
รายงานวิจัยฉบับสมบูรณ์

การพัฒนาความสามารถในการยืดตัวและความเหนียวของฟิล์มพอลิเมอร์ผสมที่สามารถย่อยสลายได้ทางชีวภาพของพลาสติกไฮดรอกซีแอลกอฮอล์และพอลิบิวทิลีนอะดิפטโคเทเรฟทาเลต

Development of Flexibility and Toughness of Plasticized Polylactide and Poly(butylenes adipate-co-terephthalate) Biodegradable Blend Films

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โครงการวิจัยนี้ได้รับทุนสนับสนุนจากงบประมาณเงินรายได้มหาวิทยาลัย ประเภททุนครูอาจารย์ มหาวิทยาลัยสงขลานครินทร์ ประจำปีงบประมาณ 2557 รหัสโครงการ SCI570376S

1. ชื่อโครงการ การพัฒนาความสามารถในการยืดตัวและความเหนียวของฟิล์มพอลิเมอร์ผสมที่สามารถย่อยสลายได้ทางชีวภาพของพลาสติกไฮดรอกซีพอลิแล็กไทด์และพอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลต

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2. ชื่อคณะผู้วิจัย

- 2.1 ชื่อ นามสกุล ดร.วรศักดิ์ เพชรวโรทัย

- 2.1.1 คุณวุฒิ ปริญญาเอก

- 2.1.2 สถานที่ทำงาน ภาควิชาวิทยาศาสตร์และเทคโนโลยีวัสดุ คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์

- 2.1.3 โทรศัพท์ 074-288398

- 2.1.4 หน้าที่หรือความรับผิดชอบในโครงการ หัวหน้าโครงการวิจัย

- 2.2 ชื่อ นามสกุล รองศาสตราจารย์ ดร.วราภรณ์ ตันรัตนกุล

- 2.2.1 คุณวุฒิ ปริญญาเอก

- 2.2.2 สถานที่ทำงาน ภาควิชาวิทยาศาสตร์และเทคโนโลยีวัสดุ คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์

- 2.2.3 โทรศัพท์ 074-288362

- 2.2.4 หน้าที่หรือความรับผิดชอบในโครงการ ที่ปรึกษาโครงการวิจัย

3. กิตติกรรมประกาศ

ขอขอบคุณภาควิชาวิทยาศาสตร์และเทคโนโลยีวัสดุ คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์ที่เอื้อเฟื้อสถานที่ใช้ในการทำการวิจัย ศูนย์เครื่องมือวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัยที่ให้ความอนุเคราะห์ในการส่งตัวอย่างทดสอบ นอกจากนี้ คณะผู้วิจัยขอขอบคุณคุณเศียร บัวแก้ว ช่างเทคนิคภาควิชาวิทยาศาสตร์และเทคโนโลยีวัสดุที่ช่วยดำเนินการแก้ไขและซ่อมเครื่องอัดรีดแบบสกรูคู่ทำให้ทางผู้วิจัยสามารถดำเนินการวิจัยต่อได้ในระยะเวลาที่กำหนด ขอขอบคุณ Dr Brian Hodgson สำหรับการช่วยตรวจทานภาษาอังกฤษสำหรับการตีพิมพ์ และขอขอบคุณ ดร.นิรันุช ภูสันติที่ช่วยในการตรวจสอบข้อมูล ร่วมวิเคราะห์และวิจารณ์ผลการทดลองในส่วน of สมบัติทางความร้อน รวมทั้ง รศ.ดร.วราภรณ์ ตันรัตนกุลที่ให้คำปรึกษาโครงการวิจัยและตรวจทานการเขียนผลงานวิจัยสำหรับการตีพิมพ์

4. บทคัดย่อ

พอลิแล็กไทด์เป็นพลาสติกย่อยสลายได้ทางชีวภาพที่รู้จักกันอย่างแพร่หลาย เนื่องจากสมบัติที่โดดเด่นหลายประการ เช่น ความแข็งแรงและมอดุลัสสูง ความใส เป็นวัสดุที่เป็นมิตรต่อสิ่งแวดล้อม ไม่เป็นพิษ และสามารถย่อยสลายได้ทางชีวภาพ เป็นต้น แต่อย่างไรก็ตาม ข้อจำกัดของพอลิแล็กไทด์ คือ การยึดตัวได้น้อยและการเกิดผลึกซ้ำซึ่งทำให้ประยุกต์ใช้ในงานด้านฟิล์มและบรรจุภัณฑ์ได้จำกัด ในงานวิจัยนี้สนใจศึกษาการปรับปรุงสมบัติการยึดตัวและความเหนียวของพอลิแล็กไทด์ ฟิล์มพอลิเมอร์ผสมของพอลิแล็กไทด์ที่มีการเติมสารพลาสติกไซเซอร์และพอลิบิวทิลีนอะดิเพตโคเทรฟเทเลตถูกเตรียมผ่านการใช้เครื่องอัดรีดแบบสกรูคู่ สมบัติการยึดตัวและความเหนียวของพอลิแล็กไทด์ถูกปรับปรุงผ่านกระบวนการก่อผลึก การเพิ่มความเป็นพลาสติก และการปรับปรุงความเข้ากันได้ ตามลำดับ พลาสติกไซเซอร์และสารก่อผลึกถูกใช้เพื่อเพิ่มความสามารถในการเคลื่อนไหวได้ของสายโซ่พอลิเมอร์และการเกิดผลึกของพอลิแล็กไทด์ ขณะที่สารเสริมสภาพความเข้ากันได้ถูกใช้เพื่อปรับปรุงอันตรกิริยาระหว่างเฟสของพอลิเมอร์ผสมของพอลิแล็กไทด์และพอลิบิวทิลีนอะดิเพตโคเทรฟเทเลต ไตรเอทิลซิเตรท ไตรคลีซิลฟอสเฟต และพอลิเอธิลีนไกลคอลถูกใช้เป็น พลาสติกไซเซอร์ที่ 0 ถึง 20 ส่วนในร้อยส่วน ขณะที่ไทเทเนียมไดออกไซด์ ทัลค์ และแคลเซียมคาร์บอเนตขนาดนาโนถูกใช้เป็นสารก่อผลึกที่ 0 ถึง 4 ส่วนในร้อยส่วน นอกจากนี้ โทลูอินไดฟีนิลไดไอโซไซยาเนตและพอลิแล็กไทด์กราฟต์มาเลอิกแอนไฮไดรด์ถูกใช้เพื่อปรับปรุงสภาพความเข้ากันได้ที่ร้อยละ 0 ถึง 9 โดยน้ำหนักของพอลิบิวทิลีนอะดิเพตโคเทรฟเทเลต ผลของปริมาณพอลิบิวทิลีนอะดิเพตโคเทรฟเทเลต ชนิดและปริมาณของพลาสติกไซเซอร์ สารก่อผลึก และสารเสริมสภาพความเข้ากันได้ รวมทั้งอัตราส่วนในการผสมที่มีต่อสมบัติทางกายภาพ สมบัติทางความร้อน ลักษณะทางสัณฐานวิทยา และสมบัติเชิงกลของพอลิเมอร์ผสมของพอลิแล็กไทด์ถูกศึกษา ผลการทดลองแสดงให้เห็นว่าการเติมสารก่อผลึกช่วยเพิ่มการยึดตัวและความทนแรงกระแทกให้กับพอลิแล็กไทด์ได้ แต่การเติมในปริมาณมากเกินไปทำให้ความทนแรงดึงลดลง เมื่อเปรียบเทียบกับแล้วพบว่าการใช้ไทเทเนียมไดออกไซด์ ให้สมบัติดีที่สุดเมื่อ ทัลค์ และแคลเซียมคาร์บอเนตขนาดนาโน นอกจากนี้ การเติมสารก่อผลึกร่วมกับพอลิบิวทิลีนอะดิเพตโคเทรฟเทเลตที่ร้อยละ 10 โดยน้ำหนักช่วยปรับปรุงการยึดตัว ความทนแรงกระแทก และเสถียรภาพทางความร้อนให้กับพอลิแล็กไทด์ได้ สำหรับการเติมพลาสติกไซเซอร์ พบว่าไตรเอทิลซิเตรทเหมาะที่จะนำมาใช้กับพอลิแล็กไทด์ พอลิแล็กไทด์กราฟต์มาเลอิกแอนไฮไดรด์แสดงให้เห็นว่าเป็นสารเสริมสภาพความเข้ากันได้ที่มีประสิทธิภาพที่ดีกว่าโทลูอินไดฟีนิลไดไอโซไซยาเนตเพื่อเพิ่มความเข้ากันได้ และปรับปรุงสมบัติต่าง ๆ ของฟิล์มพอลิเมอร์ผสม

Abstract

Poly lactide (PLA) becomes a well-known biodegradable plastic because of many outstanding advantages i.e., high strength, high modulus, transparency, environmentally friendly material, non-toxicity, and fully degradation in few weeks. However, drawbacks of PLA are brittleness and slow crystallization which limits its several usages, especially in film and packaging applications. In this work, we focus on an improvement of PLA properties in terms of flexibility and toughness. Plasticized PLA and poly(butylene adipate-co-terephthalate) (PBAT) biodegradable blend films were prepared through melt extrusion technique. Flexibility and toughness of the PLA blend films were developed by nucleation, plasticization, and compatibilization processes, respectively. Plasticizers and nucleating agents were used for enhancing chain mobility and crystallization of the PLA blend films, whereas compatibilizers were added for improving an interfacial adhesion between two phases of PLA and PBAT. PBAT acts as an impact modifier, while triethyl citrate (TEC) tricresyl phosphate (TCP), and poly(ethylene glycol) 400 (PEG 400) are used as a plasticizer. Titanium dioxide, nano-precipitated calcium carbonate (NPCC) and talc act as a nucleating agent. Furthermore, PLA and PBAT blend films were compatibilized by two types of compatibilizers (toluenediphenyl diisocyanate (TDI) and maleic anhydride (MA)). PBAT content was varied from 0 to 50 wt%, whereas plasticizer, nucleating agent, and compatibilizer levels were differed from 0 to 20 phr, 0 to 2 phr, and 0 to 9 wt% based on PBAT amounts, respectively. The effects of PBAT amounts, types and contents of plasticizer, nucleating agent, and compatibilizer, as well as blend compositions on the physical, thermal, morphological, and mechanical properties of the PLA blend films were investigated. The results indicated that the addition of a nucleating agent greatly increased the elongation at break and the impact strength of PLA; however, the tensile strength decreased especially with high amounts of loading. Comparatively, the overall properties of the PLA composites with titanium dioxide were higher than those containing NPCC and talc. For the PLA/PBAT/nucleating agent blend films, the results indicated that the presence of 10 wt% PBAT significantly improved the elongation at break, impact toughness, and thermal stability of PLA but decreased its tensile strength. Furthermore, TEC could be an effective plasticizer for PLA. PLA-g-MA showed a greater efficiency than TDI for improving the overall properties of the compatibilized PLA/PBAT blend films

5. บทสรุปผู้บริหาร

5.1 บทนำ

หนึ่งในพลาสติกย่อยสลายได้ทางชีวภาพที่เป็นที่รู้จักและยอมรับว่ามีความเป็นไปได้มากที่สุดที่นำมาใช้ทดแทนพลาสติกทั่วไป คือ พอลิแลคไทด์ (Polylactide, PLA) เนื่องจากพอลิเมอร์ชนิดนี้มีข้อดีหลายประการ อาทิ สามารถย่อยสลายได้ในระยะเวลาอันสั้น ผลิตภัณฑ์ที่ได้ไม่เป็นพิษต่อสิ่งแวดล้อม มีสมบัติเชิงกลหลายประการเทียบได้กับพลาสติกทางการค้าอย่าง พอลิเอทิลีนเทเรฟทาเลต (Poly(ethylene terephthalate), PET) และพอลิสไตรีน (Polystyrene, PS) ซึ่งมีความใส น้ำหนักเบา ขึ้นรูปเป็นผลิตภัณฑ์ต่างๆได้ง่าย และประยุกต์ใช้งานในด้านต่างๆได้อย่างหลากหลายทั้งงานด้านการแพทย์ วิศวกรรมเนื้อเยื่อ การเกษตรกรรม อุตสาหกรรมรถยนต์ รวมทั้งบรรจุภัณฑ์ต่างๆ เช่น ฟิล์ม โฟม เป็นต้น อย่างไรก็ตาม ข้อจำกัดของการใช้งานพอลิแลคไทด์คือ ราคาที่ค่อนข้างสูงเมื่อเปรียบเทียบกับพลาสติกทางการค้าจำพวกพอลิโอเลฟินส์ที่ใช้กันอย่างแพร่หลายในงานด้านบรรจุภัณฑ์ เนื่องจากเทคโนโลยีในการผลิตที่ยุ่งยากซับซ้อน นอกจากนี้ พอลิแลคไทด์ยังมีความเหนียวและยืดหยุ่นต่ำสูง แข็งแต่เปราะ รวมทั้งสมบัติการยึดตัวที่น้อย ทำให้การนำพอลิแลคไทด์ไปใช้งานในด้านต่างๆ ยังคงค่อนข้างจำกัด โดยเฉพาะอย่างยิ่ง การใช้งานเป็นฟิล์มและบรรจุภัณฑ์ แนวทางหนึ่งที่น่าสนใจที่ใช้ในการแก้ปัญหาคือ การใช้เทคโนโลยีการผสมกับวัสดุอื่นที่มีความเหนียวและยืดตัวได้ดี เพื่อปรับปรุงสมบัติการยึดตัวได้ของพอลิแลคไทด์ ตัวอย่างเช่น การผสมพอลิแลคไทด์กับพอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลต (PBAT) เป็นต้น

พอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลต (PBAT) ก็เป็นอีกหนึ่งในพลาสติกย่อยสลายได้ทางชีวภาพที่กำลังได้รับความสนใจมากขึ้นๆ เนื่องจาก ข้อโดดเด่นหลายประการ เช่น นอกจากจะสามารถย่อยสลายได้อย่างสมบูรณ์ภายในระยะเวลาไม่นาน ไม่เป็นพิษต่อสิ่งแวดล้อม สามารถนำมาใช้งานเป็นบรรจุภัณฑ์ที่เข้ากับอาหารได้แล้ว ยังมีสมบัติการยึดตัวได้สูงมากเมื่อเปรียบเทียบกับพลาสติกย่อยสลายได้ทางชีวภาพชนิดอื่นๆ ทำให้การประยุกต์ใช้งานด้านต่างๆ ของพอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลตมีความหลากหลาย อย่างไรก็ตาม แนวทางดังกล่าวยังไม่ได้รับการพัฒนาอย่างแพร่หลายนักในประเทศไทยหรือยากที่จะสามารถนำมาใช้ได้ในระดับอุตสาหกรรม เนื่องจากพอลิแลคไทด์และพอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลตนั้นเข้ากันได้ไม่ดี ทำให้สามารถเติมพอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลตลงในพอลิเมอร์ผสมได้ในปริมาณที่จำกัด เนื่องจากปริมาณร้อยละของพอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลตที่เพิ่มขึ้นทำให้เกิดการแยกเฟส (phase separation) ของวัสดุทั้งสองอย่างชัดเจน และส่งผลให้สมบัติเชิงกลของพอลิเมอร์ผสมที่ได้ต่ำลง จึงต้องมีการปรับปรุงสมบัติของวัสดุอีกหลายอย่างระหว่างการผสม เช่น การใช้สารเสริมสภาพความเข้ากันได้เพื่อเพิ่มความเข้ากันได้ของพอลิแลคไทด์และพอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลต การเติมสารก่อผลึกเพื่อช่วยเพิ่มอัตราเร็วในการเกิดผลึก และปรับปรุงสมบัติเชิงกลของพอลิเมอร์ผสม รวมทั้งการใช้พลาสติกไฮเซอร์ร่วมด้วยเพื่อให้เกิดการเสริมประสิทธิภาพในการยึดตัวได้ของพอลิเมอร์ผสม ซึ่งจากการทบทวนวรรณกรรมที่ผ่านมาของผู้วิจัยพบว่า แนวทางการใช้งานร่วมกันของทั้งสารก่อผลึก พลาสติกไฮเซอร์ และสารเสริมสภาพความเข้ากันได้

ได้ยังไม่มีการศึกษาและวิจัย มีเพียงการแยกศึกษาในแต่ละการใช้งานแบบเดี่ยว ๆ ของสารเติมแต่งซึ่งก็ปรับปรุงสมบัติได้อย่างมีประสิทธิภาพ ดังนั้น ความเป็นไปได้สูงที่การใช้งานร่วมกันจะสามารถทำให้มีการปรับปรุงสมบัติด้านความเหนียวและการยึดตัวได้ของพอลิแลกไทด์ได้อย่างมีนัยสำคัญ อันจะนำไปสู่ความก้าวหน้าในเชิงวิชาการของงานวิจัยด้านพลาสติกย่อยสลายได้ทางชีวภาพ และการใช้งานด้านต่าง ๆ ที่กว้างขวางขึ้นของพอลิแลกไทด์ ดังนั้น งานวิจัยนี้จึงมีวัตถุประสงค์เพื่อศึกษาวิธีการเตรียมฟิล์มพอลิเมอร์ผสมที่สามารถย่อยสลายได้ทางชีวภาพของพอลิแลกไทด์และพอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลตด้วยเครื่องอัดรีดแบบสกรูคู่และเครื่องกดอัด โดยศึกษาการผสมพอลิเมอร์และสารเติมแต่งต่าง ๆ เช่น สารก่อผลึก พลาสติกไซเซอร์ และสารเสริมสภาพความเข้ากันได้ที่อัตราส่วนแตกต่างกัน เพื่อปรับปรุงสมบัติความเหนียว และการยึดตัว ณ จุดขาดของพอลิแลกไทด์ ในงานวิจัยนี้เน้นทำการศึกษาผลของปริมาณของพอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลต ชนิดและปริมาณของสารก่อผลึก พลาสติกไซเซอร์ และสารเสริมสภาพความเข้ากันได้ที่มีต่อสมบัติทางกายภาพ สมบัติเชิงกล สมบัติทางความร้อน และลักษณะทางสัณฐานวิทยาของพอลิเมอร์ผสมที่เตรียมได้

5.2 วัตถุประสงค์

- เพื่อศึกษาวิธีการและสภาวะที่เหมาะสมในการเตรียมฟิล์มพอลิเมอร์ผสมที่สามารถย่อยสลายได้ทางชีวภาพของพลาสติกไซด์พอลิแลกไทด์และพอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลต
- เพื่อศึกษาผลของปริมาณของพอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลต ชนิดและปริมาณของพลาสติกไซเซอร์ สารก่อผลึกและสารเสริมสภาพความเข้ากันได้ รวมทั้ง ผลของอัตราส่วนองค์ประกอบต่าง ๆ ที่มีต่อสมบัติทางกายภาพ สมบัติเชิงกล สมบัติทางความร้อน และลักษณะทางสัณฐานวิทยาของพอลิเมอร์ผสมพอลิแลกไทด์เปรียบเทียบกับพอลิแลกไทด์บริสุทธิ์
- เพื่อปรับปรุงความสามารถในการยึดตัวและความเหนียวของฟิล์มพอลิเมอร์ผสม

5.3 สรุป

จากงานวิจัยแสดงให้เห็นได้ชัดเจนว่าแนวทางการใช้กระบวนการก่อผลึก การเพิ่มความเป็นพลาสติก และการปรับปรุงความเข้ากันได้โดยการใช้สารก่อผลึก พลาสติกไซเซอร์ และสารเสริมสภาพความเข้ากันได้สามารถปรับปรุงสมบัติการยึดตัวและความเหนียวของฟิล์มพอลิเมอร์ผสมของพอลิแลกไทด์และพอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลตได้อย่างมีประสิทธิภาพ สารก่อผลึกช่วยเร่งกระบวนการก่อผลึกให้กับพอลิเมอร์ผสมได้ผ่านกระบวนการก่อผลึกแบบเนื้อผสม (heterogeneous nucleation) เห็นได้ชัดจากการมีปริมาณผลึกที่เพิ่มขึ้น อุณหภูมิการเกิดผลึกเพิ่มขึ้น และมีอุณหภูมิการเกิดผลึกแบบเย็นที่ลดลง นอกจากนี้การเติมสารก่อผลึกร่วมกับการใช้พอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลตและสารเพิ่มความเหนียวพลาสติก ส่งผลให้ความทนแรงกระแทกและการยึดตัว ณ จุดขาดของพอลิเมอร์ผสมเพิ่ม

สูงขึ้น แสดงให้เห็นถึงความเหนียวและการยึดตัวที่สูงขึ้นของฟิล์มพอลิเมอร์ผสม โดยเฉพาะอย่างยิ่งการใช้ TiO₂ และ TEC ที่ 1 phr และ 15 phr ตามลำดับ นอกจากนี้ การเติมสารเสริมสภาพความเข้ากันได้ทั้ง TDI และ PLA-g-MA ช่วยปรับปรุงสมบัติความทนแรงดึงและความทนต่อแรงกระแทกได้ เนื่องจากการเพิ่มขึ้นของอันตรกิริยาระหว่างเฟสของพอลิแลกไทด์และพอลิบิวทิลีนอะดิเพตโคเทเรฟทาเลตสอดคล้องกับสมบัติเชิงกลและลักษณะทางสัณฐานวิทยา แต่ควรเติมในปริมาณที่เหมาะสม PLA-g-MA แสดงให้เห็นว่ามีประสิทธิภาพในการเป็นสารเสริมสภาพความเข้ากันได้ที่ดีกว่า TDI อย่างไรก็ตาม การใช้สารเติมแต่งทั้งสารก่อผลึกและสารเสริมสภาพความเข้ากันได้มีผลทำให้เสถียรภาพทางความร้อนของพอลิเมอร์ผสมลดลง (รายละเอียดดังแสดงในเอกสารแนบหมายเลข 1 ถึง 3)

จากโครงการวิจัยดังกล่าวคณะผู้วิจัยสามารถตีพิมพ์เผยแพร่ผลงานวิชาการในระดับนานาชาติ ในฐานข้อมูล Web of Science (ISI) จำนวน 2 ฉบับ ได้แก่

- Synergistic Effect of Nucleation and Compatibilization on the Polylactide and Poly(butylene adipate-co-terephthalate) Blend Films. *Chinese Journal of Polymer Science*. 2016, 34(9), 1129-1140 Published online: 28 July 2016, DOI: 10.1007/s10118-016-1834-0 (เอกสารแนบหมายเลข 1)
- Mechanical Characteristics and Thermal Behaviors of Polylactide Blend Films: Influence of Nucleating Agent and Poly(butylene adipate-co-terephthalate). *Plastics, Rubber and Composites: Macromolecular Engineering*. 2016, 45(8), 333-345 Published online: 07 July 2016, DOI: 10.1080/14658011.2016.1197556 (เอกสารแนบหมายเลข 2)

6. ภาคผนวก

6.1 สำเนาบทความที่ได้รับการตีพิมพ์แล้ว

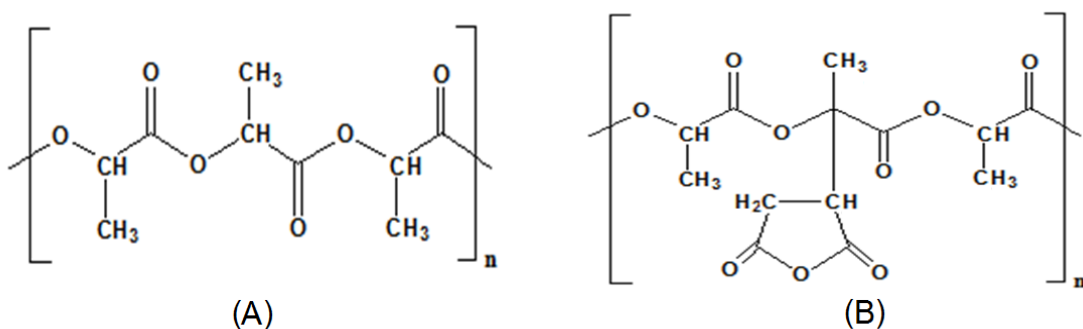
ตามเอกสารแนบหมายเลข 1 และ 2

6.2 ผลการทดลองส่วนที่ยังไม่ได้ตีพิมพ์

การศึกษาผลของการเตรียมสารเสริมสภาพความเข้ากันได้ PLA-graft-MA (PLA-g-MA)

การทดลองในส่วนนี้เป็นการเตรียมสารเสริมสภาพความเข้ากันได้ PLA-g-MA ซึ่งเตรียมได้จากการทำปฏิกิริยาการกราฟต์พอลิแลกไทด์ด้วยสารมาเลอิกแอนไฮไดรด์ที่ความเข้มข้นร้อยละ 0 – 5 ร่วมกับการใช้สาร Luperox (L101) เป็นสารริเริ่มปฏิกิริยา ที่ความเข้มข้นร้อยละ 0.1 – 0.5 ตามลำดับ เพื่อเลือกสูตรที่ดีที่สุดในการนำไปใช้สารเสริมสภาพความเข้ากันได้สำหรับในการทดลอง

ต่อไปในการปรับปรุงความเข้ากันได้ของพอลิแลกไทด์และสารเติมแต่งอื่น ๆ เนื่องจาก PLA-g-MA เป็นสารเสริมสภาพความเข้ากันได้ที่มีประสิทธิภาพสูง มีความว่องไวในการเกิดปฏิกิริยา และเป็นมิตรต่อสิ่งแวดล้อม โดยจะนำไปใช้เปรียบเทียบกับสารเสริมสภาพความเข้ากันได้ทางการค้า คือ toluene diisocyanate (TDI) โครงสร้างทางเคมีของ PLA และ PLA-g-MA แสดงในรูปที่ 1 ในการทดลองนี้ผู้วิจัยสังเคราะห์ PLA-g-MA ผ่านปฏิกิริยา reactive maleation โดยทำในเครื่องผสมแบบปิด ผลของมาเลอิกแอนไฮไดรด์ที่ความเข้มข้นร้อยละ 0 – 5 ร่วมกับการใช้สาร Luperox (L101) ที่ความเข้มข้นร้อยละ 0.1 – 0.5 ถูกติดตามโดยเทคนิค GPC ¹H-NMR และ FTIR ตามลำดับ

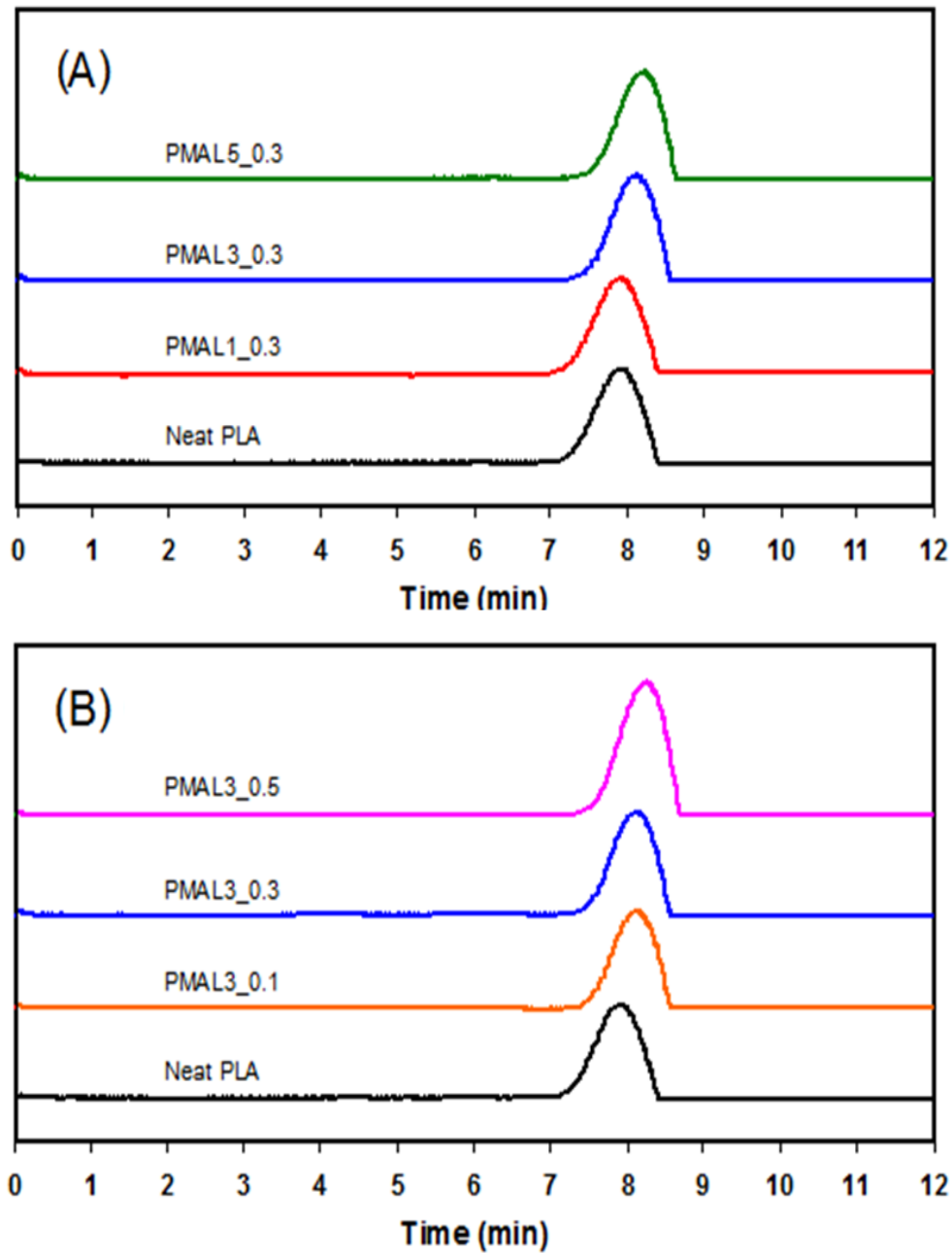


รูปที่ 1 โครงสร้างทางเคมีของ (A) neat PLA และ (B) PLA-g-MA

Characterization of neat PLA and PLA-g-MA

Molecular Weight Determination

การเปลี่ยนแปลงน้ำหนักโมเลกุลและการกระจายตัวของน้ำหนักโมเลกุลของ PLA-g-MA ถูกวิเคราะห์โดยเทคนิค gel permeation chromatography (GPC) ซึ่งใช้ tetrahydrofuran (THF) เป็นตัวทำละลายและเป็นเฟสต่อเนื่องในการทดลอง GPC chromatogram ของ neat PLA และ PLA-g-MA ที่มีการแปรปริมาณ MA และ Luperox ที่อัตราส่วนต่าง ๆ แสดงในรูปที่ 2 และตารางที่ 1 ตามลำดับ โดยทั่วไปแล้วค่าของ retention time (t) ในเทคนิคนี้จะขึ้นอยู่กับความแตกต่างของขนาดโมเลกุลของสารตัวอย่าง โมเลกุลที่เล็กกว่าจะสามารถผ่านคอลัมน์ที่อัดไว้ออกมาได้ช้ากว่าโมเลกุลที่ใหญ่กว่า เนื่องจากสายโซ่พอลิเมอร์ของโมเลกุลขนาดเล็กกว่าสามารถเคลื่อนที่เข้าไปภายในช่องว่างของอนุภาคภายในคอลัมน์ได้และถูกดักไว้ภายในจึงเคลื่อนที่ออกมาภายหลัง ในทางตรงกันข้ามสายโซ่ของโมเลกุลที่มีขนาดใหญ่กว่าไม่สามารถเคลื่อนเข้าไปภายในช่องว่างดังกล่าวได้จึงไหลออกมาอย่างรวดเร็วกว่าเมื่อเปรียบเทียบกับโมเลกุลที่มีขนาดเล็กกว่าส่งผลให้ค่า retention time (t) ของสารที่เล็กกว่ามีค่าที่มากกว่าสารขนาดใหญ่



รูปที่ 2 GPC chromatograms ของ neat PLA และ PLA-g-MA ที่ปริมาณที่แตกต่างกันของความเข้มข้นของ (A) MA และ (B) Luperox initiator

ผลการทดลองพบว่า number average molecular weight (M_n), weight average molecular weight (M_w) and PDI ของ neat PLA มีค่าประมาณ 114,000 Da, 157,600 Da, และ 1.38 ตามลำดับ (ตารางที่ 1) จากรูปที่ 2A พีกที่ได้เป็นพีกเดี่ยวของแต่ละตัวอย่างซึ่งปรากฏที่เวลาแตกต่างกันไปตามขนาดของโมเลกุลที่ต่างกัน ในส่วนของ GPC

chromatograms ของ PLA-g-MA ที่มีการเติม 0.3% L101 แสดงให้เห็นว่า retention time (t) ของสารตัวอย่างมีค่าเพิ่มขึ้นเล็กน้อยจาก 7.9 เป็น 8.3 นาที เมื่อปริมาณ MA เพิ่มขึ้นเป็นร้อยละ 5 เปรียบเทียบกับ neat PLA นอกจากนี้ ค่า M_n และ M_w ลดลงอย่างชัดเจนประมาณร้อยละ 28 และ 31 ตามลำดับ เมื่อปริมาณ MA เพิ่มขึ้นถึง ร้อยละ 5 เปรียบเทียบกับ neat PLA ผลการทดลองนี้บ่งชี้ว่าสายโซ่โมเลกุลของ PLA อาจถูกทำให้สั้นลงโดยปฏิกิริยา PLA chain scission เมื่อปริมาณ MA เพิ่มขึ้นระหว่างกระบวนการกราฟท์ พฏิกิริยาดังกล่าวมีความคล้ายคลึงกับผลการทดลองในรูปแบบที่ 2B. พีคของ PLA-g-MA ที่มีการเติม 3% MA มีค่า retention time ที่มากขึ้นเมื่อปริมาณ Luperox มากขึ้นจากร้อยละ 0.1 ถึง 0.5 เปรียบเทียบกับ neat PLA นอกจากนี้ ค่า M_n และ M_w ลดลงอย่างชัดเจนประมาณร้อยละ 35 และ 34 ตามลำดับ เมื่อปริมาณ Luperox มากขึ้นถึงร้อยละ 0.5 เปรียบเทียบกับ neat PLA

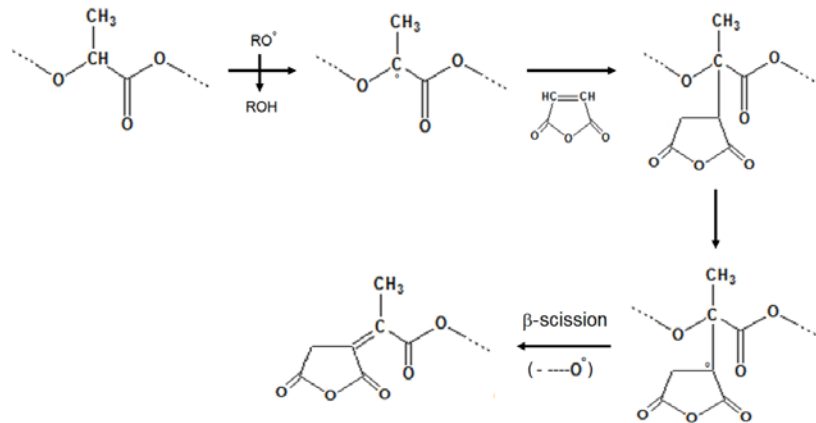
ตารางที่ 1 ข้อมูลจาก GPC chromatograms ของ neat PLA และ PLA-g-MA ที่ปริมาณที่ต่างกันของความเข้มข้นของ MA และ Luperox initiator

Sample ID	$M_n \times 10^4$ (Daltons)	$M_w \times 10^4$ (Daltons)	PDI	Retention Time (min)
Neat PLA	11.40	15.76	1.38	7.9
PMAL1_0.3	11.58	16.89	1.46	8.0
PMAL3_0.3	8.85	11.58	1.31	8.2
PMAL5_0.3	8.17	10.95	1.34	8.3
PMAL3_0.1	8.95	12.19	1.36	8.2
PMAL3_0.3	8.85	11.58	1.31	8.2
PMAL3_0.5	7.47	10.36	1.39	8.4

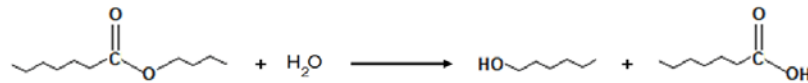
ผลการทดลองเหล่านี้แสดงให้เห็นว่าการลดลงของน้ำหนักโมเลกุลของ PLA ขึ้นอยู่กับการเติม MA และ Luperox ทั้งนี้อาจเป็นผลมาจากกลไกการตัดสายโซ่ของ PLA (β -scission, back-biting, and thermohydrolysis) ซึ่งส่งผลให้สายโซ่โมเลกุลของ PLA สั้นลงและน้ำหนักโมเลกุลเฉลี่ยลดลงระหว่างกระบวนการ PLA maleation กลไกที่เป็นไปได้ของกระบวนการตัดสายโซ่ของ PLA (PLA chain scission) ซึ่งถูกเสนอโดยงานวิจัยของ Carlson และคณะแสดงในรูปแบบที่ 3 น้ำหนักโมเลกุลของสายโซ่ PLA อาจถูกทำให้ลดลงได้ด้วย 3 กลไกดังต่อไปนี้ (A) β -scission, (B) thermohydrolysis, and (C) back-biting เริ่มจากการเกิดเป็น free radical ในสายโซ่หลักและไป

เกิดปฏิกิริยากับโมเลกุลของ MA เพื่อได้เป็น PLA-g-MA สุดท้ายเกิดผ่านกระบวนการ β -scission ทำให้เกิดการรวมกันหรือกำจัดออกของ radicals (รูปที่ 3A). อย่างไรก็ตามอาจจะเกิดจากกระบวนการ thermohydrolysis หรือ back-biting ก็เป็นได้ (รูปที่ 3B และ 3C)

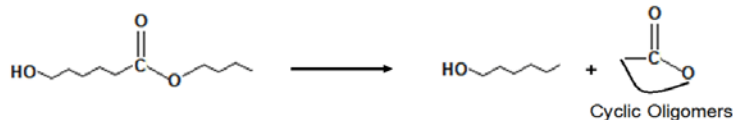
(A) β -scission



(B) Thermohydrolysis



(C) Back-biting



รูปที่ 3 Proposed chain scission mechanisms of PLA are composed of (A) β -scission, (B) thermohydrolysis, and (C) back-biting

Spectroscopy

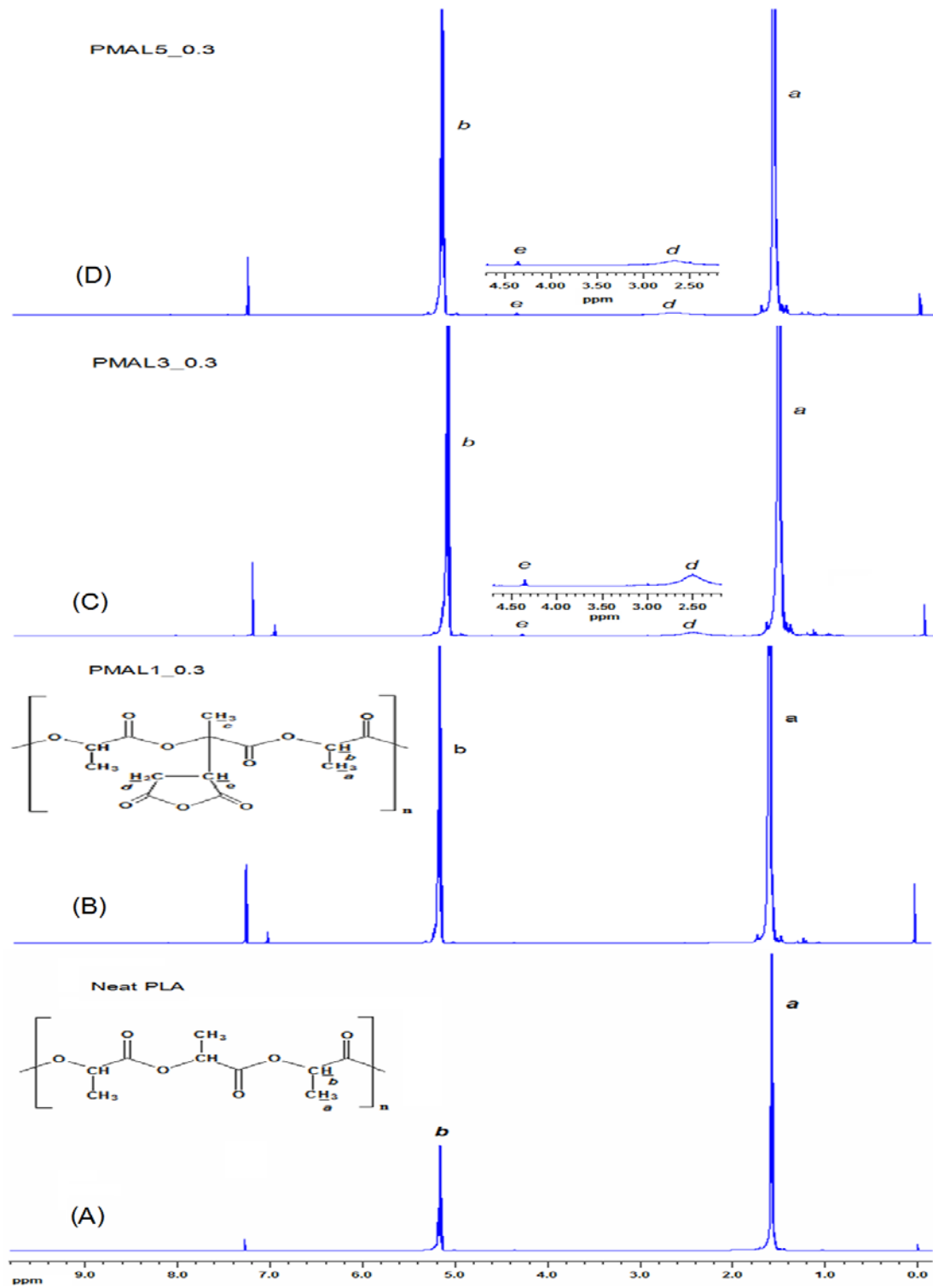
เพื่อเป็นการพิสูจน์ว่าการเติม MA และ Luperox ลงในสายโซ่หลักของ PLA ด้วยกระบวนการเกิดปฏิกิริยาแบบ maleation ที่ทำในเครื่องบดผสมแบบปิดก่อกำเนิดเป็นสาร PLA-g-MA โครงสร้างทางเคมีของสารตัวอย่างภายหลังการทดลองจำเป็นต้องได้รับการวิเคราะห์และยืนยันผลการทดลองด้วยเทคนิค $^1\text{H-NMR}$ และ FTIR Spectroscopy

¹H-NMR Spectroscopy

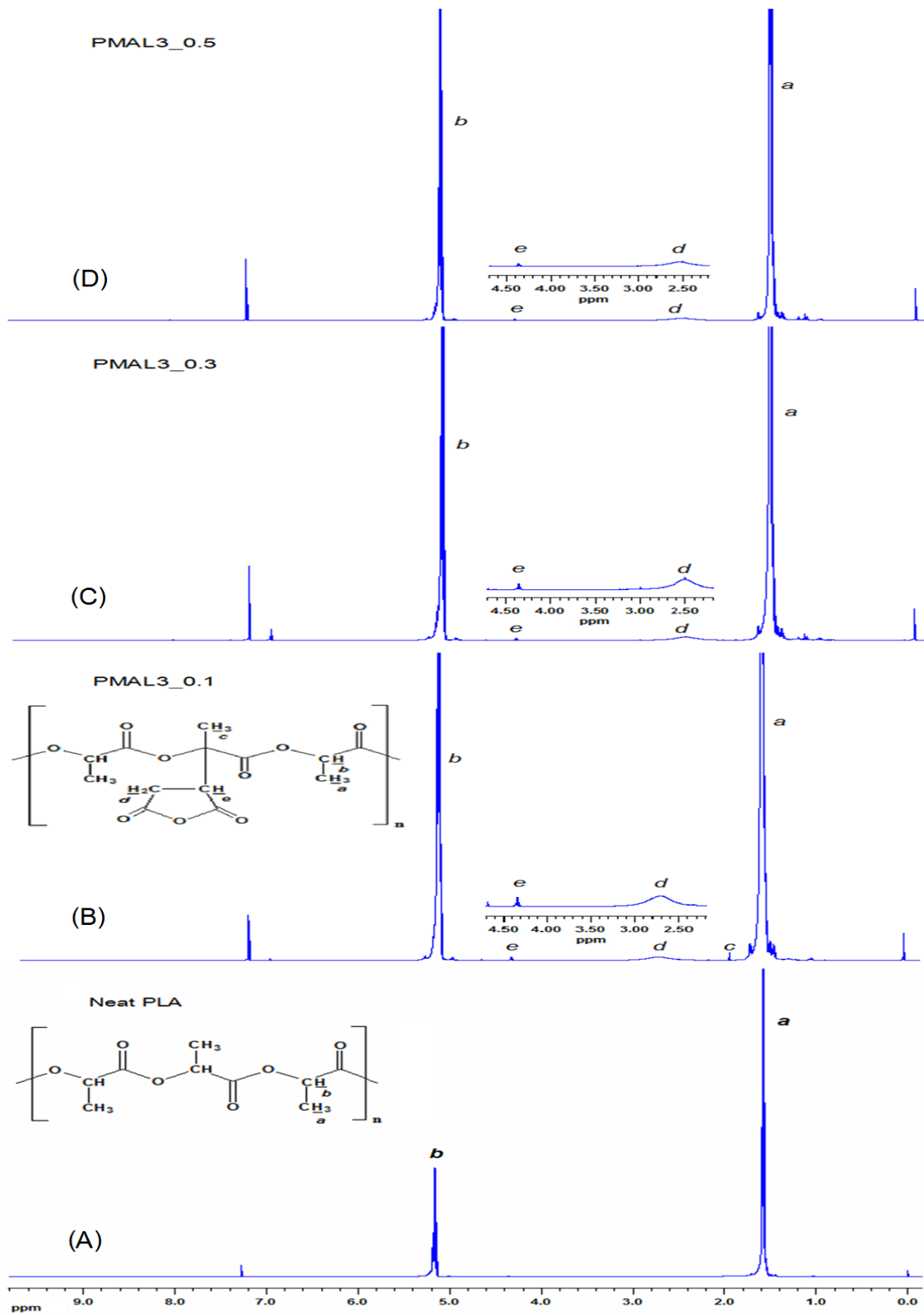
รูปที่ 4 และ 5 แสดงสเปกตรัมของสารตัวอย่างของ neat PLA และ PLA-g-MA ที่มีการแปรปริมาณของ MA และ Luperox (1 - 5 % และ 0.1 - 0.5 %) ในการทดลองนี้ Tetramethylsilane (TMS) ซึ่งปรากฏที่ chemical shift (δ) ที่ 0.00 ppm ถูกใช้เป็นสารเคมีอ้างอิง นอกจากนี้ deuterium-chloroform (CDCl_3) ซึ่งถูกใช้เป็นตัวทำละลายของ neat PLA และ PLA-g-MA ปรากฏ chemical shift (δ) ที่ 7.27 ppm ผลการทดลองพบว่า สเปกตรัมของ neat PLA แสดงให้เห็น 2 สัญญาณหลักที่ chemical shift (δ) ที่ 1.58 และ 5.17 ppm (รูปที่ 4A และ ตารางที่ 2) ซึ่งเป็นลักษณะเฉพาะของ methyl proton ($-\text{CH}_3$, (a)) และ methine proton ($-\text{CH}-$, (c)) ซึ่งต่อกับ oxygen และ carbonyl group ตามลำดับ

เปรียบเทียบกับสเปกตรัมของ neat PLA ในกรณีของสเปกตรัมของ PLA-g-MA จะพบสัญญาณเพิ่มเติมอีก 3 ชุดที่ chemical shift (δ) ที่ 1.9 2.8 และ 4.3 ppm ซึ่งให้สัญลักษณ์เป็น 'c' 'd' และ 'e' ตามลำดับ ผลที่ปรากฏนี้คล้ายคลึงกับที่รายงานในงานวิจัยของ Pan และคณะ ซึ่งศึกษาเกี่ยวกับหมู่ carboxyl และ amino groups ของ PLA ผ่านปฏิกิริยาการกราฟท์พิกที่ตำแหน่ง c สอดคล้องกับหมู่ methyl proton ที่ต่อกับ quaternary carbon atom ($\delta = 1.9$) ขณะที่พิกที่ตำแหน่ง d และ e นั้นเป็นของ methylene และ methine protons ของโมเลกุลของ anhydride ซึ่งเกิดพันธะโคเวเลนต์ต่อกับสายโซ่หลักของ PLA ระหว่างกระบวนการ maleation

จากรูปที่ 4B พบว่าสเปกตรัมของ PLA-g-MA ที่มีการเติม 1% MA และ 0.3% Luperox ไม่ปรากฏสัญญาณของพิกที่ตำแหน่ง c d และ e ในทางตรงกันข้ามเมื่อเติม MA มากกว่า 1% จะพบสัญญาณเฉพาะของ PLA-g-MA ที่ตำแหน่ง e และ d ($\delta = 4.3$ to 4.4, and $\delta = 2.5$ to 2.7 ppm) อย่างไรก็ตามพิกที่ตำแหน่ง c ไม่ปรากฏในสเปกตรัมของ PLA-g-MA ที่มีการเติม 1-3% MA และ 0.3% Luperox ในทุกกรณี ผลการทดลองแสดงให้เห็นว่าระดับของ MA ส่งผลอย่างชัดเจนต่อกระบวนการเกิดปฏิกิริยาแบบ maleation โดยการใช้เครื่องบดผสมแบบปิดสารตัวอย่างที่ 3 และ 5% MA ที่มีการเติม 0.3% Luperox อาจเป็นตัวอย่างที่เป็นไปได้ที่ประสบความสำเร็จในการสังเคราะห์สารเสริมสภาพความเข้ากันได้เป็น PLA-g-MA ในทางตรงกันข้ามการเติม MA ที่ความเข้มข้นน้อยกว่า 1% ไม่ส่งผลให้เกิดเป็น PLA-g-MA



รูปที่ 4 $^1\text{H-NMR}$ spectra ของ neat PLA และ PLA-g-MA ด้วยการเติมปริมาณของ MA ที่แตกต่างกัน (1 ถึง 5%) และ 0.3% Luperox



รูปที่ 5 ¹H-NMR spectra ของ neat PLA และ PLA-g-MA ด้วยการเติม 3% MA และปริมาณที่แตกต่างกันของ Luperox (0.1 - 0.5%)

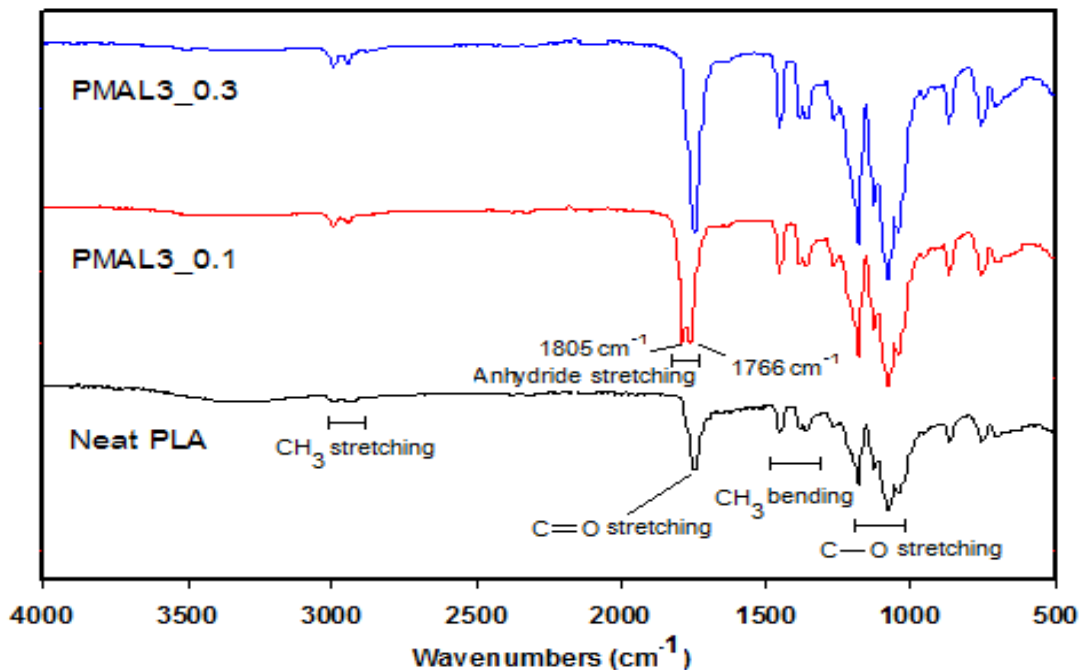
รูปที่ 5 แสดงสเปกตรัมของ neat PLA และ PLA-g-MA ที่มีการเติม 3% MA และ 0.1-0.5% Luperox ผลการทดลองพบว่าพีค d และ e ($\delta = 2.5$ to 2.7 , and $\delta = 4.3$ to 4.4 ppm) ปรากฏในสเปกตรัมของ PLA-g-MA ในทุกตัวอย่าง ที่น่าสนใจมากพบว่าพีคที่ตำแหน่ง c ปรากฏอย่างชัดเจนที่ $\delta = 1.9$ ppm ของสารตัวอย่าง PLA-g-MA ที่มีการเติม 3% MA และ 0.1% Luperox เท่านั้น (รูปที่ 13B) ผลการทดลองนี้อาจบอกเป็นนัยได้ว่าระดับความเข้มข้นที่เหมาะสมของ MA และ Luperox ที่ส่งผลอย่างมีนัยสำคัญต่อการสังเคราะห์ PLA-g-MA ที่ได้จากงานวิจัยนี้อาจจะเป็นสารตัวอย่าง PMAL5_0.3, PMAL3_0.1, PMAL3_0.3, และ PMAL3_0.5 ตามลำดับ แต่อย่างไรก็ตาม ข้อมูลที่ได้เหล่านี้จะถูกนำไปใช้พิจารณาพร้อมกับผลการทดลองในส่วน of FTIR ต่อไป

ตารางที่ 2 Chemical shifts and positions of neat PLA and PLA-g-MA on the $^1\text{H-NMR}$ spectra

Sample	Position	Chemical shift (ppm)
Tetramethylsilane (TMS)		0.00
<i>d</i> -chloroform (CDCl_3)		7.27
Neat PLA	a	1.58
	b	5.17
PLA-g-MA (PMAL3_0.1)	a	1.57
	b	5.16
	c	1.94
	d	2.71
	e	4.35

FTIR Spectroscopy

สเปกตรัมของ neat PLA และ PLA-g-MA แสดงในรูปที่ 6 ผลจากการทดลองก่อนหน้าพบว่า PMAL5_0.3, PMAL3_0.1, PMAL3_0.3, และ PMAL5_0.3 มีความเป็นไปได้ที่จะเป็นตัวอย่างที่ประสบความสำเร็จในการสังเคราะห์เป็น PLA-g-MA อย่างไรก็ตาม พบว่า PMAL5_0.3, PMAL3_0.3, และ PMAL3_0.5 ให้สัญญาณสเปกตรัม FTIR ที่คล้ายคลึงกัน แต่แตกต่างจากสัญญาณสเปกตรัมของ PMAL3_0.1 ดังนั้นในรูปที่ 14 จะใช้พีคของสาร PMAL3_0.3 เป็นตัวแทนของกลุ่ม PMAL5_0.3, PMAL3_0.3, และ PMAL3_0.5 เปรียบเทียบกับสเปกตรัมของ neat PLA และ PMAL3_0.1 ผลการทดลองพบว่า neat PLA ปรากฏสัญญาณของหมู่ฟังก์ชันต่าง ๆ ที่ช่วงของเลขคลื่น คือ 3000 - 2800, 1760 - 1700, 1500 - 1360, และ 1300 - 1000 cm^{-1} , ซึ่งเป็นลักษณะของ $-\text{CH}_3$ stretching, $\text{C}=\text{O}$ stretching, CH_3 bending, และ $\text{C}-\text{O}$ stretching ตามลำดับ (ตารางที่ 3)



รูปที่ 6 FT-IR spectra ของ neat PLA และ PLA-g-MA ในช่วงเลขคลื่นที่ 4000 ถึง 500 cm^{-1}

ในกรณีของ FTIR สเปกตรัมของ PMAL3_0.3 ผลการทดลองไม่เป็นไปตามที่คาดไว้ โดยพบว่าสเปกตรัมที่เกิดขึ้นแทบจะไม่มีแตกต่างจากสเปกตรัมที่ได้จาก neat PLA นอกจากนี้ในส่วนของพีคที่เป็นลักษณะเฉพาะของหมู่ $\text{C}=\text{O}$ stretching ใน acid anhydride ซึ่งจะปรากฏเป็นพีคคู่ที่เลขคลื่นช่วง 1830 - 1800 และ 1775 - 1740 cm^{-1} ก็ไม่สามารถถูกตรวจพบได้ใน FTIR สเปกตรัมของ PMAL3_0.3 (รวมทั้งของ PMAL5_0.3 และ PMAL3_0.5) ทั้งนี้อาจ

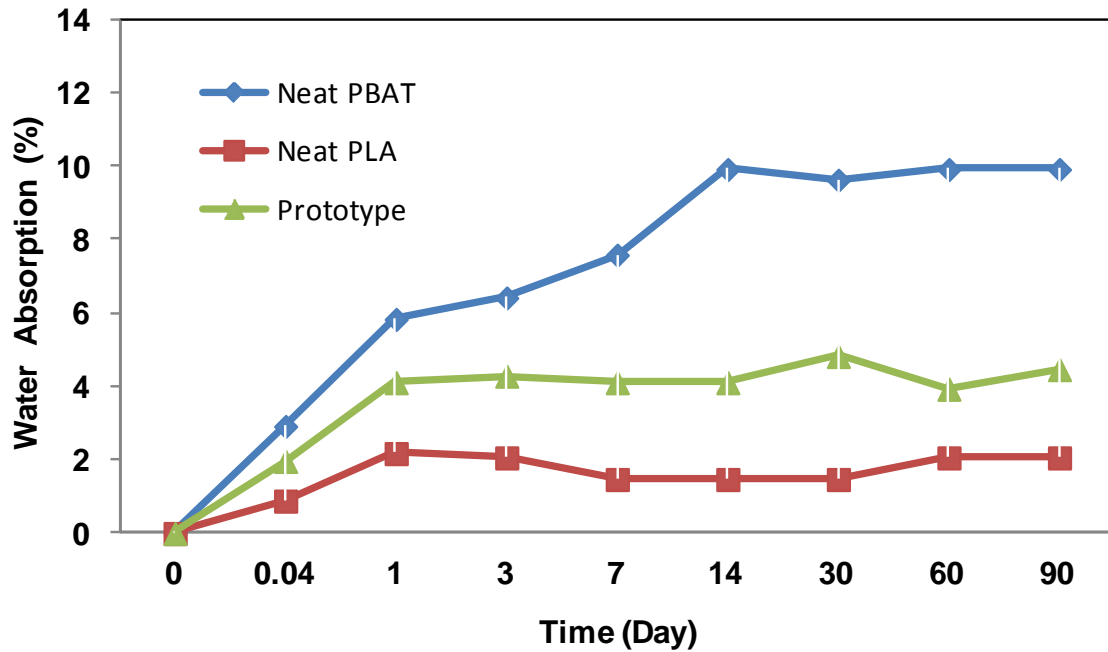
เป็นไปได้ว่าตัวอย่างดังกล่าวอาจให้ผลการกราฟพีในปริมาณที่ต่ำเกินกว่าที่จะตรวจสอบได้ด้วย FTIR แต่อย่างไรก็ตาม พิกัดลักษณะเฉพาะเหล่านี้ของหมู่ C=O stretching ใน acid anhydride ซึ่งจะปรากฏเป็นพีคคู่ที่เลขคลื่นช่วง 1830 - 1800 และ 1775 - 1740 cm^{-1} สามารถถูกตรวจพบและสังเกตเห็นได้ใน FTIR สเปกตรัมของ PMAL3_0.1 ซึ่งแสดงให้เห็นถึงการมีอยู่ของหมู่ anhydride stretching โดยพบพีคแตกเป็น 2 หัวที่ตำแหน่งประมาณ 1805 and 1766 cm^{-1} (ตารางที่ 3) ตามลำดับ

ตารางที่ 3 ข้อมูลจาก FT-IR absorptions ของ neat PLA และ PLA-g-MA

Molecular Motion	Wavenumber (cm^{-1})
<i>Neat PLA</i>	
CH ₃ stretching	3016 - 2958
C=O stretching	1751
CH ₃ bending	1454 - 1377
C-O stretching	1184 - 1049
<i>PLA-g-MA (PMAL3_0.1)</i>	
CH ₃ stretching	3005 - 2954
C=O stretching (bands of anhydrides)	1805 and 1766
CH ₃ bending	1454 - 1369
C-O stretching	1180 - 1045

Water absorption

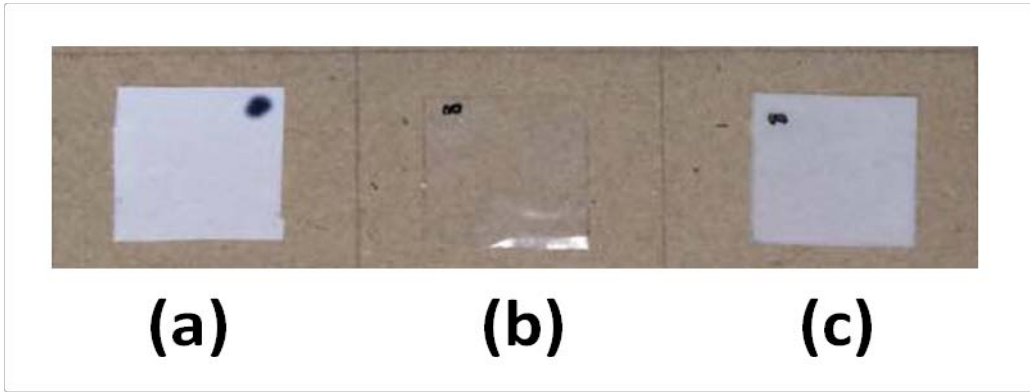
ผลของร้อยละของการดูดซึมน้ำของฟิล์มต้นแบบ (prototype) ที่เวลาตั้งแต่ 0 ถึง 90 วัน เมื่อเปรียบเทียบกับ neat PBAT และ neat PLA แสดงในรูปที่ 7 ผลการทดลองแสดงให้เห็นว่าฟิล์ม neat PLA มีร้อยละของการดูดซึมน้ำที่ต่ำมาก โดยมีการเปลี่ยนแปลงอย่างรวดเร็วแค่เพียงในช่วงต้นของการทดสอบ (1 ชั่วโมง และ 1 วัน) หลังจากนั้นให้ร้อยละการดูดซึมน้ำคงที่ที่ร้อยละ 2.06 แสดงให้เห็นว่าเป็นฟิล์มที่ไม่ชอบน้ำ แตกต่างจากฟิล์ม neat PBAT ที่มีร้อยละของการดูดซึมน้ำที่สูงกว่าอย่างชัดเจน โดยมีการเปลี่ยนแปลงอย่างรวดเร็วในช่วงต้นของการทดสอบเช่นเดียวกับ neat PLA อย่างไรก็ตามให้ค่าคงที่เมื่อผ่านไป 14 วัน โดยมีร้อยละการดูดซึมน้ำคงที่ที่ประมาณร้อยละ 9.91 ในขณะที่ฟิล์มต้นแบบที่เป็นฟิล์มพอลิเมอร์ผสมของ PLA และ PBAT นั้นให้ค่าร้อยละของการดูดซึมน้ำอยู่ระหว่างฟิล์ม neat PBAT และ neat PLA โดยมีพฤติกรรมแบบเดียวกันโดยมีการเปลี่ยนแปลงอย่างรวดเร็วในช่วงต้นของการทดสอบและคงที่เมื่อเวลาผ่านไปมีร้อยละการดูดซึมน้ำคงที่ที่ประมาณร้อยละ 4.46 ซึ่งมีค่าต่ำ



รูปที่ 7 การดูดซึมน้ำของฟิล์มต้นแบบ (prototype) ที่เวลาตั้งแต่ 0 ถึง 90 วัน เมื่อเปรียบเทียบกับ neat PBAT และ neat PLA

ลักษณะทางกายภาพและความใสของฟิล์ม

รูปที่ 8 แสดงลักษณะทางกายภาพและความใสของฟิล์ม (a) neat PBAT (b) neat PLA และ (c) ต้นแบบ (prototype) ตามลำดับ ผลการทดลองแสดงให้เห็นว่าฟิล์ม neat PBAT มีลักษณะผิวเรียบ สีขาวขุ่นคล้ายนม มีลักษณะฟิล์มแบบโปร่งแสงคือมีแสงผ่านได้บางส่วน แตกต่างจากฟิล์ม neat PLA ที่มีลักษณะผิวเรียบและใส โดยเป็นฟิล์มแบบโปร่งใสคือแสงผ่านได้ดีมาก เมื่อทดสอบด้วยเครื่อง UV-vis spectrophotometer พบว่าที่ความยาวคลื่นแสง 600 นาโนเมตร ฟิล์ม neat PBAT และ neat PLA มีร้อยละการส่องผ่านของแสงได้ในช่วงร้อยละ 45-48 และ ร้อยละ 88-90 ตามลำดับ แสดงให้เห็นอย่างชัดเจนว่าฟิล์ม neat PLA ที่ได้ส่องผ่านแสงได้ดี ในขณะที่ฟิล์ม neat PBAT แสงผ่านได้บางส่วน สำหรับการทดสอบกับฟิล์มต้นแบบ (prototype) พบว่าลักษณะทางกายภาพที่ได้คล้ายคลึงกับฟิล์ม neat PBAT นั่นคือ มีลักษณะผิวเรียบ สีขาวขุ่นคล้ายนม มีลักษณะฟิล์มแบบโปร่งแสงคือมีแสงผ่านได้บางส่วนที่ความยาวคลื่นแสง 600 นาโนเมตร ฟิล์มต้นแบบมีร้อยละการส่องผ่านของแสงได้อยู่ระหว่างฟิล์ม neat PBAT และ neat PLA ในช่วงร้อยละ 55-60 ซึ่งแสดงให้เห็นว่าแสงผ่านได้เพียงบางส่วน



รูปที่ 8 ลักษณะทางกายภาพและความใสของฟิล์ม (a) neat PBAT (b) neat PLA และ (c) ต้นแบบ (prototype)

6.3 ข้อคิดเห็นและข้อเสนอแนะสำหรับการวิจัยต่อไป

สำหรับฟิล์มพอลิเมอร์ผสมที่มีการเติมพลาสติกไซเซอร์พอลิเอธิลีนไกลคอล 400 เมื่อเวลาผ่านไปพื้นผิวของฟิล์มมีความมันเกิดขึ้น เนื่องจากเกิดการเยิ้ม (blooming effect) ซึ่งทำให้ไม่น่าใช้งานและสมบัติเชิงกลด้อยลงจึงควรมีการปรับปรุงและลดผลจากการเยิ้มที่เกิดขึ้นสำหรับงานวิจัยต่อไป นอกจากนี้ ควรปรับปรุงเพื่อเพิ่มเสถียรภาพทางความร้อนของฟิล์มพอลิเมอร์ผสมให้ดีขึ้น

6.4 บทความวิจัยที่นำเสนอในที่ประชุมวิชาการ

ตามเอกสารแนบหมายเลข 3

Synergistic Effect of Nucleation and Compatibilization on the Polylactide and Poly(butylene adipate-co-terephthalate) Blend Films*

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Abstract Polylactide (PLA) films blended with 10 wt% poly(butylene adipate-co-terephthalate) (PBAT) were prepared by using a twin screw extruder in the presence of the nucleating agent of titanium dioxide (TiO₂) and the compatibilizers of toluene diisocyanate (TDI) and PLA-grafted-maleic anhydride (PLA-g-MA). The synergistic effect of the nucleation and compatibilization on the properties and crystallization behavior of the PLA/PBAT (PLB) films was explored. The results showed that the addition of TiO₂ significantly enhanced the tensile strength and the impact tensile resistance of the PLB films while slightly decreased its thermal stability. In addition, the compatibilizers of TDI and PLA-g-MA in the system not only affected the crystallinity and cold crystallization process of the PLB films, but also increased the mechanical properties of them due to the improvement of the interfacial interaction between PLA and PBAT revealed by the morphological measurement. The synergistic effects of the nucleating agent and the compatibilizer afforded the blend films with increased tensile strength and impact tensile toughness, improved cold crystallization property and χ_c .

Keywords: Nucleation; Film; Compatibilization; Blend; Crystallization.

INTRODUCTION

Polylactide (PLA) has become one of the most promising biodegradable polymers due to its outstanding properties, such as easy processibility; non-toxicity and biodegradability in a few weeks; high strength and modulus; and transparency^[1–3]. Such polymer material has the useful applications in the fields of pharmaceuticals, biomedical science, automotive and packaging industries^[4, 5]. However, the major drawbacks of PLA including brittleness, slow crystallization rate and low crystallinity restrict its widespread usage, especially in the film packaging^[6]. One of the alternative methods to improve the ductility and flexibility of PLA is to blend a more flexible component with it. As well known, poly(butylene adipate-co-terephthalate) (PBAT) is a biodegradable aliphatic-aromatic copolyester composed of two types of comonomers. One is the butylenes terephthalate fragment from 1,4-butanediol and terephthalic acid, another one is butylene adipate moiety consisting of 1,4-butanediol and adipic acid units^[7]. The high ductility and flexibility of PBAT make it a suitable candidate for blending with PLA to improve the stiffness and toughness of the resulting polymer materials without changing the biodegradability^[8].

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To increase the crystallization rate and degree of crystallinity (χ_c) of PLA via a heterogeneous nucleation process, it is necessary to add a nucleating agent to the system. Generally, there are mainly three types of nucleating agents according to their chemical composition and reaction mechanism: the chemical nucleant, the mineral nucleant and the organic nucleant. Among them, titanium dioxide (TiO_2) shows the excellent abilities for improving the nucleation, the crystallization, and modifying the properties of several polymers^[9, 10]. For example, some papers have reported that TiO_2 could act as a UV stabilizer for PLA thin films owing to its UV shielding effect and the barrier properties^[11, 12]. However, blending TiO_2 with PLA is uncommon possibly because of the transparency reduction of the resulting materials. It has been revealed that some nucleating agents such as modified montmorillonite (MMT), clay, talc and the flexible polymers of poly(ϵ -caprolactone) (PCL) and poly(butylene adipate-co-terephthalate) (PBAT) have often been used as the nucleating agents blended with PLA^[13–17]. The typical examples are reported by Wang and Xiao *et al.* who used PBAT to enhance the crystallization rate, nucleation density, impact strength, and flexibility of the blended polymers^[15, 16]. However, the lack of compatibility with PLA made the polymers to have the poor mechanical properties, especially the strength and elongation of the final products. In order to enhance the mechanical performances of PLA polymers, a compatibilizer is required for enhancing the interfacial adhesion of the blends. Several effective compatibilizers *i.e.*, maleic anhydride (MA)^[18, 19], dioctyl maleate (DOM)^[20], isocyanate compounds^[21, 22], multifunctional epoxy^[23], and PLA-graft-maleic anhydride (PLA-g-MA)^[24, 25] *etc.* have been used to improve the compatibility of PLA and its blends. In addition, the compatibilizer should also act as a chain extender to react with functional groups from both the matrix and the filler, and enable the formation of polymeric chains and increase the molecular weight of the polymer^[26, 27].

In the previous work, we explored the appropriate blending ratio of PLA and PBAT (PLB) to achieve the polymers with better properties^[22]. In this article, we report the preparation of the films from PLA blended with 10 wt% PBAT. We expect to improve the crystallization and compatibilization of the blend films by the synergistic effects of a nucleating agent for expanding the crystallization temperature window and a compatibilizer for optimizing the interfacial interaction between PLA and PBAT so as to increase the mechanical performances. Moreover, the influences of the TiO_2 amount and the compatibilizer on the tensile, impact tensile, thermal, and morphological properties of the PLB films have also been discussed.

EXPERIMENTAL

Materials

The PLA resin (PLA 4043D) was from NatureWork LLC (Cargill-Dow, Minneapolis, MN) and used as a polymer matrix. The PLA pellets were transparent with a density of 1.24 g/cm³. The glass transition temperature (T_g), melting temperature (T_m), and decomposition temperature (T_d) of the neat PLA were characterized by differential scanning calorimetry (DSC) and a thermogravimetric analyzer (TGA) with values of about 60, 154, and 337 °C, respectively. The polydispersity (PDI) and weight average molecular weight of the neat PLA was determined by the gel permeation chromatography (GPC) by using tetrahydrofuran (THF) as the eluent with the results of 1.46 and 130 kDa, respectively. PBAT (Ecoflex F BX7011) with a density of 1.26 g/cm³ was from the BASF Corporation (Ludwigshafen, Germany). The T_g , T_m and T_d of the PBAT as determined by DSC and TGA were about –30, 110, and 410 °C, whereas their PDI and weight average molecular weight were 1.32 and 170 kDa (GPC analysis in THF), respectively. Titanium dioxide (TiO_2) with a volume mean diameter of 0.727 μm analyzed by laser particle size analyzer (LPSA) was from Chemipan Co., Ltd., Bangkok, Thailand. Toluenediphenyl diisocyanate (TDI) and maleic anhydride (MA) were purchased from Siam Chemical Industry Co., Ltd., Bangkok, Thailand.

Material Preparation

The PLA, PBAT and TiO_2 were dried in a vented oven at 60 °C overnight and stored in a desiccator before use. TiO_2 was used as the nucleating agent with varying amounts from 1 phr to 4 phr for accelerating the crystallization rate of PLA, whereas the TDI and PLA grafted maleic anhydride (PLA-g-MA) were used as a

compatibilizer with different amount from 1 wt% to 7 wt% based on the PBAT content for improving the interfacial interactions between PLA and PBAT. The PLA-g-MA was synthesized in an internal mixer (D-47055, PLASTI-CORDER Lab station, Brabender, Duisburg, Germany) by the free radical reaction with 2,5-dimethyl-2,5-di-(*tert*-butylperoxy) hexane (Luperox101) as an initiator. The blend composition ratio of PLA to PBAT was fixed at 90 and 10 for all experiments. PLA, PBAT and TiO₂ were pre-mixed before extrusion process. The mixture was melted in a co-rotating twin screw extruder (PRISM TSE 16TC, Thermo Electron Corporation, Karlsruhe, Germany) having an L/D ratio of 15 and a screw diameter of 15.6 mm. The temperature profiles of the extrusion were controlled on three zones ranging from 110 °C to 180 °C with a screw speed of 30 r/min. After the extrusion, the pellets were dried in a vented oven at 60 °C overnight and then compression-molded into the films by a hydraulic press (KT-7014, Kao Tieh Machinery Industrial, Taichung, Taiwan) under optimum conditions: the holding temperature of 180 °C; the pressure of 10.34 MPa; a cycle time of 25 min. The PLA/PBAT (PLB) blend with compatibilizer was also prepared in the same way in order to obtain a compatibilized blend film. Sample formulations and its abbreviations are displayed in Table 1.

Table 1. The formulations of PLA/PBAT (PLB) blend films with various contents of TiO₂ and different types of compatibilizer

Formulation	PLA (wt%)	PBAT (wt%)	TiO ₂ (phr)	Compatibilizer contents based on PBAT (wt%)	
				TDI	PLA-g-MA
PLB	90	10	–	–	–
PLBO1	90	10	1	–	–
PLBO2	90	10	2	–	–
PLBO4	90	10	4	–	–
PLBO1T1	90	10	1	1	–
PLBO1T3	90	10	1	3	–
PLBO1T5	90	10	1	5	–
PLBO1T7	90	10	1	7	–
PLBO1P1	90	10	1	–	1
PLBO1P3	90	10	1	–	3
PLBO1P5	90	10	1	–	5
PLBO1P7	90	10	1	–	7

Material Characterization

Tensile properties

The tensile test of rectangular film specimens with a size of 15 mm width, 150 mm length, and about 250 μm thickness was performed on a universal testing machine (LR 100k, LLOYD, Fareham, UK) using a crosshead speed of 10 mm/min and a gauge length of 100 mm, according to the ASTM D882-09. A load cell of 1 kN was employed for the testing of all blend film samples. The specimens were stored overnight at room temperature before testing. At least five specimens of each film were tested and the results were averaged to obtain a mean value.

Impact tensile testing

A standard type IV impact tensile specimens of the blend films were evaluated by an impact tester (Zwick 5102 Pendulum, Zwick/Roell Group, Ulm, Germany) using a deflection angle of 160°, an exchangeable pendulum of 1 J, with an impact velocity of 2.93 m/s, and a pendulum length of 225 mm, according to DIN EN ISO 8256:2004. All specimens were stored overnight at room temperature before testing. The average values were obtained by repeating the test experiment at least five times. The thickness of the films was determined by an analog thickness gauge. The impact energy (E_{Im}) can be calculated by using the following Eq. (1):

$$E_{\text{Im}} = \frac{E_{\text{Ab}}}{w \times d} \quad (1)$$

where E_{Im} : the impact tensile energy or impact tensile strength, E_{Ab} : the absorbed energy, w : the width of the specimen, and d : the thickness of the specimen.

Thermal stability

The decomposition temperature of the uncompatibilized and compatibilized PLB/TiO₂ blends was characterized by a thermogravimetric analyzer (TGA; TG/DSC STA 449 F3 Jupiter, NETZSCH Instruments, Selb, Germany). The TGA technique was used to determine the thermal stability of the blend films before and after the addition of TiO₂ and the compatibilizer. Test specimens (about 4–6 mg) were placed in a crucible (70 μL) in each TGA experiment. The operation was performed in a nitrogen atmosphere using a heating rate of 20 K/min from 50 °C to 600 °C. The percentage of weight loss for all samples was examined.

Crystallization and thermal behaviors

A differential scanning calorimeter (DSC; DSC 200 F3 Maia, NETZSCH Instruments, Selb, Germany) was used to investigate the crystallization behaviors and thermal transitions of the blend films. For each DSC analysis, the film sample (approximately 6–8 mg) was encapsulated in a hermetically sealed aluminum pan (30 μL). A first heating scan was operated from room temperature to 180 °C at a heating rate of 10 K/min and held at 180 °C for 3 min to eliminate the thermal history of all of the samples. Then, it was cooled to –60 °C with a cooling rate of 10 K/min. Finally, in a second heating scan it was reheated to 180 °C at a heating rate of 10 K/min to evaluate the non-isothermal crystallization behaviors of the films. All experiments were carried out under nitrogen atmosphere. The glass transition temperature (T_g), crystallization temperature (T_c), cold crystallization temperature (T_{cc}), melting temperature (T_m), specific crystallization enthalpy (ΔH_c), specific cold crystallization enthalpy (ΔH_{cc}), and specific melting enthalpy (ΔH_m) of the samples were also recorded. The χ_c of the PLB blend films was calculated by using the following Eq. (2):

$$\chi_c \% = \frac{(\Delta H_m - \Delta H_{cc})}{(1 - W_f) \cdot \Delta H_m^0} \times 100 \quad (2)$$

where W_f is the weight fraction of the filler and ΔH_{m0} is the melting enthalpy of the 100% crystalline PLA that is equal to 93.6 J/g^[28].

Electron microscope analysis

The fractured surface morphology of the PLB blend films was characterized using a scanning electron microscope (SEM; Quanta 400, FEI Company, Hillsboro, OR). The tensile fractured surface of the sample was sputter-coated with a thin layer of gold in order to avoid any electrostatic charge and poor resolution during the testing procedure. The SEM was operated at an accelerating voltage of 20 kV to image the films at 2000X magnification.

RESULTS AND DISCUSSION

Characterization of Nucleated PLB Films

Mechanical properties

Tensile testing The tensile properties of the PLB films with different amounts of TiO₂ are presented in Fig. 1. Compared to the neat PLB with a tensile strength of 32.87 MPa and an elongation at break of 11.59%, the tensile strength of the PLB films was significantly affected by the addition of TiO₂. No obvious strength reduction was observed with a small amount of TiO₂ in the system; while the PLB film with 4 phr TiO₂ showed the distinct strength decrease by almost 32%. The elongation at break of the film displayed a similar changing tendency. Lower amount of TiO₂ improved the extension of the PLB films; when over 1 phr of TiO₂ was added, the extension of PLB film increased by almost 40% (data as shown in Table 2), but a severe decrease of elongation at break was observed. This is attributed to the nucleating effect of TiO₂, which accelerated the crystallization rate and increased the degree of crystallinity (χ_c) of the PLB molecular chains. Moreover, the tensile of the film showed a significant decrease when further increasing the TiO₂ amount. We speculate this is because of the non

uniform distribution of TiO_2 in the film with the agglomeration and defects from the overloading of TiO_2 molecules.

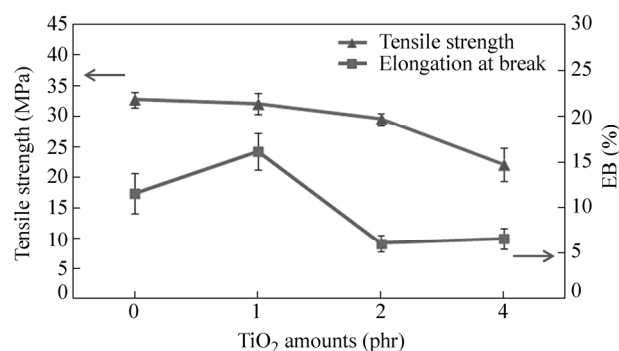


Fig. 1 The tensile properties of PLA/PBAT blend films with various TiO_2 contents

Table 2. The mechanical properties of PLA/PBAT (PLB) blend films without and with TiO_2

Sample ID	Tensile strength (MPa)	Elongation at break (%)	Impact resistance (kJ/m^2)
PLB	32.87 ± 1.13	11.59 ± 2.19	280 ± 12
PLBO1	32.06 ± 1.76	16.16 ± 2.00	439 ± 18
PLBO2	29.64 ± 0.84	6.09 ± 0.89	487 ± 11
PLBO4	22.06 ± 2.74	6.63 ± 1.11	422 ± 15

Impact tensile testing To understand the effect of nucleation on the mechanical performance, impact-tension behavior of the PLB films was evaluated. Data from the impact tension testing can be reported in terms of the impact tensile toughness or impact tensile resistance. Table 2 shows the impact tensile resistance of the PLB films without and with TiO_2 (1 to 4 phr). The neat PLB has an impact tensile strength of (280 ± 12) kJ/m^2 , indicating a quite low value of the absorbed energy. Interestingly, the impact tensile energy of the PLB films was greatly enhanced in the presence of TiO_2 , leading to an impressive increase of the impact tensile strength. For example, the impact tensile resistance of the PLB increased to 439, 487 and 422 kJ/m^2 when the TiO_2 amount was increased from 1, to 2, and to 4 phr, respectively. That meant the impact tensile toughness of the PLB films increased by about 50% to 70% due to the nucleating agent of TiO_2 accelerated the rate of crystallization and increased the χ_c . Here, the crucial point for improving the toughness of the PLB film is the crystallinity of PLB induced by the addition of the nucleating agent^[29]. The greater number of tie-molecules that resulted from heterogeneous nucleation and the crystallization enhanced the capability of the nucleated PLB films to absorb energy^[30]. The DSC measurement yet confirmed the enhanced crystallinity. However, no significant effect was observed for the nucleated PLB films' impact tensile resistance when different concentration of TiO_2 was used.

Thermal properties

Thermogravimetric analysis Figure 2 displays the TGA thermograms of the PLB films with various concentrations of TiO_2 . The neat PLB revealed two stages of decomposition. The first stage at about 330 °C was attributed to the loss of the PLA matrix, whereas the second stage appeared at around 400 °C, corresponding to the thermal degradation of PBAT. The TGA results showed that the thermal stability of the PLB slightly decreased with an increase of the TiO_2 amount from 0 to 4 phr. The weight percentage of char residual at 550 °C and the weight loss temperature at 10% and 50% of the films are reported in Table 3. With the addition of 4 phr TiO_2 , the temperature for the weight loss of 10% and 50% was reduced by about 5 and 8 K, respectively; in contrast, the percentage of the char residual at 550 °C increased. It might be implied that the nucleation effect of TiO_2 enhanced the crystallization of the PLA and PBAT chains, which generated a larger number of tiny crystals that played an important role in reducing the thermal stability of the PLB films.

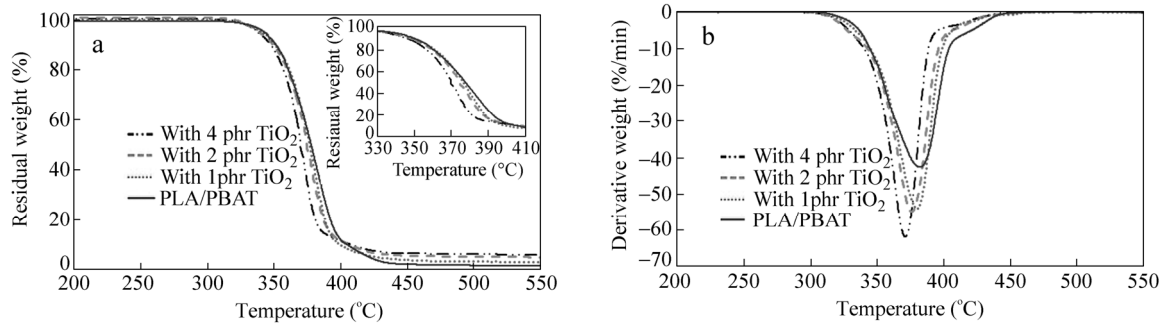


Fig. 2 The thermograms of PLA/PBAT blend films with different TiO₂ amounts (a) TGA and (b) DTG

Table 3. The thermal properties of PLA/PBAT (PLB) blend films without and with TiO₂

Sample ID	Temperature at weight loss (°C)		Char residual at 550 °C (%)	Thermal transition temperature (°C)					H_c (J/g)	H_{cc} (J/g)	H_m (J/g)	χ_c (%)
	10%	50%		T_g	T_c	T_{cc}	T_{m1}	T_{m2}				
PLB	351.3	377.8	1.4	54.7	–	111.9	148.4	155.3	–	–24.9	26.9	31.9
PLBO1	351.1	376.6	2.7	56.9	–	103.6	144.5	154.1	–	–27.8	28.1	33.7
PLBO2	349.4	374.4	4.8	56.5	–	104.5	145.3	155.2	–	–28.1	29.6	35.9
PLBO4	346.5	369.4	5.8	59.8	–	106.8	147.8	156.6	–	–30.4	32.4	39.8

Differential scanning calorimetry The cooling and second heating cycles of the DSC thermograms for the neat PLB and the PLB films with TiO₂ are shown in Figure 3(a) and 3(b), respectively. The neat PLB has a glass transition temperature (T_g) at 54.7 °C, an exothermic cold crystallization temperature (T_{cc}) at 111.9 °C, and a double melting temperature (T_m) at 148.4 and 155.3 °C, respectively. The double melting phenomenon was related to the α and α' crystal formation^[31, 32] observed at the α and α' crystallization formation temperature region. Furthermore, it was affected by the crystallization time, molecular weight, and cooling rate. The lower temperature of the melting (T_{m1}) was concerned in the crystallization of PLA during the heating process, and the higher temperature of melting (T_{m2}) corresponded to the crystallization of PLA upon cooling^[33, 34]. The T_c of the neat PLB did not appear in the cooling cycle due to the high cooling rate (10 K/min). As a result, the recrystallization of the laminated PLA occurred, leading to the appearance of T_{cc} in the second heating cycle.

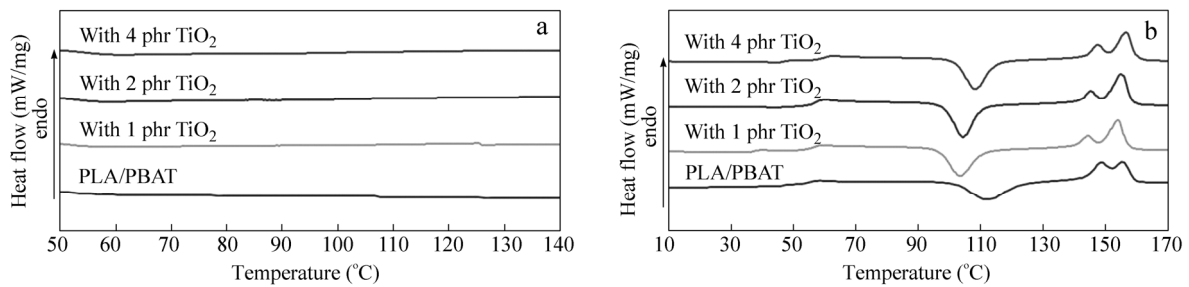


Fig. 3 The DSC thermograms of PLA/PBAT blend films without and with TiO₂ (a) cooling and (b) second heating cycles

In addition, the cold crystallization behavior (Fig. 3b) of the PLB films containing different amount of TiO₂ was also observed when heating the samples in the DSC measurement. The neat PLB and the PLB films nucleated with TiO₂ showed the typical thermal transitions in terms of T_g , T_{cc} and two overlapping T_m values. No T_c was found in the cooling cycle (Fig. 3a). Nevertheless, the film with TiO₂ showed a lower T_{cc} values in the range from 103.6 °C to 106.8 °C in the DSC heating cycle as compared with the neat PLB sample with the T_{cc} of 112 °C (Table 3). This may be due to the fast nucleation process and the short crystallization time of the PLB

induced by TiO_2 . The addition of TiO_2 also promoted the χ_c of PLB and might generated perfect crystals with an increment of the T_{m2} . Moreover, the heat of fusion (ΔH_m) and the χ_c significantly increased with the increase of TiO_2 amount from 1 phr to 4 phr, indicating that TiO_2 was an effective nucleating agent for initiating the heterogeneous nucleation of the PLB films. We observed that T_g of the PLB increased with the addition of TiO_2 because it facilitated the formation of crystalline domains that restrained the mobility of the polymer chains. This result was in agreement with the tensile properties of PLB showing a decreased value of elongation at break when the amount of TiO_2 increased. In our case, 1 phr TiO_2 is proved as the optimum amount for improving the properties of the films, including the elongation at break, the impact toughness, and the crystallization rate.

Characterization of the Compatibilized PLB/ TiO_2 Films

Mechanical properties

Tensile testing To evaluate the effect of nucleation and compatibilization on the mechanical properties of the PLB/ TiO_2 film, two types of compatibilizer (TDI and PLA-g-MA) were used to combine in the PLB/ TiO_2 film. Figure 4 shows the tensile properties of the compatibilized PLB/ TiO_2 films. The results showed us that when 3 wt% TDI was added, the tensile strength of the PLB/ TiO_2 increased by almost 25% as compared to the sample without TDI; while increasing TDI to more than 5 wt%, the mechanical strength of the PLB/ TiO_2 films was reduced. Furthermore, the elongation at break of the compatibilized PLB/ TiO_2 films decreased progressively in the present of TDI. A similar tendency was observed when the PLA-g-MA content was increased in PLB/ TiO_2 films. For example, compatibilized PLB/ TiO_2 films with 3 wt% PLA-g-MA achieved the highest tensile strength, whereas the tensile strength of the films obviously reduced if the amount of PLA-g-MA was more than 3 wt%. This implied that the tensile properties of PLB/ TiO_2 films are compatibilizer concentration dependence. We speculate the tensile strength increase is attributed to the improvement of interfacial interactions by the compatibilizer which enhances the wetting and adhesion bond strength between PLA and PBAT. The diisocyanate groups of TDI interacted with both the hydroxyl and carboxyl groups of the PLA and PBAT to form strong urethane and amide linkages. In contrast, the ester linkages were formed from maleic anhydride groups of PLA-g-MA and the hydroxyl groups of PLA and PBAT, such leading to the enhancement of the interfacial adhesion in the PLB films, as evidenced by the morphological images. The proposed reaction mechanisms of TDI and PLA-g-MA with the PLB blend are illustrated in Fig. 5. The reaction between PLB and compatibilizer may occur *via* three competitive routes, a) chain extension of the PLA and PLA, b) compatibilization of the PLA and PBAT, and c) chain extension of the PBAT and PBAT. The chain extension reaction increases the molecular weight, whereas the compatibilization improves the interfacial adhesion. However, the overloading of the compatibilizer may cause the particle agglomeration to leave more defects in the polymeric films with reduced tensile strength and the elongation at break. We may conclude that the optimum concentration of the compatibilizer for the PLB/ TiO_2 films is lower than 5 wt%.

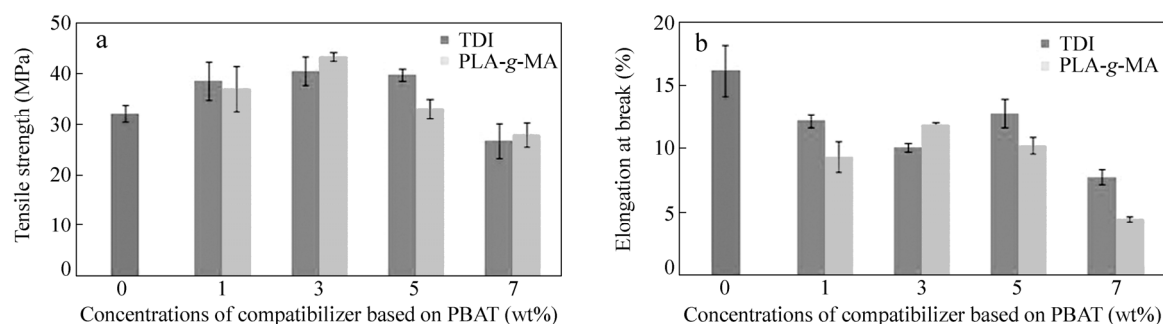


Fig. 4 The tensile properties of PLB/ TiO_2 blend films with TDI and PLA-g-MA (a) tensile strength and (b) elongation at break at various compatibilizer concentrations

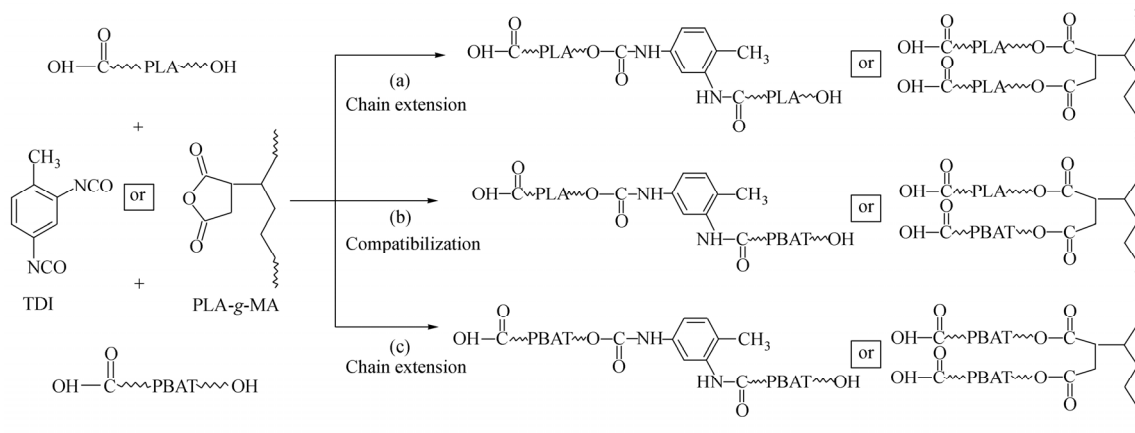


Fig. 5 Proposed mechanism for the compatibilization reaction of PLB, TDI, and PLA-g-MA

Impact tensile testing Figure 6 displays the impact tensile strength of the PLB/TiO₂ films with different concentrations of compatibilizer. The impact tensile resistance of the PLB/TiO₂ films is obviously improved in the presence of TDI and PLA-g-MAs that are proved as the good compatibilizers for PLA and PBAT depending on their concentrations. For example, the impact tensile strength of PLB/TiO₂ films compatibilized with 1 phr of TDI and PLA-g-MA reached 623 and 492 kJ/m², corresponding to increase by about 41% and 12%, as compared to that of uncompatibilized film (439 kJ/m²). This implied that some initial cracks in the PLA matrix was retarded because of the enhancement of interfacial interaction between the PLA and PBAT aided by the compatibilizer. However, we noticed that the impact tensile resistance of the compatibilized PLB/TiO₂ films reduced in a higher concentration of the compatibilizer.

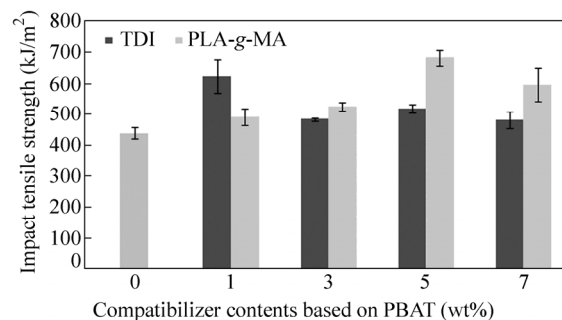


Fig. 6 The impact tensile strength of PLB/TiO₂ blended films with different contents of TDI and PLA-g-MA

Morphological study

Scanning electron microscope The SEM micrographs of the tensile fractured surface of the neat PLB and the PLB/TiO₂ films are shown in Fig. 7. The SEM images depict the neat PLB (Fig. 7a) and the PLB/TiO₂ (Fig. 7b) films with a large number of holes on the fractured surface due to the pulling out of PBAT particles. Furthermore, a lot of isolated PBAT were clearly observed, indicating the poor interfacial adhesion between PLA and PBAT. These results implied that the cracking might occur between the PLA matrix and the PBAT particles to generate many holes and isolated PBAT particles on the fractured surface of the neat PLB and the PLB/TiO₂ films because PBAT was not well wetted by PLA^[35].

As shown in Figs. 7(c) and 7(d), most of PBAT were surrounded and embedded by the PLA matrix after compatibilization using TDI and PLA-g-MA. More uniform and less isolated PBAT particles were clearly seen on the tensile fractured surface of the compatibilized films, indicating the significant improvement of adhesive

bonding and the interfacial interaction of PLA and PBAT in the presence of compatibilizer. Such function of the compatibilizer for the improvement of wetting and bonding at the interface of the blends was also observed and clearly explained by Wu^[36].

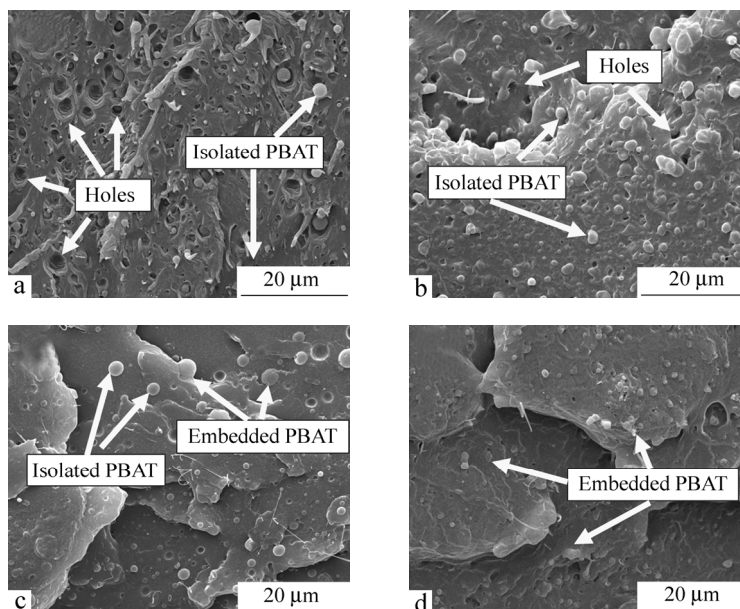


Fig. 7 The SEM images of the tensile fractured surface of (a) neat PLB, (b) nucleated PLB blended with 1 phr TiO_2 , (c) nucleated PLB/ TiO_2 blended with 3 wt% TDI, and (d) nucleated PLB/ TiO_2 blended with 3 wt% PLA-g-MA

Thermal properties

Thermogravimetric analysis The influences of the types and contents of the compatibilizer on the thermal stability of the PLB/ TiO_2 films are displayed in Fig. 8. The TGA and DTG thermograms of the PLB/ TiO_2 films showed two steps of decomposition at about 330 and 400 °C, relating to the T_d onset of the PLA and PBAT polymeric chains, respectively. Table 4 summarizes the temperature of weight loss 10% and 50% for the compatibilized PLB/ TiO_2 films. It can be seen that the weight loss temperature is affected by the TDI and PLA-g-MA content. The temperature for the weight loss of 10% and 50% gradually decreased as a function of the compatibilizer concentration, and at high concentration of compatibilizer (7 wt% based on PBAT), especially for the compatibilizer of PLA-g-MA, the weight loss temperature was lower. The TGA data indicated that the thermal stability of the PLB/ TiO_2 films with compatibilizer was lower than that of uncompatibilized film. At the

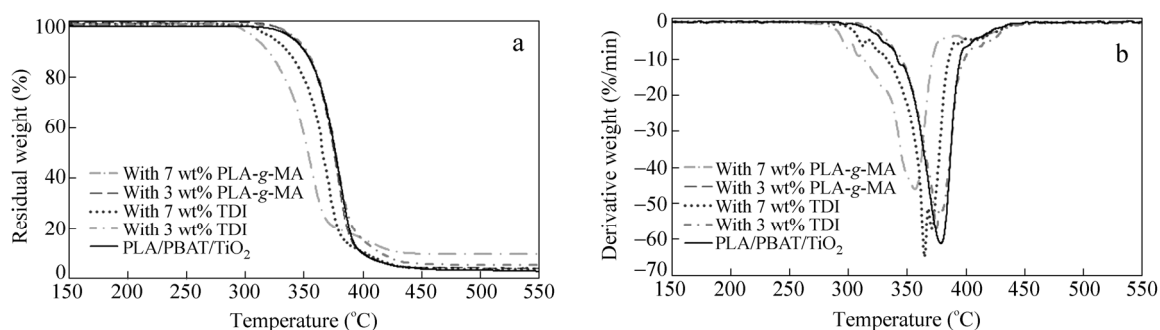


Fig. 8 The thermograms of nucleated PLB/ TiO_2 blend films with different compatibilizer amounts (a) TGA and (b) DTG

high concentration of TDI and PLA-g-MA, more defects of the crystal might present in the compatibilized PLB/TiO₂ films. Those imperfect crystals play an important role for decreasing the thermal stability, which were obviously observed in the DTG thermograms (Fig. 8b). The T_d of the compatibilized PLB/TiO₂ films shifted to the lower value when 7 wt% of the compatibilizer was added.

Table 4. The TGA and DSC data of PLA/PBAT (PLB) blend films compatibilized with different contents of TDI and PLA-g-MA

Sample ID	Temperature at weight loss (°C)		Char remaining at 550 °C (%)	Thermal transition temperature (°C)					H_c (J/g)	H_{cc} (J/g)	H_m (J/g)	χ_c (%)
	10%	50%		T_g	T_c	T_{cc}	T_{m1}	T_{m2}				
	PLBO1	351.1		376.6	2.7	56.9	–	103.6				
PLBO1T1	350.4	376.9	1.9	58.6	–	109.4	147.9	154.4	–	–25.4	25.7	31.2
PLBO1T3	352.4	376.2	3.5	63.9	–	116.2	150.5	156.5	–	–24.3	25.8	31.7
PLBO1T5	350.8	374.4	2.8	59.1	–	110.8	149.2	154.7	–	–26.3	26.8	33.7
PLBO1T7	336.4	365.4	2.5	58.2	–	107.9	145.8	154.3	–	–21.9	22.7	29.2
PLBO1P1	351.2	375.4	2.8	58.1	–	107.3	147.3	154.7	–	–24.9	25.9	31.4
PLBO1P3	344.0	373.2	2.2	56.2	–	105.1	144.9	154.5	–	–29.3	28.8	35.4
PLBO1P5	342.1	371.0	2.6	57.5	–	103.4	145.6	154.8	–	–25.5	30.2	38.0
PLBO1P7	316.1	352.2	5.3	58.3	–	101.0	143.6	154.3	–	–29.3	36.2	46.6

Differential scanning calorimetry Figures 9(a) and 9(b) illustrate the DSC profiles on the cooling and the second heating cycles of the PLB/TiO₂ films with and without compatibilizer. There was no significant change on the crystallization during the cooling process for both the uncompatibilized and compatibilized PLB/TiO₂ films. As listed in Table 4, it is suggested that the TDI and PLA-g-MA have the similar effect on the T_g , T_{cc} and T_m of the PLB/TiO₂ films. The addition of compatibilizer to the films increased the T_{cc} , indicating that the cold crystallization process on the heating cycle (Fig. 9b) was retarded. In addition, PLA-g-MA as a compatibilizer shifted the T_{cc} to the lower temperature and had a much less influence on the cold crystallization process than that of TDI. These experimental data implied that the crystallization of the PLB/TiO₂ films was slowed with the addition of TDI and PLA-g-MA because both of them as the compatibilizer improved the interfacial adhesion of PLA and PBAT, and as the chain extender extended the polymeric chain length and increased the molecular weight of PLA and PBAT. As a consequence, the crystallization of polymeric chains was significantly reduced, T_c disappeared, and T_{cc} increased. Moreover, as another important factor, the concentration of compatibilizer also influenced the crystallization of the PLB/TiO₂ films. As discussed above, the improvement of the properties of the compatibilized PLB/TiO₂ films was associated with the reaction between the maleic anhydride groups of the PLA-g-MA, the diisocyanate groups of TDI and the carboxylic and hydroxyl groups of PLA and PBAT, which might result in the agglomeration when higher concentration of compatibilizer was introduced in the system.

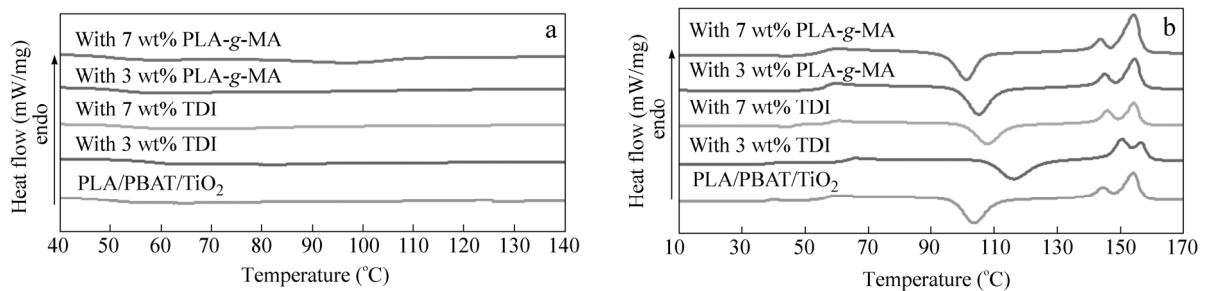


Fig. 9 The DSC thermograms of nucleated PLB/TiO₂ blend films with various compatibilizer contents (a) cooling and (b) the second heating cycles

The T_g and T_m of the compatibilized PLB/TiO₂ films were not changed when compared to those of uncompatibilized ones. The T_g of the PLB/TiO₂ films with TDI and PLA-g-MA slightly increased in the range of

58 °C to 63 °C and 56 °C to 58 °C, respectively. Whereas, the T_m of the compatibilized PLB/TiO₂ films also displayed the double melting characteristic but there was no obvious difference in both the T_{m1} and T_{m2} values. Interestingly, different concentration of compatibilizer resulted in the change of the χ_c of the compatibilized PLB/TiO₂ films (Fig. 10). The results revealed that the χ_c of the compatibilized PLB/TiO₂ films increased as a function of PLA-g-MA concentration in contrast to TDI. For example, the relative χ_c of the compatibilized PLB/TiO₂ films with 7 wt% PLA-g-MA increased by almost 40% while it was slightly decreased when the films with 7 wt% TDI. From the T_{cc} and χ_c results, we may suggest that the incorporation of PLA-g-MA into the PLB/TiO₂ films slightly retards the cold crystallization process but progressively induces crystallinity. PLA-g-MA is a more efficient compatibilizer than TDI for improving the χ_c and the cold crystallization of the PLB/TiO₂ films. This could be explained that the PLA-g-MA functioned as both a compatibilizer and a nucleating agent *via* a heterogeneous nucleation and compatibilization process for the compatibilized PLB/TiO₂ films. As for TDI, it only acted as a compatibilizer.

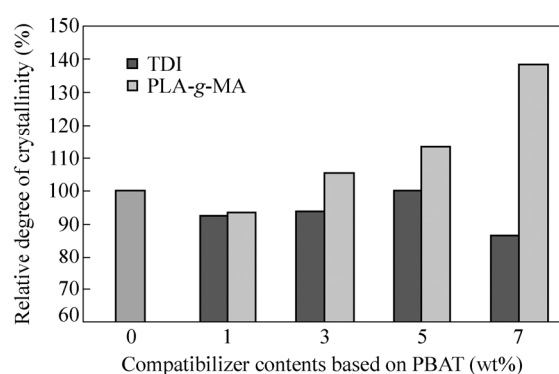


Fig. 10 The relative degree of crystallinity of nucleated PLB/TiO₂ blend films with various compatibilizer contents

CONCLUSIONS

TiO₂ has been successfully used as a nucleating agent for producing PLB films *via* heterogeneous nucleation. The addition of TiO₂ accelerated the cold crystallization process of the PLB films by decreasing the T_{cc} and enhancing the χ_c compared to the neat PLB. Furthermore, the impact tensile resistance and elongation at break of the PLB films increased by the addition of TiO₂ with the optimal amount of 1 phr. However, overloading the amount of TiO₂ caused the decrease of the tensile strength, elongation at break, and thermal stability of the PLB films.

In the cases of the PLB/TiO₂ films, the results revealed that the tensile strength and impact tensile resistance sharply increased with the presence of both TDI and PLA-g-MA due to the improvement of the interfacial interaction between PLA and PBATs. An appropriate concentration of the compatibilizer for balancing the properties of the compatibilized PLB/TiO₂ films is important. The mechanical performances and thermal stability of the films were significantly reduced by overloading TDI and PLA-g-MA. PLA-g-MA showed a greater efficiency than TDI for improving the overall properties of the compatibilized PLB/TiO₂ films in terms of tensile properties, impact tensile toughness, morphology, cold crystallization and the χ_c .

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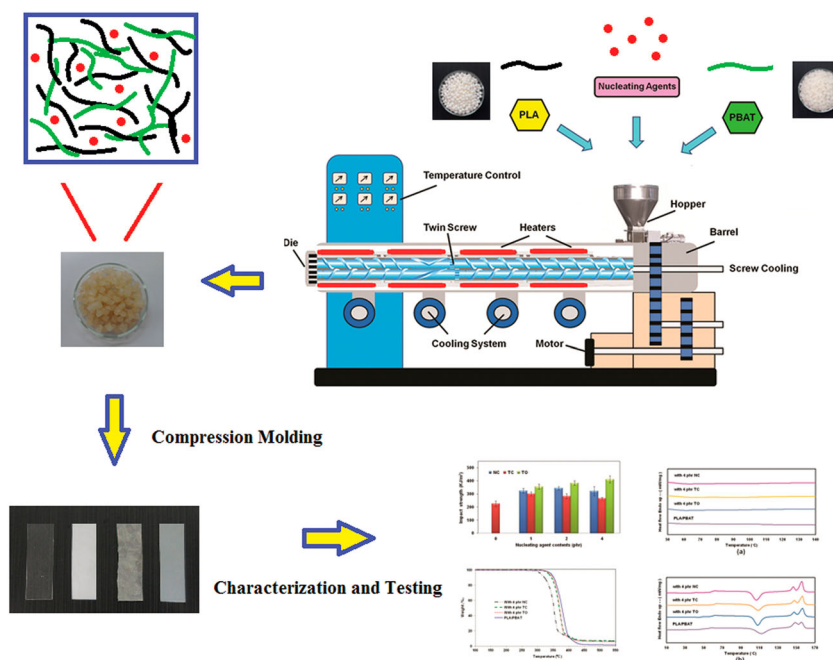
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Mechanical characteristics and thermal behaviours of polylactide blend films: influence of nucleating agent and poly(butylenes adipate-co-terephthalate)

W. Phetwarotai^{*1,2}, V. Tanrattanakul^{1,2} and N. Phusunti³

Polylactide (PLA) blend films with poly(butylenes adipate-co-terephthalate) (PBAT) and a nucleating agent were prepared by the melt compounding technique. Thermal stability of the PLA decreased with added nucleating agent; in contrast, the decomposition temperature increased with the presence of PBAT. In addition, the differential scanning calorimetry thermograms demonstrated that the heterogeneous nucleation and cold crystallisation processes of the PLA blend films were accelerated.

The influence of the type and level of the nucleating agent and the presence of PBAT on the tensile properties, impact resistance, thermal stability and non-isothermal crystallisation behaviours of the PLA blend films were investigated. Both the PLA/nucleating agents and the PLA/PBAT/nucleating agent blends showed significant effects from the changes in the nucleation process on their tensile properties, impact toughness and thermal behaviour. Furthermore, the impact energy that the PLA blends absorbed during the entire impact tension test was obviously enhanced by the increased content of the nucleating agent.



Keywords: Blend, Film, Nucleation, Crystallisation, Biodegradable, Toughness, Impact, Tensile

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Introduction

Poly(lactide) (PLA) is one of the most promising bio-based semi-crystalline polymers that has received considerable attention in recent years. PLA has been used for many applications i.e. biomedical, pharmaceutical, agricultural and automotive fields.^{1–3} This is because they have several advantages i.e. non-toxicity, ease of processability, transparency, gas permeability, mechanical strength and biodegradability.^{4–7} At present, PLA has become an extremely useful alternative material to replace some conventional petroleum-based plastics such as polyolefins, polystyrene and poly(ethylene terephthalate). Unfortunately, there are some drawbacks such as its slow crystallisation rate, low crystallinity and complete brittleness that restricts its usage for many applications, especially in the film packaging industry.^{8–10} The slow crystallisation rate leads to a long processing cycle time and a low production efficiency for PLA products.^{11,12}

To promote the crystallisation rate, crystallinity and nucleation of PLA, a nucleating agent has been selectively used. Theoretically, the nucleating agent can initiate a great number of nuclei via a heterogeneous nucleation process, resulting in the improvement of the crystallisation behaviours of its polymer. This is associated with changes in terms of its surface free energy, crystal size and spherulitic density during the melting processing and moulding. Therefore, mixing the PLA polymer with an appropriate nucleating agent may be a potential method to modify the mechanical properties and crystallisation behaviour of PLA. In this manuscript we have selected to use poly(butylene adipate-co-terephthalate) (PBAT) as a flexible filler to try to balance the high brittleness of PLA and the low stiffness of PBAT. PBAT, an aliphatic-aromatic copolyester derived from 1,4-butanediol, adipic acid and terephthalic acid, is a biodegradable plastic with a high flexibility and elongation but low strength.^{13–15} PBAT has been widely used for food packaging and in agricultural films.^{16,17} PLA and PBAT are reported to be immiscible over their entire composition range due to the differences in their polarity.^{18,19} However, the immiscible blending can lead to promotion of the nucleation and crystallisation, as previously reported in some other blend pairs such as PLA/polycaprolactone (PCL),²⁰ PLA/poly(vinylidene fluoride) (PVDF),²¹ iPP/ethylene-propylene-diene terpolymers²² and polycarbonate/poly(ethylene oxide).²³

As a result, the motivation of this research was to improve the PLA limitations for extending more applications for film packaging. We envision that mixing of the nucleating agent and PBAT, would not only accelerate the crystallisation process through heterogeneous nucleation, but would also enhance the toughness of PLA. In this study, PBAT was used to modify the toughness and the crystallisation rate of PLA by incorporating a nucleating agent. The influence of different types and levels of nucleating agent on the characterisations of the PLA blend films was investigated. In addition, the synergistic effect of the nucleating agent and PBAT on the tensile properties, its impact on its toughness, thermal stability and the crystallisation behaviours of the PLA blends was also studied.

Experimental

Materials

PLA resin (PLA 4043D) was from NatureWork LLC (Cargill-Dow, Minneapolis, MN, USA) for use as a polymer matrix. The PLA pellets were transparent with a density reported by the manufacturer of 1.24 g cm^{-3} , according to the ASTM D1505. The glass transition temperature (T_g), melting temperature (T_m) and decomposition temperature (T_d) of neat PLA was characterised by differential scanning calorimetry (DSC) and a thermogravimetric analyser (TGA) at about 60, 154 and 337°C , respectively. The polydispersity (PDI) and the weight average molecular weight of neat PLA was 1.46 and 130 kDa as determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF). PBAT (Ecoflex F BX7011) with a density of 1.26 g cm^{-3} was from BASF Corporation (Ludwigshafen, Germany). The T_g , T_m and T_d of PBAT were determined by DSC and TGA and were about -30 , 110 and 410°C , whereas its PDI and weight average molecular weight were 1.32 and 170 kDa (GPC analysis in THF), respectively. Nano precipitated calcium carbonate (NC) was from Behn Meyer Chemical, Co., Ltd, Bangkok, Thailand. Talc (TC) and titanium dioxide (TO) were from Chemipan, Co., Ltd, Bangkok, Thailand.

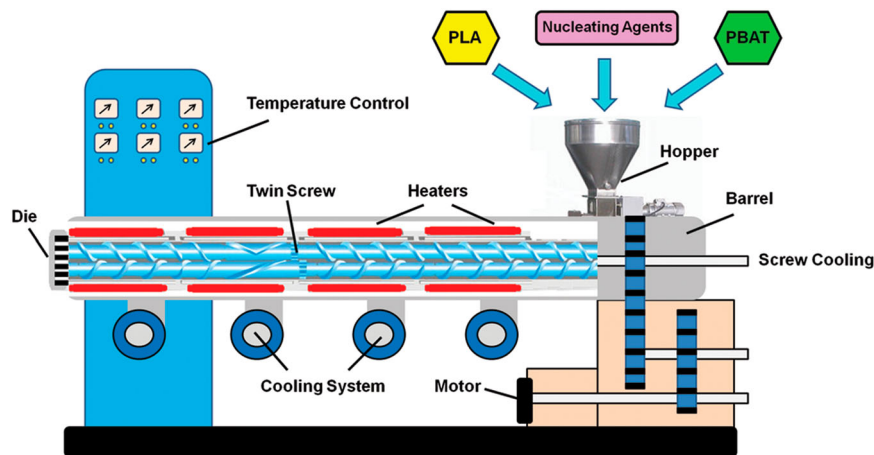
Material preparation

The PLA, PBAT and nucleating agent were dried in a vented oven at 60°C overnight and stored in a desiccator before usage. TC, NC and TO were used as the nucleating agent using different levels from 1 to 4 phr for enhancing the crystallisation rate of PLA. In the case of binary compounding, the weight ratio of PLA to PBAT was fixed at 90 to 10 for all experiments. PLA, PBAT and the nucleating agent were pre-mixed by a high speed mixer with a speed of 60 rev min^{-1} for 10 min before the extrusion process. The mixture was then melted in a co-rotating twin screw extruder (PRISM TSE 16TC, Thermo Electron Corporation, Karlsruhe, Germany) having a screw diameter of 15.6 mm and L/D ratio of 15. A schematic representation for the preparation of the blend is displayed in Fig. 1. The temperature profiles of the extrusion process were controlled on three zones ranging from 110 to 180°C with a screw speed of 30 rev min^{-1} . After extrusion, the compounds were dried in a vented oven at 60°C overnight and then compression-molded into the film specimens using a hydraulic press (KT-7014, Kao Tieh Machinery Industrial, Taichung, Taiwan) under optimum conditions; a holding temperature of 180°C ; pressure, 1500 psi; cycle time, 25 min. The neat PLA was also taken in the same way in order to be used as a reference material. Sample formulations and their abbreviations are displayed in Table 1.

Characterisation and testing

Tensile properties

The tensile test for the rectangular film specimens with a size of 15 mm wide, 150 mm long and about $250 \mu\text{m}$ thickness was performed on a universal testing machine (LR 100k, LLOYD, Fareham, UK) using a crosshead speed



1 A schematic representation of the preparation of the material

of 10 mm min⁻¹ and a gauge length of 100 mm, according to the ASTM D882-09. A 1 kN load cell was employed for testing the films of neat PLA and the PLA blend. All specimens were stored overnight at room temperature before testing. At least five specimens of each film were tested and the results were averaged to obtain a mean value.

Impact tensile testing

Standard type IV, impact tensile specimens of neat PLA and PLA blend films were evaluated by an impact tester (Zwick 5102 Pendulum, Zwick/Roell Group, Ulm, Germany) using a deflection angle of 160°, an exchangeable pendulum of 1 J, an impact velocity of 2.93 m s⁻¹, and a pendulum length of 225 mm. All specimens were stored overnight at room temperature before testing. At least five specimens were tested according to DIN EN ISO 8256:2004 and the results were averaged to obtain a mean value. The thickness of the films was determined by an analogue thickness gauge. The average thickness was obtained from at least five samples for each film. For calculating the impact energy (*E_{Im}*) the following equation (1) was used:

$$E_{Im} = \frac{E_{Ab}}{w \times d} \tag{1}$$

where *E_{Im}*: determining impact energy or impact strength, *E_{Ab}*: absorbed energy of specimen, *w*: width of specimen and *d*: thickness of specimen.

Thermal stability

The decomposition temperature of the neat PLA and its blends were characterised using a TGA (TG/DSC STA 449 F3 Jupiter, NETZSCH Instruments, Selb, Germany). The TGA technique was used to determine the thermal stability of the PLA films before and after the addition of the nucleating agent and PBAT. Samples (about 4–6 mg) were cut from the neat and PLA blend films and placed in a crucible (70 μL) to use in each TGA experiment. The operation was performed in a nitrogen atmosphere with a heating rate of 20°C min⁻¹ from 50 to 600°C. The percentage of weight loss for all samples was evaluated.

Crystallisation and thermal behaviours

A differential scanning calorimeter (DSC; DSC 200 F3 Maia, NETZSCH Instruments, Selb, Germany) was used to evaluate the crystallisation behaviours and any thermal transitions of the PLA blend films. For each DSC analysis, approximately 6–8 mg of samples was encapsulated in a hermetically sealed aluminium pan

Table 1 Sample formulations of neat PLA and the PLA blend films with different types and contents of nucleating agent

Formulation	PLA (wt-%)	PBAT (wt-%)	Nucleating agents (phr)		
			NC	TC	TO
Neat PLA	Neat PLA	100	–	–	–
Nucleated PLA	PLA/NC 1	100	1	–	–
	PLA/NC 2	100	2	–	–
	PLA/NC 4	100	4	–	–
	PLA/TC 1	100	–	1	–
	PLA/TC 2	100	–	2	–
	PLA/TC 4	100	–	4	–
	PLA/TO 1	100	–	–	1
	PLA/TO 2	100	–	–	2
	PLA/TO 4	100	–	–	4
	Nucleated PLA/PBAT	PLA/PBAT	90	10	–
PLA/PBAT/NC 4		90	10	4	–
PLA/PBAT/TC 4		90	10	–	4
PLA/PBAT/TO 4		90	10	–	–

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(30 μL). A first heating scan was operated from room temperature to 180°C at a heating rate of 10°C min⁻¹ and held at 180°C for 3 min to remove the thermal history of all samples. Then, it was cooled to -60°C with a cooling rate of 10°C min⁻¹. Finally, in a second heating scan samples were heated to 180°C at a heating rate of 10°C min⁻¹ to determine the non-isothermal crystallisation behaviours of the films. All experiments were carried out in a nitrogen atmosphere. The glass transition temperature (*T_g*), crystallisation temperature (*T_c*), cold crystallisation temperature (*T_{cc}*), melting temperature (*T_m*), specific cold crystallisation enthalpy (ΔH_{cc}) and specific melting enthalpy (ΔH_m) of the samples were recorded. The degree of crystallinity (χ_c) of the neat PLA and PLA blend films was calculated using the following equation (2):

$$\chi_c = \frac{(\Delta H_m - \Delta H_{cc})}{(1 - W_f) \cdot \Delta H_m^0} \times 100 \quad (2)$$

where *W_f* is the weight fraction of the filler and ΔH_m^0 is the melting enthalpy of the 100% crystalline PLA that was equal to 93.6 J g⁻¹.²⁴

Morphological studies

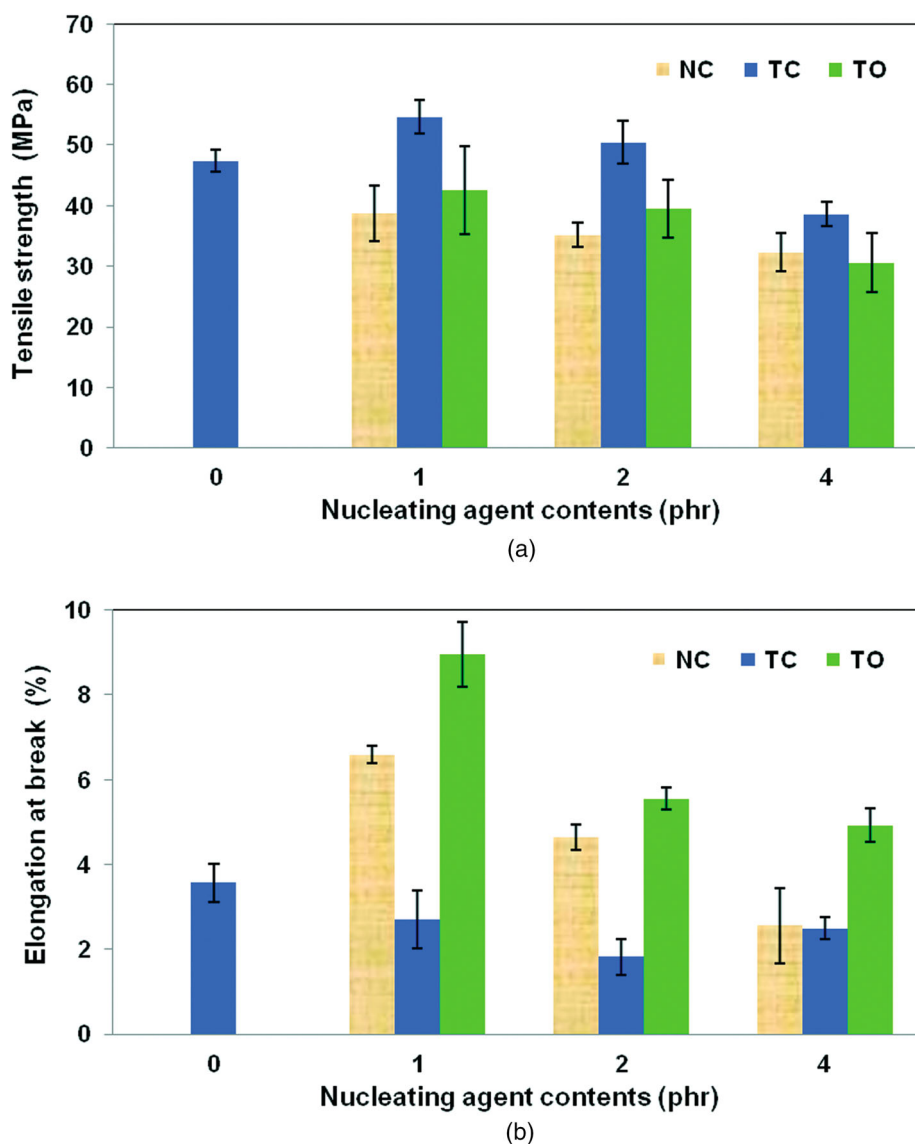
Fracture surfaces after tensile testing were evaluated by a scanning electron microscope (SEM; JSM 6480, JEOL, Tokyo, Japan). The fractured surface of the PLA blend films was sputter coated with a thin layer of gold prior to experiment. The SEM was operated at 15 kV to image the films. Furthermore, an energy dispersive spectroscopy (EDS; 7573 INCAx-sight EDS, Oxford Instruments, Concord, MA, USA) on SEM was used to identify the particle elements and disperse state of the PLA blend films.

Results and discussion

PLA/nucleating agent blends

Tensile properties

Tensile strength and elongation at break of neat PLA and PLA blend films with various types and concentrations of nucleating agent are displayed in Fig. 2a and b, respectively. Neat PLA had a high tensile strength (about



2 The tensile properties of neat PLA and the PLA blend films with various types and concentrations of nucleating agent a tensile strength and b elongation at break

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50 MPa) but the elongation at break was quite low (about 3.6%). Neat PLA had a high glass transition temperature (T_g) of 60.1°C and displayed a glass-like brittle behaviour at room temperature due to the freezing of the molecular chains into the polymer. In the glassy state, a large scale molecular motion of the PLA main chains did not occur because of the limitation of the relative free volume, that led to a lower volume expansion coefficient in this region.²⁵ The addition of TC (i.e. <4 phr) to the PLA blend films produced an increase of their tensile strength. The tensile strength on the PLA/TC blends increased with each increment of TC level; however, the percentage of the elongation at break gradually decreased. Furthermore, at 4 phr of TC, the tensile strength of the composite films significantly decreased to 38.56 MPa compared to that of the blends containing 1 phr (54.63 MPa). It might result from some agglomeration of TC that occurred at high concentrations.

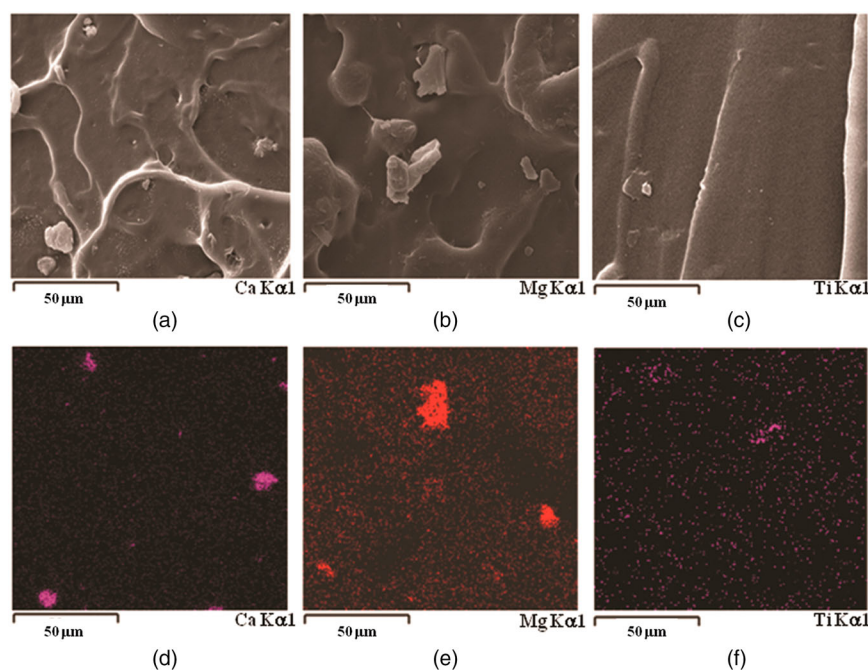
In contrast, the presence of NC and TO in the PLA matrix composites led to a slight decrease of the tensile strength but there was an impressive increase of the elongation at break, especially with small amounts of the nucleating agent (1 phr). This could be explained in that the addition of nucleating agent might lead to an increase in both the degree of crystallinity (χ_c) and the smaller spherulitic size that resulted in the enhancement of the elongation at break of the PLA blend films as supported by the morphological studies. Figure 3 shows the SEM and energy dispersive spectroscopy on SEM (EDS/SEM) images at 1000× magnification of the tensile fracture surface of the PLA blend films with 1 phr of nucleating agent. The EDS/SEM results revealed that NC, TC and TO particles were well-dispersed in the PLA matrix with the typical appearance as in Fig. 3a–f. Moreover, the tensile fracture surface of the PLA blend film with 1 phr of NC and TO (Fig. 3d and f) showed more homogeneous dispersion of nucleating agent than that with TC (Fig. 3e) which helped to improve their

mechanical properties. On the other hand, with a further increase of the nucleating agent (i.e. >1 phr), the tensile properties of the PLA blend films apparently decreased. This is probably because some agglomeration of the overloading nucleating agent particles occurred and this led to more defects and cracks in the composites. This is one possible reason why the tensile properties of the PLA blend films at the higher levels of the nucleating agent obviously decreased. These behaviours could be observed in both of the PLA blend films with NC and TO. However, comparatively, the overall elongation at break of the blend films with NC and TO was higher than that of the neat PLA. This result was supported by the DSC data because the χ_c of the blend films was closely related to their mechanical properties.

Impact tension

Generally, impact testing is used to determine the capability of the material to withstand a suddenly applied load in terms of the impact toughness or the impact energy. Moreover, toughness of the material is related to its ability to absorb energy during the impact testing. Therefore, brittle materials have a lower toughness or impact resistance than ductile material due to the lower energy absorption. Normally, the crystal size, crystal amount and crystal perfection of materials may also significantly affect the value of the impact strength because they may lead to an increase or decrease of the stress concentration that was related to the absorbed energy. Neat PLA was semi-crystalline with a 19.8% degree of crystallinity (as shown in Table 2) due to its slow crystallisation rate. Crystallinity and the rate of crystallisation of PLA were enhanced by using an appropriate nucleating agent that may lead to a decrease of its life cycle time for productivity.

From equation (1), the impact energy (E_{Im}) or impact strength of the neat PLA and PLA blend films was



3 SEM and energy dispersive spectroscopy on SEM (EDS/SEM) images at 1000× magnification of the tensile fracture surface of PLA blend films with 1 phr of nucleating agent a, d NC, b, e TC and c, f TO

Table 2 Data from the TGA and DSC thermograms of neat PLA and PLA blend films with various types and levels of nucleating agent

Formulation	T_d (°C) onset	Temperature (°C) at weight loss		Thermal transitions (°C)					
		10%	50%	T_g	T_c	T_{cc}	T_{m1}^*	T_{m2}^*	χ_c (%)
Neat PLA	336.5	347.3	372.8	60.1	–	125.9	–	154.4	19.8
PLA/NC 1	333.8	348.1	375.6	61.3	94.4	103.4	147.4	157.9	29.7
PLA/NC 2	315.2	337.2	360.6	58.4	–	100.4	144.6	155.4	41.7
PLA/NC 4	310.3	326.5	351.4	61.6	–	108.9	148.3	156.7	33.6
PLA/TC 1	340.1	355.1	376.8	58.2	92.9	–	144.4	155.2	37.6
PLA/TC 2	335.6	350.5	374.7	55.6	92.4	–	144.9	154.9	37.2
PLA/TC 4	321.7	334.4	359.2	54.7	86.2	96.2	143.2	155.4	38.8
PLA/TO 1	335.8	350.0	375.5	56.9	–	111.2	147.2	156.2	43.7
PLA/TO 2	334.9	348.7	370.7	56.4	–	109.2	145.9	155.7	41.2
PLA/TO 4	331.6	344.6	369.9	58.2	–	115.7	148.4	156.4	40.2

* T_{m1} : lower melting temperature, T_{m2} : higher melting temperature.

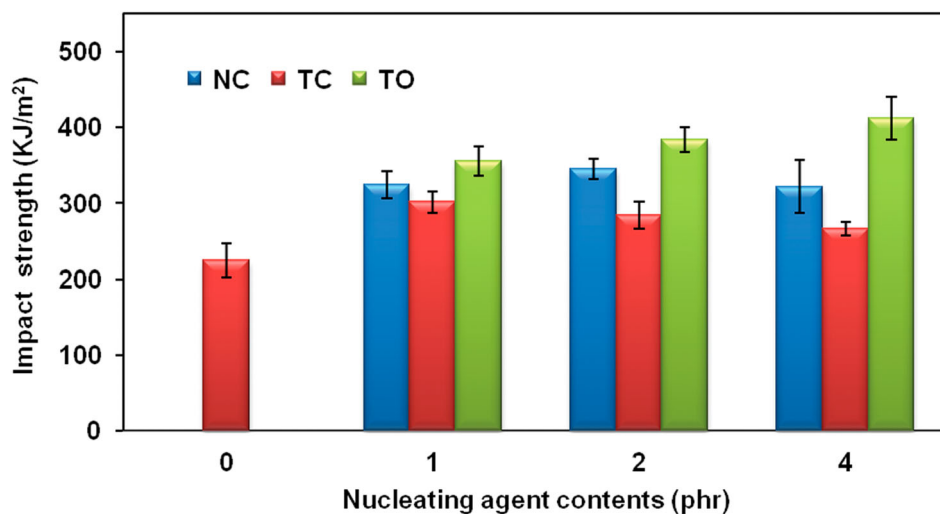
calculated. The impact strength of the neat PLA and the PLA blend films with different types and concentrations of nucleating agent is displayed in Fig. 4. The impact strength of the neat PLA was 225 kJ m^{-2} which indicated its brittle behaviour due to the low value of the absorbed energy. As expected, the PLA blend films with the addition of the nucleating agent had an increased tendency in terms of their resistance to impact. For example, the impact strength of the PLA blends with TO was increased to 356, 384 and 412 kJ m^{-2} when the TO level increased from 1 to 2 and 4 phr, respectively. In other words, the percentage of the impact energy of the PLA composite films with TO was enhanced by almost 58, 71 and 83%, respectively, compared to that of the neat PLA. Furthermore, similar results were observed in the PLA blend with NC and TC. The results of similar experiments have been previously reported by Arends²⁶ and Zhang *et al.*²⁷ They explained that changing of the spherulite size in the polymer with the addition of a nucleating agent was a key reason for the increment of toughness. With the presence of the nucleating agent, a lot of small spherulites were produced that led to a large number of tie-molecules that led to an increased ability of the material to absorb energy.

Also the increase of the impact strength may be due to a decrease of the internal stresses in the micro regions of the

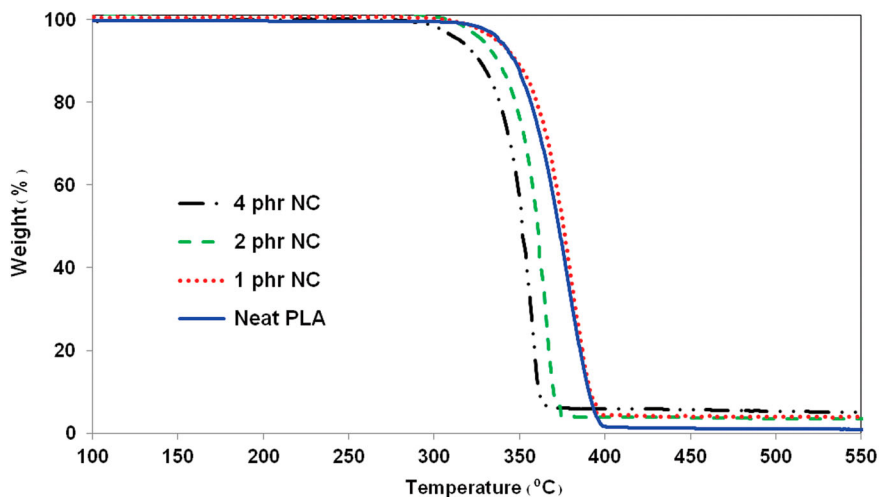
PLA composites. The role of these stresses in the change of the impact resistance can be explained via the cracking mechanism as follows: the presence of a nucleating agent in PLA accelerated the crystallisation process and promoted a large number of tiny crystals which then reinforced the resistance of a suddenly applied load. Therefore, the micro deformations grow first at the crystal boundaries rather than on the PLA matrix when the stresses were applied by impact tension. This is one possible reason why the impact resistance of the PLA blend films with TC, NC and TO was obviously improved compared to that of neat PLA.

Thermal stability

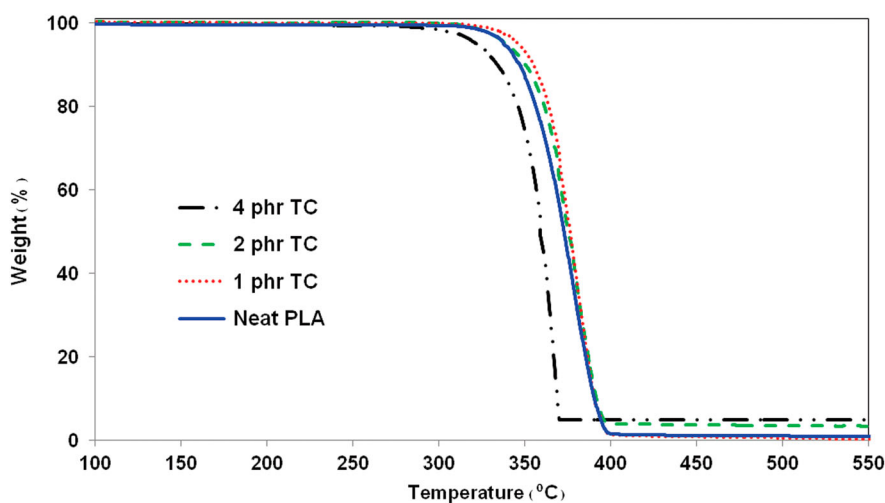
The TGA technique was used to investigate the thermal stability and decomposition temperature (T_d) of the neat PLA and PLA blend films. Figure 5a–c shows the effect of the different types and levels of nucleating agent on the thermal stability of the PLA composites. The neat PLA showed only one step of decomposition from about 336 to 390°C that was attributed to the thermal decomposition of the PLA backbone. The temperatures at 10 and 50% of weight loss of the neat PLA were 347 and 372°C, respectively (as shown in Table 2). Surprisingly, the TGA thermograms (Fig. 5a) revealed that the onset of the T_d



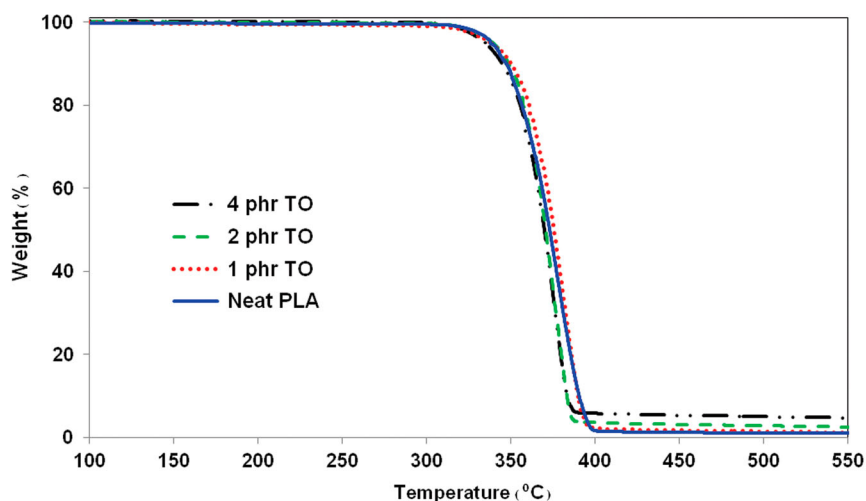
4 Impact toughness of neat PLA and the PLA blend films with different types and concentrations of nucleating agent



(a)



(b)

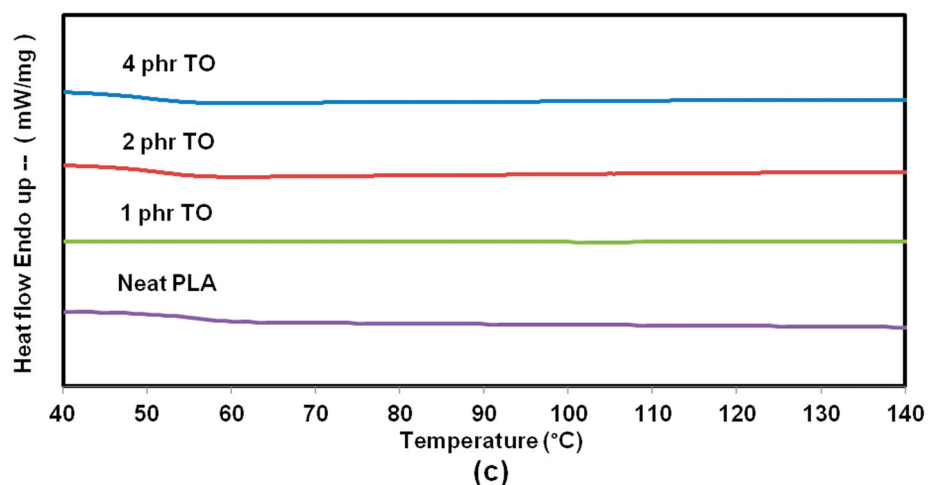
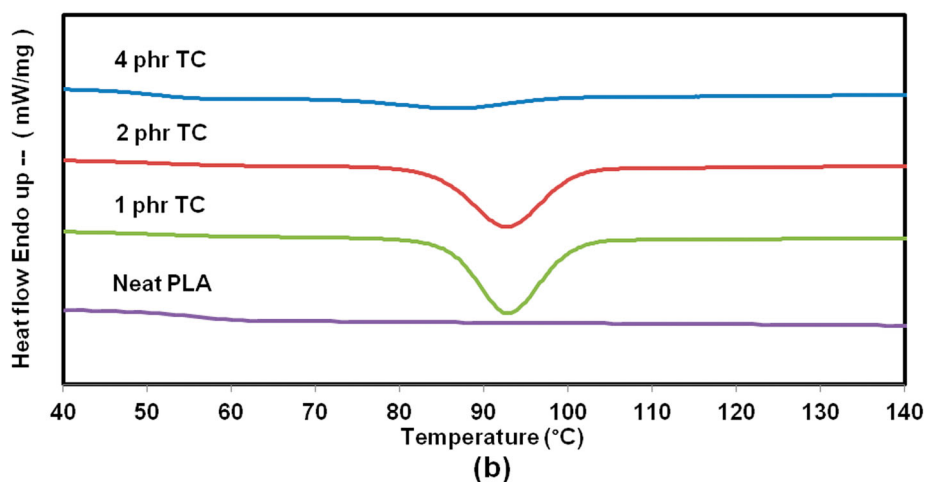
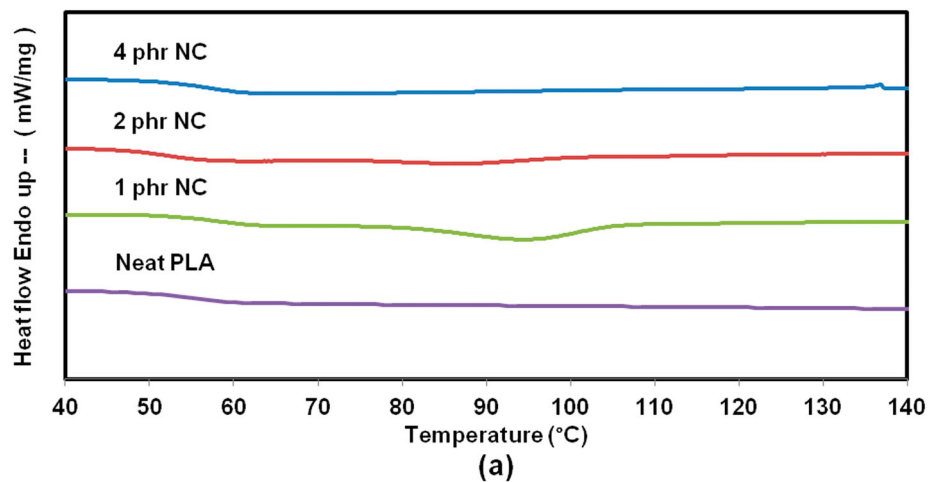


(c)

5 TGA thermograms of neat PLA and PLA blend films with various levels of nucleating agent a NC, b TC and c TO

of the PLA blend films with NC was significantly reduced with an increase of the content of the nucleating agent (from 1 to 4 phr) with a decrease from 333.8 to 310.3°C compared to that of the neat PLA. For example, the thermal stability of the PLA composites with 4 phr NC

decreased by about 26°C compared to the neat PLA. Furthermore, the TGA data indicated that the temperature used for a 10% weight loss of the PLA/NC blend decreased to 348.1°C (1 phr NC), 337.2°C (2 phr NC) and 326.5°C (4 phr NC), respectively. A similar tendency of the



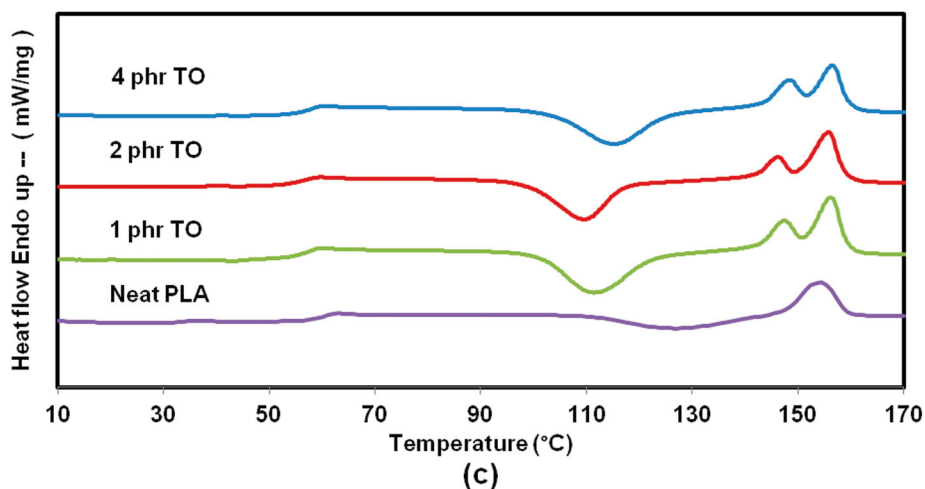
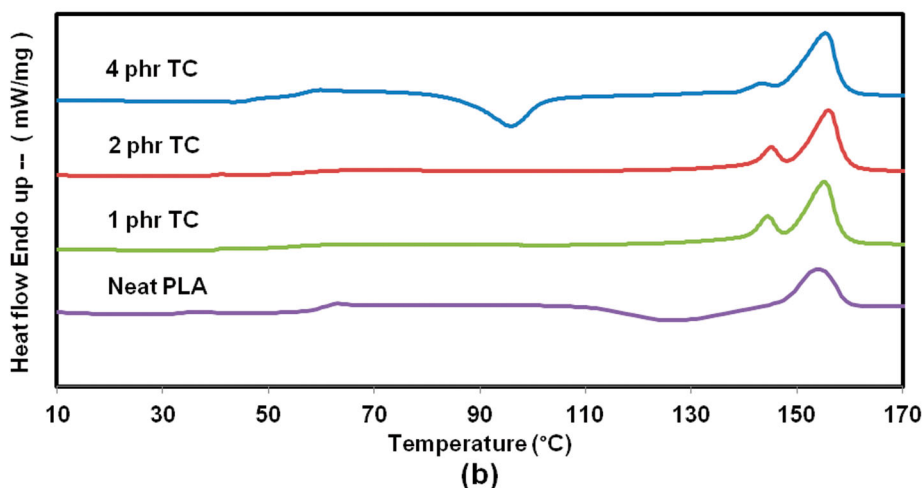
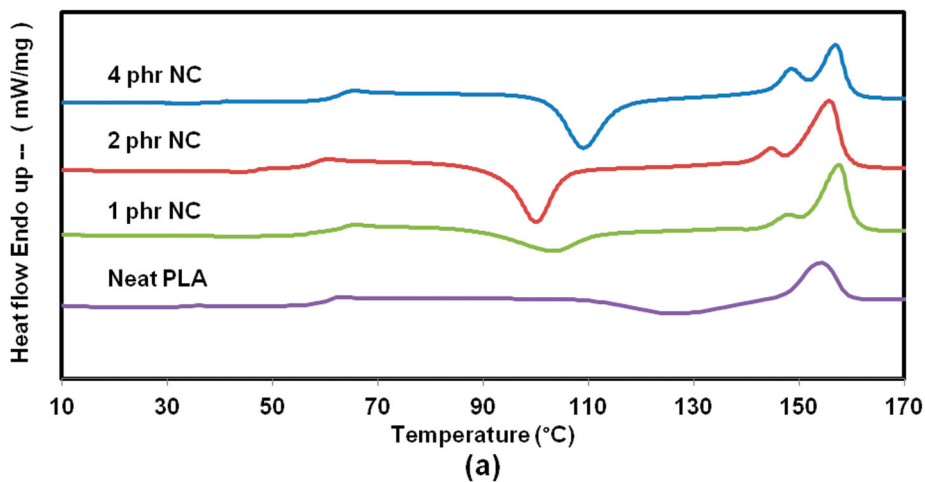
6 Cooling curves in the DSC thermograms of neat PLA and PLA blend films with various contents of nucleating agent a NC, b TC and c TO

temperature used for a 50% weight loss was noticed. These results might be the result of the presence of NC that could obviously be enhanced by the larger number of nuclei that led to a greater amount of tiny crystals in the PLA matrix. Those very small sized PLA crystals played an important role on the large depression of the thermal stability of the PLA/NC composite films. These behaviours could also be observed in the PLA blend films with the TC and TO as shown in Fig. 5b and c, respectively. However, it seems that the thermal stability of the blend films with a higher

TO was higher than that with NC. From Table 2, at 4 phr of nucleating agent, the T_d onset values of the composite films were about 310°C (PLA/NC) and 332°C (PLA/TO), as an example.

Crystallisation and thermal behaviours

The DSC technique was used to determine the crystallisation behaviour and thermal transitions of neat PLA and the PLA blend films. DSC cooling and the 2nd



7 2nd heating curves in the DSC thermograms of neat PLA and PLA blend films with different levels of nucleating agent a NC, b TC and c TO

heating curves of neat PLA and PLA blends with various types and amounts of nucleating agent are shown in Figs. 6 and 7, respectively. The DSC data indicated that the crystallisation temperature (T_c) of neat PLA depended upon the cooling rate. The T_c of neat PLA was not observed because of the high cooling rate ($10^\circ\text{C min}^{-1}$). Hence, at the 2nd heating the DSC thermogram of the neat PLA, an exothermic peak associated with a cold crystallisation temperature (T_{cc}) was noticed at 125.9°C due to the recrystallisation of the PLA lamellae. This evidence confirmed that the crystallisation rate

of neat PLA was too slow to occur in one cooling step that led to a partial re-alignment of its molecular chains in the 2nd heating step. A single endothermic signal that was the melting temperature (T_m) appeared at 154.4°C , whereas its degree of crystallinity was quite low at about 19.8% (Table 2).

A similar behaviour of a non-isothermal crystallisation could also be observed in both of the PLA blend films with NC and TO. The DSC cooling curves in Fig. 6 indicated that an exothermic peak of the PLA blends did not appear during the cooling step; however, the T_{cc} peak

was clearly observed in the heating step. It was of interest, that with an increase of the TO content, the T_{cc} values were shifted towards a lower temperature (109–115°C) compared to that of the neat PLA (125.9°C) under the same conditions. These tendencies were similarly reported in the PLA blends with NC. The presence of both NC and TO led to decrease of the T_{cc} , and accelerated the crystallisation rate of PLA. However, adding too much of NC and TO (i.e. 4 phr) led to a slight decrease of the T_{cc} . This might be because the efficiency of the nucleating agent was retarded by some agglomeration of the particles. Furthermore, these DSC data indicated that the χ_c of the PLA blend films was improved by 30–44%, compared to the neat PLA (19.8%). A doubling of the melting temperature of the PLA blends was clearly observed over the range of 143–148°C (T_{m1}) and 155–158 °C (T_{m2}), respectively. Generally, the influence of the T_c , crystallisation time, molecular weight, heating and cooling rates were significantly affected by the double melting behaviour.²⁸ The lower peak of melting (T_{m1}) was probably related to the crystallisation of the PLA during the heating cycle and the higher peak of melting (T_{m2}) should correspond to the crystallisation of PLA during the cooling process.^{28,29}

In the case of the PLA blend films with TC, different thermal behaviours were observed. In the cooling step, the DSC thermograms showed the obvious T_c signal that was related to the induction of the PLA crystallisation when a small amount of TC was added to the composite films. The T_c values appeared at about 86–92°C which indicated that the crystallisation of the PLA/TC composite was completed during the cooling process. Therefore, recrystallisation of PLA molecular chains did not occur in the 2nd heating scan leading to the disappearance of the T_{cc} peak. Nevertheless, the blend films with 4 phr TC showed small signals in both the T_c and T_{cc} . This might result from some agglomeration of the overload of TC particles present in the PLA composites. Double melting peaks that resulted from the perfect and imperfect crystals were also observed. Furthermore, the addition of TC into the composites led to a significant increase of χ_c . These results revealed that the presence of TC in the PLA composites significantly affected the non-isothermal crystallisation behaviour of the films. The addition of TC to the composites led to a faster crystallisation rate and greater crystallinity compared to that without the nucleating agent. In summary, (1) the crystallisation behaviour of the neat PLA and its composites was dependent on the type and amount of the nucleating agent, (2) NC, TC and TO played an important role in accelerating the crystallisation rate and increasing the crystallinity of the PLA and (3) TC, NC and TO were effective nucleating agents for PLA.

PLA/PBAT/Nucleating agent blends

Tensile properties

A flexible polymer like PBAT was used to complex with PLA to enhance the flexibility and toughness of neat PLA. Table 3 shows the tensile properties of neat PLA and the PLA/PBAT (90/10 w/w) blend films with different types of nucleating agent (4 phr). The elongation at break of the PLA was greatly improved after the addition of PBAT from 3.6% (neat PLA) to 11.6%. In contrast, the tensile strength of the films was significantly decreased by the presence of 10 wt-% PBAT (32.9 MPa), compared to the neat PLA (47.4 MPa). Normally, such behaviour

was observed when the softer material (PBAT) was mixed with a more brittle material (PLA). Furthermore, the poor adhesion between the two phases of PLA and PBAT led to a reduction of the tensile strength.

When the nucleating agent was added into the composite films, both tensile strength and elongation at break decreased significantly. The tensile strength of the PLA/PBAT composites decreased to 24.7 (4 phr NC), 27.7 (4 phr TC) and 22.2 MPa (4 phr TO), respectively. The reduction of the strength was about 20–30%, whereas the decrease of the elongation at break was about 50–70%, compared to the PLA/PBAT composite without nucleating agent. From these results it seems as though there was an incompatibility of PLA, PBAT and the nucleating agent that occurred. Furthermore, the particles of the dispersed PBAT and nucleating agent acted as stress concentrators and caused defects and cracks in the composites, that resulted in a low tensile strength and elongation at break. Such behaviour was observed in all the different compositions of the PLA/PBAT blend films.

Impact tension

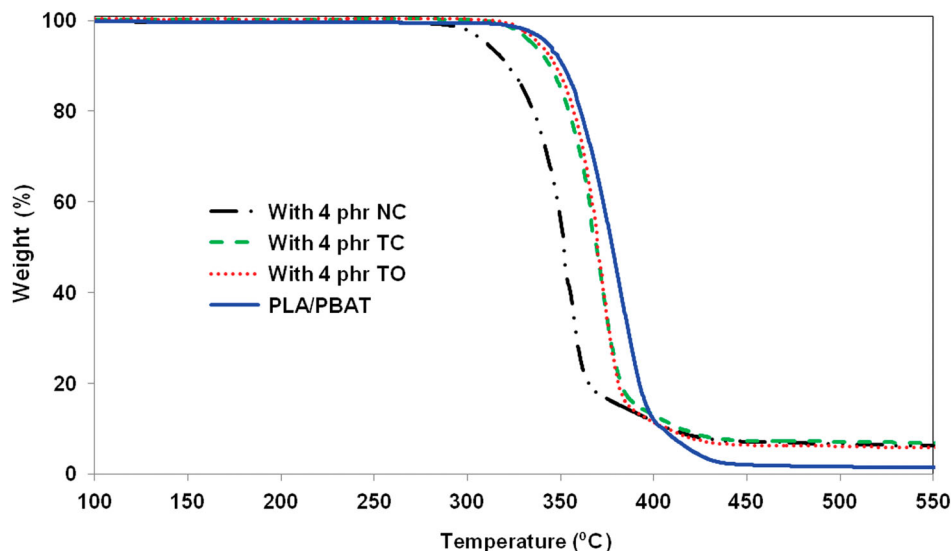
Although the presence of a nucleating agent in the PLA/PBAT blend films had a negative effect on the tensile properties, the tensile-impact resistance was greatly improved. As shown in Table 3, the impact strength of PLA was enhanced from 225 to 280 kJ m⁻² by adding 10 wt-% PBAT because the phenylene groups in the PBAT main chains played an important role for improving the energy absorption. Furthermore, the impact strength of the PLA/PBAT (90/10 w/w) blends increased to 326, 512 and 422 kJ m⁻² in the presence of NC, TC and TO, respectively. As discussed above in topic 'Impact tension', the presence of a nucleating agent in the PLA accelerated the crystallisation process and created a large number of small crystals that enhanced the energy of resistance from a suddenly applied load. Therefore, the impact resistance of the PLA blend films containing a nucleating agent was obviously increased. It was of interest, that these results clearly showed the synergistic effect of adding PBAT and a nucleating agent into the PLA blend films that resulted in a strong improvement of the toughness.

Thermal stability

The TGA thermograms of the PLA/PBAT blend films without and with various types of nucleating agent are displayed in Fig. 8. The PLA/PBAT film showed two steps of thermal degradation. The first stage was approximately at 335–340°C and was attributed to the decomposition of the PLA main chains, while the second step was about 400–

Table 3 Tensile properties and tensile-impact resistance of neat PLA and PLA/PBAT blend films without and with various types of nucleating agent

Film samples	Tensile strength (MPa)	Elongation at break (%)	Tensile-impact resistance (kJ m ⁻²)
Neat PLA	47.39 ± 1.85	3.57 ± 0.45	225 ± 20
PLA/PBAT	32.87 ± 1.13	11.59 ± 2.19	280 ± 12
PLA/PBAT/NC 4	24.72 ± 1.64	4.18 ± 0.31	326 ± 8
PLA/PBAT/TC 4	27.72 ± 1.27	5.25 ± 0.35	512 ± 14
PLA/PBAT/TO 4	22.06 ± 2.74	6.63 ± 1.11	422 ± 15



8 TGA thermograms of PLA/PBAT (90/10 w/w) blend films without and with different types of nucleating agent

410°C and was associated with the loss of PBAT, and indicated the presence of PLA and PBAT phases in the films. Furthermore, the TGA result revealed that the thermal stability of PBAT was higher than that of PLA.

For investigating the thermal stability of the PLA/PBAT blends without and with a nucleating agent, the temperatures used for decomposing the samples to 10 and 50% weight loss were determined. As shown in Table 4, the temperatures at 10 and 50% weight loss of the PLA/PBAT composite films without nucleating agent were approximately 351 and 378°C, respectively. These values of the blend films apparently decreased with the addition of nucleating agent. Similar results of a decreased T_d onset were observed in both the first and second decomposition steps. These data implied that the thermal stability of the PLA/PBAT blend films decreased with the presence of NC, TC and TO due to the changes in the size and specific surface area of the crystals that were related to the heat of decomposition. However, the PLA blend with 4 phr TO had a higher thermal stability than those with NC and TC.

Crystallisation and thermal behaviours

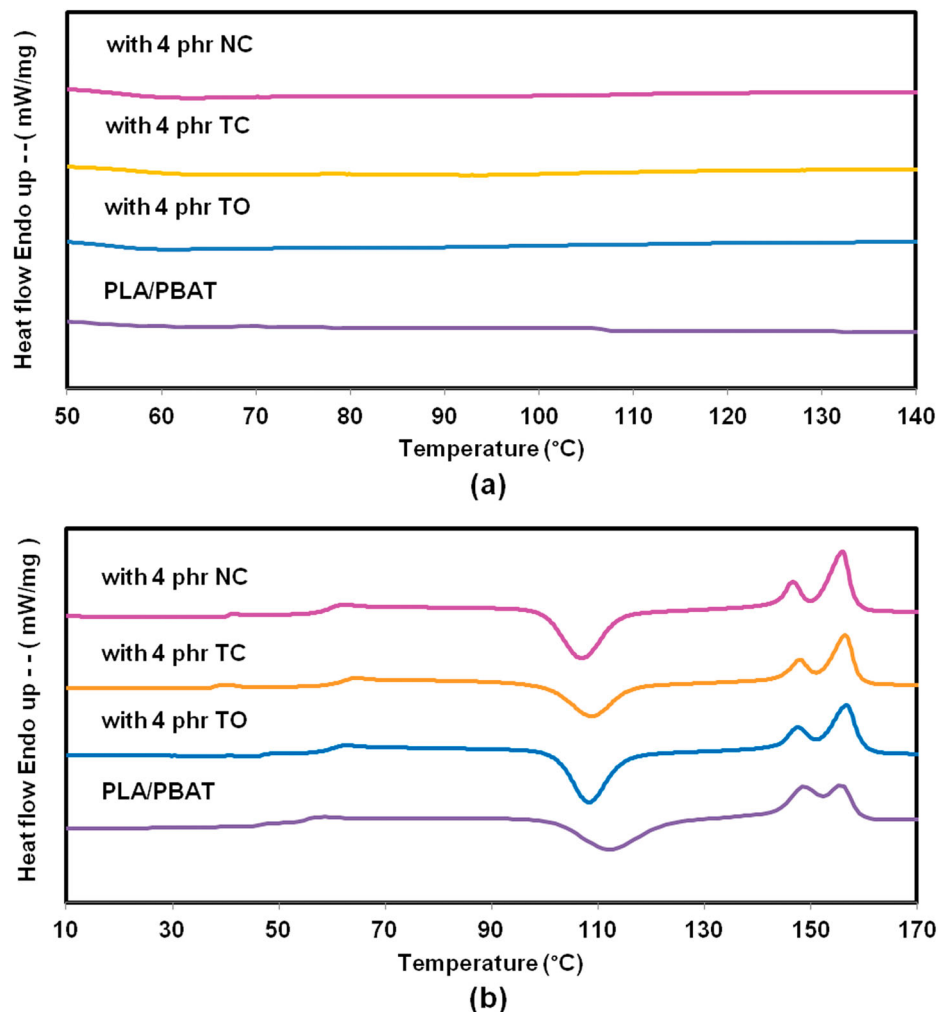
The DSC thermograms of the PLA/PBAT (90/10 w/w) blend films without and with different types of nucleating agent are shown in Fig. 9. The T_g , T_{cc} and χ_c of PLA/PBAT (90/10 w/w) films without a nucleating agent were 54.7°C, 111.9°C and 28.7%, respectively. In addition, the T_{m1} and T_{m2} appeared at around 148 and 155°C as shown in Table 4. The exothermic peak that corresponded

to the T_c did not appear in the DSC cooling process of the PLA/PBAT films. These data indicated that crystallisation of the PLA/PBAT composites was not completely formed during the cooling step. Therefore, the recrystallisation process was taking place and led to the obvious T_{cc} curve during the 2nd heating scan (Fig. 9b). The T_g of the PLA/PBAT film without the nucleating agent decreased by almost 5.5°C (from 60.1 to 54.7°C) compared to that of the neat PLA because the presence of the PBAT phase helped to enhance the chain mobility of the PLA matrix and led to a significant increase of the elongation at break, as evidenced by the tensile properties. It was of interest, that the T_{cc} of PLA decreased dramatically after complexing with the PBAT from 125.9°C (neat PLA) to 111.9°C, and indicated that the PBAT accelerated the cold crystallisation of PLA. The T_{cc} of PLA significantly decreased by almost 14°C after mixing with 10 wt-% PBAT. A similar result was reported recently by Pan *et al.*²¹ They found that the immiscible blending of PLA and PVDF promoted the crystallisation and nucleation of the PLA matrix. The proposed mechanism of the PVDF-promoted crystallisation of PLA was that of an interface-assisted and heterogeneously epitaxial nucleation. Furthermore, Sakai *et al.*²⁰ investigated the effect of blending PCL with PLA on the crystallisation and thermal behaviour. They reported that the accelerated crystallisation of PLA that had occurred during the cold crystallisation in the PLA/PCL blending system was associated with the mechanism of interface-assisted nucleation.

Table 4 Thermal properties of PLA/PBAT blend films without and with various types of nucleating agent

Formulation	T_d (°C) onset		Temperature (°C) at weight loss		Thermal transitions (°C)					
	First	Second	10%	50%	T_g	T_c	T_{cc}	T_{m1}^*	T_{m2}^*	χ_c (%)
PLA/PBAT	336.1	410.3	351.3	377.8	54.7	–	111.9	148.4	155.3	28.7
PLA/PBAT/NC 4	306.4	383.6	321.8	351.8	60.2	–	107.6	146.6	155.8	34.5
PLA/PBAT/TC 4	328.5	400.5	344.2	369.1	61.5	–	108.1	147.1	156.1	31.1
PLA/PBAT/TO 4	330.7	398.7	346.5	369.4	59.8	–	106.8	147.8	156.6	36.0

* T_{m1} : lower melting temperature, T_{m2} : higher melting temperature.



9 DSC thermograms of PLA/PBAT (90/10 w/w) blend films without and with different types of nucleating agent *a* cooling and *b* 2nd heating curves

With the addition of a nucleating agent, the thermal transitions of the PLA/PBAT blend films were significantly affected. First, the T_g value of the composites increased to 60.2, 61.5 and 59.8°C when NC, TC and TO, respectively were present. The increase of T_g that occurred because of the reduction of PLA chain mobility led to more brittle behaviour together with evidence for the depression of both the tensile strength and the elongation at break. Second, the double melting behaviour of PLA were hardly affected and this indicated that different types of nucleating agent made little change to the size and perfection of the crystals of the PLA/PBAT composite. Third, no crystallisation peak was detected during the cooling process at 10°C min⁻¹ but the cold crystallisation peak was clearly noticed during the heating that followed. The T_{cc} values decreased by approximately 5°C (in the range of 106.8–108.1°C) with the addition of a nucleating agent. This implied that addition of the nucleating agent facilitated the crystallisation rate of the blends. An increment of crystallinity was also observed. These results indicated that TO was a more efficient nucleating agent for PLA and PLA/PBAT blend films than NC and TC.

Conclusions

The type and amount of nucleating agent affected the properties and crystallisation behaviours of PLA blend

films. The addition of a nucleating agent greatly increased the elongation at break and the impact strength of PLA each being associated with a change of the spherulite size that enhanced its crystallinity; however, the tensile strength decreased especially with high amounts of loading due to some agglomeration of the nucleating agent particles. Furthermore, the T_d onset of PLA decreased with each extra amount of added nucleating agent. Comparatively, the overall properties of the PLA composites with TO were higher than those containing NC and TC. Based on the non-isothermal crystallisation, we have summarised that the addition of the nucleating agent into the composite films promoted heterogeneous nucleation and enhanced the crystallisation process of PLA. The appearance of T_c during the cooling process and the decrease of the exothermic T_{cc} during the cold crystallisation was due to the acceleration of the crystallisation rate into the PLA molecular chains, and this was supported by the DSC results.

For the PLA/PBAT/nucleating agent blend films, the results indicated that the presence of 10 wt-% PBAT significantly improved the elongation at break, impact toughness and thermal stability of PLA but decreased its tensile strength. Moreover, the crystallisation rate of PLA was promoted via the immiscible blending with PBAT and the cold crystallisation processes was due to the synergistic effects of PLA and PBAT. With the addition of a nucleating agent, a T_g increment of the

PLA/PBAT composites was observed. Nevertheless, the χ_c and the crystallisation rate of the blends were also enhanced. The experimental data indicated that TO was a more efficient nucleating agent for the PLA and PLA/PBAT blend films than NC and TC.

Acknowledgements

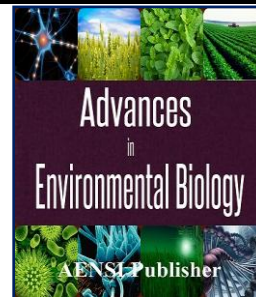
This work was supported by a grant from Prince of Songkla University, contract no.SCI570376S. We gratefully thank the Development and Promotion of Science and Technology Talents Project (DPST). Thanks also to Dr Brian Hodgson for assistance with the English.

Conflict of interest

The authors declare that they have no conflict of interest.

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Nucleation and Compatibilization of Poly (butylene adipate-co-terephthalate) and Polylactide Biodegradable Composite Films

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ABSTRACT

Poly(butylene adipate-co-terephthalate) (PBAT) and polylactide (PLA) biodegradable composite films were hot-melted via a twin screw extruder. The influences of PLA contents, nucleating agent types and compatibilizer levels on the tensile, thermal, physical, and morphological properties of the composite films were investigated. PLA contents were varied from 10 to 50 wt%. Nanoprecipitated calcium carbonate (NPCC) and talc were used as a nucleating agent at 2 phr. Whereas, toluenediphenyl diisocyanate (TDI) was used as a compatibilizer at different concentrations (1 to 9 wt% based on PLA contents) to enhance an interfacial adhesion between PBAT and PLA. The presence of PLA, nucleating agent, and compatibilizer had significant effect on mechanical strength, elongation, morphology, and thermal behaviors of the PBAT/PLA biodegradable composite films. The results showed that tensile strength of the composites was increased with increment of PLA contents; in contrast, elongation at break was substantially decreased due to phase separation of PBAT and PLA according to SEM results. In addition, thermal stability and crystallization of PBAT composite films were affected with the addition of PLA. However, a presence of nucleating agent and an appropriate level of TDI led to significant improvement of the tensile properties of the PBAT composites compared with the uncompatibilized ones. These effects are in agreement with morphological results.

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INTRODUCTION

Poly(butylene adipate-co-terephthalate) (PBAT) is one of the most attractive biodegradable polymers because its high elongation, flexibility, and toughness [1, 2]. PBAT could be used in widespread applications; i.e., biomedical material, food container, and film packaging. However, low modulus and low strength were significant limitations of PBAT [3]. Reinforcing PBAT with other polymers is one of well-known techniques to improve its drawbacks. Commercial polymers such as polystyrene (PS) and poly(ethylene terephthalate) (PET) may be considered as a good alternative material for strengthening PBAT. On the other hand, the production process, usage, and waste of these polymers lead to addition of PLA could be used to reinforce the strength of PBAT composite films. For example, the tensile strength of PBAT composite films with 50 wt% of PLA was increased about 32 % compared to that of neat PBAT. However, elongation at break of PBAT/PLA (50/50 w/w) composite films was only about 3 % resulting from incompatibility between two phases of PBAT and PLA [7]. Hence, the nucleating agent and the compatibilizer were used to improve tensile properties and compatibility of the PBAT/PLA composite films. As a result, the objectives of this work were focused on the preparation of PBAT/PLA biodegradable composite films at various compositions. Two types of nucleating agent (talc and nano-precipitated calcium carbonate (NPCC)) were investigated. PLA was used as a reinforcing polymer, while toluenediphenyl diisocyanate (TDI) was used as a compatibilizer at different amounts (1 to 9 wt%) based on PLA contents to enhance an interfacial adhesion between PBAT and PLA.

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*Experimental:**Materials:*

PBAT resin (Ecoflex F BX7011) acted as polymer matrix with a density of 1.26 g/cm³ was purchased from BASF Corporation. The glass transition temperature (T_g) and melting temperature (T_m) of PBAT were about -30 and 110 °C (DSC analysis), while its weight average molecular weight (M_w) and polydispersity index (PDI) were 170 kDa and 1.32 (GPC analysis in THF), respectively. Polylactide (PLA 4042D, M_w = 130 kDa, PDI = 1.46, T_g = 58 °C, T_m = 152 °C, density = 1.24 g/cm³) was purchased from NatureWork LLC. NPCC and talc used as a nucleating agent were supplied from Behn Meyer Chemical Co., Ltd., Bangkok, Thailand and Siam Cement Group (SCG Chemicals) Co., Ltd., Rayong, Thailand, respectively. TDI obtained from Siam Chemical Industry Co., Ltd., Bangkok, Thailand was used as a compatibilizer for improving interfacial adhesion of PBAT and its composites.

Table 1: Sample formulations of neat PBAT and PBAT/PLA biodegradable composite films with various types of nucleating agent and different levels of PLA and TDI.

Sample ID	PBAT contents (wt%)	PLA contents (wt%)	Nucleating agent contents (phr)		TDI levels (wt% based on PLA)
			Talc	NPCC	
Neat PBAT	100	0	-	-	-
PBPL10	90	10	-	-	-
PBPL20	80	20	-	-	-
PBPL30	70	30	-	-	-
PBPL40	60	40	-	-	-
PBPL50	50	50	-	-	-
PBPL10Ta	90	10	2	-	0
PBPL10TaTD1	90	10	2	-	1
PBPL10TaTD3	90	10	2	-	3
PBPL10TaTD5	90	10	2	-	5
PBPL10TaTD7	90	10	2	-	7
PBPL10TaTD9	90	10	2	-	9
PBPL10NP	90	10	-	2	0
PBPL10NPTD1	90	10	-	2	1
PBPL10NPTD3	90	10	-	2	3
PBPL10NPTD5	90	10	-	2	5
PBPL10NPTD7	90	10	-	2	7
PBPL10NPTD9	90	10	-	2	9

Sample Preparation:

The PBAT/PLA composites were prepared through a counter-rotating twin screw extruder (L/D = 15/1, TSE 16 TC, PRISM). PLA was used as a reinforcing polymer at different concentrations (10 to 50 wt%), whereas NPCC and talc acted as a nucleating agent were fixed at 2 phr, respectively. TDI were used as compatibilizer at various levels from 1 to 9 wt% based on PLA contents for enhancing an interfacial adhesion between two phases of the composite films. Sample formulations and its abbreviations were displayed in Table 1. The temperature profiles and screw speed of twin screw extruder were controlled on three zones ranging from 110 to 180 °C and 30 rpm, respectively. The extruded pellets were dried in a vented oven at 60 °C overnight and then compression-molded into the film specimens by hydraulic press (Scientific, Labtech Engineering).

Characterization and Testing:

Rectangular film specimens of tensile testing with the size of 15 mm wide, 150 mm long, and about 250 μm thickness were performed using a universal testing machine, according to the ASTM D882-02. Scanning electron microscope (SEM) was employed to characterize the fractured surface of neat PBAT and PBAT/PLA composites. The fractured surface of the films was coated with a thin layer of gold before being scanned. The SEM was operated at 15 kV to image the films.

Thermal stability of the composite films was evaluated by using a thermogravimetric analyzer (TGA) under nitrogen atmosphere using a heating rate of 20 °C/min from 50 to 600 °C. Thermal behaviors of the films were characterized by a differential scanning calorimeter (DSC). Sample size with an average weight of 10 - 12 mg encapsulated in a hermetically sealed aluminum pan was prepared for each test. Thermal history of all samples was removed by first heat scanning from 25 °C to 180 °C and hold for 3 min to eliminate any thermal history of all samples, followed by quenching the sample with liquid nitrogen to -60 °C, and finally heating again to 180 °C at cooling and heating rates of 10 °C/min, respectively. All experiments were carried out under nitrogen atmosphere. The glass transition temperature (T_g), crystallization temperature (T_c), cold crystallization temperature (T_{cc}), and melting temperature (T_m) were evaluated, respectively.

RESULTS AND DISCUSSION

Tensile strength and elongation at break of neat PBAT and PBAT/PLA composite films with different amounts of PLA (10 to 50 wt%) are displayed in Figure 1a and 1b, respectively. Neat PBAT showed a ductile behavior with very high elongation at break of 111 % but low tensile strength of only about 6 MPa (Table 2). In addition, the presence of PLA in PBAT composite films led to an increment of tensile strength but significant

decreasing of elongation at break compared to neat PBAT. These results indicated that the addition of PLA could be used to reinforce the strength of PBAT composite films. For example, the tensile strength of PBAT composite films with 50 wt% of PLA was increased about 32 % compared to that of neat PBAT. However, elongation at break of PBAT/PLA (50/50 w/w) composite films was only about 3 % resulting from incompatibility between two phases of PBAT and PLA [7]. Hence, the nucleating agent and the compatibilizer were used to improve tensile properties and compatibility of the PBAT/PLA composite films.

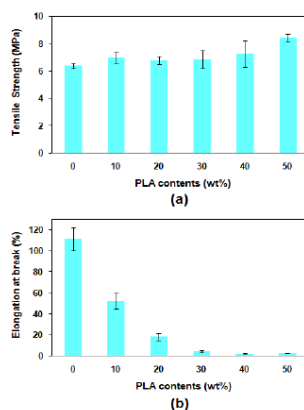


Fig. 1: Tensile properties of neat PBAT and PBAT/PLA composite films with different PLA contents (a) tensile strength and (b) elongation at break

Table 2: Tensile properties of neat PBAT and PBAT/PLA biodegradable composite films with various amounts of PLA from 10 to 50 wt%.

Sample ID	Tensile strength (MPa)	Elongation at break (%)
Neat PBAT	6.38 ± 0.20	111.02 ± 11.24
PBPL10	6.95 ± 0.39	52.40 ± 7.32
PBPL20	6.79 ± 0.28	18.19 ± 3.57
PBPL30	6.84 ± 0.65	4.29 ± 0.75
PBPL40	7.27 ± 0.97	2.13 ± 0.39
PBPL50	8.43 ± 0.29	2.77 ± 0.25

Physical appearances of neat PBAT and the PBAT/PLA (70/30 w/w) composite films are displayed in Figure 2a and 2b, respectively. The results illustrated that elongation of neat PBAT film was obviously increased by forming a neck within a narrow region of a width, indicating ductile behavior of neat PBAT. In contrast, the PBAT/PLA (70/30 w/w) composite film was brittle material without formation of elongation area which was in agreement with tensile properties. The more PLA content was added the lower elongation at break of the PBAT biodegradable composite films was (as shown in Table 2).

Figure 3 displays the SEM micrographs of fracture surface of neat PBAT, neat PLA, and PBAT composite films with different contents of PLA. In Figure 3, the SEM micrograph of neat PBAT (3a) displayed smooth fracture surface which was a typical characteristic of ductile material; in contrast, that of neat PLA (3d) illustrated rougher fracture surface which was associated with brittle polymer, respectively. For PBAT/PLA composite film, the SEM images showed the obvious phase separation between PBAT and PLA (Figure 3b and 3c). A large number of PLA particles on the fracture surface of the films were found. Furthermore, many gaps in fracture surface of the composites which were resulting from pulling away and debonding of PLA particles from PBAT matrix were obviously noticed. These results revealed the incompatibility between two phases of PBAT and PLA which was in agreement with tensile properties of the PBAT/PLA biodegradable composite films without compatibilizer. This is a reason why the tensile properties of the films significantly decreased with the increasing of PLA.

The influence of PLA amounts (0 to 40 wt%) on the thermal stability of neat PBAT and its composites is displayed in Figure 4 and Table 3. TGA thermograms indicated that neat PLA had an initial weight loss at about 330 °C, responding to thermal decomposition of PLA main chains, whereas neat PBAT illustrated a single main stage of thermal degradation at about of 370 °C, related to the decomposition of PBAT. Furthermore, TGA thermograms of PBAT/PLA films revealed 2 steps of thermal degradation. The first step was approximately 330 to 350 °C which was attributed to the decomposition of PLA, whereas the second stage was about 370 to 390 °C which was associated with the loss of PBAT. These results indicated the presence of PBAT and PLA in the biodegradable composite films.

For evaluating the thermal stability of neat PBAT and its biodegradable composites, the temperature at 20 wt% weight loss of sample was calculated. As shown in Table 3, the temperature used for removing 20 wt% of neat PBAT was 401.7°C . The temperature at 20 wt% weight loss of the blend films apparently decreased

(from 395.3 to 367.9 °C) when the PLA amount increased (from 10 to 40 wt%). These results implied that thermal stability of the PBAT/PLA biodegradable films decreased with the increment of PLA amount. The PBAT/PLA composite films were lower thermal stability than neat PBAT at all compositions. This was resulting from PLA phase with lower thermal stability ($T_d = 330$ °C). As a result, with increasing of PLA and PBAT ratio, thermal stability of composite was lower than ones of neat PBAT. Furthermore, data from TGA thermograms revealed that percentage of char remaining at 550 °C of neat PBAT (4.93 %) was higher than that of neat PLA (0.74 %). The results showed that weight of char remaining of the sample was slightly reduced with the increasing of PLA content. It might be explained that thermal stability of PLA significantly affected to the presence of char residue in composite films.

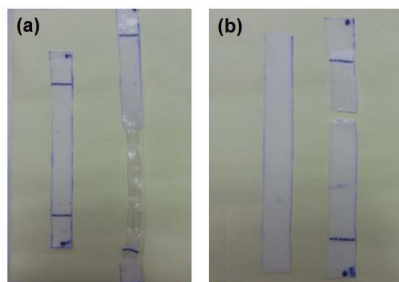


Fig. 2: Physical appearances of rectangular film specimens of (a) neat PBAT and (b) PBAT/PLA (70/30 w/w) composite before and after tensile testing.

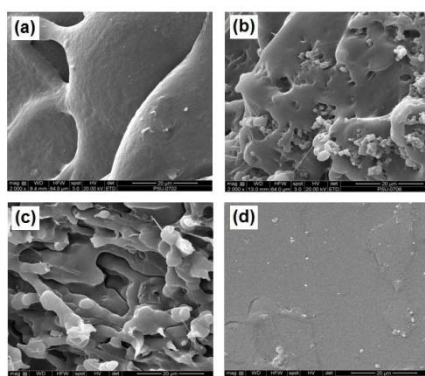


Fig. 3: SEM micrographs of the fracture surface of (a) neat PBAT, (b) PBAT/PLA (90/10 w/w) composite, (c) PBAT/PLA (60/40 w/w) composite, and (d) neat PLA films.

Figure 5 show the cooling (5a) and 2nd heating (5b) curves of DSC thermograms of neat PBAT, neat PLA, and PBAT biodegradable composite films with different concentrations of PLA. Furthermore, the data of thermal transition temperature, i.e., the glass transition temperature (T_g), crystallization temperature (T_c), cold-crystallization temperature (T_{cc}), and melting temperature (T_m), characterized by a differential scanning calorimetry (DSC) are conclusively displayed in Table 4.

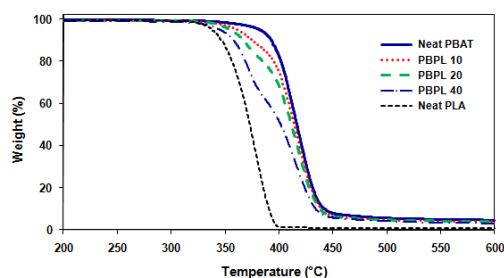


Fig. 4: TGA thermograms of neat PBAT, neat PLA, and PBAT biodegradable composite films with 10 to 40 wt% of PLA.

Table 3: Data from TGA thermograms of neat PBAT, neat PLA, and PBAT biodegradable composite films with different amounts of PLA.

Sample ID	Temperature at 20 % of Weight Loss (°C)	Char remaining at 550 °C (%)
Neat PBAT	401.7	4.93
PBPL10	395.3	4.25
PBPL20	386.3	4.10
PBPL40	367.9	3.43
Neat PLA	356.5	0.74

The effect of PLA contents on the DSC thermograms was clearly observed. DSC thermogram of neat PLA displayed the T_g at about 59.2 °C and a melting endothermic peak at 152.5 °C which represented to residual crystallinity. Similar results have been previously reported by Martin and Averous [8]. Besides, T_{cc} peak appeared at 124.9 °C in the 2nd heating curve of DSC thermogram of neat PLA. This thermal behavior implied that crystallization of neat PLA in cooling step was not completed due to high cooling rate. As a result, T_{cc} peak could be observed in 2nd heating step of DSC thermogram of neat PLA because some parts of PLA chains were re-crystallized. In case of neat PBAT, its thermogram showed a T_g at approximately -30 °C whereas, a broader peak of T_m appeared at around 123.2 °C and no T_{cc} which was similarly reported by Jiang *et al* and Yeh *et al* [7, 9]. Neat PLA showed the thermal behavior of a brittle material with higher T_g (compared to room temperature); in contrast, neat PBAT exhibited that of a flexible polymer with lower T_g . These results indicated the thermal characteristics of neat PLA and neat PBAT.

When higher level of PLA (from 10 to 40 wt%) was added into the PBAT biodegradable films, T_g was significantly increased from 45.8 °C to 53.7 °C. It might be due to brittle behavior of PLA which prompted chain stiffness of PBAT/PLA biodegradable composite films. In addition, T_{cc} of the PBAT composite films was obviously observed at about 105 to 106 °C with the increment of PLA levels from 10 to 40 wt%. Both decreasing of T_c and increasing of T_{cc} in the DSC thermograms of composite films indicated that the crystallization behaviors of the films became slower with the presence of PLA. In other words, the addition of PLA retarded crystallization process of PBAT/PLA biodegradable composite films. However, from 2nd heating curves of DSC thermograms, the presence of PLA into the composite film led to obvious appearance of T_m which related to degree of crystallinity and mechanical properties of composite films. This is one of reasons why the tensile properties of the composite films increased with the increasing of PLA levels.

Table 4: DSC data of neat PBAT, neat PLA, and PBAT composite films with various amounts of PLA.

Film Samples	Thermal Transitions (°C)				
	T_g	T_c	T_{cc}	T_{m1}	T_{m2}
Neat PBAT	-29.6	96.1	-	123.2	-
PBPL 10	45.8	75.4	105.9	145.4	152.3
PBPL 20	52.4	74.3	106.1	145.6	152.4
PBPL 40	53.7	69.6	105.4	145.8	154.1
Neat PLA	59.2	58.4	124.9	-	152.5

Influence of different types of nucleating agent and various levels of TDI on the tensile strength and elongation at break of the PBAT/PLA composite films is exhibited in Figure 6. These results indicated that the tensile strength of the PBAT composite films with 2 phr of nucleating agents (both NPCC and talc) increased with the increment of TDI amounts, while the elongation at break sharply increased with 7 wt% TDI based on PLA content. These results were obviously observed in both of the nucleated PBAT/PLA composite films with NPCC and talc. As shown in Table 5, the nucleated PBAT/PLA composite films with 7 wt% TDI gave the highest tensile properties over the whole composition range. The mechanical data indicated that the tensile strength and elongation at break of the PBAT/PLA/talc composite films with 7 wt% TDI increased about 33 % and 15 %, respectively, whereas those of PBAT/PLA/NPCC composite films with 7 wt% TDI increased about 42 % and 20 %, respectively comparing to the films without TDI. Significantly, the addition of compatibilizer composed of diisocyanate functional group led to interfacial adhesion improvement of the binary mixing [10, 11]. These results can be summarized that on the one hand adding too less level of TDI (i.e., less than 7 wt%) was insufficient for improving the interfacial addition between PBAT and PLA phases, but on the other hand, adding too much amount of TDI (i.e., more than 7 wt%) might cause some cracks in the composites, which led to the reduction of the tensile properties. Thus, the addition of 7 wt% TDI in the nucleated PBAT/PLA composite films could be an appropriate concentration to improve and strengthen the interfacial adhesion of PBAT and PLA, leading to the increasing of tensile properties of the films.

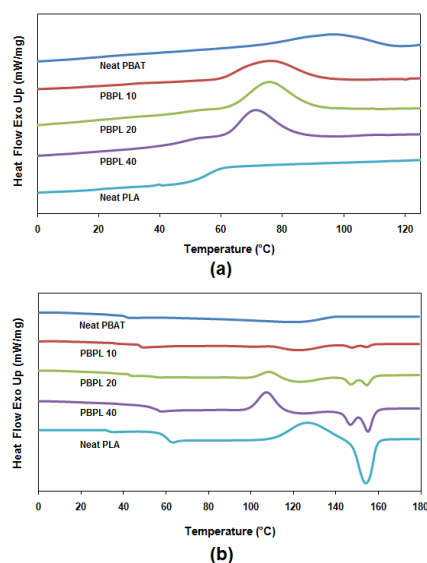


Fig. 5: DSC thermograms of neat PBAT, neat PLA, and PBAT biodegradable composite films with various PLA levels; (a) cooling and (b) 2nd heating curves.

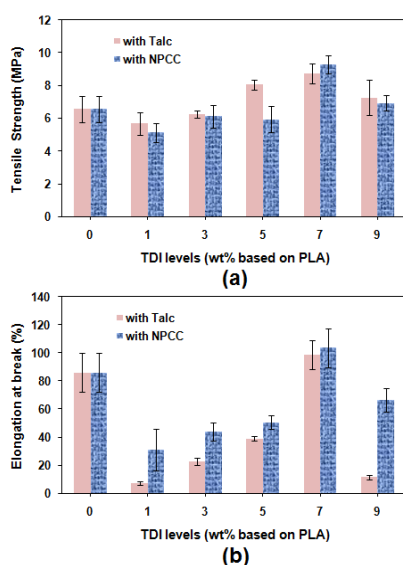


Fig. 6: Effect of different nucleating agent types and various TDI levels (1 to 9 wt% based on PLA contents) on the tensile properties of PBAT/PLA (90/10 w/w) composite films; (a) tensile strength and elongation at break

Table 5: Tensile properties of PBAT/PLA (90/10 w/w) biodegradable composite films with various types of nucleating agents and different concentrations of TDI.

Sample ID	Tensile strength (MPa)	Elongation at break (%)
PB PL10 Ta	6.55 ± 0.82	85.83 ± 13.90
PB PL10 Ta TD1	5.67 ± 0.68	7.40 ± 1.44
PB PL10 Ta TD3	6.26 ± 0.21	22.66 ± 2.76
PB PL10 Ta TD5	8.04 ± 0.30	39.09 ± 1.43
PB PL10 Ta TD7	8.72 ± 0.60	98.67 ± 10.36
PB PL10 Ta TD9	7.26 ± 1.09	11.52 ± 1.40
PB PL10 NP	6.55 ± 0.82	85.83 ± 13.90
PB PL10 NP TD1	5.12 ± 0.59	31.13 ± 14.86
PB PL10 NP TD3	6.11 ± 0.68	44.02 ± 6.30
PB PL10 NP TD5	5.94 ± 0.79	50.62 ± 4.95
PB PL10 NP TD7	9.27 ± 0.54	103.52 ± 13.65
PB PL10 NP TD9	6.93 ± 0.47	66.54 ± 8.44

SEM images of the fracture surface after tension of nucleated PBAT/PLA composite films without and with 7 wt% TDI based on PLA amount is illustrated in Figure 7. For SEM images of the PBAT/PLA/talc (90/10/2) and PBAT/PLA/NPCC (90/10/2) composite films without compatibilizer (Figure 7a and 7b), the phase separation between PBAT and PLA was noticed at where some PLA particles detached from PBAT matrix prompting to a large number of holes on the composite fracture surface. These results clearly revealed the incompatibility of PBAT and PLA. The cracking mechanism of the nucleated PBAT/PLA composite films without TDI might predominately take place via the matrix of the agglomerated PLA particles than at the interface between PBAT and PLA.

Nevertheless, a smoother and more uniform fracture surface between PBAT and PLA were showed in the SEM images of compatibilized PBAT/PLA biodegradable composite with talc and NPCC (Figure 7c, 7d). The addition of compatibilizer (7 wt% of TDI based on PLA content) significantly influenced to the fracture surface of the films. Both compatibilized PBAT/PLA/talc and PBAT/PLA/NPCC composite films indicated that the PLA particles were finely dispersed into the PBAT composite films, compared to those without compatibilizer. Many cavities on the fracture surface of the nucleated composite films with TDI evidently decreased. These behaviors indicated that some interfacial adhesion between two phases of PBAT and PLA was obviously improved with the addition of TDI. It might be implied that the toughening mechanism of the PBAT/PLA composite films with the presence of TDI occurred through the interface between PBAT and PLA. These results supported the tensile properties of the nucleated PBAT/PLA composite films which previously discussed.

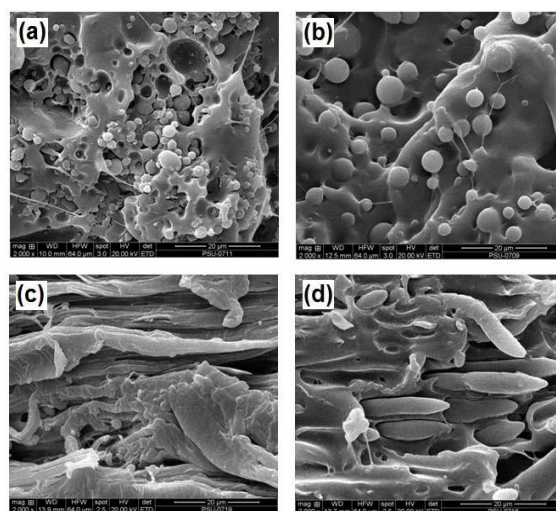


Fig. 7: SEM micrographs of the fracture surface after tension of PBAT/PLA/talc (90/10/2) composites (a) without and (c) with 7 wt% TDI and PBAT/PLA/NPCC (90/10/2) composites (b) without and (d) with 7 wt% TDI, respectively.

Conclusion:

Tensile strength of the PBAT/PLA biodegradable composite films was improved with the increment of PLA content; in contrast, elongation at break was significantly decreased due to phase separation between PBAT and PLA, supported by SEM results. Furthermore, data from TGA and DSC thermograms revealed that thermal stability of the composite films was slightly decreased and the crystallization was retarded with the addition of PLA. However, incompatibility between two phases of PBAT and PLA could be improved by using compatibilizer. The addition of TDI on the both of PBAT/PLA/talc and PBAT/PLA/NPCC composite films led to the enhancement of interfacial adhesion and the reduction of phase separation into the composites, as evidenced by tensile and morphological studies. From these data, the appropriate compatibilizer concentration for enhancing the properties of the nucleated composite films was 7 wt% of TDI based on PLA amounts.

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