

**GREEN COMPOSITES BASED ON RAMIE FABRICS AND POLYLACTIC
ACID (PLA)**

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**DEPARTMENT OF TEXTILE & FIBRE ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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ACID (PLA)**

by

Swati

Department of Textile and Fibre Engineering

Submitted

In fulfilment of the requirements of the degree of Doctor of Philosophy

to the



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Dedicated to my family

CERTIFICATE

This is to certify that the thesis titled “**Green composites based on Ramie fabrics and Polylactic Acid (PLA)**”, being submitted by **Ms Swati** to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy**, is a record bonafide research work carried out by her. She has worked under our guidance and supervision and fulfilled the requirements for submitting the thesis, which has attained the standard required for a Ph.D. degree.

The results in this thesis have not been submitted in part or whole to any other university to award any degree or diploma.

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Swati

ABSTRACT

The use of bio-based polymers like polylactic acid (PLA), polycaprolactone, poly (butylene adipate terephthalate) and polyhydroxy butyrate, etc., has proven to be a viable replacement of conventional petroleum-based polymers as they pose a significant threat to the environment and result in speedy depletion of fossil fuels. Owing to its comparable properties with other commodity polymers, the utilisation of PLA in various fields like packaging, biomedical, fibre production, etc., has increased over time. The use of PLA in biocomposites is limited due to its low impact strength and moderate ductility. Thus, this research attempts to tailor PLA properties using sustainable additives like plasticisers, fillers, and natural fibres. Also, the degradation behaviour of PLA mixed with these additives has been explored by soil burial method.

The effect of incorporating halloysite nanotubes (HNT) and polyethylene glycol (PEG) on mechanical and thermal properties of PLA its composites were investigated in the first chapter of this research work. Various concentrations of PEG and HNT were used with PLA, and films were prepared using the solvent casting method. The addition of PEG increased elongation at break but reduced the tensile strength. However, the addition of HNT in PLA/PEG compensated for the loss in tensile strength. Adding 3 wt.% HNT into PLA blend involving 5 wt.% PEG increased its elongation at break by 640% and tensile strength by 22%. At the same time, no significant change in Young's modulus was observed. The dynamic mechanical analysis showed significant improvement in storage modulus of PLA/PEG/HNT films in the rubbery region. Ramie fabric-reinforced PLA composites were manufactured using neat PLA and PLA films with additives by compression moulding technique. The results showed that the addition of PEG decreases the tensile strength, elongation at break and flexural strength compared to ramie/neat PLA composites. But impact strength of ramie/PLA composites improved significantly after the addition of PEG in PLA. On the contrary, the addition of 5 wt.% HNT improved the tensile strength and flexural strength of ramie/PLA composite with marginal loss in elongation. PEG and HNT's addition did not improve the mechanical performance of ramie/PLA composites; however, HNT alone improved their tensile strength and toughness significantly.

The efficacy of selective additives with unique characteristics, namely an impact modifier (lotader AX8900), a plasticiser (TEC) and a reinforcement (HNTs), was studied in improving the performance-based properties of PLA. The aforementioned additives were

extruded with PLA in different mass ratios, and resulting composites were evaluated for rheological, mechanical, and thermomechanical characteristics. The addition of 10 wt.% of lotader in PLA showed optimum tensile properties with approximately 14 times higher elongation at break than neat PLA and negligible fall in tensile strength. When TEC was combined with lotader, the elongation at break improved by 18 times compared to neat PLA. The dynamic mechanical analysis of neat and modified PLA films showed that incorporating HNT in neat PLA or PEG-modified PLA films improved its storage modulus in the rubbery region significantly and shifted $\tan \delta$ towards higher temperatures. When HNT was added to the TEC modified PLA, the performance above the transition temperature was also improved.

In the second part, ramie fabric-reinforced PLA composites were manufactured using compression moulding with neat and modified PLA films with additives (lotader, TEC and HNTs) as a matrix and evaluated their mechanical performance. Tensile testing results revealed that the tensile and flexural strength of ramie/PLA composites remained unaffected after adding lotader. On the other hand, TEC and HNT with lotader adversely affected its tensile and flexural strength. The impact strength of ramie/PLA composites containing lotader showed significant improvement. The same was also observed when both TEC and lotader were used together. The comprehensive study revealed that the optimised concentration of lotader, i.e., 10 wt.% with TEC, significantly improved PLA and ramie/PLA composites' performance.

The use of natural fibre as reinforcement has some disadvantages associated with the hydrophilic nature, causing an inferior interface, resulting in low mechanical properties of composites when used to reinforce hydrophobic matrices. Here, the surface of ramie fabric was modified from hydrophilic to hydrophobic to improve the interfacial interaction between ramie and PLA. Ramie fabric was treated with silane and alkali (i.e., sodium hydroxide and ammonium hydroxide), followed by investigating the effect of treatment on the mechanical and morphological properties of ramie fabric. In the second step, PLA composites with untreated and treated ramie fabrics were prepared using a compression moulding technique, followed by evaluating their mechanical performance and thermomechanical analysis. Silane treated ramie fabrics displayed a decrease in tensile strength with a slight increase in elongation at break. Ramie/PLA composites having silane treated ramie fabric with ammonia and sodium hydroxide showed 10 and 12% improvement in the tensile strength. This improvement can be attributed to better interfacial

adhesion between the more hydrophobic silane treated ramie fibres and PLA matrix. After silane treatment with ammonia and sodium hydroxide, the impact strength of ramie/PLA composites improved. In ramie/PLA composites, the silane treatment of ramie resulted in higher storage modulus at the onset of transition temperature than untreated ramie-based composites. The results imply that silane treatment improves the fibre-matrix interface, thereby enhancing the stress transfer from matrix to fibre. As a result, tensile, impact and dynamic mechanical properties improved.

Being a bio-based polymer, it was crucial to study the degradation behaviour of PLA and its composites with ramie. This part of the work deals with the effect of plasticisers (lotader, PEG and TEC) on the biodegradability of PLA and its composites with HNT and ramie fabric by soil burial method. The samples were tested for their morphological characteristics, mechanical properties, thermal properties, and any chemical changes in the structure to analyse the degradation quantitatively. After 60 days of incubation at 40 °C, the tensile strength of neat PLA films deteriorated by ~22.5%. However, the additives, i.e., lotader, TEC, PEG and HNT, increased the degradation rate of PLA, enhancing the deterioration of tensile strength up to 66% in the case of PLA-lotader film. In case of ramie/PLA composites, the drop in tensile strength was higher initially, i.e., up to 20 days, but reduced after that. After soil burial, thermal analysis of PLA films showed that the crystallinity of PLA films increased as the amorphous regions were attacked preferentially by microorganisms than the crystalline phase. Ramie/PLA composites, where ramie fabric treated with diammonium phosphate degraded extensively at the end of incubation, showed a complete loss of tensile strength after 60 days of soil burial. The EDX analysis of the soil from DAP treated ramie/PLA composites showed improvement in phosphorus content. This implies that after degradation, these composites can improve the fertility of soil.

पारंपरिक पेट्रोलियम पर आधारित बहुलकों के अत्यधिक उपयोग से जीवाश्म ईंधन का तेजी से हास हो रहा है और यह बहुलक पर्यावरण के लिए एक महत्वपूर्ण खतरा बने हुए हैं। जैव आधारित बहुलक जैसे कि पॉलीलैक्टिक एसिड (पी.एल.ए.), पॉलीकैप्रोलैक्टोन, पॉली (ब्यूटलीन एडीपेटे टेरेफ्थैलेट) और पॉलीहाइड्रोक्सी ब्यूटायरेट वर्तमान समय की ज़रूरत बन गये हैं। इन जैव आधारित बहुलकों के तुलनीय गुणों के कारण यह अन्य पण्य बहुलकों के प्रतिस्थापन साबित हुए हैं। विभिन्न क्षेत्रों जैसे पैकेजिंग, बायोमेडिकल, रेशों के उत्पादन आदि में पी.एल.ए. का उपयोग समय के साथ बढ़ रहा है। हालाँकि, बायोकंपोजिट्स में पी.एल.ए. का उपयोग इसकी कम संघट्ट प्रतिरोध क्षमता और मध्यम लचीलेपन के कारण सीमित है। इस शोध में प्लास्टिसाइज़र, पूरक और प्राकृतिक रेशे जैसे संधारणीय योज्य का उपयोग करके पी.एल.ए. के गुणों का सुधार करने का प्रयास किया गया है। इसके अतिरिक्त, इस शोध में योज्य के साथ मिश्रित पी.एल.ए. को मिट्टी में दफ़न करके उसके जैवनिम्नीकरण व्यवहार का भी अन्वेषण किया गया है।

पी.एल.ए. के मैकेनिकल और तापीय गुणों पर हैलोसाइट नैनोट्यूब (एच.एन.टी.) और पॉलीथीन ग्लाइकोल (पी.ई.जी.) को शामिल करने के प्रभाव की जांच की गई। पी.एल.ए. के साथ पी.ई.जी. और एच.एन.टी. की विभिन्न सांद्रता का उपयोग करके, सॉल्वेंट कास्टिंग विधि द्वारा फिल्मों का निर्माण किया गया। पी.ई.जी. के डालने से पी.एल.ए. की दीर्घीकरण क्षमता में वृद्धि हुई परन्तु तनाव-पुष्टि में कमी पाई गयी। हालाँकि, एच.एन.टी. को जब पी.एल.ए./ पी.ई.जी. में मिलाया गया तो तनाव-पुष्टि में हुए नुकसान की भरपाई हो गयी। ३ भार % एच.एन.टी. को जब ५ भार % पी.ई.जी. वाली पी.एल.ए. फिल्म्स के साथ मिश्रित किया गया तो इन फिल्म्स की दीर्घीकरण क्षमता में ६४०% की वृद्धि हुई और तनाव-पुष्टि २२ % की वृद्धि हुई। इसके साथ ही यंग प्रत्यास्तथा गुणांक में कोई खास बदलाव नहीं देखा गया। गतिशील यांत्रिक विश्लेषण ने रबर क्षेत्र में पी.एल.ए./पी.ई.जी./एच.एन.टी. फिल्म्स के भंडारण प्रत्यास्तथा में महत्वपूर्ण सुधार दिखाया। रैमी कपड़े से प्रबलित पी.एल.ए. कंपोजिट्स को संपीड़न मोल्लिंग तकनीक द्वारा योज्य के साथ व योज्य बिना, पी.एल.ए. फिल्म्स का उपयोग करके निर्मित किया गया। परिणामों से पता चला कि पी.ई.जी. को डालने से रैमी / पी.एल.ए. कंपोजिट की तनाव-पुष्टि, दीर्घीकरण क्षमता और बंकन सामर्थ्य कम हो जाता है। परन्तु पी.ई.जी. डालने से रैमी/पी.एल.ए. कंपोजिट की संघट्ट प्रतिरोध में काफी सुधार हुआ। इसके विपरीत, ५ भार % एच.एन.टी. के संयोजन से रैमी/पी.एल.ए. कंपोजिट की तनाव-पुष्टि और बंकन सामर्थ्य में सुधार हुआ, हालाँकि दीर्घीकरण क्षमता में मामूली नुकसान हुआ। पी.ई.जी. और एच.एन.टी. को एकसाथ डालने से रैमी/पी.एल.ए.

कंपोजिट के यांत्रिक प्रदर्शन में सुधार नहीं हुआ; हालांकि, अकेले एच.एन.टी. ने रैमी/पी.एल.ए. कंपोजिट की तनाव-पुष्टि और कठोरता में काफी सुधार किया।

इस शोध में अद्वितीय विशेषताओं वाले विभिन्न योज्य जैसे कि संघट्ट प्रतिरोध संशोधक (लोटाडर AX8900), प्लास्टिसाइज़र (टे. ई. सी.) और पूरक (एच.एन.टी.) का उपयोग पी.एल.ए. के प्रदर्शन-आधारित गुणों में सुधार करने के लिए किया गया। इन विभिन्न योज्य को पी.एल.ए. के साथ अलग-अलग मात्रा में पिघला के उत्सारित किया गया था, और परिणामी कंपोजिट का मूल्यांकन रियोलॉजिकल, मैकेनिकल और थर्मोमैकेनिकल विशेषताओं के लिए किया गया था। पी.एल.ए. और लोटाडर (१० % मात्रा) में मिलाने से मिश्रण की दीर्घीकरण क्षमता में अमिश्रित पी.एल.ए. तुलना में लगभग १४ गुना की वृद्धि पाई गयी। जब पी.एल.ए. और लोटाडर के साथ टे.ई.सी. भी मिलाया गया तो यह पाया गया कि दीर्घीकरण क्षमता में अमिश्रित पी.एल.ए. तुलना में १८ गुना सुधार हुआ। अमिश्रित और संशोधित पी.एल.ए. फिल्मों के गतिशील यांत्रिक विश्लेषण से पता चला है कि अमिश्रित पी.एल.ए. या संशोधित पी.एल.ए. फिल्मों में एच.एन.टी. के समावेश ने रबड़ क्षेत्र में अपने भंडारण प्रत्यास्तथा में काफी सुधार किया और इसके परिणामस्वरूप उच्च तापमान की ओर टैनδ में बदलाव हुआ । जब एच.एन.टी. को टे.ई.सी. संशोधित पी.एल.ए. में मिलाया गया, तो पारगमन तापमान से ऊपर प्रदर्शन में भी सुधार हुआ था।

इस खंड के दूसरे भाग में अमिश्रित और संशोधित पी.एल.ए. की फिल्मों का उपयोग करके रैमी कपड़े से प्रबलित पी.एल.ए. कम्पोजिटस का निर्माण किया गया और साथ ही उनके यांत्रिक प्रदर्शन का मूल्यांकन किया गया। परीक्षण के परिणामों से पता चला कि रैमी/पी.एल.ए. कंपोजिट की तनाव-पुष्टि और बंकन सामर्थ्य लोटाडर के मिश्रण बाद अप्रभावित रही। दूसरी ओर, लोटाडर के साथ टे.ई.सी. और एच.एन.टी. ने इन कम्पोजिटस की तनाव-पुष्टि और बंकन सामर्थ्य पर प्रतिकूल प्रभाव डाल दिया। लोटाडर युक्त रैमी/पी.एल.ए. कंपोजिट की संघट्ट प्रतिरोध क्षमता में महत्वपूर्ण सुधार दिखाई दिया । ऐसा तब भी देखा गया जब टे.ई.सी. और लोटाडर दोनों का एक साथ इस्तेमाल किया गया। व्यापक अध्ययन से पता चला है कि लोटाडर की अनुकूलित मात्रा (१० % मात्रा) को टे.ई.सी. के साथ मिलाने पी.एल.ए. बहुलक और रैमी/पी.एल.ए. कंपोजिट के प्रदर्शन में उल्लेखनीय रूप से सुधार हुआ है।

प्राकृतिक रेशों को बहुलकों के सुदृढीकरण में उपयोग करने के कुछ नुक्सान भी हैं। प्राकृतिक रेशे जलस्रेही होते हैं तथा जब इनका उपयोग जलभीत बहुलकों के सुदृढीकरण के लिए किया जाता है तो अंतरफलक कमजोर बनता है और कम्पोजिटस के यांत्रिक गुण अच्छे नहीं होते हैं। शोध के इस भाग में रैमी कपड़े की सतह को जलस्रेही से जलभीत बनाया गया ताकि रैमी और पी.एल.ए. के

बीच अंतरफलक परस्पर क्रिया में सुधार किया जा सके। रैमी कपड़े को सिलेन और क्षार (यानी सोडियम हाइड्रोक्साइड और अमोनियम हाइड्रोक्साइड) के साथ निरूपण किया गया, जिसके बाद रैमी कपड़े के यांत्रिक और रूपात्मक गुणों पर निरूपण के प्रभाव की जांच की गई। दूसरे चरण में, अनुपचारित और उपचारित रैमी कपड़े के साथ पी.एल.ए. कंपोजिट को संपीड़न मोल्लिंग तकनीक का उपयोग कर तैयार किया गया उनके यांत्रिक प्रदर्शन और थर्मोमैकेनिकल विश्लेषण का मूल्यांकन किया। सिलेन उपचारित रैमी कपड़े तोड़ने तक दीर्घीकरण क्षमता में मामूली वृद्धि के साथ तनाव-पुष्टि में कमी दर्ज की गयी। अमोनिया और सोडियम हाइड्रोक्साइड के साथ सिलेन उपचारित रैमी कपड़े वाले रैमी/पी.एल.ए. कंपोजिट ने तनाव-पुष्टि में १० और १२% सुधार दिखाया। इस सुधार के लिए जलभीत सिलेन उपचारित रैमी कपड़े और पी.एल.ए. के बीच बेहतर अंतरफलक परस्पर क्रिया को जिम्मेदार ठहराया जा सकता है। अमोनिया और सोडियम हाइड्रोक्साइड के साथ सिलेन उपचार के बाद, रैमी/पी.एल.ए. कंपोजिट की संघट्ट प्रतिरोध क्षमता में सुधार हुआ। रैमी/पी.एल.ए. कंपोजिट के मामले में, रैमी के सिलेन उपचार के परिणामस्वरूप अनुपचारित रैमी आधारित कंपोजिट की तुलना में पारगमन तापमान की शुरुआत में उच्च भंडारण प्रत्यास्तथा होती है। परिणामों का मतलब है कि सिलेन निरूपण रेशे और बहुलक की अंतरफलक परस्पर क्रिया में सुधार करता है, और इस तरह बहुलक से रेशे में तनाव हस्तांतरण को बढ़ाता है। नतीजतन, तनाव-पुष्टि, संघट्ट प्रतिरोध क्षमता और गतिशील यांत्रिक गुणों में सुधार होता है।

जैव-आधारित बहुलक होने के कारण, पी.एल.ए. और रैमी के साथ इसके कम्पोजिट्स के अवक्रमण व्यवहार का अध्ययन करना महत्वपूर्ण था। शोध के हिस्से में जैवनिम्नीकरण गति पर प्लास्टिसाइजर (लोटाडर, पी.ई.जी. और टे.ई.सी.), पूरक (एच.एन.टी.) और संघट्ट प्रतिरोध संशोधक (लोटाडर AX8900) युक्त पी.एल.ए. तथा अमिश्रित पी.एल.ए. फिल्म्स और रैमी के साथ इसके कम्पोजिट्स पर इनका प्रभाव देखने के लिए मिट्टी में दवाने की विधि का उपयोग किया गया। मिट्टी में दवाने के बाद समय-समय पर नमूनों को उनकी रूपात्मक विशेषताओं, यांत्रिक गुणों, उष्ण गुणों और संरचना में हुए किसी भी रासायनिक परिवर्तन का विश्लेषण किया गया। ४०°C पर ६० दिनों के ऊष्मायन के बाद, अमिश्रित पी.एल.ए. फिल्मों की तनाव-पुष्टि ~ २२.५% कम हो गई। हालांकि, संशोधित पी.एल.ए. यानी, लोटाडर, टे.ई.सी., पी.ई.जी. और एच.एन.टी. के साथ मिश्रित पी.एल.ए. की तनाव-पुष्टि गिरावट दर में वृद्धि देखी गयी। पी.एल.ए.-लोटाडर फिल्म के मामले में तनाव-पुष्टि में ६६% तक की गिरावट आई। रैमी /पी.एल.ए. कंपोजिट के मामले में, तनाव-पुष्टि में २० दिनों तक ज्यादा गिरावट हुई, लेकिन उसके बाद गिरावट की दर कम हो गई। मिट्टी को दफनाने के बाद, पी.एल.ए. फिल्मों के उष्ण विश्लेषण से पता चला है कि पी.एल.ए. फिल्मों की स्फटिकता में वृद्धि हुई

है क्योंकि स्फटिक क्षेत्र की तुलना में सूक्ष्मजीवों द्वारा अनाकार क्षेत्रों पर हमला करना आसान होता है। डायमोनियम फॉस्फेट के साथ निरूपित किए गए रैमी कपड़े से सुदृढ़ पी.एल.ए. कंपोजिट, मिट्टी में दफन होने के ६० दिनों के बाद पूर्णतया नष्ट हो गए। मिट्टी के ई.डी.एक्स विश्लेषण से यह पता चला कि डायमोनियम फॉस्फेट के साथ निरूपित रैमी /पी.एल.ए. कंपोजिट का निम्नीकृत होने से मिट्टी की उर्वरता बढ़ गयी।

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