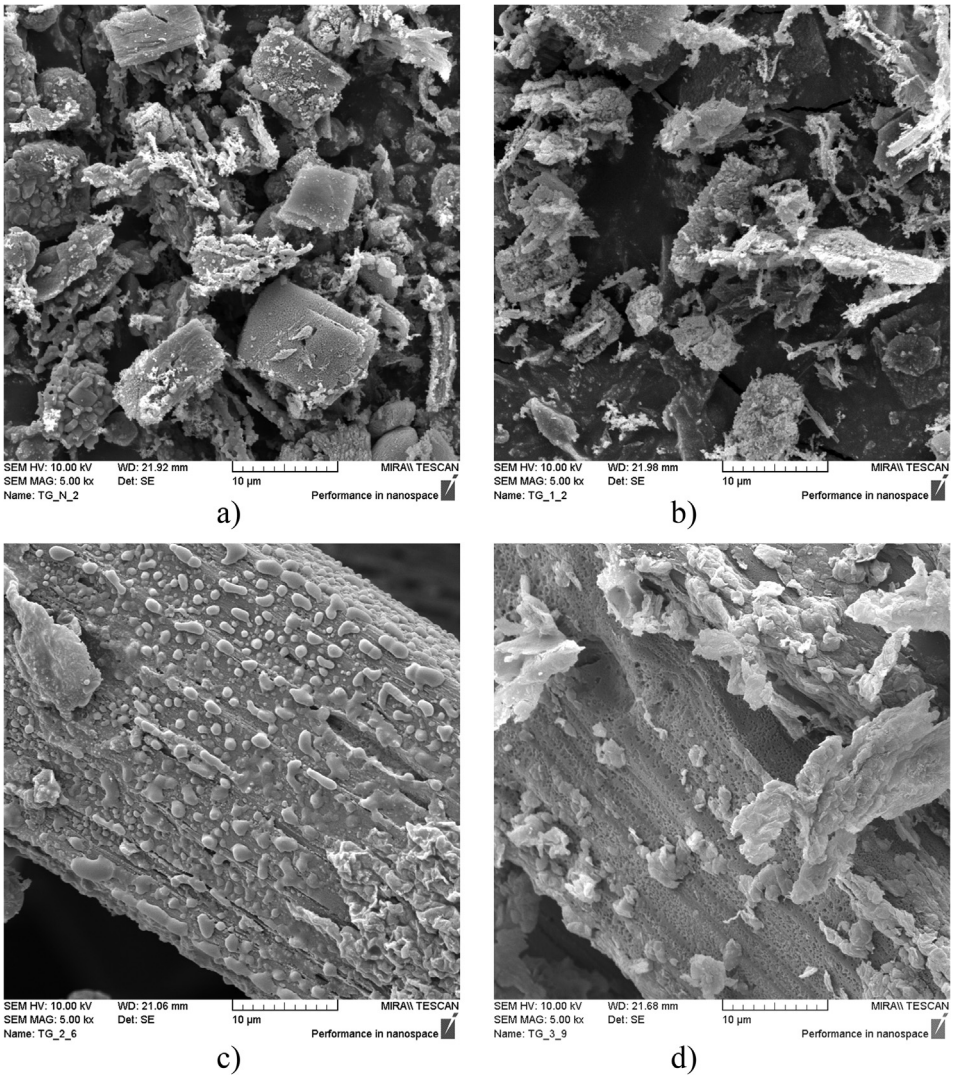

Fig. 6. SEM micrographs of chars after TGA of: a) CR composite; b) C1 composite; c) C2 composite; d) C3 composite.

indicated the incorporation of crosslinker (CA) as well. Fibre matrix debonding and fibre pull-out were more evident in the composite CR than in C1 (Fig. 3a and b), indicating that the interfacial adhesion between the matrix and reference fibre was lower. It was supported by lower mechanical properties, in comparison with the C1 mechanical properties (Table 2 [37]). Improved thermal properties in the C3 composite may be due to fibre morphology change. However, on adding MMT into the composites (C2), the fractured surface of the composite (Fig. 3c) was found to be very brittle and full fibre/matrix debonding was observed, indicating reduced mechanical properties of the C2, in comparison with the other tested composites. The C3 composite showed smoother fractured surface

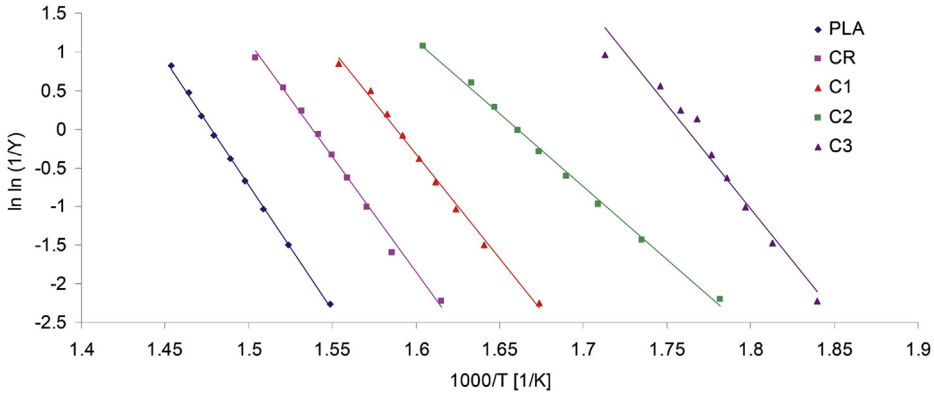

Fig. 7. Broido plot of ln ln (1/Y) against 1000/T [K] the slope of which is related to the activation energy [kJ/mol].

Table 4
Kinetic parameters of PLA and its composites by Broido method.

Sample	Activation energy, E_a [kJ/mol]	R^2
PLA[a]	268.67	0.9990
CR[b]	247.56	0.9942
C1[c]	224.16	0.9961
C2[d]	156.59	0.9971
C3[e]	222.86	0.9661

[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.

(Fig. 3d), which might be due to the fact that the combination of the MMT and CA particles increased the interaction with PLA matrix, which resulted in less pulled-out fibres from the fractured surface, in comparison with the CR, C1 and C2 composites. The overall results indicated that introducing nanoclay and crosslinker to the *S. junceum* L. fibre/PLA composites improved their thermal properties, confirming the synergistic effects of the fibre and clay in the composites. Therefore, improved thermal properties of the composite materials reinforced with fibres treated only with MMT was not expected, due to the increase of the number of air voids (Fig. 4) and less stiff structure, in comparison with the MMT/CA modified fibres.

4.3. Nanoclay pre-treatment and its influence on the thermal properties of Spartium and PLA composites

The influence of MMT and MMT/CA on the thermal properties of the biocomposites was investigated by TGA as shown in Fig. 5.

The analysis of higher temperature (higher than 300 °C) decomposition of biocomposites showed improved thermal stability for the MMT treated fibres reinforced composites, regarding their residual weight after thermal treatment at 800 °C. The improvement could be attributed to the presence of clays in the treated fibres. Table 3 (derived from Fig. 5) shows the initial decomposition temperature (T_i), maximum pyrolysis temperature (T_m), decomposition temperature (T_D) at different weight loss and residual weight (RW) of the composites. T_i decreased from 354 °C (PLA) to 328 °C (C2) and this behaviour could be attributed to the material processing [32,38]. The T_D values of the crosslinked MMT composite (C3) were higher than for the uncrosslinked MMT composite (C2). This might be due to the formation of crosslinking caused by the interaction between the CA and hydroxyl groups of cellulose or polymer. The MMT treated composites showed an additional increase in RW values over MMT untreated samples.

The composite chars formed from the MMT treated fibres, characterized upon TGA, appeared to be very different compared to the untreated ones. These chars obtained from the MMT treated composites (Fig. 6c) were quite firm, while the samples without the FR treatment were completely damaged. The sample C2 (Fig. 6c) had more firm and intact surface compared to the sample C3 (Fig. 6d) which showed partially damaged surface. It was the reason why the sample C2 had higher residual weight after thermal treatment than C3. Applied magnification of 5 kx offered a clear view of possible nanoclay effect, where the migration of nanofiller from the inner part of the fibre to the surface (Fig. 6c and d), after thermal treatment at 800 °C, could be observed.

The activation energy of PLA reinforced *S. junceum* L. biocomposites study was obtained using constant heating rate [16,18]. The activation energy of thermal degradation was calculated through Broido method for all the tested composites. Fig. 7 presents the linear plots for pure PLA, CR, C1, C2 and C3 composites, while average activation energies measured in the temperature range from 340 to 400 °C were calculated from the slope of these curves, as shown in Table 4, together with the R^2 values for the same lines. The temperature range from 340 to 400 °C was chosen as it presented the second stage and the fastest step of degradation. Although the reaction mechanism of all the tested composites was similar, according the plotted lines, the activation energy showed lower thermal stability of the C2 composite (156.59 kJ/mol), compared to other tested composites.

Microscale combustion calorimetry (MCC) is a proper test for the efficacy of flame retardant in polymers from just a few milligrams sample. The test method is a thermal analysis method that improves upon previous methods by directly measuring the heat of combustion of the gases evolved during controlled heating of the samples [39–41]. According to the MCC results, the heat release rate (HRR) curves of PLA composites reinforced with different treated fibres of *S. junceum* L. and the corresponding combustion data are presented in Fig. 8 and Table 5. Lower heat release values (W/g) were obtained in the case of composites reinforced with the MMT treated fibres (C2 and C3) demonstrating much higher flammability than reference composite and the composite treated with NaOH (e. g. CR and C1). Meanwhile, the total heat release (kJ/g) decreased in Spartium reinforced polymer composites, compared to the pure PLA, the highest reduction being 20% when the fibres modified with MMT were incorporated in the composite (C2). The C2 composites exhibited a tendency of earlier start of the decomposition process (at approx. 374 °C) in comparison with the C3 composites (approx. 387 °C) because of the low initial thermal

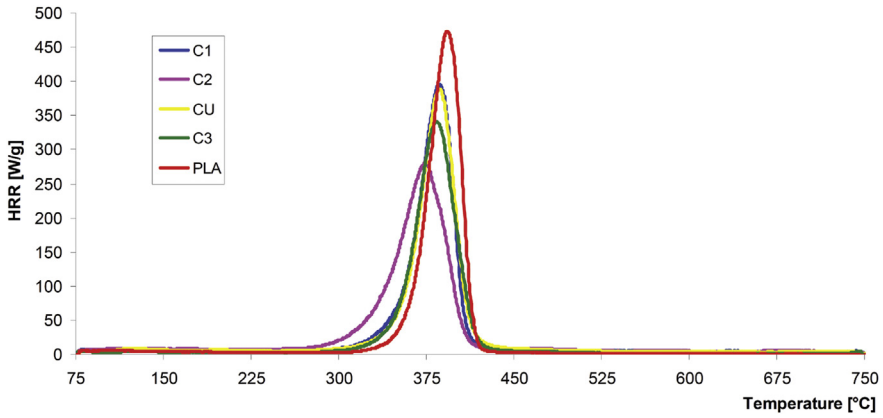

Fig. 8. HRR curves of the PLA composites reinforced with differently treated fibres of *Spartium junceum* L..

Table 5
Data recorded in MCC experiment, where TPHRR is maximum temperature of peak heat release rate.

Samples	PLA[a]	CR[b]	C1[c]	C2[d]	C3[e]
Heat release capacity, J/(g*K)	469.7	386.3	389.0	302.0	383.3
Peak heat release rate, (W/g)	475.1	388.4	395.6	280.9	341.4
TPHRR, (°C)	396.5	386.7	387.5	374.4	387.3
Total heat release, (kJ/g)	17.1	14.4	14.8	13.8	14.8

[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.

stability of the C2 composites. All the results presented above show that the composites reinforced with *S. junceum* L. fibres can improve the flame retardancy of pure PLA polymer.

5. Conclusion

The effect of nanoclay and crosslinking agent citric acid on the thermal properties of PLA biocomposites was studied. Having in mind that CA is known as an eco friendly crosslinker, with a positive impact on the FR properties of cellulose fibres, better thermal properties of tested biocomposite were expected.

The incorporation of CA improved the thermal properties of the MMT composites via the interaction of the carboxylic group of the crosslinker with the hydroxyl group of nanoclay and *S. junceum* L., although the overall results showed a decrease in thermal stability, which may be due to improper amount of incorporated nanoclay, resulting in higher number of air voids in the biocomposite. Therefore, it could be conclude that thermal stability of the MMT modified biocomposites increased on the addition of CA as a crosslinking agent. However, the type of the method used to produce biocomposites, as well as the nature, amount and deposition of nanoclay, significantly influenced thermostability of the composite obtained.

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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).

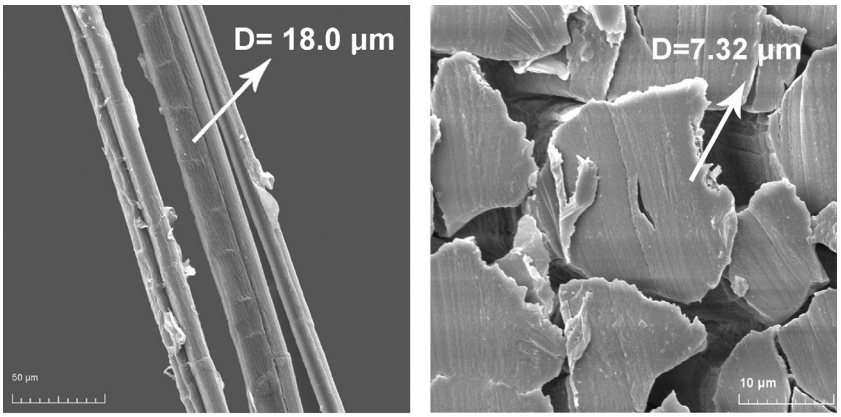

Figure 1 SEM micrographs of *Spartium junceum* L. fibres (a) longitudinal image of elementary fibre as a part of technical fibre and (b) cross section image of elementary fibre.

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.

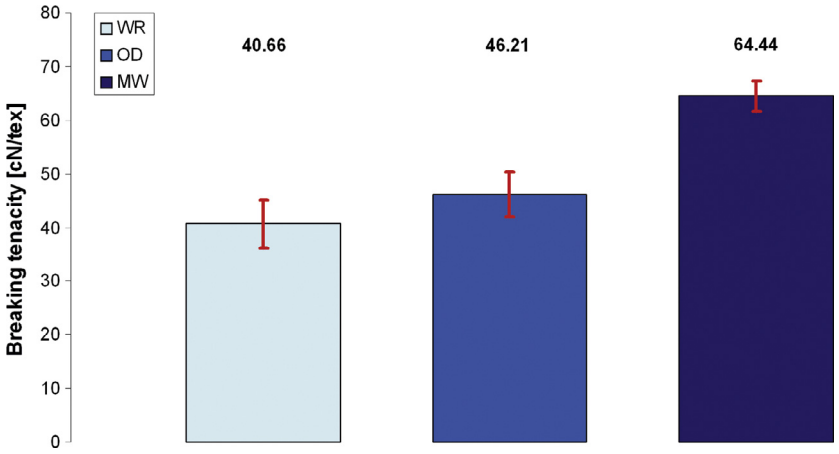

Figure 2 The results of measuring breaking tenacity of *Spartium junceum* L. reference fibres after different maceration methods, where: WR – water retting; OD – osmotic degumming; MW – microwave treatment.

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

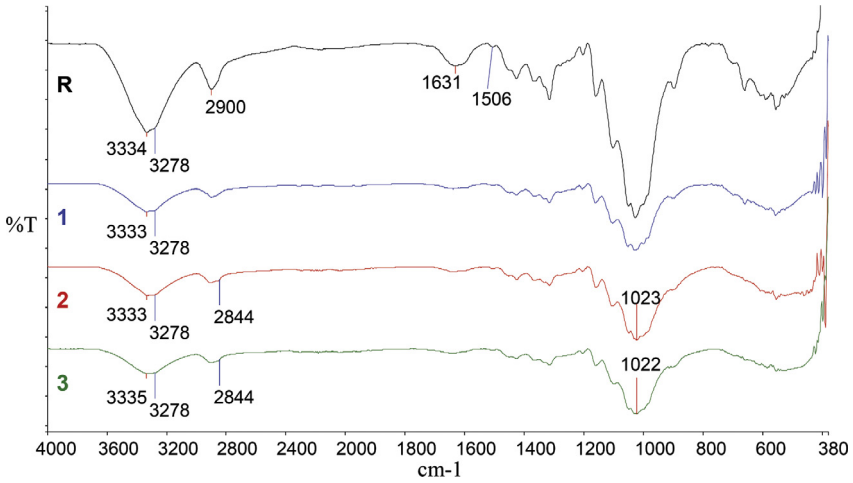

Figure 3 IR spectra of *Spartium junceum* L. fibres, where: R – the reference fibres; 1 – the fibres treated with NaOH; 2 – the fibres treated with MMT; and 3 – the fibres treated with MMT and CA.

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-

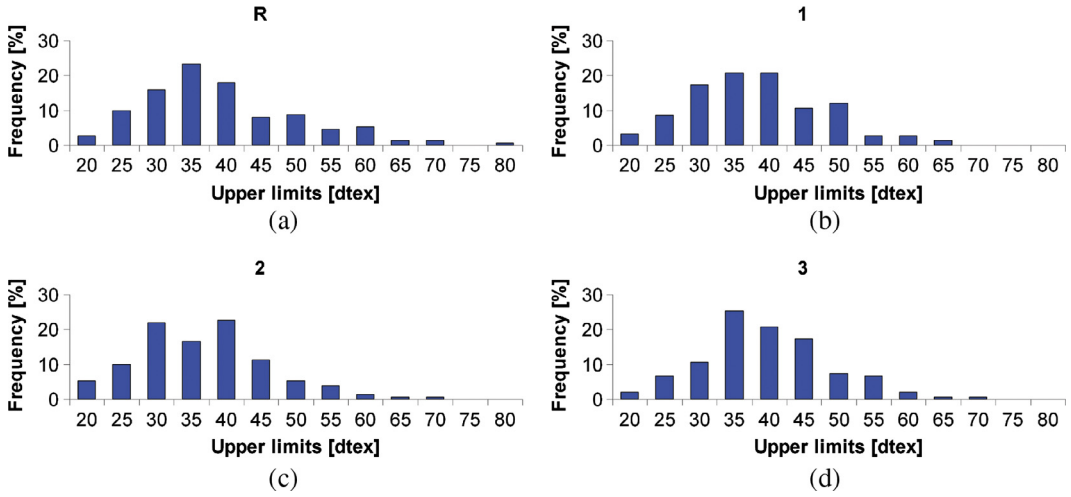

Figure 4 Frequency of fineness for 150 measurements of (a) the reference fibres (R); (b) the NaOH-treated fibres (1); (c) the MMT-treated fibres (2); and (d) the MMT- and CA-treated fibres (3).

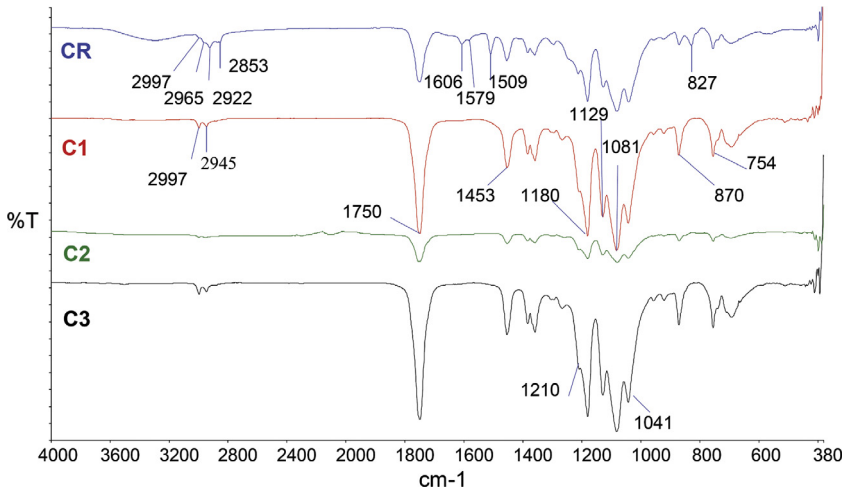

Figure 5 IR spectra of PLA polymer reinforced with *Spartium junceum* L. fibres, where: CR – composite reinforced with reference fibres; C1 – composite reinforced with the fibres treated with NaOH; C2 – composite reinforced with the fibres treated with MMT; C3 – composite reinforced with the fibres treated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

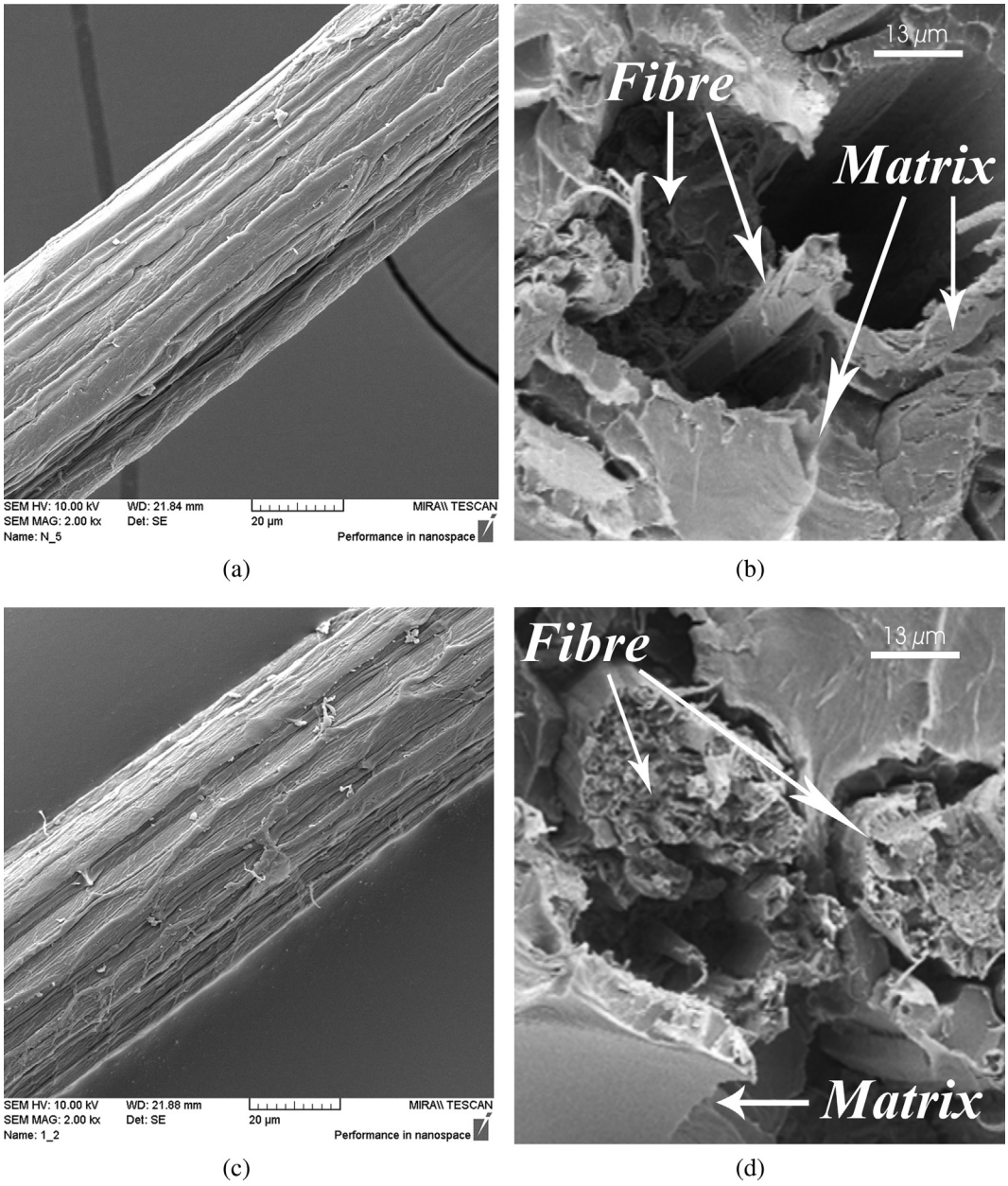

Figure 6 Scanning electron micrographs of the fibre reinforced composites and tensile fracture surface of the composites, where: (a) the reference fibre (R); (b) fractured surface of the CR composite; (c) the NaOH-treated fibre (1); and (d) fractured surface of the C1 composite.

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

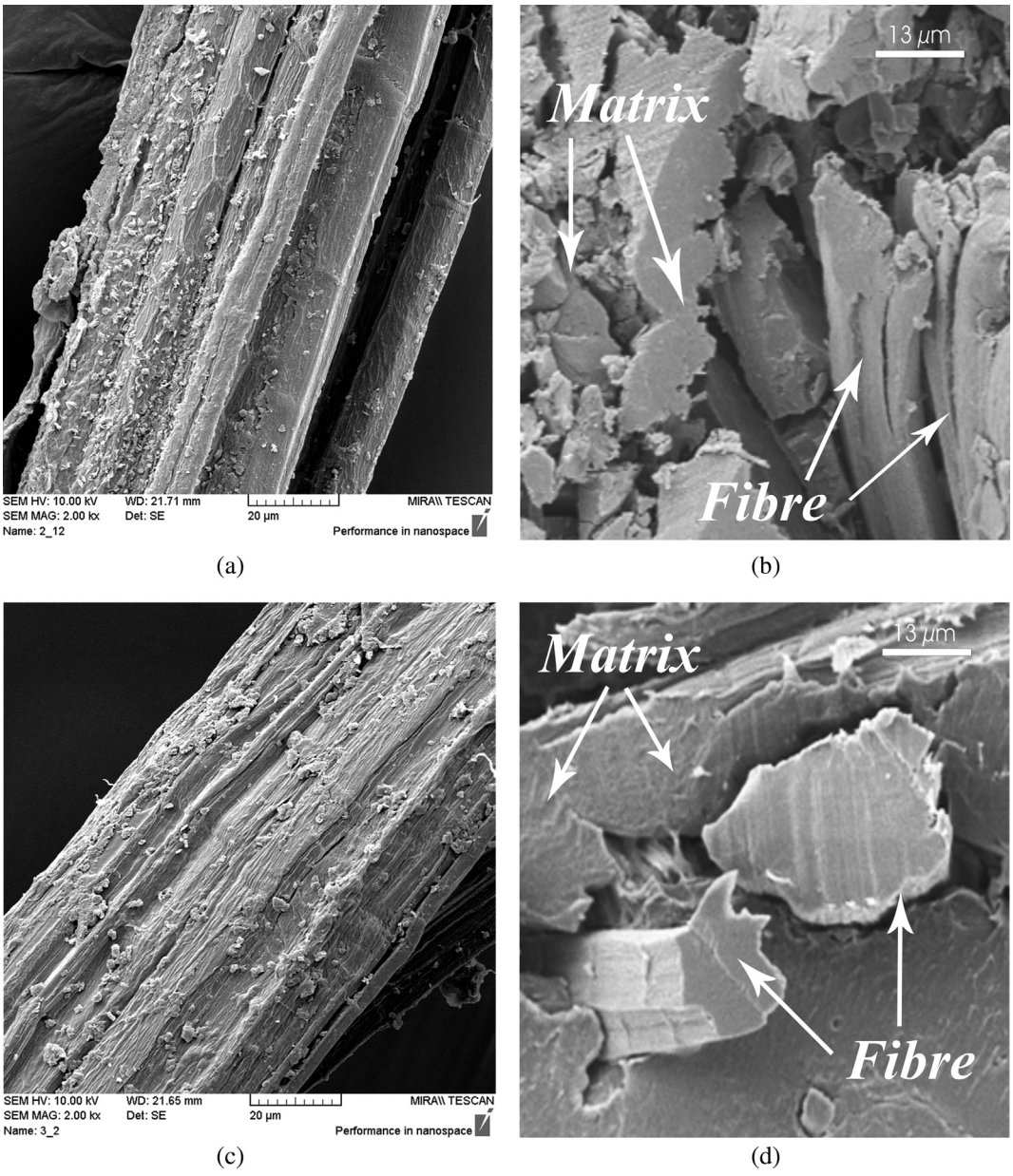

Figure 7 Scanning electron micrographs of the fibre reinforced composites and tensile fracture surface of the composites, where: (a) the fibre treated with MMT (2); (b) fractured surface of the C2 composite; (c) the fibre treated with MMT and CA (3); and (d) fractured surface of the C3 composite.

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.

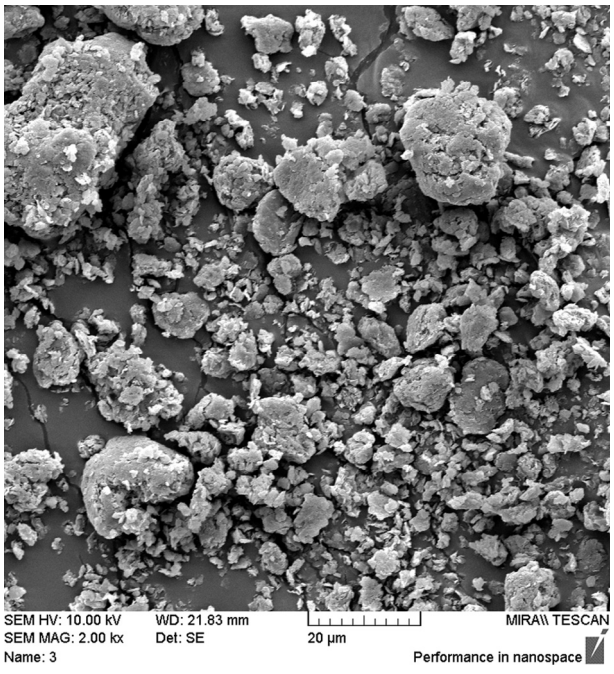

Figure 8 SEM micrograph of pure nanoclay (MMT).

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;

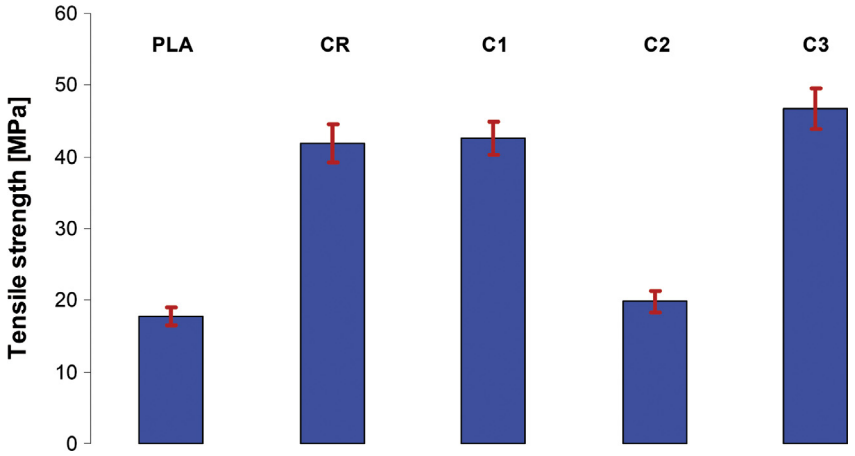

Figure 9 Tensile strength of tested composites where: PLA – pure PLA polymer prepared by the same method as the composites; CR – composite reinforced with the reference fibres; C1 – composite reinforced with the NaOH-treated fibres; C2 – composite reinforced with the MMT-treated fibres; C3 – composites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

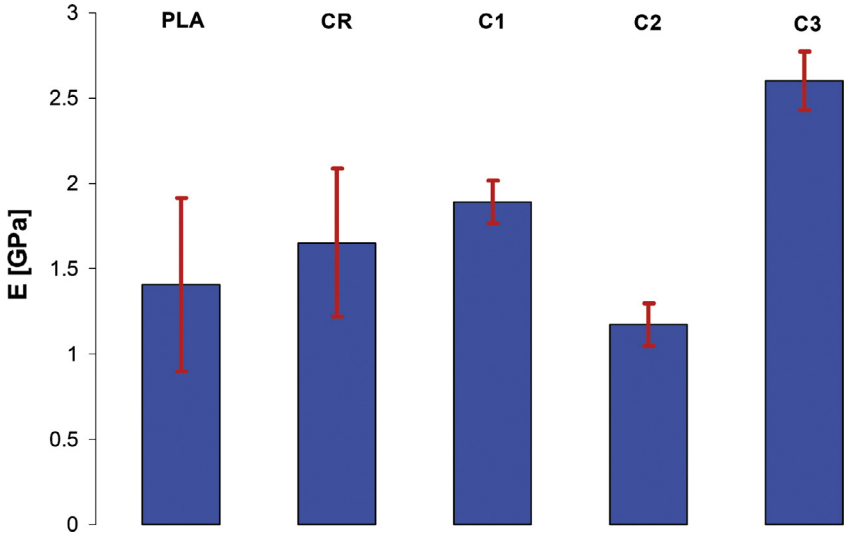

Figure 10 Young modulus of tested composites where: PLA – pure PLA polymer prepared by the same method as the composites; CR – composite reinforced with the reference fibres; C1 – composite reinforced with the NaOH-treated fibres; C2 – composite reinforced with the MMT-treated fibres; C3 – composites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

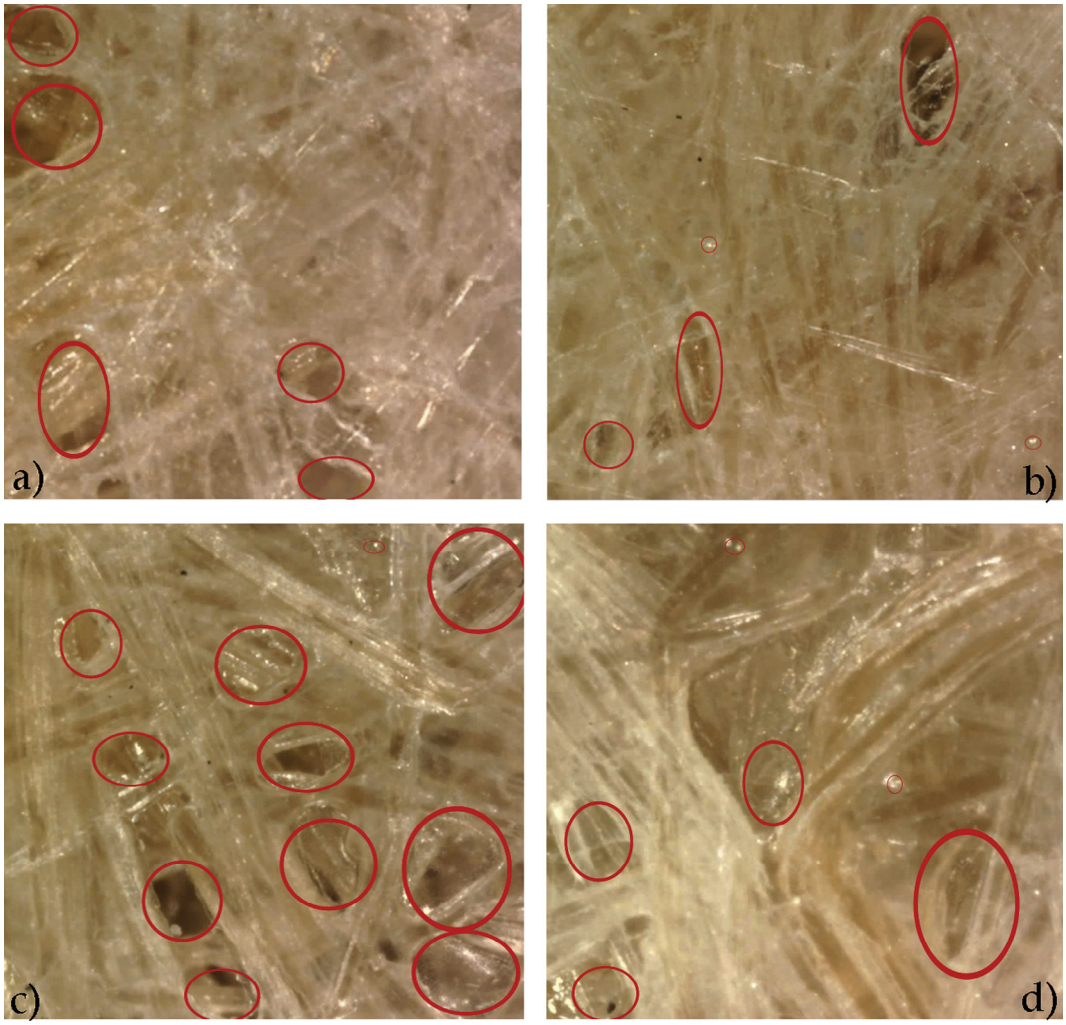

Figure 11 Dino-Lite digital microscope images at 50× magnification presenting voids on the surface of: (a) CR composite; (b) C1 composite; (c) C2 composite; and (d) C3 composite.

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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7.4 Enhancement of *Spartium junceum* L. fibres properties - IOP Conference Series-Materials Science and Engineering 254 (2017), article number: 022005 - *reused with permission from publisher*

Enhancement of Spartium junceum L. fibres properties

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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 elektrokinetic 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 Sodyum Hypophosphite 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 1 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 1 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.

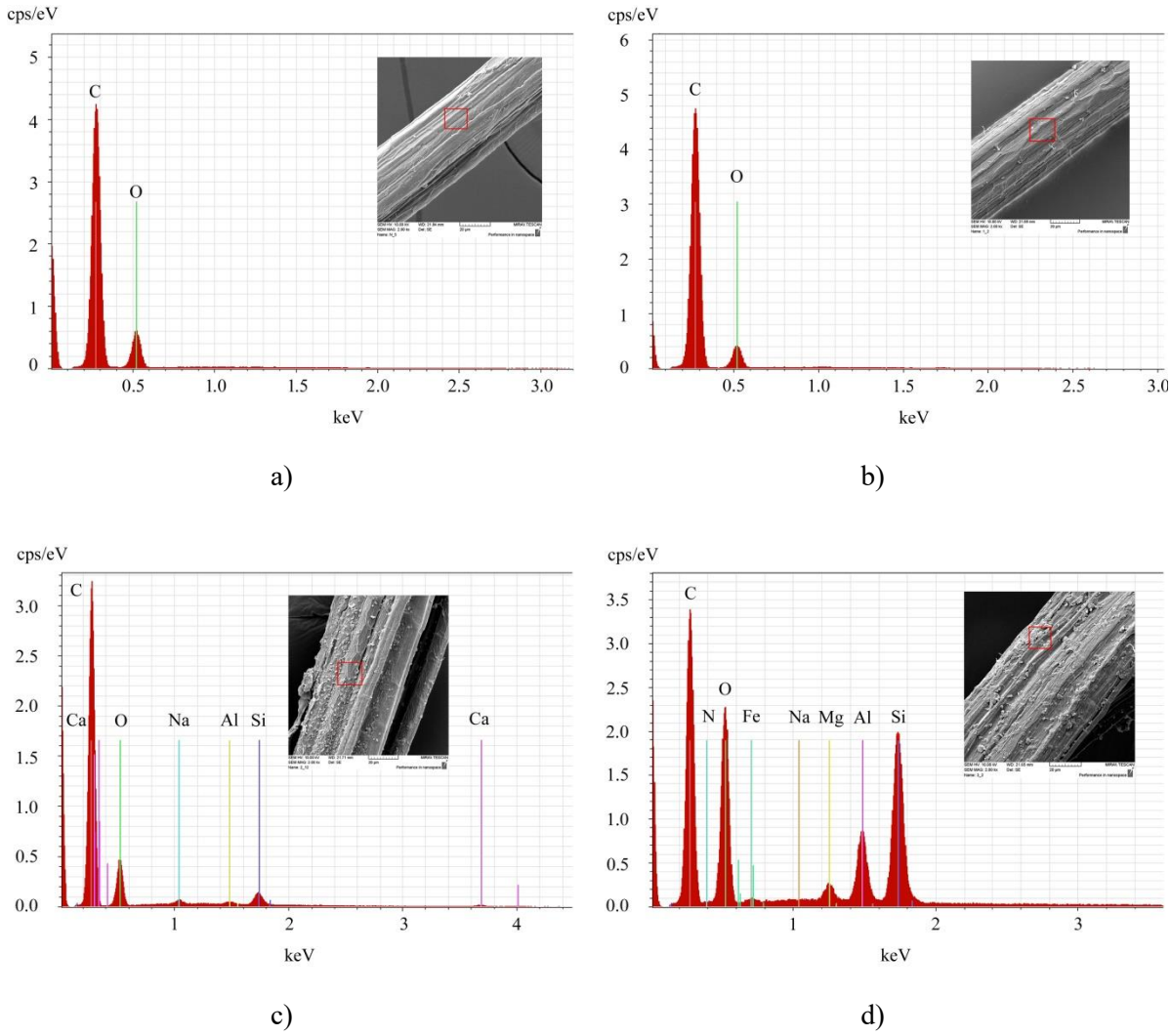

Figure 1. EDS spectra and SEM images of a) RF; b) 1F; c) 2F and, d) 3F.

In order to investigate hydrophilic/hydrophobic nature of Spartium junceum L. fibres, their ζ-potential- pH dependence was determined in 1 mM KCl electrolyte solution. Figure 2 shows different ζ-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 ζ-plateau value compared to RF. RF and 2F fibres have a small negative ζ-potential plateau values and both of them display a rapid increase of the negative ζ-potential below pH 5. Rapid increment of ζ-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 ζ-potential=0, at low pH values (around pH 2, extrapolated) and the ζ-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 ζ-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.

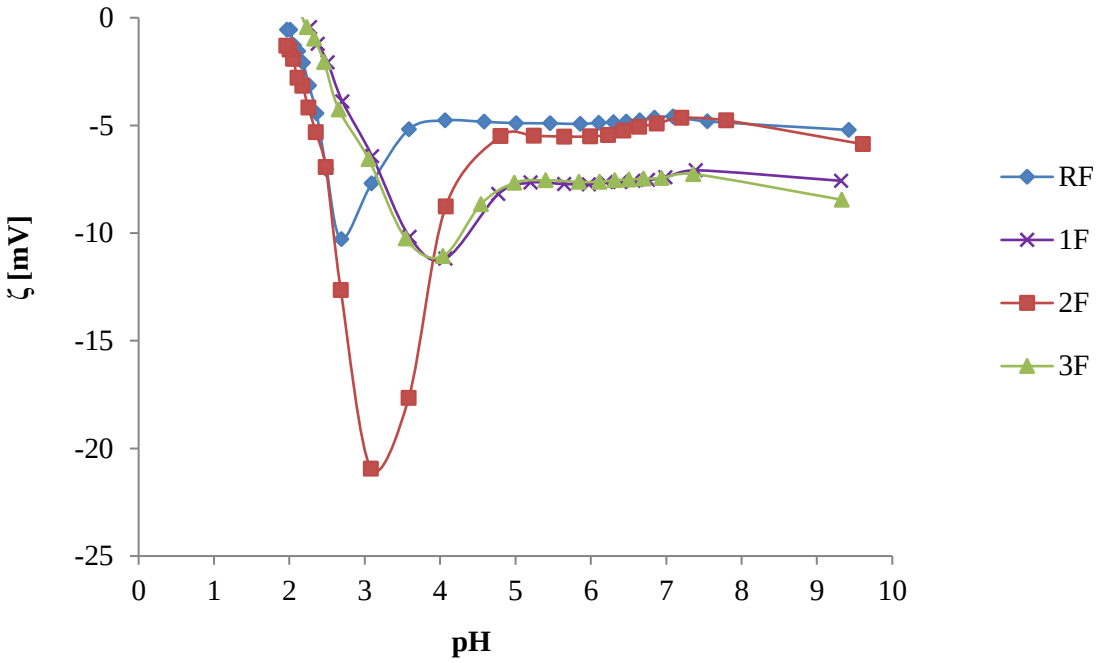

Figure 2. ζ-potential- pH dependence of reference and modified Spartium junceum L. fibres.

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 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.

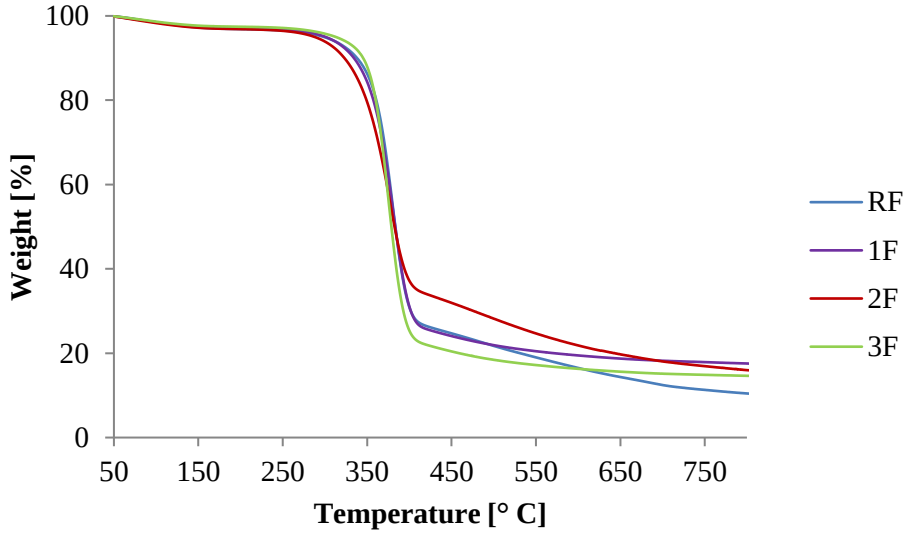

Figure 3. TGA curves of reference and modified Spartium junceum L. fibres.

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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7.5 The potential of nanoclay modified *Spartium junceum* L. fibres used as reinforcement in PLA matrix composites for automotive applications - International journal of Nanotechnology 15 (2018) 8/9/10, p. 695-700 - *reused with permission from publisher*

The potential of nanoclay modified *Spartium junceum L.* fibres used as reinforcement in PLA matrix composites for automotive applications

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Abstract: Novel bionanocomposite material has been developed using nanoclay modified *Spartium junceum L.* fibres and PLA matrix. Its potential for the automotive industry was examined. *Spartium junceum L.* fibres were previously treated with montmorillonite nanoclay (MMT) and citric acid (CA) in order to enhance bionanocomposite thermal and mechanical properties to comply with the automotive industry requirements. After a macromechanics analysis, a comparison was made between experimental and theoretical modelling results. The evaluated tensile modulus and tensile strength of theoretical Hirsch model were in good agreement with those of the tested composites. Tensile strength and modulus of the newly developed advanced material were improved by 164% and 86% respectively, as compared to the pure PLA matrix.

Keywords: *Spartium junceum L.*; natural fibres; nanoclay; micromechanical modelling; automotive industry.

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1 Introduction

We are aware nowadays of pros (low density, environmentally friendly, renewable, less cost materials) and cons (sensitivity to moisture, large variation of properties, limited length, poor compatibility between the fibres and the matrix) for the usage of natural fibres as reinforcement in composite materials. The most common application of these materials is in construction and automotive industry. Natural fibre reinforcements are generally divided into wood (most commonly used in building and construction) and non-wood fibres (flax, *Spartium junceum L.*, etc.) which are the materials of choice for automotive applications [1]. The usage of natural fibre reinforced composites (NFRC) in automotive industry is favoured by the Directive 2000/53/EC of European Union. In order to make NFRC even more attractive to automotive producers, it is necessary to improve their properties such as: uniformity in fibre properties, better adhesion between the fibre and the matrix, UV resistance, moisture repellence and flame retardancy. Improvements in mechanical properties are visible comparing our previous research [2,3] with the present results.

2 Experimental

PLA polymer (6200D) was obtained from Nature Works LLC while montmorillonite clay (MMT) and NaOH were purchased from Sigma-Aldrich, UK. *Spartium junceum L.* was collected in Croatia, in the area of the town of Šibenik.

Fibres obtained by the maceration process with NaOH carried out in a microwave oven are used as reference fibres (R). Fibres were modified with NaOH (1), MMT (2) and a mixture of MMT and citric acid – MMT/CA (3) in order to improve composite interfacial, mechanical and thermal properties. Polymer was melted in the vacuum oven at 170°C and hot pressed together with 20 wt. % of short fibres in a compression moulding machine at 170°C under 1 tonne pressure for 5 minutes.

Micromechanical characterisation of composites and prediction of its tensile strength (σ^C) and tensile modulus (E^C) were performed on the basis of mathematical models: Modified rule of mixtures with Cox-Krenchel equations and Hirsch model. According to the literature [4,5] applied models are most commonly used in the case of short fibre randomly oriented composites.

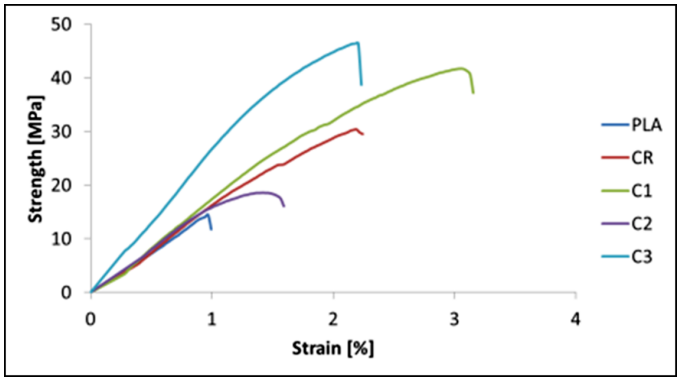
3 Results and discussion

Fibre surface treatment is one of the possible ways to enhance the properties of the natural fibre reinforced composites. Mechanical properties of *Spartium junceum L.* fibres differ after various chemical modifications. Tensile strength results of the nanoclay treated samples indicated improvement in strength compared to the reference fibres [3].

Figure 1 presents stress-strain curves of composite materials reinforced with R, 1, 2 and 3 fibres. Pure PLA material breaks at lower strain than others, indicating its brittle nature. Furthermore, tensile strength of pure PLA proved to be very low. Introduction of modified fibres and additives resulted in significant increase in its mechanical properties. Improvements in strength of 136.8%, 141.2%, 12.0% and 164.0% were observed for composite materials CR, C1, C2 and C3, respectively, in comparison to the pure PLA. The reason for low mechanical properties of the sample C2 was attributed to the decrease of interface bond between fibre and matrix, caused by larger amount of air voids observed inside the C2 sample [3]. Figure 2 shows a comparison of the experimental and theoretical tensile strength and tensile modulus values. Tensile strength of matrix within modified rule of mixtures (mRoM) was calculated by interpolating the stress-strain curve of PLA matrix while other parameters are presented in Table 1.

The behaviour of tensile stress until fluency point fitted the following equation for any strain (ε): $\sigma^M = -1.6464\ \varepsilon 2 + 16.264\ \varepsilon - 0.235$.

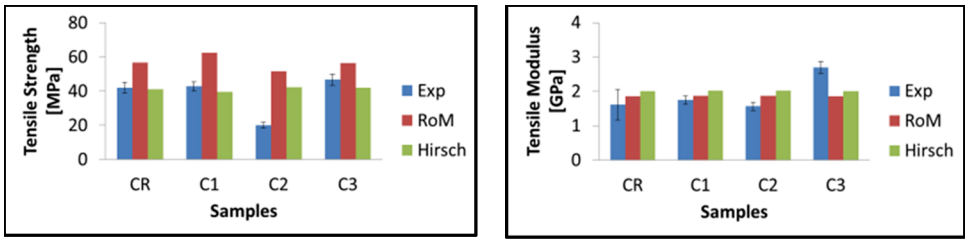
Figure 1 Stress-strain curves of pure PLA and CR, C1, C2, and C3 composite materials (see online version for colours)



Since the fibres are arranged in planar random fashion, the efficiency factor in RoM model was expressed according to Fu and Lauke [6] for the prediction of the tensile strength values and using Cox-Krenschel model for the tensile modulus values, while the length and interface factor can be obtained through knowing interfacial shear strength and critical fibre length [4,7]. The obtained value of the interfacial shear strength, considering

the matrix strength and according to Von Mises criterion, was 10.21 MPa. This criterion predicted (τ) value quite well, provided the composites were correctly bonded [4]. The mean fibre length (L) was assumed to be 2.5 mm since it was already reported in the literature that composite production technology and processes influence the decrease of fibre length inside the composite material [7]. The Cox-Krenschel model uses parameters such as: β, which is the coefficient of stress concentration rate at the ends of the square packing fibres, L stands for the fibre length inside the composite material, r is the fibre radius and v the Poisson's ratio of the matrix, which is assumed to be 0.36 for PLA matrix [4,5]. Properties such as the tensile strength of the fibre (σ^F) and matrix (σ^M), volume fractions of the fibre (V^F) and matrix (V^M), as well as the tensile modulus of fibre (E^F) and matrix (E^M) are the fundamental quantities to be used to predict composite properties. The Hirsch model is a combination of parallel and series models where β is the parameter that determines the fibre-matrix stress transfer and markedly differs from the Cox-Krenschel's β. According to the literature [5], β is influenced by the fibre orientation and stress concentration effects at the fibre ends. The values of $\beta = 0.4$ and 0.1 have been most usually reported as the values that adequately reproduce results obtained experimentally for natural fibre composites but the agreement between the experimental and theoretical values in the case of composites reinforced with randomly oriented fibres was found only when $\beta = 0.1$.

Figure 2 (a) Experimental and predicted tensile strength values in NFC; (b) experimental and predicted tensile modulus values in NFC (see online version for colours)



(a) **(b)**

Table 1 Equations and parameters used in modified rule of mixtures (mRoM)

		Orientation factor (η_0)	*Length factor* (η_l)	*Fibres diameter* (d^F) (μm)	
mRoM	Tensile strength (σ^C)	0.375	$\eta_l = (\tau^* L^F)/(d^F * \sigma^F)$	CR	55.26
	$\sigma^C = \eta_0 * \eta_l * \sigma^F * V^F + \sigma^M * V^M$	[6,7]		C1	54.62
	Young's modulus (E^C)	0.2	$\eta_l = 1 - (\tanh((\beta * L^F)/2)/(\beta * L^F)/2)$	C2	53.45
	$E^C = \eta_0 * \eta_l * E^F * V^F + E^M * V^M$	[3,6]	$\beta = 1/r\sqrt{(E^M/(E^F(1-v)\mathrm{Ln}\sqrt{(\pi/4 * V^F)}))}$	C3	55.78

Predicted tensile strength values of mRoM were higher than experimental ones which is the consequence of bonding quality between the fibres and matrix and fibres discontinuity. The compatibility factor f_C was found to be a good indicator of the interface quality. In well bonded composites the values were within the range 0.16–0.20 [4]. Our f_C results for CR, C1, C2 and C3 composites were 0.18, 0.19, 0.17, and 0.17, respectively, indicating good interface which is not in the agreement with the previous

results of low strength for the C2 sample (12% of increment in strength compared to pure PLA, which denoted inapropriate interface). Hirsch model offers good correlation between the experimental and theoretical results. Predicted tensile strength values were ca. 10% lower than the experimental values, except for the C2 sample. It can be assumed that the interface quality in this sample was very poor, in comparison with C3 sample, where citric acid (CA) has been added as an eco-friendly crosslinker with a positive impact on flame retardant properties of cellulose fibres [3]. Predicted tensile modulus values were higher than experimental values, except for the C3 sample, where predicted values were 30% and 20% lower for mRoM and Hirsch model, respectively. The reasons which may affect predicted results are: usage of models which fit well enough for randomly oriented fibrous reiforcement but are developed for homogenous and isotropic fibres [1] and formation of microvoids between the fibre and matrix [5].

4 Conclusion

Modified *Spartium junceum L.* fibres were used as reinforcement in the NFRC materials with the aim to improve their mechanical properties. Tensile strength and tensile modulus of the composite reinforced with MMT and CA treated Spartium fibres (C3) were increased by 164.0% and 85.7% respectively, compared to pure PLA sample. Obtained results confirmed improvements of mechanical properties of applied samples in comparison to our previous series – reinforced with unmodified fibres and without any crosslinker. A comparison of experimental and theoretical results of NFRC tensile properties was conducted using modified Rule of Mixtures and Hirsch model. The predicted values of tensile properties were only comparable with the experimental coefficient of variation in the case of CR sample, while the predicted values of tensile strength showed partially good agreement only for Hirsch model. Further improvements of novel biocomposites require the enhancement of the affinity between hydrophilic fibre (nanoclay modified *Spartium junceum L.* fibres) and hydrophobic PLA matrix.

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7.6 Spanish Broom (*Spartium junceum* L.) – Feedstock for bioplastic and bioenergy industry - The Hollistic Approach to Environment 9 (2019) 3, p. 44-52 - *reused with permission from publisher*

SPANISH BROOM (*SPARTIUM JUNCEUM L.*) – FEEDSTOCK FOR BIOPLASTIC AND BIOENERGY INDUSTRY

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ABSTRACT

Spanish Broom (*Spartium junceum* L.) is a Mediterranean plant of various usage possibilities. Its fibres were known since ancient time but in some point of last century, more accurately in 1950s, their production was abandoned due to the negative economic effect. Another drawback was large time consumption, especially during the old tradition method – Spanish Broom maceration in salt water. Nowadays, due to technology development and ecological awareness, it is much easier to produce Spanish Broom fibres of enhanced quality. One of the fibre extraction methods is the one assisted with microwave oven. Demerit of such fibre production is in large residue content after obtaining fibres - approx. 90 % of initial Spanish Broom weight.

Due to the need for finding sustainable solutions in the development of new materials, the usage of Spanish Broom fibres in the service of reinforcement for biopolymer poly (lactic acid) (PLA) matrix was investigated. Obtained results target our further research into the direction of Spanish Broom fibres and PLA application in the production of green composites. The aim of this research was to prove that developed product can be categorized under the biodegradable group by investigating its degradation properties using serine endopeptidase enzyme. The results show positive degradation effect while using 50 wt.% (on weight of material) enzyme concentration during a 5-day treatment.

Stem residues of Spanish Broom plant derived from salty water and microwave maceration were further investigated for their potential as raw material for second-generation biofuel production. Examination of its energy properties consisted of determination of proximate and ultimate properties of the biomass. The results show low moisture content (6.5 % - 7.5 %), ash content below 5 % and higher values of fixed carbon and volatile matter content of 13.2 % and 75 %, respectively. Higher heating values that were determined (17.2 - 18.8 MJ/kg) indicate a high quality biomass that can be used most effectively in solid biofuel production.

***Keywords**: Spartium junceum L., Spanish Broom, poly(lactic acid), composites, biodegradation, Savinase enzyme, biomass, solid biofuel*

INTRODUCTION

Spartium junceum L. (SJL) is a shrub-like Mediterranean plant from the family of legumes, Figure 1. It is the only species in the genus Spartium L. It grows up to 1 – 1.5 m, whereas only older plants grow into smaller trees between 4 to 5 m of height and 15 to 20 cm of thickness. It produces intensively yellow flowers, between May and July, and its shoots mature between August and October [1]. Its flowers, seeds, stem, leaves and even root are used for the production of natural dyestuff or oil, the latest being used both for the nutritional purposes, as well as for the essence of perfumes and scents [1].

Figure 1. Representation of SJL plant and its structural above ground axis, which is raw material for fibre production; Left to right: SJL shrub during bloom; Freshly harvested SJL stem; Scanning electron micrograph of SJL fibres extracted from the SJL stem [1]

SJL plant belongs to Fibre crops group based on the Agriculture crop classification, and therefore it has been recognized as excellent raw material for fibre production [2]. Wide distribution of fibre crops is based on the fact that such crops manage to grow in all climate environments (except extremely dry and cold conditions) whose diversity could influence the fibre properties. Therefore, each climate region has one or more fibre crop varieties, which could be utilized delivering economic benefits to rural areas.

SJL fibres belong to the group of bast fibres, sharing similar physico-chemical and mechanical properties with flax fibre which is representative of the bast fibre group [3]. The importance of fibre crops has been known since ancient time in terms of raw materials for garment production or textile products like ropes [1]. Nowadays, the interest is focused on their usage in agriculture, construction, medicine, automotive or chemical industry [4 - 6].

Kovacevic et al. [7] investigated usage of SJL fibres as reinforcement in polymer matrix for possible application in automotive industry. One of the critical issues of novel research targeting products to be used in automotive industry is application of green and biodegradable materials [8]. 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. These materials are relatively cheap, they have specific properties, contributing to the neutralization of CO_2, and they are biodegradable. Although PLA is biodegradable, the basic understanding of its enzymatic degradation related to its blending with another biodegradable polymer still requires better understanding [9 - 12].

However, both fibre and green composites' production, results in large quantities of residues. In 2013, during Summer school ''From Production to final Use'', Cosentino [13] reported on SJL yield as naturally occurring or cultivated crop in the overall areas of 2.5 – 5.0 t ha^{-1} and 4.0 – 7.5 t ha^{-1}, respectively. The fibre yield is usually between 7 - 12 %, depending upon the variety from which it is extracted. These residues, obtained after fibre soaking, are in the liquid form as well as in the crude form, and from the aspect of current global circular economy and bioeconomy strategies, they should be managed somehow.

Hence, the aim of this research was to determine biodegradability of SJL/PLA composite material, and to gain knowledge in the potential of utilizing crude residues after SJL fibre extraction for energy production *via* direct combustion [14].

EXPERIMENTAL

Materials

SJL fibres were obtained from the Spanish Broom plant, which was harvested in the area of town Šibenik, Croatia. The plant was collected in the wilderness of nature and harvesting was done by hand using specialized scissors. After fibre extraction through several maceration processes [15 - 17], the plant residue was collected and air-dried for further investigation as biomass for solid biofuel production.

Materials used for biodegradability test were already prepared composite materials made of PLA, SJL fibres and Montmorillonite nanofiller (MMT) which were subjected to enzymatic degradation [17, 18]. The Fluka buffer solutions were used for setting of pH 9.0 (borax/hydrochloric acid). Enzyme Savinase 16 L was obtained from Strem Chemicals, Inc. It belongs to class of proteases, more accurately it is serine endopeptidase that catalyses selective hydrolysis of ester bonds. It is in liquid form with optimum conditions being 30 - 70 °C, pH 8 - 10 and activity of 16 Kilo Novo Protease Unit KNPU (S/g).

Biodegradability

The weights of the samples were measured prior to immersing them in separate vials containing approx. 1 mL of buffer (pH 9) and Savinase enzyme. The buffer solution was prepared in a 25 mL flask by adding $2.66 \cdot 10^{-5}$ mol/mL $CaCl_2$, 5 mL 1 % Triton solution and 100, 250 and 500 mg respectively of Savinase enzyme, while pH 9 buffer was added to the 25 mL mark on the volumetric flask. Since measurements were made on the basis of 5 parallel tests, every single test vial was filled up with 1 mL of buffer/enzyme solution containing 4, 10 and 20 mg of Savinase and approx. 20 mg of investigated composite material. The enzymatic degradation was performed in the laboratory oven operated at 37 °C for 5 days.

Prior to immersing into the enzyme solution, the samples were cut into rectangular shape and weighed. The samples were than dried in an oven (Elektrosanitarij, Croatia) at 105 ± 5 °C until reaching the constant mass. Every 24 hours, upon immersing into the enzyme solution, samples were thoroughly washed with deionised water and dried again in an oven at 105 ± 5 °C for 24 hours. The weights of the samples after enzymatic degradation were measured and the effect of the enzymatic degradation was determined after 24, 72 and 120 hours by weight loss. The percentage of weight loss after enzymatic degradation ($\Delta m_{24,72,120}$) was calculated according the equation (1):

$$\Delta m_{24,\,72,\,120} = (W_i - W_{24,\,72,\,120})/W_i \cdot 100 \qquad (1)$$

where W_i is the initial weight measured after oven drying at 105 ± 5 °C; $W_{24,\,72,\,120}$ is the weight after enzymatic degradation within a certain time (24 h, 72 h and 120 h).

Biofuels properties

Residue samples after fibre extraction were grounded in a laboratory grinder (IKA Analysentechnik GmbH, Germany). Three replicates of each sample were measured in order to provide reproducibility of the analysis. The biomass samples were analysed according to following standard methods: moisture content (HRN EN 18134-2:2015), ash content (HRN EN ISO 18122:2015), coke content and volatile matter (HRN EN 15148:2009) and fixed carbon (by difference). Carbon, hydrogen, nitrogen and sulphur were determined by the method of dry combustion in a Vario Macro CHNS analyser (Elementar Analysensysteme GmbH, Germany) according to the standard methods HRN EN 15104:2011 and HRN EN 15289:2011, while oxygen content was calculated by difference according to the following formula, where db stands for dry basis:

$$O\,(\%\,db) = 100 - C(\%\,db) - H(\%\,db) - N(\%\,db) - S(\%\,db) - \text{ash}\,(\%\,db) \qquad (2)$$

Heating value was determined according to the HRN EN 14918:2010 standard method by using an oxygen bomb calorimeter (IKA C200 Analysentechnik GmbH, Germany). Heating value is presented as MJ/kg on dry basis.

RESULTS AND DISCUSSION

Description of used samples is presented in Table 1.

Table 1. Description of samples and test conditions in biodegradability examination

Zero sample	Enzyme	Time
PLA – neat polymer	Savinase 16 L – serine endopeptidase Concentrations: 20 %, 50 % and 100 % on weight of zero material. Test conditions: pH 9, T = 37 °C	Samples were exposed to enzymatic treatment for 24, 72 and 120 hours
CR – composite material made of PLA and SJL (reference - untreated) fibres		
C1 - composite material made of PLA and SJL (NaOH treated) fibres		
C2 - composite material made of PLA and SJL (MMT nanoclay treated) fibres		
C3 - composite material made of PLA and SJL (MMT and citric acid CA treated) fibres		

The results of pure PLA and its composites biodegradability are shown in Figure 2. A biodegradation experiment was conducted in the period of five days. According to the weight loss measurements it could be concluded that fibre reinforcements increased the degradation rate compared to neat PLA. Biodegradation rate of PLA composites depends on the biodegradability of all components and the nature of their miscibility [9]. It has been already concluded in our previous research that due to weak adsorption force between the clay particles and the fibre surface - Sample C2 show inappropriate interface properties, which influences faster degradation of such composite material. By comparing used enzyme concentrations, it is visible that the best results were obtained with 50 % Savinase enzyme after 5 days of treatment. Recent study of Singh et al. [10] showed that the incorporation of MMT into PLA increased the biodegradation rate and the effect depends on the organic modifier used in the clays, thus degradation depends on the presence of excess –OH groups in the MMT and its dispersion through matrix which is also visible through experiment group 50%E120h.

Katović et al. investigated properties of SJL fibres and their associated residues after various extraction methods – traditional sea water retting and microwave assisted alkali retting [15]. They have compared chemical composition content of SJL stem before and after fibre extraction and found out that chemical composition of residue after extraction depends on the chosen extraction method. Microwave assisted alkali treated residues have shown increase in cellulose and lignin content compared to sea water retted residues for approximately 5 % and 14 %.

Considering such increase in lignin content and the fact that after SJL fibre extraction approx. 90 % of residue remains unused, we came to the point for further investigation of possible usage of SJL residues as feedstock in bioenergy production.

In order to achieve solid biofuel standardization, ISO TC 238 is working on drafting and publishing of international solid biofuel standards, which set out the expected values of fuel properties for various types of biomass, i.e. proximate and ultimate analysis and determination of heating values [19].

The non-combustible and combustible properties of the SJL residues after fibre extraction by sea water retting and microwave assisted alkali retting are shown in Tables 2 and 3.

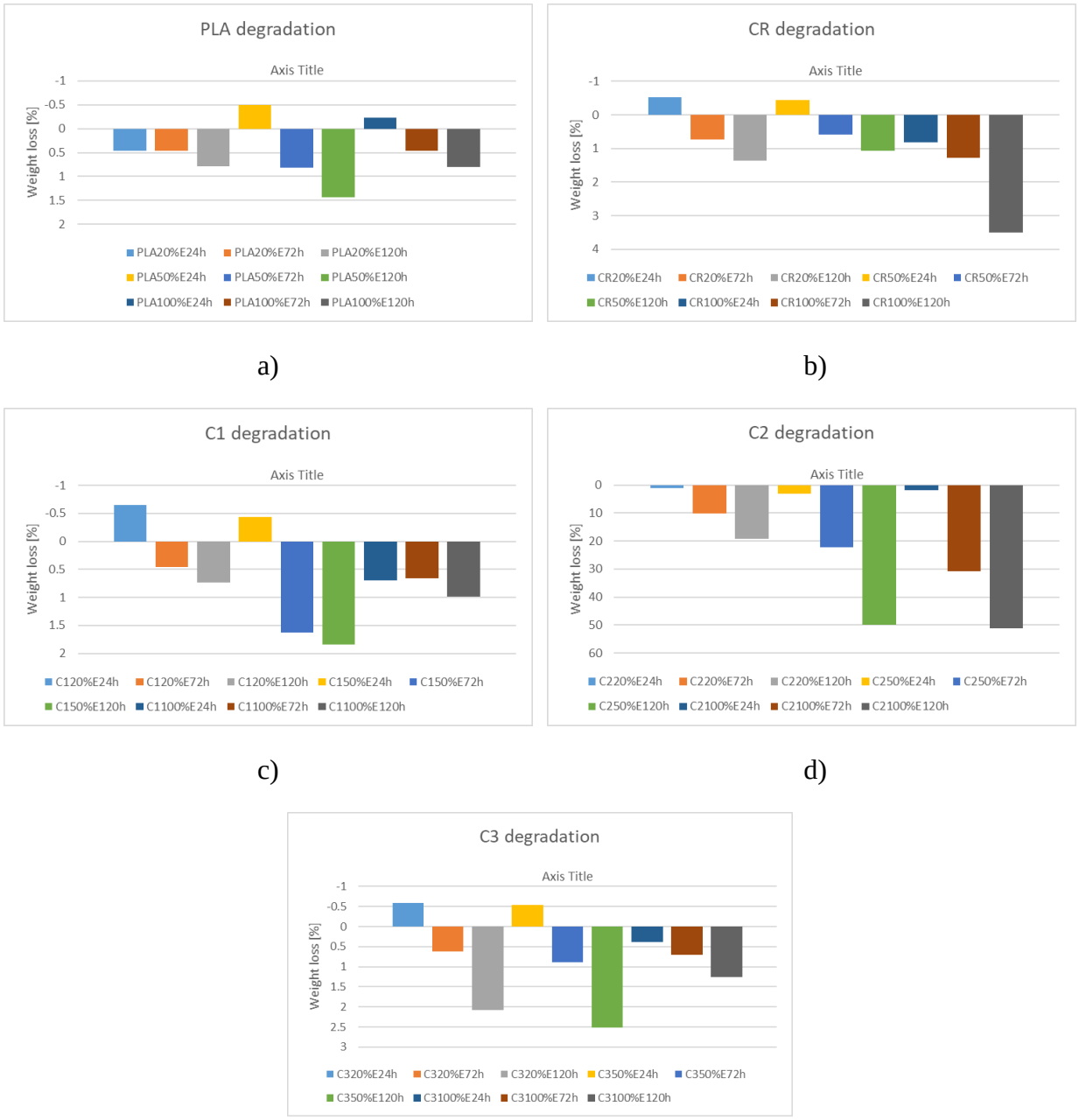

Figure 2. Weight loss percentage of PLA and its composites after enzymatic degradation, symbol explanations in Table 1

Table 2. Non-combustible matter content in the SJL residues after fibre extraction

	MC (%, db)	AC (%, db)	FC (%, db)	Coke (%, db)	Nitrogen (%)
0	6.45 a ± 0.156	2.38 a ± 0.095	7.60 a ± 2.705	9.98 a ± 2.698	0.97 a ± 0.022
Sea Water	7.46 b ± 0.133	4.37 b ± 0.301	10.47 a ± 1.897	14.84 a ± 1.819	0.39 b ± 0.012
Microwave	6.53 a ± 0.092	4.77 b ± 0.045	13.22 a ± 2.701	18.00 ba ± 2.668	0.18 c ± 0.004
Significance	< 0.05*	< 0.05*	0.3160 NS	< 0.05*	< 0.05*

where db – dry basis; MC – moisture content; AC – ash content; FC – fixed carbon; Different letters within a column indicate significant differences at the 5 % level; significance * $p < 0.05$, NS – non significant.

Table 3. Combustible matter content with higher and lower heating values in the SJL residues after fibre extraction

	Carbon (%)	Sulphur (%)	Hydrogen (%)	Oxygen (%)	VM (%, db)	HHV (MJ/kg)	LHV (MJ/kg)
0	46.51 a ± 0.167	0.28 a ± 0.039	7.12 a ± 0.062	45.12 a ± 0.044	83.50 b ± 2.60	18.83 a ± 0.058	17.28 a ± 0.057
Sea Water	43.46 c ± 0.127	0.29 a ± 0.010	6.07 a ± 0.918	49.80 a ± 0.793	77.76 a ± 1.85	17.23 a ± 0.122	15.90 ba ± 0.121
Microwave	44.13 b ± 0.039	0.18 ab ± 0.007	6.76 a ± 0.000	48.75 ba ± 0.050	75.52 a ± 2.64	18.16 a ± 1.112	16.69 a ± 1.112
Significance	< 0.05*	< 0.05*	0.1467 NS	< 0.05*	< 0.05*	0.0907 NS	0.1293 NS

where db – dry basis; VM – volatile matter; HHV – higher heating value; LHV – lower heating value; Different letters within a column indicate significant differences at the 5 % level; significance * $p < 0.05$, NS – non significant.

All samples show significant difference in the non-combustible matter content, except fixed carbon values, where the content is not affected by different method of fibre extraction. The latter was proven by the ANOVA analysis. Fixed carbon represents covalently bonded carbon where higher content of bonded carbon correlates with the higher quality of biomass [20].

Moisture content is important for the purpose of the raw material storage [21]. Residues after microwave assisted extraction show no significant difference in moisture content compared to samples prior to fibre extraction. It is usually advised to keep the moisture content in biomass within the limits of 10 - 15 % since higher moisture content can cause endothermic reaction [21, 22].

Ash is undesirable component of biomass, considering its catalytic influence on thermal decomposition. Higher ash amount points to higher carbon and gas concentrations. Melting point of biomass ash is low, so during thermal process melted ash produces slagging, which prevents energy transfer and lowers combustion efficiency [20]. The obtained ash content of residues after different fibre extractions show no significant difference. Its content is approx. 4.5 %, which is within the expected limits, since SJL belongs to herbaceous and agricultural biomass group that commonly reveals higher ash content than wood biomass, because of different chemical composition and higher mineral share, such as potassium, calcium, magnesium or phosphorus, which are ash-forming elements [23].

Coke content is considered as positive property of biomass and in Table 2 an increase in coke content for residues after microwave assisted extraction process can be observed.

The proximate analysis of two different biomass samples derived from different extraction methods show that volatile matter content is reduced while fixed carbon content increased, pointing to lower concentrations of light hydrocarbons like CO, CO_2, H_2, moisture and tars in the samples which underwent microwave assisted extraction of fibres [21-23].

Table 3 shows that by increasing carbon and hydrogen content, higher heating value also increases because C and H oxidised during combustion by exothermic reactions (formation of CO_2 and H_2O) [24]. The highest heating values were obtained for residues after microwave assisted fibre extraction, with HHV of 18.16 MJ/kg and related LHV of 16.69 MJ/kg.

Although, SJL biomass from residues after fibre extraction show satisfying properties for solid biofuel production. It could be also pre-treated by using biomass torrefaction technology through which physical or chemical characteristics of biomass are modified on purpose, before it is used for final

conversion into a useful energy carrier. Such pre-treatment significantly reduces chlorine and other undesirable components of raw biomass making it more suitable for power generation in pulverised coal fired power plants [25].

CONCLUSION

In this paper, Spanish Broom products in the form of composite material reinforced with its fibres and in the form of residues left after fibre extraction were investigated.

Biodegradation of PLA/SJL composites has been successfully performed by using Savinase 16 L enzyme for 5 days. The best results regarding loss of weight were obtained by 50 % of enzyme concentration which is in fact too high quantity to be used for enzymatic treatments. Therefore, further research will be carried out with several different enzymes suitable for the degradation of PLA and natural fibres. Although, biodegradable plastic won't solve all the problems related to plastic, hopefully it will reduce the environmental impact compared to fossil-based plastic.

Since the most important role of Spanish Broom crop is its utilization for the bast fibre production, a huge disadvantage is in organic residue left after the fibre extraction that represents almost 90 wt% of initial stem weight from which fibres were extracted. In present day we are witnessing the rise of biomass energy industry since the European Commission has set a long-term goal to develop a competitive, resource efficient and low carbon economy by 2050.

Based on the obtained results of moisture, ash, fixed carbon, coke, volatile matter, nitrogen, sulphur, carbon, hydrogen and oxygen content, as well as the obtained heating values, it can be concluded that the residues after fibre extraction can be further utilized as raw material for solid biofuel production in order to achieve more efficient and sustainable production, leading to EU goals of circular economy and bioeconomy.

From the results obtained in this study, it can be concluded that Spanish Broom besides its application in biocomposites' production, is also a promising crop for various applications in biofuels industry.

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8 BIOGRAPHY

Zorana Kovačević was born in Split, Croatia in 1984. After graduating from mathematics and natural sciences Grammar School, she enrolled Design of Clothing and Textiles at the University of Zagreb, Faculty of Textile Technology. For her accomplishments during the undergraduate study she received the Dean's award in 2007 for the best 4th year student, and in 2009, she received acknowledgement for the accomplishments during undergraduate study. She graduated in June 2009, with the diploma thesis: Advanced cotton materials for special purposes, and gained the professional title of graduated engineer of Textile technology. Since September 2009, she has been employed at the Faculty of Textile Technology, working on the FP7 project titled: FP7-REGPOT-2008-1-229801: T-Pot, coordinated by Prof. Sandra Bischof. In 2010, Zorana has started the postgraduate course Textile science and technology at the University of Zagreb, Faculty of Textile Technology. During her work at the Faculty of Textile Technology, Zorana Kovačević has been involved in the following European and national projects: Alternative eco-friendly processing and methods of cellulose modification (2007-2012), E! 5785 FLAMEBLEND (2010-2013), Revitalization of textile production of *Spartium juncem* L. – Development of an indigenous Croatian product: From weed to fabric (2012), ADVANCETEX (2014-2019), MI-TSRC (2018-2020), BIOCOMPOSITES (2019-2023). During her PhD study, Zorana attended several research secondments (Institute for Natural Fibres and Medicinal Plants, Poznan, Poland in duration of two months and Brunel University, London, UK in the duration of three months), summer schools and trainings. Zorana has been a member of the Organizing Committee of the International Textile, Clothing & Design Conference and has received Certificate of Excellence issued by DAAAM International, Vienna, Austria (2010 and 2012) for the successful organization of these conferences. Additionally, Zorana has been awarded with EMS scholarship for participation to the 15th European Microscopy Congress in 2012, Dean's award for scientific excellence in 2013 and TSRC award in 2016 for the best scientific paper of early stage career researchers. As an assistant, Zorana Kovačević has been involved in practical training at the graduate and undergraduate study for following courses: Textile finishing, Textile finishing operations, Dry finishing, High performance finishing, Finishing processes management, Textile fibres and materials and Advanced fibres identification methods. During her scientific research, Zorana has published 1 book, 1 book chapter, 6 reviewed journal papers and 18 scientific papers in conference proceedings.

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LIST OF PUBLICATION	
QUALIFICATION PAPERS	
1.	Kovačević, Z.: Pamučni materijali unaprijeđene vrijednosti za posebne namjene / Advanced cotton materials for special purposes / Master thesis, University of Zagreb Faculty of Textile Technology 12th June 2009, Supervisor: Prof. Edita Vujasinović PhD.
A. SCIENTIFIC WORK	
1.	**SCIENTIFIC PAPERS**
	Paper index according abstract and citation database: Web of Science Core Collection: 5 Science Citation Index Expanded (SCI-EXPANDED)-1955-PRESENT: 4 Conference Proceedings Citation Index – Science (CPCI-S)-1990-present:1 SCOPUS: 6 **Cited by:** Web of Science Core Collection: 33 Web of Science (from All Databases):38 SCOPUS:38 Google scholar: 69 **H-index:** Web of Science Core Collection: 2 Web of Science (from All Databases): 3 SCOPUS: 3 Google scholar: 4
1.1.	**Book**
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