

**TOUGHENING OF POLYBENZOXAZINE BY SILK SERICIN-g-PLA/MARL  
BIOCOMPOSITES**



Juthamas Mahajaroensiri

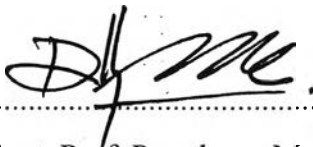
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**Thesis Advisors:** Assoc. Prof. Rathanawan Magaraphan  
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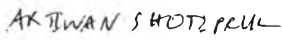
  
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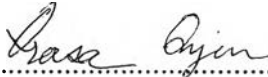
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## ABSTRACT

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Juthamas Mahajaroensiri: Toughening of Polybenzoxazine by Silk Sericin-g-PLA/Marl Biocomposites.

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Polylactide (PLA) is the most widely known biodegradable polymer in use today. Additionally, natural proteins in silk, sericin, have been increasingly used. This work emphasized the synthesis of a graft copolymer, Sericin-g-PLA, in the presence of surface treated marl as a filler, followed by blending with polybenzoxazine to harden the obtained biocomposite. Polybenzoxazine precursor was synthesized from aliphatic diamine, bisphenol-A, and paraformaldehyde by using the faster quasi-solventless approach with 88% yield. The synthesized polybenzoxazine precursor was blended with marl having surface modified by (3-aminopropyl) trimethoxy-silane. The chemical structures of the graft copolymer and polybenzoxazine precursor were confirmed by FTIR and NMR. The results from SEM revealed the better interfacial adhesion between the graft copolymer and the polymer matrix after modification surface of marl. The results of DSC and TGA techniques showed that graft copolymer filled with modified marl can lower the curing temperature of polybenzoxazine; meanwhile, the thermal stability was increasing. The effects of the polybenzoxazine content on the mechanical properties of the biocomposite, particularly flexural strength and impact strength, were exhibited that the biocomposite from 20% graft copolymer added modified marl with polybenzoxazine gave the highest flexural modulus and impact strength.

## บทคัดย่อ

จุฑามาศ มหาเจริญศิริ : การเพิ่มความแข็งแรงให้กับพอลิเบนซอกซาซีนโดยใช้วัสดุคอมพอสิตชีวภาพซึ่งเตรียมได้จากกราฟโคพอลิเมอร์ของโพรตีนไหมเซริซิน, พอลิแลคไทด์, และดินสอพอง (Toughening of Polybenzoxazine by Silk Sericin-g-PLA/Marl Biocomposite) อ. ที่ปรึกษา : รศ. ดร. รัตนาวรรณ มกรพันธุ์และ ดร. ธัญญลักษณ์ ฉายสุวรรณ 188 หน้า

ปัจจุบันพลาสติกย่อยสลายได้ เช่น พอลิแลคไทด์ถูกพัฒนาให้เหมาะสมกับการใช้งาน และได้รับการยอมรับอย่างกว้างขวาง นอกจากนี้ยังมีพอลิเมอร์ที่ได้จากสัตว์จำพวกสารโพรตีนกาวไหมเซริซินก็ได้รับความนิยมในการใช้งานมากยิ่งขึ้นด้วย ดังนั้นงานวิจัยนี้จึงเน้นการสังเคราะห์โคพอลิเมอร์แบบกราฟของกาวไหมเซริซินกับพอลิแลคไทด์ โดยใช้ดินสอพองที่มีการปรับปรุงพื้นผิวมาเป็นสารเติมแต่ง จากนั้นจึงทำการผสมพอลิเบนซอกซาซีนเพื่อเพิ่มความแข็งแรงของผลิตภัณฑ์คอมพอสิตชีวภาพที่ได้ พอลิเบนซอกซาซีนในขั้นเริ่มต้นสังเคราะห์ได้จากสารไดเอมีนสายโซ่ตรง, บิสฟีนอล-เอ, และพาราฟอร์มัลดีไฮด์โดยใช้วิธีเสมือนไม่ใช้ตัวทำละลายซึ่งเป็นวิธีที่พัฒนาขึ้นใหม่ ทำให้ใช้เวลาในการสังเคราะห์น้อยลงโดยที่ได้มวลรวมของสารสังเคราะห์ในปริมาณเทียบเท่ากับการใช้วิธีเดิม (ร้อยละ 88) พอลิเบนซอกซาซีนสังเคราะห์ขั้นต้นจะถูกนำมาผสมกับดินสอพองที่ทำการปรับปรุงพื้นผิวโดยใช้สาร (3-อะมิโนโพรพิล)ไตรเมทอกซี-ไซเลนโครงสร้างทางเคมีของกราฟโคพอลิเมอร์ และพอลิเบนซอกซาซีนขั้นต้นจะถูกวิเคราะห์และยืนยันโดยใช้เครื่องฟลูออเรสเซนซ์สเปกโทรสโกปี จากภาพถ่ายด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดแสดงให้เห็นว่า กราฟโคพอลิเมอร์ซึ่งมีดินสอพองที่ได้ปรับปรุงพื้นผิวเป็นสารเติมแต่งและพอลิเบนซอกซาซีนสามารถยึดติดกันได้ดีขึ้น เทคนิคดีฟเฟอเรนเชียลเทอร์มอลอะนาไลซิสและเทอร์โมกราวิเมตริกอะนาไลซิสถูกนำมาใช้เพื่อศึกษาการบ่ม และคุณสมบัติทางความร้อนของพอลิเบนซอกซาซีนและวัสดุคอมพอสิตชีวภาพ ซึ่งจากผลการทดลองพบว่ากราฟโคพอลิเมอร์ที่เติมดินสอพองซึ่งได้รับการเติมแต่งพื้นผิว จะทำให้อุณหภูมิการบ่มของสารพอลิเบนซอกซาซีนลดลงได้ ในขณะที่เดียวกันก็ช่วยเพิ่มคุณสมบัติทางความร้อนของวัสดุคอมพอสิตด้วย นอกจากนี้งานวิจัยยังทำการศึกษาผลของปริมาณพอลิเบนซอกซาซีน ต่อคุณสมบัติเชิงกลของวัสดุคอมพอสิต โดยการทดสอบด้วยเครื่องกดโค้งงอและเครื่องรับแรงกระแทก ซึ่งจากผลการทดลองพบว่าที่สัดส่วนผสมร้อยละ 20 ของกราฟโคพอลิเมอร์ที่มีดินสอพองซึ่งได้ทำการเติมแต่งพื้นผิวสามารถรับแรงในการกดโค้งงอและแรงกระแทกได้สูงที่สุด

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**ABBREVIATIONS**

LA	Lactide
PLA	Poly lactide
BZ	Benzoxazine
PBZ	Polybenzoxazine
Sericin-g-PLA	Silk sericin protein copolymer graft poly lactide
SA	Silane coupling agent
S acid	Stearic acid