STUDIES ON FIBROUS BIOCOMPOSITES PREPARED WITH NETTLE (*Girardinia diversifolia*) YARN AND FABRIC REINFORCEMENTS IN POLY(LACTIC ACID) MATRIX

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by

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Dedicated to Prof. Jyoti Prakash Goswami and Mrs. Durba Ash Das

for their endless love and encouragement.

CERTIFICATE

This is to certify that the thesis entitled "**Studies on Fibrous Biocomposites Prepared with Nettle (*Girardinia diversifolia*) Yarn and Fabric Reinforcements in Poly(lactic acid) Matrix**", being submitted by Ms. Parna Nandi to the Indian Institute of Technology Delhi, for the award of "Doctor of Philosophy" is a record of bonafide research work carried out by her in the Department of Textile and Fibre Engineering, IIT Delhi. She has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis.

To the best of my knowledge, the results contained in this thesis have not been submitted in part or full to any other university or institute for the award of any degree or diploma.

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ABSTRACT

In this study, a series of nettle/PLA unidirectional biocomposites was prepared by varying the weight content of nettle yarn preform and the biocomposites were tested for physical, mechanical, thermal, and biodegradation properties with a focus on automotive dashboard and door panel applications. As the preform content increased, the static and dynamic mechanical properties of the biocomposites increased initially and decreased afterwards. The biocomposite prepared with equal weight fraction of nettle preform and PLA demonstrated the highest tensile strength (52.56 MPa), flexural strength (42.73 MPa), impact strength (30.96 kJ/m^2), and tensile (Young's) modulus (4.73 GPa). The same biocomposite showed the highest storage and loss moduli and the lowest damping factor at temperatures ranging from 30 °C to 115 °C. The micromechanical analysis revealed that the tensile strength and Young's modulus of the biocomposites could be anticipated by considering the tensile properties of the constituent materials. The morphological and thermal analyses of the biocomposite prepared with 50 % preform content demonstrated good reinforcement wettability, thermal stability (up to 254.62 °C), and high crystallinity (53.13 %). The same biocomposite showed remarkable biodegradability and enrichment of soil nutrients during soil burial tests. Overall, this biocomposite was found to be very promising for dashboards and door panels applications.

Another set of biocomposites was developed by using nettle (*Girardinia diversifolia*) woven fabric and PLA fibres in varied mass fractions. The prepared biocomposites were evaluated for physical, mechanical, thermal, and biodegradation properties. The biocomposite prepared with equal mass fractions of nettle and PLA showed the highest tensile strength (39.87 MPa), Young's modulus (4.37 GPa), flexural strength (50.96 MPa), and impact strength (35.95 kJ/m^2). This biocomposite was found to be quite light-weight (1155 kg/m^3). It exhibited excellent thermal stability till 309 °C. It showed remarkable dynamic mechanical behavior with highest storage modulus (3.9 MPa), loss modulus (0.2 GPa), and lowest damping factor (0.04). After 20 days of burial in soil, this biocomposite lost 10.57 % of its weight and 37.42 % of its strength. The biocomposite made from equal weights of nettle woven reinforcement and PLA matrix showed a great potential for automotive dashboard panel application.

Also, this research work witnessed improved reinforcement-matrix interface by silanisation of the reinforcement surfaces, and the resulting nettle/PLA biocomposites showed enhancement in mechanical, thermo-mechanical, and biodegradation properties. Tri-ethoxy silyl propyl methacrylate (TES-PM) and amino propyl tri-ethoxy silane (APTES) were grafted onto cellulosic nettle reinforcement at various concentrations. The morphological, structural, chemical, and mechanical properties of the nettle woven reinforcement and the degree of silanisation were determined to ensure a high-quality grafting. Functional moiety and concentration of silane coupling agent were found to affect interfacial strength of the biocomposites. It was shown that an appropriate coupling agent with an optimal concentration improved the static mechanical (tensile, flexural, and impact), dynamic mechanical (storage & loss moduli and damping factor), and biodegradation properties of the biocomposites without changing the thermal properties much.

Further, this work employed n-octyl coupling agent to obtain a stronger interface between the nettle reinforcement and the PLA matrix. This resulted in higher static and dynamic mechanical strengths of the biocomposites. Even with a low concentration of n-octyl silane, the mechanical properties of the biocomposites improved. The low density of grafted n-octyl silane guaranteed a complex design of the biocomposite. The developed process and the obtained end-product could be economical since less n-octyl coupling agent was needed. Moreover, n-octyl silane altered fibre cell walls, resulting in an increased dimensional stability, fungal resistance and thermally stability of the biocomposites. All products were recyclable and biodegradable.

Lastly, PLA fiberwebs and multi-ply nettle woven reinforcement were employed in this work to develop nettle/PLA biocomposites with varied reinforcement orientations. Piling of nettle fabrics resulted in improved tensile, flexural, impact, and thermal properties of the biocomposites. The best among all the biocomposites developed in this study was found to be the three-layered woven fabric reinforced PLA biocomposite with a reinforcing orientation of 0°/45°/90°. The tensile strength, Young's (tensile) modulus, flexural strength, impact strength, storage modulus, and loss modulus of the biocomposite were determined as 55.25 MPa, 6.30 GPa, 85.83 MPa, 63.74 J/m^2, 10.08 GPa, and 0.75 GPa, respectively. Though thermal stability of biocomposite was found to be unaffected, the crystallinity rose by 25.84 %. The degradation kinetics and the activation energy of the biocomposite were determined by employing differential fitting of Arrhenius model. This biocomposite lost 15.06 % weight and 50.56 % strength after 20 days of burial in soil.

सारांश

इस अध्ययन में, नेटल/पीएलए के एकदिश बायोकॉम्पोजिट्स की एक श्रृंगारिक शृंखला तैयार की गई जिसमें नेटल यार्न प्रीफॉर्म के भार की मात्रा को बदलकर और बायोकॉम्पोजिट्स को भौतिक, यांत्रिक, तापीय, और जैव अपघटन गुणधर्मों के लिए परीक्षित किया गया, जिसमें ऑटोमोटिव डैशबोर्ड और दरवाजा पैनलों के अनुप्रयोगों पर ध्यान केंद्रित था। प्रीफॉर्म की मात्रा बढ़ने से, बायोकॉम्पोजिट्स की स्थिर और गतिशील यांत्रिक गुणधर्म आरंभिक रूप से बढ़े और बाद में कम हो गए। नेटल प्रीफॉर्म और पीएलए के समान भार अंश वाले बायोकॉम्पोजिट ने सर्वाधिक तनाव प्रतिष्ठा (52.56 एमपीए), फ्लेक्सरल प्रतिष्ठा (42.73 एमपीए), प्रभाव प्रतिष्ठा (30.96 किलोजूल/वर्ग मीटर), और तनाव (यंग) मॉड्यूलस (4.73 जीपीए) प्रदर्शित किया। इसी बायोकॉम्पोजिट ने 30 °C से 115 °C तापमान तक सर्वाधिक भंडारण और लॉस मॉड्यूलस और सबसे कम डैम्पिंग कारक प्रदर्शित किया। माइक्रोमैकेनिकल विश्लेषण ने दिखाया कि अणु सामग्रियों की तनावी गुणधर्मों को ध्यान में लेकर बायोकॉम्पोजिट की तनाव प्रतिष्ठा और यंग मॉड्यूलस का पूर्वानुमान किया जा सकता है। प्रीफॉर्म की 50 % मात्रा के साथ तैयार बायोकॉम्पोजिट की मॉर्फोलॉजिकल और तापीय विश्लेषण ने अच्छी पुनर्निर्माण जलन क्षमता, तापीय स्थिरता (254.62 °C तक), और उच्च क्रिस्टैलिनिटी (53.13 %) प्रदर्शित की। इसी बायोकॉम्पोजिट ने मिट्टी में दफन के दौरान अद्भुत जैव अपघटनीयता और मिट्टी के पोषक तत्वों का समृद्धिकरण दिखाया। सम्पूर्ण रूप से, यह बायोकॉम्पोजिट डैशबोर्ड और दरवाजा पैनलों के अनुप्रयोगों के लिए बहुत उम्मीदवार पाया गया।

बायोकॉम्पोजिट्स के एक और सेट का विकास (गिरार्डिनिया डिवर्सिफोलिया) बुने हुए नेटल के कपड़े और पीएलए रेशे का उपयोग करके विभिन्न भार अंशों में किया गया। तैयार किए गए बायोकॉम्पोजिट्स का भौतिक, यांत्रिक, तापीय, और जैव अपघटन गुणधर्मों के लिए मूल्यांकन किया गया। नेटल और पीएलए के समान भार अंशों से तैयार किए गए बायोकॉम्पोजिट ने सर्वाधिक तनाव प्रतिष्ठा (39.87 एमपीए), यंग मॉड्यूलस (4.37 जीपीए), फ्लेक्सरल प्रतिष्ठा (50.96 एमपीए), और प्रभाव प्रतिष्ठा (35.95 किलोजूल/वर्ग मीटर) प्रदर्शित की। यह बायोकॉम्पोजिट काफी हल्का (1155 किलोग्राम/ घन मीटर) पाया गया। इसने 309 °C तक उत्कृष्ट तापीय स्थिरता प्रदर्शित की। इसने सर्वाधिक भंडारण मॉड्यूलस (3.9 एमपीए), लॉस मॉड्यूलस (0.2 जीपीए), और सबसे कम डैम्पिंग कारक (0.04) के साथ उल्लेखनीय गतिशील यांत्रिक व्यवहार प्रदर्शित किया। मिट्टी में 20 दिनों के बाद, इस बायोकॉम्पोजिट ने अपने वजन का 10.57 % और अपनी मजबूती का 37.42 % खो दिया।

बुने हुए नेटल के रीइंफोर्समेंट और पीएलए मैट्रिक्स के समान वजन से बनी बायोकॉम्पोजिट ऑटोमोटिव ने डैशबोर्ड पैनल अनुप्रयोग के लिए एक बड़ी संभावना को प्रदर्शित किया ।

इसके अलावा, इस अनुसंधान काम ने रीइंफोर्समेंट-मैट्रिक्स इंटरफेस में रीइंफोर्समेंट सतहों के सिलेनेशन द्वारा सुधार का साक्षात्कार किया, और परिणामस्वरूप नेटल/पीएलए बायोकॉम्पोजिट्स में यांत्रिक, थर्मो-यांत्रिक, और जैवअपघटन गुणधर्मों में सुधार हुआ। ट्राई-इथोक्सी सिलिल प्रोपिल मेथाक्रिलेट (टीईएस-पीएम) और एमिनो प्रोपिल त्राई-इथोक्सी सिलेन (एपीटीईएस) को विभिन्न अंशों पर सेलुलोजिक नेटल रीइंफोर्समेंट पर जांचा गया। बुने हुए नेटल रीइंफोर्समेंट और सिलेनेशन की ग्रेड को सुनिश्चित करने के लिए संरचनात्मक, रासायनिक, और यांत्रिक गुणधर्मों की जाँच की गई। सिलेन कप्लिंग एजेंट की कार्यात्मक धातु और उत्तेजक मात्रा का प्रभाव बायोकॉम्पोजिट की इंटरफेसियल मजबूती पर प्रभाव डालता है यह दिखाया गया कि बिना तापीय गुणधर्मों को बदले, उपयुक्त कप्लिंग एजेंट और सर्वोत्तम मात्रा के साथ बायोकॉम्पोजिट के स्थिर मैकेनिकल (तनाव, फ्लेक्सरल, और प्रभाव), गतिशील मैकेनिकल (स्टोरेज, लॉस मॉड्यूलस, और डैम्पिंग कारक), और जैवअपघटन गुणधर्मों में सुधार होता है।

इसके अतिरिक्त, यह काम n-ऑक्टाइल कप्लिंग एजेंट का उपयोग करता है ताकि नेटल रीइंफोर्समेंट और पीएलए मैट्रिक्स के बीच मजबूत इंटरफेस प्राप्त किया जा सके। इससे बायोकॉम्पोजिट की स्थिर और गतिशील यांत्रिक शक्तियाँ बढ़ गई। n-ऑक्टाइल सिलेन की कम मात्रा के साथ भी बायोकॉम्पोजिट के यांत्रिक गुणधर्मों में सुधार हुआ। कम घनत्व में लगाये गए n-ऑक्टाइल सिलेन ने बायोकॉम्पोजिट के एक जटिल डिज़ाइन को निश्चित किया। n-ऑक्टाइल कप्लिंग एजेंट की कम आवश्यकता की वजह से विकसित प्रक्रिया और प्राप्त उत्पाद आर्थिक हो सकते हैं। इसके अलावा, n-ऑक्टाइल सिलेन नेटल की फाइबर सेल दीवारों को बदल देता है, जिससे बायोकॉम्पोजिट की वास्तविक स्थिरता, कवक प्रतिरोध और ऊष्मीय स्थिरता में वृद्धि होती है। सभी उत्पाद पुनर्चक्रणीय और जैविक थे।

अंत में, इस काम में पीएलए फाइबरवेब्स और बहुपरत बुने हुए नेटल रीइंफोर्समेंट का प्रयोग किया गया था ताकि विभिन्न रीइंफोर्समेंट दिशाओं के साथ नेटल/पीएलए बायोकॉम्पोजिट्स विकसित किए जा सकें। नेटल के कपड़े को सटाने से बायोकॉम्पोजिट्स की तनाव, फ्लेक्सरल, प्रभाव, और ऊष्मीय गुणधर्मों में सुधार हुआ। इस अध्ययन में विकसित सभी बायोकॉम्पोजिट्स में से सर्वश्रेष्ठ तीन-परती बुने हुए कपड़े से रीइंफोर्स्र्ड पीएलए बायोकॉम्पोजिट प्राप्त हुआ, जिसमें 0°/45°/90° का रीइंफोर्समेंट अनुविधान था। बायोकॉम्पोजिट की तानाव

प्रतिष्ठा, यंग (तनाव) मॉड्यूलस, फ्लेक्सरल प्रतिष्ठा, प्रभाव प्रतिष्ठा, स्टोरेज मॉड्यूलस, और लॉस मॉड्यूलस को अनुमानित किया गया, जो कि 55.25 एमपीए, 6.30 जीपीए, 85.83 एमपीए, 63.74 किलोजूल / वर्ग मीटर, 10.08 जीपीए, और 0.75 जीपीएए पाया गया। हालांकि बायोकॉम्पोजिट की तापीय स्थिरता प्रभावित नहीं हुई, लेकिन क्रिस्टलाइनिटी 25.84 % बढ़ गई। बायोकॉम्पोजिट की अपघटन की गतिकी और सक्रिय कार्यक्षमता को अरेनियस मॉडल के विभाजनीय समायोजन का उपयोग करके निर्धारित किया गया। इस बायोकॉम्पोजिट ने मिट्टी में गाड़ने के 20 दिनों के बाद 15.06 % वजन और 50.56 % मजबूती खो दी।

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LIST OF SYMBOLS

$C_6H_{12}O_6$	Glucose
C_{r}	Percentage crystallinity of reinforcement
I_{002}	Maximum intensity of diffraction of the (002) lattice peak at 2θ angle
I_{am}	Intensity of diffraction of the amorphous region at 2θ angle
θ	Bragg's angle
R	Flexural rigidity of yarn, measured by a "SHIRLEY" weighted ring yarn stiffness tester
d	Deflection of ring
R_1	Scale reading at lowest point of ring before adding a mass
R_2	Scale reading at lowest point of ring after adding a mass
M	Mass of ring
L	Circumference of ring
Z	Specific value corresponding to the value of $\frac{d}{L}$
ρ_{c}	Density of biocomposite
$w_{c,a}$	Weight of biocomposite in air
$w_{c,h}$	Weight of biocomposite in hexene
$\rho_{c,t}$	Theoretical density of biocomposite
w_r	Mass fraction of reinforcement
ρ_r	Density of reinforcement
w_m	Mass fraction of matrix
ρ_m	Density of matrix
V_p	Void content of biocomposite
T_m	Melting temperature of biocomposite
ΔH_m	Melting enthalpy of biocomposite
T_c	Crystallization temperature of biocomposite
ΔH_c	Crystallization enthalpy of biocomposite
X_c	Degree of crystallinity of biocomposite

$\Delta H^0{}_{\mathrm{m}}$	Melting enthalpy of completely crystallized PLA matrix
W_{i}	Weight of biocomposite specimen before soil buried
W_{f}	Weight of biocomposite specimen before soil buried
σ_{i}	Tensile strength of biocomposite specimen before soil buried
σ_{f}	Tensile strength of biocomposite specimen before soil buried
D	Size of crystallite
K	Scherrer's constant
β	Full-width of peak at half-maximum at 2θ
λ	Wavelength of the x-ray radiation
σ_c	Tensile strength of biocomposite
σ_r	Tensile strength of reinforcement
V_r	Volume fraction of reinforcement
σ_m	Tensile strength of matrix
V_m	Volume fraction of matrix
η	Orientation efficiency factor
α	Average angle of inclination of the fibres from the loading direction
D	Yarn diameter
Z	Yarn twist
T_g	Glass transition temperature of biocomposite
K_{PLA}	Thermal conductivity of PLA matrix
K_{nettle}	Thermal conductivity of nettle reinforcement
$E^{\prime}$	Storage modulus of biocomposite
$E^{\prime\prime}$	Loss modulus of biocomposite
$\tan\delta$	Damping factor of biocomposite
C	Bending length of woven fabric
l	Length of overhang of woven fabric
G	Flexural rigidity of woven fabric
W	Areal density of woven fabric
q	Bending modulus of woven fabric
g	Fabric thickness

$\mathcal{X}$	Empirical interfacial factor in between matrix and reinforcement
$\rho_{\text{TES-PM}}$	Density of TES-PM
ρ_{APTES}	Density of APTES
M	Molar weight of a hydrolysed silane
α	Thermal degradation of biocomposite
t	Conversion time
$k(T)$	Temperature-dependent rate constant of conversion
T	Absolute reaction temperature
$f(\alpha)$	Temperature-independent function of conversion
n	Order of reaction
β	Rate of heating
A	Pre-exponential/ frequency factor
E	Activation energy
R	Universal gas constant
R^2	Coefficient of determination
ΔH_{cc}	Cold crystallization enthalpy of biocomposite
A	Adhesion coefficient between matrix and reinforcement
V_f	Volume fraction of reinforcement
$\tan \delta_c$	Damping factor for biocomposite
$\tan \delta_m$	Damping factor for neat PLA matrix

LIST OF ABBREVIATIONS

PLA	Poly(lactic acid)
PET	Poly(ethylene terephthalate)
ELV	End-of-life-vehicle
NFRBC	Natural Fibre Reinforced Bio-matrix Composite
NFC	Natural fibre-reinforced composites
APTES	Amino propyl tri-ethoxy silane
PHA	Poly(hydroxy alkanoates)
g/L	Gram per liter
BFPRO	Business of forest products, Japan
ATP	Adenosine triphosphate
NADH	Reduced nicotinamide adenine dinucleotide
ROP	Ring-opening polymerization
DSC	Differential scanning calorimetry
LOI	Limiting oxygen index
RTM	Resin transfer moulding
VARTM	Vacuum-assisted resin transfer moulding
PDS	Product design specification
UD	Unidirectional
XRD	X-ray diffractogram
FT-IR	Fourier transform infrared
EDX	Energy dispersive X-ray
ASTM	American society for testing and materials
SEM	Scanning electron microscopy
TGA	Thermo gravimetric analysis
DTG	Differential thermogravimetry
DMA	Dynamic mechanical analysis
ANOVA	Analysis of variance
RoM	Rule of mixtures

DP	Degree of polymerization
PHBV	Poly(3-hydroxybutyrate hydroxyvalerate)
ATRIR	Attenuated total reflection infra-red
NFC	Natural fibre-reinforced composites
TES-PM	Tri-ethoxy silyl propyl methacrylate
w/w	Weight by weight
TEnOS	Tri ethoxy n-Octyl silane
v/v	Volume by volume
CD	Cross-direction
MD	Machine-direction