

**การเตรียมกราฟต์โคพอลิเมอร์ระหว่างเมทิลเมทาคริเลตกับยางธรรมชาติ  
โดยกระบวนการอิมัลชันพอลิเมอร์ไรเซชัน**  
**Graft copolymerization of methyl methacrylate onto natural rubber  
prepared by emulsion polymerizations**

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### บทคัดย่อ

ศึกษาผลของการกราฟต์เมทิลเมทาคริเลตบนยางธรรมชาติที่มีต่อร้อยละประสิทธิภาพการกราฟต์และร้อยละการเปลี่ยนแปลงมอนอเมอร์โดยศึกษาผลที่มีต่อชนิดและปริมาณของตัวริเริ่มปฏิกิริยา รวมทั้งศึกษาโครงสร้างและสมบัติของโคพอลิเมอร์ โดยใช้เทคนิค FT-IR และศึกษาสมบัติทางความร้อนโดยใช้เทคนิค TGA พบว่าร้อยละประสิทธิภาพการกราฟต์ของโคพอลิเมอร์ที่สังเคราะห์โดยใช้โพแทสเซียมเปอร์ซัลเฟตเป็นตัวริเริ่มปฏิกิริยาเท่ากับร้อยละ 97.18 ซึ่งมีค่าสูงกว่าโคพอลิเมอร์ที่สังเคราะห์โดยคิวมินไฮโดรเปอร์ออกไซด์ที่ได้เท่ากับร้อยละ 40.86 และสภาวะที่เหมาะสมในการสังเคราะห์คือ ใช้ความเข้มข้นของตัวริเริ่มปฏิกิริยาเท่ากับ 0.5 % โดยโมล สำหรับการศึกษาสมบัติทางความร้อนของกราฟต์โคพอลิเมอร์ที่สังเคราะห์พบว่าดีกว่าของพอลิเมทิลเมทาคริเลตและยางธรรมชาติ จากการพิสูจน์เอกลักษณ์ของโคพอลิเมอร์ โดยเทคนิค FT-IR พบว่าแสดงพีคที่ 1722 และ 826  $\text{cm}^{-1}$  ซึ่งแสดงถึงการกราฟต์ของพอลิเมทิลเมทาคริเลตบนยางธรรมชาติ

### Abstract

The grafting efficiency of the methyl methacrylate (MMA) monomer onto natural rubber was studied. The effect of the synthesis variables such as the type of initiators and amount of initiator on the grafting efficiency and conversion were investigated. Structures and properties were characterized by FT-IR spectroscopy and their thermal behavior was studied by thermogravimetric analysis. It was found that the grafting efficiency of grafted copolymer using potassium persulphate as initiator higher than that using cumene hydroperoxide. In addition, 0.5 mole% of potassium persulphate gave highest level of grafting efficiency for range of the amount of the initiators in this study. Thermal properties of grafted copolymers are better than that of poly(methyl methacrylate)(PMMA) and natural rubber. The appearance of 1722 and 826  $\text{cm}^{-1}$  bands in the FT-IR spectra of the grafted copolymers indicated that MMA had been successfully grafted onto natural rubber.

**คำสำคัญ:** ยางธรรมชาติ, พอลิเมทิลเมทาคริเลต, กราฟต์โคพอลิเมอร์ไรเซชัน

**Keywords:** Natural Rubber, Poly(methyl methacrylate), Graft copolymerization

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## 1. Introduction

Natural rubber (NR) is obtained in the form of latex, which is an extrudate from the *Hevea brasiliensis* tree. The NR-based products are made either directly from concentrated latex or the latex is coagulated and dry rubber is used as the raw material. In order to develop NR-based raw materials and to extend its used, several chemical modifications of natural rubber have been tried, both in latex and in solution (B. George et al, 2006). Chemical modification of natural rubber via vinyl graft copolymerization constitutes a powerful means of improving natural rubber properties which graft copolymerization is a technique for modifying the chemical and physical properties of natural and synthetic polymers (Isam Y.M. Qudsieh et al, 2004). It is well known that the introduction of a small amount of grafting can lead to major changes in mechanical properties (W. Arayaprane et al, 2002).

In this work, a grafted copolymer of natural rubber and methyl methacrylate(MMA) which is a hydrophobic monomer was prepared with emulsion polymerization technique. The effects of two types of initiators and amount of methyl methacrylate on the grafting efficiency and conversion were investigated. After removal of the homopolymer, the grafted copolymer was characterized by Fourier transform infrared spectroscopy (FTIR), Thermal gravimetric dynamic thermal analysis (TG/DTA).

## 2. Experimental

### 2.1. Materials

Natural rubber latex containing 60% dried rubber was supplied by Thai Hua,Ltd.(Udontani, Thailand). Methyl methacrylate was supplied by

Aldrich and used after the stabilizer was removed by an aluminum oxide column. The redox initiator, cumene hydroperoxide ( $\text{CHP}-\text{C}_9\text{H}_{12}\text{O}_2$ ) was obtained from Aldrich /tetraethylene pentamine ( $\text{TEPA}-\text{C}_8\text{H}_{23}\text{N}_5$ ) was obtained from Aldrich. The thermal initiator, potassium persulphate ( $\text{PPS}-\text{K}_2\text{S}_2\text{O}_8$ ) was obtained from Aldrich and used as received acetone was purchased from Carlo Erba. The emulsifier, sodium lauryl sulphate ( $\text{SLS}-(\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na})$ ) was obtained from Ajax and sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) was obtained from Aldrich, as buffer.

### 2.2. Methods

#### 2.2.1. Graft copolymerization

The natural rubber was mixed with methyl methacrylate in a three-necked 100 ml round-bottomed flask and stirred for 1 hr. at room temperature. After that sodium lauryl sulphate was charged to the mixture and flushed with nitrogen for 15 min. Then aqueous solution of tetraethylene pentamine was added to the mixture. After that cumene hydroperoxide was added dropwise into the mixture (when thermal initiator, potassium persulphate was used). The reaction were allowed to proceed for 24 hr and then the mixture was discharged into Petri dish and dried in the oven at 70 °C. The tetraethylene pentamine was used only in the presence of cumene hydroperoxide. PMMA homopolymer was separated from polymer product by soxhlet extraction. Using acetone as the solvent. The purified grafted copolymer was dried in an oven at 60 °C to a constant weight. For using potassium persulphate as initiator, Grafted copolymer was carried out as described above.

The grafting efficiency(GE) and conversion were calculated by the following relationship:

$$\% \text{Grafting efficiency (GE)} \quad (1)$$

$$= \frac{\text{weight of graft copolymer}}{\text{total weight of graft copolymer and weight of homopolymer}} \times 100$$

$$\% \text{Conversion} \quad (2)$$

$$= \frac{\text{total weight of homopolymer and total weight of monomer grafted on NR}}{\text{total weight of monomer}} \times 100$$

### 2.3. Characterization

#### 2.3.1. Fourier transform infrared spectroscopy (FTIR)

Grafted copolymer product were characterized by Fourier transform infrared spectroscopy (Perkin Elmer model Spectrum One).

#### 2.3.2. Thermogravimetric and differential thermal analysis (TG/DTA)

Thermal properties of grafted polymer were examined by TG/DTA (Perkin elmer model Pyris Diamond 6300) at the heating rate of 10 °C per minute in the dried air.

### 3.2. Thermal properties

TG/DTA thermogram of NR and grafted copolymer at heating rate of 10 °C/min in dried air are shown in Figure 2–3. In the DTG thermogram, the major peak was observed at 370 °C. This corresponded with the complete degradation of NR. In the case of grafted polymer, the major peak was observed at 379 °C. Natural rubber shows the maximum weight loss temperature of grafted polymer was higher than NR (Figure 2–3). It reveals that grafting can improve the thermal properties of NR (Liu Y. et al, 2002).

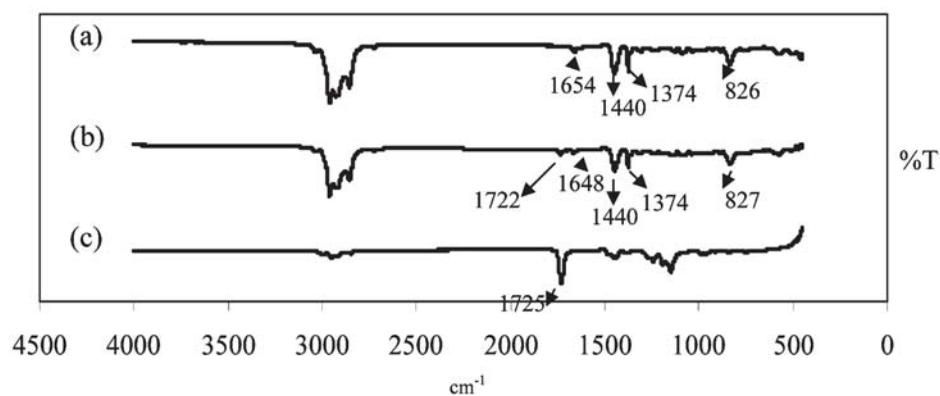
### 3.3. Effect of initiators

The effect of initiator on %GE and %conversion of grafted copolymer are shown in Figure 4–5. Grafting level increase with increasing initiator concentration until it reach the plateau and if the initiators concentration increase furture, %GE starts to decline. The decrease of %GE when the amount of initiator was increased may be due to increasing in the homopolymer formation which competes with the grafting reaction for available monomer (Liu Y. et al, 2002).

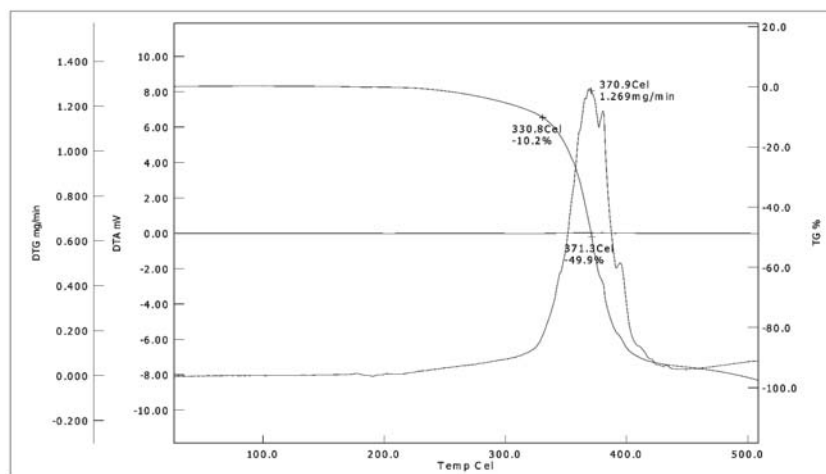
## 3. Results and discussion

### 3.1. FT-IR characterization

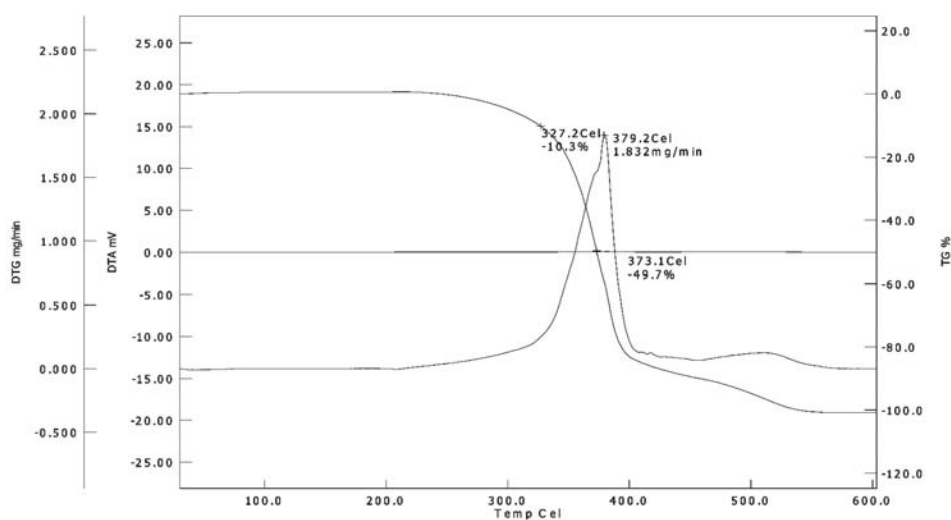
The FT-IR spectra of poly(methyl methacrylate) (PMMA), ungrafted natural rubber and grafted copolymer are shown in Figure 1. PMMA showed a characteristic band at 1725 cm<sup>-1</sup> for carbonyl group of ester stretching vibration (Figure 1(c)). The peak at 1722 cm<sup>-1</sup> for grafted copolymer indicated the presence of PMMA chains on natural rubber which was not prominent in case of IR spectra of ungrafted natural rubber. Moreover, the band at 1440 cm<sup>-1</sup> and 1374 cm<sup>-1</sup> in Figure 1(b) confirmed CH-aliphatic group.



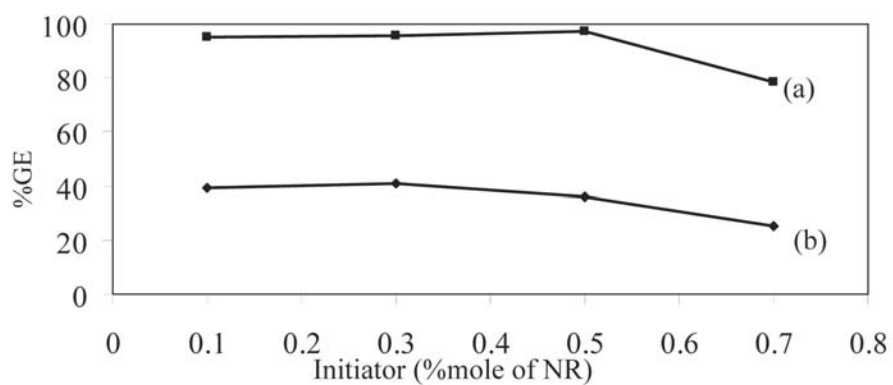
**Figure 1.** FTIR spectra of (a) ungrafted natural rubber; (b) PMMA grafted natural rubber and (c) PMMA.



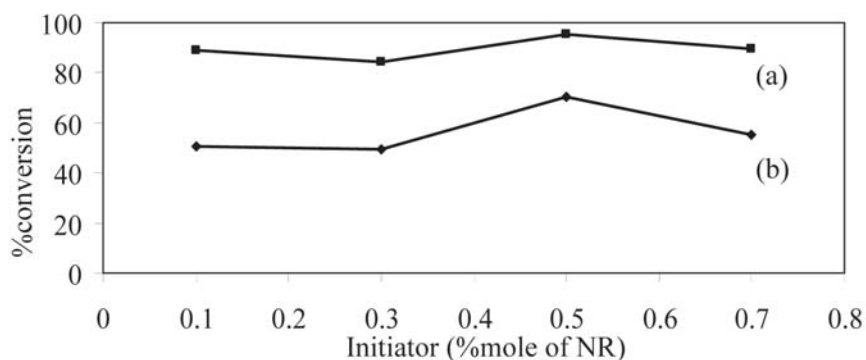
**Figure 2.** The TG/DTA thermogram of NR sample at heating rate of 10 °C/min in dried air.



**Figure 3.** The TG/DTA thermogram of PMMA grafted natural rubber sample at heating rate of 10 °C/min in dried air.



**Figure 4.** Effect of initiators on % grafting efficiency of PMMA grafted natural rubber (a) Thermal initiator (b) Redox initiator.



**Figure 5.** Effect of initiators on % conversion of PMMA grafted natural rubber (a) Thermal initiator (b) Redox initiator.

#### 4. Conclusions

The grafting efficiency of grafted copolymer using thermal initiator (potassium persulphate) was higher than that using redox initiator (cumene hydroperoxide/tetraethylene pantamine). The highest level of grafting efficiency (97.2%) obtained using 0.5 mol% of potassium persulphate, 20 mole% of MMA at 70 °C. The appearance of 1721  $\text{cm}^{-1}$  band in the FTIR spectrum of the grafted copolymer indicated that MMA had been successfully grafted onto natural rubber. Thermal properties shown that grafting can improve the thermal properties of NR

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