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บนยางธรรมชาติ

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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

THE EFFECT OF REDOX INITIATOR ON GRAFT COPOLYMERIZATION OF  
METHYL METHACRYLATE ONTO NATURAL RUBBER



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ศูนย์วิทยทรัพยากร  
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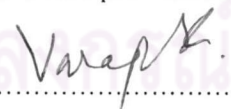
  
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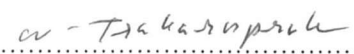
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งานวิจัยนี้เป็นการศึกษาผลของตัวริเริ่มปฏิกิริยาแบบรีดอกซ์ต่อการกราฟต์เมทิลเมทาคริเลตบนยางธรรมชาติโดยอิมัลชันพอลิเมอไรเซชัน โดยตัวริเริ่มปฏิกิริยาแบบรีดอกซ์ 3 ชนิดที่แตกต่างกัน คือ คิวมินไฮโดรเพอร์ออกไซด์/เทระเอทิลีนเพนทามีน เทอร์-บิวทิลไฮโดรเพอร์ออกไซด์/เทระเอทิลีนเพนทามีน และโพแทสเซียมเปอร์ซัลเฟต/โซเดียมไทโอซัลเฟต สำหรับตัวริเริ่มปฏิกิริยาแต่ละชนิดได้ศึกษาภาวะที่เหมาะสมในการเตรียมยางธรรมชาติกราฟต์ โดยตรวจสอบหมู่ฟังก์ชันด้วย FT-IR และ NMR หาน้ำหนักโมเลกุลเฉลี่ยและการกระจายน้ำหนักโมเลกุลด้วย GPC ตรวจสอบสมบัติทางความร้อนของยางธรรมชาติกราฟต์ด้วย DSC ศึกษาสัณฐานวิทยาของยางกราฟต์ด้วยเมทิลเมทาคริเลตด้วย TEM พบว่าเมทิลเมทาคริเลตเกิดปฏิกิริยากราฟต์โคพอลิเมอไรเซชันที่บริเวณผิวอนุภาคยาง

ตัวริเริ่มปฏิกิริยาคิวมินไฮโดรเพอร์ออกไซด์ละลายได้ดีมากในน้ำมัน และเทอร์-บิวทิลไฮโดรเพอร์ออกไซด์ละลายได้ดีปานกลางในน้ำมัน ทำปฏิกิริยาร่วมกับเทระเอทิลีนเพนทามีนที่ละลายได้ดีปานกลางในน้ำ พบว่าคิวมินไฮโดรเพอร์ออกไซด์ให้ค่าประสิทธิภาพการกราฟต์ที่สูงกว่า ตัวริเริ่มปฏิกิริยาแบบที่ละลายน้ำได้คือโพแทสเซียมเปอร์ซัลเฟต/โซเดียมไทโอซัลเฟต ดังนั้นจึงเติมไวทิลนีโอเดคะโนเอตลงในตัวริเริ่มปฏิกิริยาโพแทสเซียมเปอร์ซัลเฟตเพื่อส่งเสริมให้เกิดกราฟต์ของเมทิลเมทาคริเลตบนยางธรรมชาติและลดปริมาณพอลิเมทิลเมทาคริเลตซึ่งเกิดในน้ำ พบว่าร้อยละของประสิทธิภาพการกราฟต์ของ เมทิลเมทาคริเลตบนน้ำยางธรรมชาติโดยคิวมินไฮโดรเพอร์ออกไซด์ เทอร์-บิวทิลไฮโดรเพอร์ออกไซด์ และโพแทสเซียมเปอร์ซัลเฟต มีค่า 84.4 74.5 และ 61.1 ตามลำดับ ซึ่งสอดคล้องกับค่าร้อยละของพอลิเมทิลเมทาคริเลตที่เกิดในน้ำ ซึ่งมีค่า 7.2 12.0 และ 17.8 สำหรับการริเริ่มปฏิกิริยาคิวมินไฮโดรเพอร์ออกไซด์ เทอร์-บิวทิลไฮโดรเพอร์ออกไซด์ และโพแทสเซียมเปอร์ซัลเฟต ตามลำดับ การเติมไวทิลนีโอเดคะโนเอตทำให้เกิดแอลลิทิกเรดิคัลบนโซ่พอลิโอไซพรีนซึ่งเอื้อต่อการเกิดกราฟต์ด้วยมอนอเมอร์ชนิดอื่น งานวิจัยนี้สรุปได้ว่าคิวมินไฮโดรเพอร์ออกไซด์/เทระเอทิลีนเพนทามีนเป็นระบบของตัวริเริ่มปฏิกิริยาที่ดีของการกราฟต์น้ำยางธรรมชาติด้วยไวทิลมอนอเมอร์ นอกจากนี้ยังได้อธิบายกลไกของการส่งเสริมการเกิดปฏิกิริยากราฟต์โคพอลิเมอไรเซชัน

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KEYWORD : NATURAL RUBBER / METHYL METHACRYLATE / REDOX INITIATOR / GRAFT COPOLYMERIZATION

TEERANUCH KOCHTHONGRASAMEE : THE EFFECT OF REDOX INITIATOR ON GRAFT COPOLYMERIZATION OF METHYL METHACRYLATE ONTO NATURAL RUBBER.

THESIS ADVISOR : PROF. SUDA KIATKAMJORNWONG, Ph.D., THESIS CO-ADVISOR : PROF. PATTARAPAN PRASASSARAKICH, Ph.D. 131 pp. ISBN 974-03-1515-1.

This research investigated the effect of redox initiator on natural rubber graft methyl methacrylate by emulsion polymerization. Three different types of redox initiator namely cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA), tert-butyl hydroperoxide (TBHPO)/TEPA, and potassium persulfate ( $K_2S_2O_8$ )/sodium thiosulfate ( $Na_2S_2O_3$ ). The optimum reaction condition for each redox initiator on grafting of natural rubber was studied. Functional groups of grafted natural rubber by FT-IR and NMR, molecular weights and their distribution by GPC, thermal properties by DSC, and morphology by TEM were carried out. It was found that the poly(methyl methacrylate) graft copolymerization resides on the surface of rubber particles.

CHPO dissolves very well in the oil phase, and TBHPO dissolves moderately in the oil phase as well. Each can interact with TEPA in aqueous phase. CHPO was found to give a higher grafting efficiency.  $K_2S_2O_8$  / $Na_2S_2O_3$  is water-soluble initiator. To promote a greater grafting efficiency and lower homopolymer content of poly(methyl methacrylate) in the aqueous phase, vinyl *neo*-decanoate (VneoD), a grafting promoter was then added in the latter. It was found that the percentages of grafting on methyl methacrylate on natural rubber latex initiated by CHPO, TBHPO, and  $K_2S_2O_8$  are 84.4, 74.5, and 61.1, respectively, which are in good agreement with percentages of poly(methyl methacrylate) formed in the aqueous phase as 7.2, 12.0, and 17.9 by CHPO, TBHPO, and  $K_2S_2O_8$ . The role of added VneoD is to produce allylic radicals on polyisoprene chains that favor the grafting reaction with other vinyl monomers. This research concludes that CHPO/TEPA is a good redox system for grafting of vinyl monomers on natural rubber latex. Additionally, this research also describes the reaction mechanism that promotes such a graft copolymerization.

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จุฬาลงกรณ์มหาวิทยาลัย

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## ABBREVIATIONS

NR	: Natural Rubber
MMA	: Methyl Methacrylate
PMMA	: Poly(methyl methacrylate)
DRC	: Dry Rubber Content
FT-IR	: Fourier Transform Infrared Spectroscopy
NMR	: Nuclear Magnetic Resonance Spectroscopy
TEM	: Transmission Electron Microscopy
DSC	: Differential Scanning Calorimetry
phr	: Parts per hundred of rubber
hr	: Hour
Tg	: Glass Transition Temperature
GE	: Grafting Efficiency
pp.	: Page
VneoD	: Vinyl <i>neo</i> -decanoate