แอดไมเซลลาร์พอลิเมอไรเซชันของพอลิ (เมทิล เมทาคริเลต) และ พอลิ (2- ไฮดรอกซีเอทิล เมทาคริเลต) บนอนุภาคยางธรรมชาติ

Admicellar polymerization of poly (methyl methacrylate) and poly (2-hydroxyethyl methacrylate) onto natural rubber particles using mixed surfactants

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บทคัดย่อ

ทำการศึกษาการเคลือบฟิล์มบางของพอลิ(เมทิล เมทาคริเลต) (PMMA) และพอลิ (2-ไฮดรอกซีเอทิลเมทาคริเลต) (PHEMA) บนอนุภาคยางธรรมชาติ โดยวิธีแอดไมเซลลาร์พอลิเมอไรเซชัน กระบวนการแอดไมเซลลาร์พอลิเมอไรเซชันเกิดขึ้น 3 ขั้นตอน ได้แก่ การเกิดแอดไมเซลล์ของเซทิลไตรเมทิลแอมโมเนียม โบรไมด์ (CTAB) การการละลายเข้าไปในชั้น Bilayer (adsolubilization) ของมอนอเมอร์ (MMA และ HEMA) และการพอลิเมอไรเซชัน (polymerization) จากผล FT-IR พบว่าเกิดแอดไมเซลลาร์พอลิเมอไรเซชันของ PMMA เพียงอย่างเดียวที่เคลือบอนุภาคยางธรรมชาติ

Absract

Thin-film coating of poly (methyl methacrylate) (PMMA) and poly (2-hydroxyethyl methacrylate) (PHEMA) onto natural rubber particles was prepared by admicellar polymerization. The thin-film polymerization process occurs in three steps, namely, the formation of surfactant admicelles of Hexadecyltrimethylammonium bromide (CTAB), the partitioning of the hydrophobic monomer (MMA) and the hydrophilic monomer (HEMA) into admicelles and the in situ polymerization of the adsolubilized monomer. The FT-IR results confirmed that only PMMA could be successfully coated onto natural rubber via the admicellar polymerization.

คำสำคัญ: แอดไมเซลลาร์พอลิเมอไรเซชัน, เฮกซะเดซิลไตรเมทิลแอมโมเนียมโบรไมด์
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1. Introduction

Admicellar polymerization (AP) is a method to produce a polymer thin-film coated on the surface. AP is a three-step process in which the first step involves admicellar formation. Admicelle or surfactant bilayer on the substrate surface is formed when the surfactant concentration is controlled just below the critical micelle concentration (CMC). The second step constitutes monomer adsolubilization in which the monomer is solubilized into the hydrophobic interior of the surfactant bilayer. The third step comprises a polymerization reaction of adsolubilized monomer. Water-soluble initiators are added to start the polymerization. Theoretically, the mechanism of polymerization in the bilayer is similar to that of emulsion polymerization. After the completion of the polymerization reaction, the upper layer of surfactant is removed by thoroughly washing with water (Wei, 2003). Admicellar polymerization is illustrated in Figure 1 (Pongprayoon and Yanumet, 2002). The technique is reported to be quite versatile and is applicable to a variety of surfaces. Various potential applications have been proposed for thin-films formed by this technique, e.g., in composite materials, health care products, microelectronic and electronic devices (Sachin and Douglas,1995).In this research, the formation of poly(methyl methacrylate) (PMMA) and poly (2-hydroxyethyl methacrylate) (PHEMA) films onto natural rubber particles using mixed-surfactant of cationic surfactant (CTAB) and SDS has been studied. The thin-film of PMMA or PHEMA was expected to form on NR latex particles via the admicellar polymerization. FT-IR technique was employed to study admicellar polymerization of these monomer on NR.

2. Experimental

2.1. Materials

Concentrated NR latex was purchased from Thai-Hua Company Thailand. An anionic surfactant Sodium dodecyl sulphate (SDS) was obtained from APS Ajax Finechem. A cationic surfactant Hexadecyltrimethylammonium bromide (CTAB) was obtained from Fluka. Ammonium Hydroxide (NH_4OH) was obtained from J.T.Baker. A cationic initiator 2,2' Azo-bis (2-methylpropionamidine) (AIBA), Methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) were obtained from Aldrich.

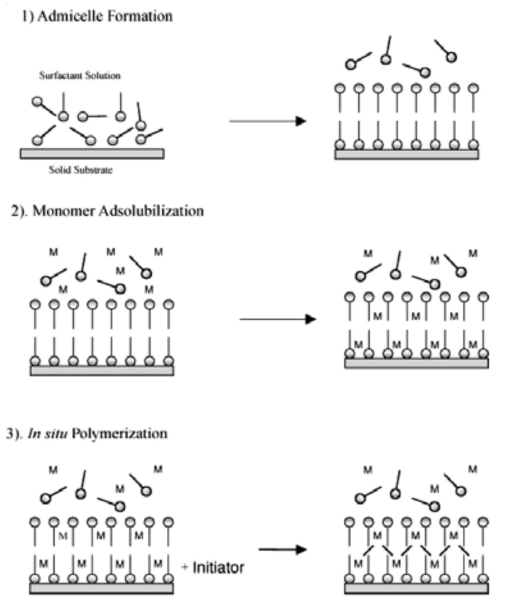

Figure 1. Admicellar polymerization process.

Table 1 Materials used in the admicellar polymerization.

Reagents	Reaction 1	Reaction 2	Reaction 3	Reaction 4	Reaction 5	Reaction 6
NR (g)	200	200	200	200	200	200
MMA (g)	11.78	11.78	11.78	-	-	-
HEMA (g)	-	-	-	15.31	15.31	15.31
SDS (g)	22.5	22.5	22.5	22.5	22.5	22.5
CTAB (g)	0.13	0.10	0.07	0.13	0.10	0.07
AIBA (g)	0.3	0.3	0.3	0.3	0.3	0.3
NaCl (mL)	5	5	5	5	5	5
DI water (mL)	400	400	400	400	400	400

2.2. Methodology

The NR latex was purified by centrifugation at 10000 rpm for 20 minutes at 30 °C and were redispersed the upper layer in ammonium hydroxide 5% v/v solution. Afterwards the resultant NR latex was diluted in DI water to 40% w/w. Admicellar polymerization of poly(methyl methacrylate) (PMMA) and poly(2-hydroxyethyl methacrylate) (PHEMA) onto natural rubber particles were carried out at various cationic surfactant concentrations. The conditions of polymerization of MMA and HEMA onto NR particles are shown in Table 1. NR latex was charged in a 3-neck round bottom flask. Then SDS solution, 0.15M NaCl and CTAB solution were added into the reactor. The reactor was equipped with a mechanical stirrer. The mixture was stirred and heated using water bath for 24 h to allow the CTAB adsorption. After this period, MMA monomer or HEMA monomer was added into the reactor and allowing the monomer adsolubilization for 3 h at 30 °C. AIBA was then injected into the reactor and the temperature was raised to 70 °C to initiate the polymerization under N_2 atmosphere. After 3 h, the reaction was stopped by immersing the reactor in the ice bath for 10 min. The resultant latex was centrifuged at 5300 rpm for 60 min. Then latex was dialyzed againt with deionized water for 1 week to removed excess surfactant. Finally, the latex was dried in an oven at 60°C for 24 h.

2.3. Characterization

Fourier transform infrared spectroscopy (FT-IR) (Perkin Elmer Spectrum one) was used to study the chemical composition of the product. Samples were scanned over the frequency range of 4000-400 cm $^{-1}$.

3. Results and discussion

Figure 2a shows FT-IR spectra of PHEMA, NR and PHEMA-coated on NR particles at different concentrations of CTAB. NR spectrum showed characteristic peaks of isoprene unit at 1647 and 825 cm^{-1} referred to C=C stretching and C=CH bending, respectively. PHEMA showed characteristic peaks at 3378, 1704 and 1146 cm^{-1} corresponding to -OH stretching, C=O stretching and C-O stretching, respectively. However, -OH stretching peak of PHEMA which prepared by admicellar polymerization on NR can not be observed which may be due to the limitation of monomer adsolubilization into the bilayer of CTAB.

Figure 2b PMMA showed characteristic peaks at 1718 and 1180 cm^{-1} attributed to C=O stretching and C-O stretching of MMA unit. FT-IR spectra of PMMA-coated on NR which prepared by admicellar polymerization revealed both characteristic peaks of NR and PMMA indicating that PMMA could be incorporated into CTAB bilayer on NR particles via admicellar polymerization.

4. Conclusion

In this research, admicellar polymerization of PMMA and PHEMA on NR particles were studied. To avoid micelle formation, the concentrations of CTAB used below CMC of CTAB. The products were characterized by FT-IR in which the spectra of PMMA showed the combination of characteristic peaks of NR and PMMA. On the other hand, PHEMA did not polymerized admicelles of CTAB due to the high water soluble of HEMA monomer.

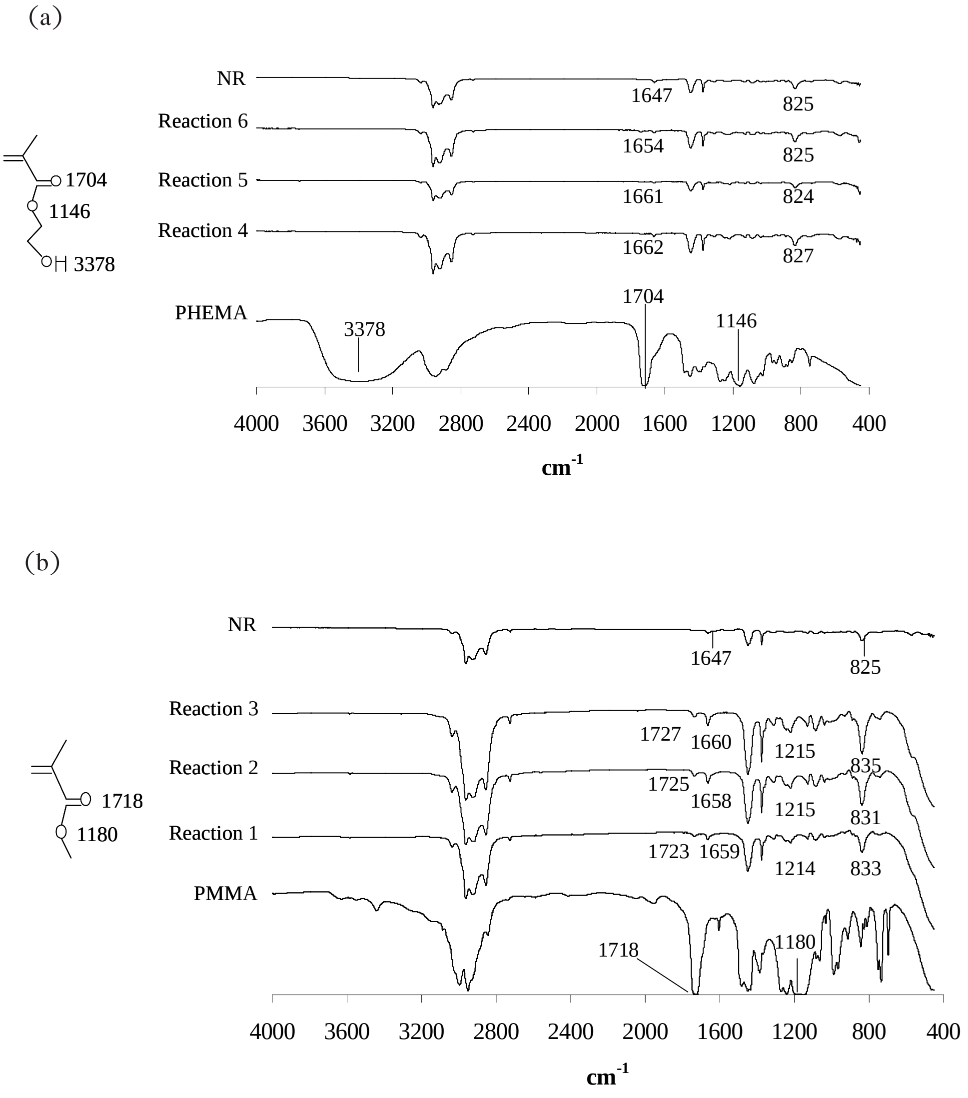

Figure 2. FT-IR spectrum of admicellar polymerization of (a) PHEMA and (b) PMMA.

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