# STUDIES ON POLY(L-LACTIDE) BASED BLOCK COPOLYMERS AND BLENDS

**DEBANGA BHUSAN KONWAR**

**DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING**

**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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**by**

**DEBANGA BHUSAN KONWAR**

Department of Materials Science and Engineering

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*Dedicated to My Parents and Pallavi*

# CERTIFICATE

This is to certify that the thesis entitled **"Studies on Poly(L-lactide) based Block Copolymers and Blends"** being submitted by **Mr. Debanga Bhusan Konwar** to the Indian Institute of Technology Delhi, New Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him. Mr. Debanga Bhusan Konwar has worked under my guidance and supervision and has fulfilled the requirements for the submission of his thesis, which to our knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any University or Institute for the award of any degree or diploma.

**Dr. Josemon Jacob**
Professor
Department of Materials
Science and Engineering
Indian Institute of Technology Delhi
New Delhi, India-110016

**Dr. Bhabani K. Satapathy**
Associate Professor
Department of Materials
Science and Engineering
Indian Institute of Technology Delhi
New Delhi, India-110016

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Debanga Bhusan Konwar

# ABSTRACT

Poly(lactic acid) (PLA) is one of the most commercially successful bio-based degradable polymer with high strength, high stiffness, good bio-compatibility and excellent transparency. However, neat PLA suffers from major disadvantage, notably brittleness (low strain-at-break and high modulus), which restricts its use in applications where toughness and impact resistance are required, particularly for durable applications such as in automotive and electronics. Copolymerization and blending with another rubbery polymer are simple, effective ways to modify brittle property of PLA.

In the first section, a series of six-armed star diblock copolymers based on poly(L-lactic acid) PLLA and poly(ε-caprolactone) (PCL) were synthesized by ring opening polymerization (ROP) using stannous octoate as catalyst. The effect of star architecture and length of outer PLLA block on the thermal, rheological and mechanical properties of the copolymers was studied. The melting point and the degree of crystallinity were found to be lower in the case of copolymers as compared to their linear counterparts. The crystallite size corresponding to PLLA component remained the maximum where PCL content was the highest, as estimated by Sherrer's equation based on wide angle X-ray diffraction (WAXD) data. Dynamic rheological studies revealed that the star polymer shaped block copolymers were susceptible to angular frequency (shear deformations) due to presence of large free volume. Atomic force microscopy (AFM) studies revealed that copolymers exhibited microphase separated morphology with elongated (worm-like) microdomains. Dynamic mechanical analysis (DMA) revealed that storage moduli were higher in the case of copolymer with high PLLA content due to higher crystallization and increase in PLLA block length.

In the next section, a series of ABA type triblock copolymers based on biodegradable poly(butylene carbonate) (PBC) and PLLA were synthesized with PBC as the core and varying

the PLLA outer block length. The influence of outer PLLA chain length on structural, thermal, morphological and mechanical properties of triblock copolymers were studied. A significant reduction in the crystallinity of the PBC component was observed in the triblock copolymers as evidenced by differential scanning calorimetry (DSC) and WAXD. A systematic increase in the crystallinity of the PLLA blocks was observed with increasing chain length of PLLA. The triblock copolymers undergo a transition from micro-phase separated lamellar morphology to macro-phase separated unstable morphology in the composition domain of ~ 45-55 wt% of PLLA. A *pseudo*-ductile to *quasi*-brittle transition was observed in the composition range of ~ 45-55 wt% of PLLA corresponding to a change in morphology as confirmed by mechanical analysis.

Another series of ABA type triblock copolymers based on biodegradable aliphatic polycarbonate and PLLA were synthesized with PLLA as the outer block and varying the aliphatic polycarbonate middle block i.e. poly(hexamethylene carbonate), poly(octamethylene carbonate) and poly(decamethylene carbonate). In the first step, a series of hydroxyl terminated aliphatic polycarbonate has been prepared by step growth polymerization of corresponding diols (1,6-hexanediol, 1,8-ocatne diol, 1,10-decane diol) and dimethyl carbonate using NaH as catalyst and they were used as a macroinitiator in the second step to introduce outer block. The influences of middle aliphatic polycarbonate block on structural, thermal, morphological and mechanical properties of the triblock copolymers were investigated.

In the last section of this study, two different series of PLA based blends were developed and studied. First, a series of PLA/PLLA-*b*-PBC-*b*-PLLA blends were developed to study the effect of PLLA-*b*-PBC-*b*-PLLA triblock copolymers as well as PLA wt% on the thermal, mechanical and morphological properties of the blend. DSC studies showed that the triblock

copolymer acted not only as a plasticizer, but also as a nucleating agent depending upon the outer PLLA block length. With shorter PLLA segment of triblock copolymers, $T_g$ and $T_c$ of the blends decrease, owing to the higher content of PBC content. However, triblock copolymers with relatively longer PLLA segment showed unique nucleation effects for PLLA, leading to the elevation of melting point of PLLA. The morphologies as well mechanical properties of blends were also found to depend upon the outer PLLA block length.

Additionally, another PLA/PCL binary blend was developed with comparable PLA to PCL ratio as in six armed PLA/PCL block copolymers. A comparative study of thermal, rheological, morphological and mechanical properties of PLA/PCL blends and copolymers were done. The $T_m$ and the degree of crystallinity were found to be lower for the copolymers than the blends due to poor folding property of star copolymers. Dynamic rheology revealed that the star polymers have lower elastic modulus, storage modulus and viscosity as compared to the corresponding blends with similar composition.

# सार

पॉली (लैक्टिक एसिड) (पीएलए) सबसे अधिक व्यावसायिक रूप से सफल जैव-आधारित गिरावट योग्य बहुलक है जिसमें उच्च शक्ति, उच्च कठोरता, अच्छी जैव-संगतता और उत्कृष्ट पारदर्शिता है। हालांकि, साफ पीएलए प्रमुख नुकसान, विशेष रूप से पित्तता (कम तनाव-पर-ब्रेक और उच्च मॉड्यूलस) से ग्रस्त है, जो अनुप्रयोगों में इसके उपयोग को प्रतिबंधित करता है जहां विशेष रूप से टिकाऊ अनुप्रयोगों जैसे ऑटोमोटिव और इलेक्ट्रॉनिक्स के लिए कठोरता और प्रभाव प्रतिरोध की आवश्यकता होती है। कोपालिमेराइजेशन और एक और रबड़ बहुलक के साथ मिश्रण पीएलए की भंगुर संपत्ति को संशोधित करने के लिए सरल, प्रभावी तरीके हैं।

पहले खंड में, पॉली (एल-लैक्टिक एसिड) पीएलएलए और पीसीएल के आधार पर छह-सशस्त्र स्टार डिब्बॉक कोपोलीमर्स की एक श्रृंखला को उत्प्रेरक के रूप में स्टैनस ऑक्टोएट का उपयोग करके रिंग ओपनिंग पॉलिमरराइजेशन (आरओपी) द्वारा संश्लेषित किया गया था। कोपोलिमर्स के थर्मल, रियोलॉजिकल और मैकेनिकल गुणों पर स्टार आर्किटेक्चर और बाहरी पीएलएलए ब्लॉक की लंबाई का प्रभाव अध्ययन किया गया था। पिघलने बिंदु और क्रिस्टलीयता की डिग्री को उनके रैखिक समकक्षों की तुलना में कोपोलिमर्स के मामले में कम पाया गया था। पीएलएलए घटक से संबंधित क्रिस्टलीय आकार अधिकतम बनी हुई है जहां पीसीएल सामग्री उच्चतम थी, जैसा कि शेरर के समीकरण द्वारा व्यापक कोण एक्स-रे विवर्तन (डब्ल्यूएक्सडी) डेटा के आधार पर अनुमान लगाया गया था। गतिशील रियोलॉजिकल अध्ययन से पता चला है कि स्टार पॉलिमर के आकार वाले ब्लॉक कोपोलिमर बड़े मुक्त मात्रा की उपस्थिति के कारण कोणीय आवृत्ति (कतरनी विकृति) के लिए अतिसंवेदनशील थे। परमाणु बल माइक्रोस्कोपी (एएफएम) के अध्ययन से पता चला है कि कोपोलीमर्स ने विस्तारित (कीड़े की तरह) माइक्रोडोमेन्स के साथ माइक्रोफेज अलग रूपरेखा का प्रदर्शन किया। डायनामिक मैकेनिकल विश्लेषण (डीएमए) ने खुलासा किया कि उच्च क्रिस्टलाइजेशन और पीएलएलए ब्लॉक की लंबाई में वृद्धि के कारण उच्च पीएलएए सामग्री वाले कोपोलीमर के मामले में स्टोरेज मॉड्यूलि अधिक थी।

अगले खंड में, बायोडिग्रेडेबल पॉली (ब्यूटिलीन कार्बोनेट) (पीबीसी) और पीएलएलए के आधार पर एबीए प्रकार ट्रिबॉक कॉपोलिमर्स की एक श्रृंखला को पीबीसी के साथ कोर के रूप में संश्लेषित किया गया था और पीएलएलए बाहरी ब्लॉक की लंबाई अलग-अलग थी। जनजातीय कॉपोलिमर्स के संरचनात्मक, थर्मल, और यांत्रिक गुणों पर बाहरी पीएलएलए श्रृंखला की लंबाई का प्रभाव अध्ययन किया गया था। पीबीसी घटक की क्रिस्टलीनिटी में एक महत्वपूर्ण कमी ट्रायलॉक कोपोलीमर्स में देखी गई थी, जैसा अंतर स्कैनिंग कैलोरीमेट्री (डीएससी) और डब्ल्यूएक्सडी द्वारा प्रमाणित किया गया था। पीएलएलए ब्लॉक की क्रिस्टलिनिटी में व्यवस्थित वृद्धि पीएलएलए की बढ़ती श्रृंखला लंबाई के साथ देखी गई थी। ट्राइबॉक कॉपोलिमर्स को पीएलएलए के ~ 45-55 वाट% के संयोजन डोमेन में सूक्ष्म चरण से अलग लैमेलर मॉर्फोलॉजी से मैक्रो-चरण अलग अस्थिर रूपरेखा से संक्रमण से गुजरना पड़ा। यांत्रिक विश्लेषण द्वारा पुष्टि के रूप में मॉर्फोलॉजी में बदलाव के अनुरूप पीएलएलए के 45-55 वाट% की संरचना रेंज में अर्ध-भंगुर संक्रमण के लिए एक छद्म-लचीलापन देखा गया था।

बायोडिग्रेडेबल एलीफाटिक पॉली कार्बोनेट और पीएलएलए के आधार पर एबीए प्रकार ट्राइबॉक कॉपोलिमर्स की एक अन्य श्रृंखला को पीएलएलए के साथ बाहरी ब्लॉक के रूप में संश्लेषित किया गया था और एलीफाटिक पॉली कार्बोनेट मध्य ब्लॉक i.e. पॉली (हेक्सामाइथिलीन कार्बोनेट), पॉली (ऑक्टमाथिलीन कार्बोनेट) और पॉली (डीकामेथिलीन कार्बोनेट) को बदल दिया गया था। पहले चरण में, हाइड्रोक्साइल समाप्त अल्फाटिक पॉली कार्बोनेट की एक श्रृंखला को संबंधित डायल के चरण वृद्धि बहुलक (1,6-हेक्साडेडियोल, 1,8-ओकटेन डायल, 1,10-डीसीन डायल) और डीएचथिल कार्बोनेट द्वारा उत्प्रेरक के रूप में NaH का उपयोग करके तैयार किया गया है। और बाहरी ब्लॉक को पेश करने के लिए दूसरे चरण में उन्हें मैक्रोइनिएटर के रूप में इस्तेमाल किया गया था। जनजातीय कॉपोलिमर्स के संरचनात्मक, थर्मल, और यांत्रिक गुणों पर मध्यम पॉली कार्बोनेट  ब्लॉक के प्रभाव की जांच की गई।

इस अध्ययन के अंतिम खंड में, पीएलए आधारित मिश्रणों की दो अलग-अलग श्रृंखला विकसित और अध्ययन की गई थीं। सबसे पहले, पीएलए / पीएलएलए-बी-पीबीसी-बी-पीएलएलए मिश्रणों की एक श्रृंखला पीएलएलए-बी-पीबीसी-बी-पीएलएलए ट्राइबॉकॉक कोपोलीमर्स के प्रभाव के साथ-साथ थर्मल, मैकेनिकल और मॉर्फोलॉजिकल गुणों पर पीएलए वाट% के प्रभाव का अध्ययन करने के लिए विकसित की गई थी। मिश्रण डीएससी अध्ययन से पता चला है कि ट्राइबेलॉक कोपोलिमर न केवल प्लास्टाइज़र के रूप में काम करता था, बल्कि बाहरी पीएलएलए ब्लॉक की लंबाई के आधार पर एक न्यूक्लियटिंग एजेंट के रूप में भी काम करता था। पीबीसी सामग्री की उच्च सामग्री के कारण, ट्रिबॉक कॉपोलिमर्स के छोटे पीएलएलए सेगमेंट के साथ, मिश्रणों का टीजी और टीसी कम हो जाता है। हालांकि, अपेक्षाकृत लंबे पीएलएलए सेगमेंट के साथ ट्राइबेलॉक कोपोलीमर्स ने पीएलएलए के लिए अद्वितीय न्यूक्लियेशन प्रभाव दिखाए, जिससे पीएलएलए के पिघलने बिंदु की ऊंचाई बढ़ गई। मिश्रणों के साथ-साथ मिश्रणों के यांत्रिक गुण बाहरी पीएलएलए ब्लॉक की लंबाई पर निर्भर करते हैं।

इसके अतिरिक्त, एक अन्य पीएलए / पीसीएल बाइनरी मिश्रण को तुलनात्मक पीएलए के साथ पीसीएल अनुपात में छह सशस्त्र पीएलए / पीसीएल ब्लॉक कोपोलीमर्स के रूप में विकसित किया गया था। पीएलए / पीसीएल मिश्रणों और कोपोलिमर के थर्मल, रियोलॉजिकल, मॉर्फोलॉजिकल और मैकेनिकल गुणों का तुलनात्मक अध्ययन किया गया। स्टार कोपोलीमर्स की खराब तहखाने की संपत्ति के कारण टीएम और क्रिस्टलीटी की डिग्री कोपलिमर के लिए मिश्रणों की तुलना में कम पाया गया था। गतिशील रियोलॉजी ने खुलासा किया कि स्टार पॉलिमर के पास समान संरचना के साथ संबंधित मिश्रणों की तुलना में कम लोचदार मॉड्यूलस, स्टोरेज मॉड्यूलस और चिपचिपाहट है।

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## List of abbreviations and symbol

| | |
|---|---|
| NMR | Nuclear magnetic resonance |
| FT-IR | Fourier transform-infrared spectroscopy |
| GPC | Gel permeation chromatography |
| DSC | Differential scanning calorimetry |
| TGA | Thermogravimetric analysis |
| DMA | Dynamic mechanical analysis |
| $M_n$ | Number average molecular weight |
| $M_w$ | Weight average molecular weight |
| E' | Storage (Elastic) modulus in DMA |
| E" | Loss (Viscous) modulus in DMA |
| WAXD | Wide angle X-ray diffraction |
| POM | Polarized electron microscopy |
| G' | Storage modulus in parallel plate rheology |
| G" | Loss modulus in parallel plate rheology |
| $T_g$ | Glass transition temperature |
| $T_m$ | Melting point |
| PLLA | Poly(L-lactide) |
| PCL | Poly(ε-caprolactone) |
| SEM | Scanning electron microscopy |
| AFM | Atomic force microscopy |
| SAXS | Small-angle X-ray scattering |
| $T_c$ | Crystallization temperature |
| $T_g$ | Glass transition temperature |
| $T_m$ | Melting temperature |
| $T_{max}$ | Temperature corresponding to maximum degradation |
| WAXD | Wide Angle X-ray Diffraction |
| $X_c$ | Degree of crystallinity |
| $\Delta H_m$ | Enthalpy of melting (fusion) |
| $\eta^*$ | Complex viscosity |