

## The synthesis of core-shell natural rubber with polymethyl methacrylate

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### Abstract

In this research, core-shell natural rubber was synthesized by grafting polymethyl methacrylate (PMMA) onto natural rubber (NR) by using seed emulsion polymerization and CHPO/TEPA as initiators. The effect of surfactant types (SDS, SLES and Oleic acid), surfactant concentrations (1, 1.5 and 2 phr) and MMA monomer concentrations (80, 100 and 120 phr) were investigated. The suspensions of NR-g-PMMA were converted to powder form by spray drying. The potential use of the NR-g-PMMA powder was also investigated as an impact modifier for polylactic acid (PLA). For the effect of surfactant, SDS was found to be the most effective in dispersing the PMMA-grafted NR (NR-g-PMMA), where the use of SDS at 1.5 phr provided the smallest particle size with the highest %yield. For the effect of monomer to NR ratio, it was found that the lowest MMA content of 80 phr provided the smallest particle size of grafted NR with the highest %yield, where too high content (120 phr) led to coagulation of NR particles. This might be from the flocculating effect of free PMMA. The TEM micrograph of NR-g-PMMA latex produced using 1.5 phr of SDS and 100 phr of MMA revealed the complete coverage of NR core by PMMA shell. From the preliminary investigation of NR-g-PMMA as an impact modifier for PLA, it was found that the grafted NR aggravated the toughness of PLA/NR blends. It was suspected that some impurities in the grafted product might lead to degradation of PLA. Moreover, the presence of PMMA homopolymer might lead to the brittleness of the blend.

**Keywords:** natural rubber, emulsion polymerization, graft copolymer, spray drying, polymer blend

## 1. Introduction

Natural rubber (NR) is an important polymer produced from natural resource. NR has higher elasticity and tensile strength because it contains water, phospholipids, lipids, proteins, carbohydrates and other organic and inorganic compounds [1]. However, the uses of NR blended with other polymers are limited because of the stickiness of NR and the immiscibility with polar polymer. Graft copolymerization is one of techniques that is used to improve the properties and interfacial compatibility of NR with other fillers or polymers. The core-shell particles may be synthesized by the graft copolymerization of NR latex with various types of monomer. From previous research, methyl methacrylate monomer (MMA) had been widely used to produce grafted natural rubber latex [2-5] because MMA contains carbonyl groups making it more compatible with polyesters [2]. Besides, PMMA could be formed as hard polymer shell by emulsion polymerization on soft NR core [3]. Graft-copolymer of NR with MMA had been carried out by using various types of initiator. Kochthongrasamee et al. [4] studied effects of redox initiator on MMA grafted NR by emulsion polymerization. It was found that CHPO/TEPA is a better redox system for grafting of MMA monomer on natural rubber latex. However, the PMMA-grafted natural rubber produced by this method has never been used for producing core-shell NR powder. Therefore, in this study, core-shell natural rubber was synthesized by grafting PMMA onto natural rubber by using seed emulsion polymerization and CHPO/TEPA as initiators, with NR as the core and PMMA as the shell. Then, the grafted NR was converted into powder by spray drying. In this case, it was expected that the grafted NR could be converted into powder because the PMMA shell should be hard enough for preventing agglomeration of rubber particles. From this study, it was expected that grafted NR powder could be easily applied for many applications in plastic industry.

## 2. Experimental

### 2.1 Material

NR latex containing 60 wt.% dried rubber was purchased from Rubber Research Institute (Thailand). Block rubber (NR grade STR5L) was produced by Srijaroen Rubber Co.,Ltd (Thailand). PLA 4043D was produced by NatureWorks LLC with the melt flow index and the specific gravity of 6.0 g/10 min and 1.24 g/cc, respectively. Methyl methacrylate (MMA) was obtained

from Acros Organics, MMA was purified to remove inhibitor by washing with 10 wt.% NaOH solution followed by washing with distilled water until its pH was neutral. Potassium hydroxide (KOH) was purchased from Suksapan Panich (Thailand). Sodium dodecyl sulfate (SDS) and Oleic acid were produced by Ajax Finechem Pty Ltd. and Panreac respectively. Sodium Lauryl Ether Sulfate (SLES) was obtained from Honghvat Co.,Ltd. and cumene hydroperoxide (CHPO, 80%) and tetraethylene-pentamine (TEPA) were purchased from Sigma-Aldrich.

### 2.2 Synthesis of NR-g-PMMA

35 g of NR latex (60% DRC) was placed in a three neck round bottom flask reactor along with 70 cm<sup>3</sup> of 10 wt.% potassium hydroxide (KOH) solution. The KOH solution was added to control the pH of NR latex as lower pH led to coagulation of rubber particles. Then, the surfactant (1, 1.5 or 2 phr) which was used as an emulsifier was added while stirring. The mixture was deoxygenated by passing through the nitrogen gas bubbles for 30 min at room temperature. The MMA monomers (80, 100 or 120 phr) was then added continuously while stirring for 30 min. Then the mixture was heated up to 50°C before the initiator CHPO (0.5 phr) was added. After 15 min of mixing, the TEPA (0.5 phr) was added. The reaction was then allowed to proceed for 4 hr under continuous stirring to complete the polymerization

### 2.3 Characterization of NR-g-PMMA latex.

The morphology of NR-g-PMMA latex was determined by using a Transmission Electron Microscopy (TEM model HT7700) at 120 kV. To prepare samples for TEM, the grafted NR latex was diluted 300 times with distilled water. Then, 1 drops of a 2% aqueous solution of osmium tetroxide (OsO<sub>4</sub>) was used to stain the rubber particles for 1 day. A drop of the diluted latex was placed on a carbon-coated Formvar film deposited on a copper grid and dried in a desiccator. The particle size distribution of NR-g-PMMA latex was measured by Optical microscope (Model SKM-904). The NR-g-PMMA latex was diluted 5 times with distilled water before measuring particle size to prevent agglomeration of rubber particles.

### 2.4 Preparation of NR-g-PMMA powder

NR-g-PMMA powder was prepared by the Buchi Mini Spray Dryer B-290 with the inlet air temperature of 130°C.

The feed and air flow rate were set at 1.4 ml/min and 600 NI/hr, respectively. The spray dried powder was kept in a desiccator prior to use. The variation between weight of NR-g-PMMA powder from spray drying and weight of solid content in NR-g-PMMA latex can be calculated using the percent yield from equation (1):

$$\% \text{ yield} = \frac{\text{weight of NR-g-PMMA powder from spray drying}}{\text{weight of total solid content in NR-g-PMMA latex}} \times 100 \quad (1)$$

where the solid content in NR-g-PMMA latex is the sum of the weights of MMA monomers, and rubber particles in NR-g-PMMA latex.

### 2.5 Polymer blend preparation

PLA was dried in a vacuum oven at 80°C for 6 hr to eliminate moisture before mixing. PLA blends were prepared using an internal mixer (Brabender internal mixer, 350E) at the temperature of 160°C with a rotor speed of 60 rpm for 15 min. The compositions of all blends are shown in Table 1. After mixing in an internal mixer, the impact test specimens were prepared by compression molding at 170°C using the compression pressure of 90 bar for 20 min.

### 2.6 Characterization of PLA/NR blends

The impact test was measured according to ASTM D256 by the Izod impact test with a Rasil impactor. The rectangular-shaped test specimens with dimensions of 12.7×63.5×3 mm<sup>3</sup> were tested using the pendulum size of 1 J at 3.46 m/s.

**Table 1** Blend Compositions

Symbols	PLA (wt.%)	NR (wt.%)	NR-g-PMMA (wt.%)
PLA/NR-g-PMMA (90/10)	90	-	10
PLA/NR/NR-g-PMMA (90/7/3)	90	7	3
PLA/NR/NR-g-PMMA (90/9/1)	90	9	1

## 3. Results and Discussion

### 3.1 The effect of type and amount of surfactants

The particle size and %yield of the natural rubber latex grafted with various types and concentrations of surfactants are shown in Table 2 and 3, respectively. The grafted product consisted of 100 phr of MMA as a monomer, and 0.5 phr each of CHPO and TEPA as redox initiators. The reaction was carried out at 50°C for 4 hours. When using 1.5 phr of SDS, the average particle size of the grafted natural rubber latex was the smallest and the %yield of the grafted natural rubber powder was the highest. The effectiveness of the surfactant could be correlated with the critical micelle concentration (CMC) of the surfactants, which is the maximum concentration without micelles. The formation of micelles is undesirable as it would be the place for the undesirable polymerization of free PMMA. From Table 2, the CMC of SDS was the highest indicating that SDS could be added in a large amount without forming free PMMA. Therefore, too high surfactant concentration would lead to the formation of free PMMA, which was undesirable as PMMA is another brittle polymer. The contamination of brittle PMMA in PLA could make the blend even more brittle. Moreover, the free PMMA in the suspension could result in coagulation of NR particles due to depletion effect leading to a larger NR particle size. On the other hand, at too-low concentration of surfactant (below CMC), the surfactant would be insufficient to completely cover NR surfaces leading also to coagulation of NR particles and thus to a larger NR particle size. The images of NR-g-PMMA particles with various types and concentrations of surfactants are shown in Figure 1. Note that the CMCs of SDS, oleic acid, and SLES shown in Table 2 in mol/L are equivalent to 1.5, 0.017 and 0.12 phr, respectively.

**Table 2** The average particle sizes of grafted natural rubber latex with various types and amounts of surfactants

Name	Surfactant	CMC (mol/L)	Particle size ( $\mu\text{m}$ )		
			1 phr	1.5 phr	2 phr
NR-g-PMMA	SDS	$8.2 \times 10^{-3}$	$17.39 \pm 11.84$	$4.20 \pm 0.75$	$10.12 \pm 4.86$
NR-g-PMMA	Oleic acid	$1 \times 10^{-4}$	$10.91 \pm 3.87$	$13.29 \pm 6.98$	$9.60 \pm 4.37$
NR-g-PMMA	SLES	$0.7 \times 10^{-3}$	$10.38 \pm 10.39$	$10.88 \pm 3.54$	$8.71 \pm 6.32$

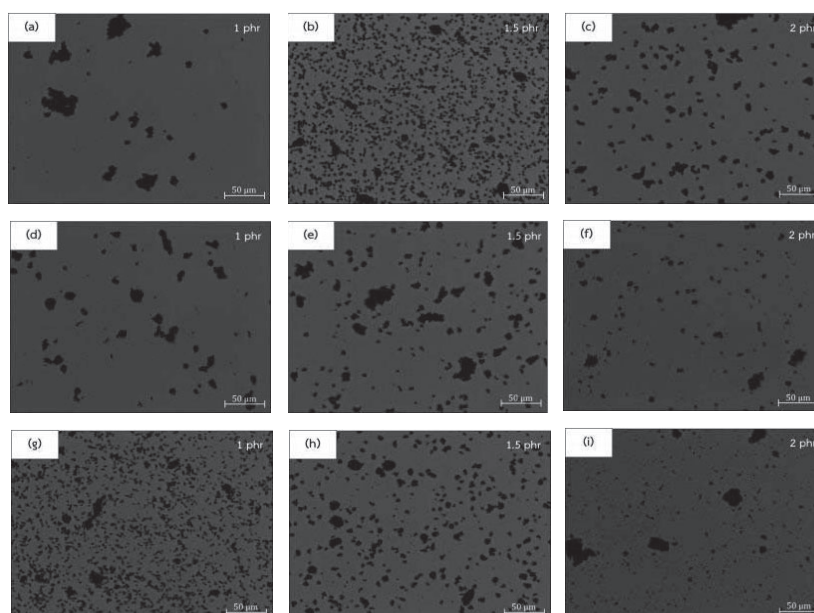
**Table 3** %yield of grafted natural rubber powders using various surfactants at 1.5 phr

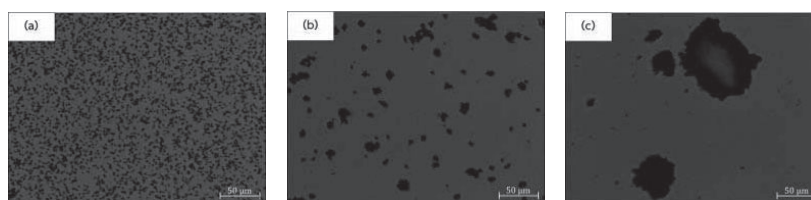
Name	surfactant	Yield (%)
NR-g-PMMA	SDS	43.48
NR-g-PMMA	Oleic acid	15.02
NR-g-PMMA	SLES	11.34

### 3.2 The effect of monomer concentration

In this part, the concentration of MMA was varied from 80, 100 and 120 phr. It was found that the grafted NR tended to coagulate more at MMA concentration higher than 100 phr, as shown in Figure 2. This is probably because the increasing monomer content led to higher degree of homopolymerization reaction of PMMA than graft copolymerization onto NR particles. The free PMMA homopolymer could lead to bridging and thus, coagulation of NR

particles, which was reflected by the increase in NR particle size as shown in Table 4. In the spray-drying step, it was found that the smaller NR particle size was better for the spray-drying process as a large NR particle size led to spray nozzle coagulation. Here, the grafted NR using 80 phr of MMA provided higher %yield than that using 100 phr due to the smaller NR particle size. On the other hand, the grafted NR using 120 phr of MMA could not be spray dried at all due to the coagulation during the reaction

**Figure 1** The images of NR-g-PMMA particles using various types and concentrations of surfactants; (a)-(c) SDS; (d)-(f) oleic acid; (g)-(i) SLES; all of them used 1, 1.5 and 2 phr, respectively



**Figure 2** The images of NR-g-PMMA particles at the concentrations of MMA monomer of (a) 80 phr, (b) 100 phr and (c) 120 phr

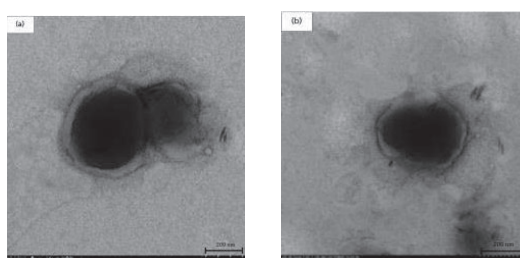
**Table 4** The average particle size of grafted natural rubber latex and %yield of grafted natural rubber powders using various MMA concentrations

Sample	Particle size ( $\mu\text{m}$ )	Yield (%)
NR-g-PMMA (with MMA 80 phr)	$4.26 \pm 0.94$	39.83
NR-g-PMMA (with MMA 100 phr)	$11.40 \pm 3.83$	15.90
NR-g-PMMA (with MMA 120 phr)	$20.39 \pm 29.83$	N/A

\*N/A = Not Available

### 3.3 Morphology of the grafted natural rubber

The grafted NR using 1.5 phr of SDS and 100 phr of MMA was selected for morphology observation because it provided the highest %yield of grafted NR powder. The TEM images are presented in Figure 3. The phase contrast of NR and PMMA was enhanced by using  $\text{OsO}_4$  staining. It was known that  $\text{OsO}_4$  could react with functional groups of unsaturated double bonds, as well as with hydroxyl and amine groups [6]. In the micrographs, it was found that the NR as the core was darkened due to the reaction of unsaturated double bonds ( $\text{C}=\text{C}$ ) with  $\text{OsO}_4$ . A layer around NR represented the PMMA shell formed in grafting polymerization. However, the rubber particles in the images are not spherical due to the coagulation of NR during the grafting process.



**Figure 3** Transmission electron micrographs of the grafted NR latex ( $\text{OsO}_4$  stain) ( $\times 25,000$ )

### 3.4 Impact test

The use of grafted NR powder as an impact modifier for PLA has been investigated by blending PLA with NR and grafted NR at the ratio of PLA/NR/NR-g-PMMA of 90/9/1 and 90/7/3. From the impact test, it was found that the impact strength of PLA/NR blended with grafted NR was lower than neat PLA. This might be because the encapsulated NR powder contained too high PMMA content leading to brittleness of the blend.

## 4. Conclusion

The core-shell natural rubber was synthesized by grafting PMMA onto natural rubber using emulsion polymerization. It was found that, the surfactant and monomer concentrations affected the particle sizes of grafted NR latex and %yield of grafted NR powder. The optimal condition that provided the smallest particle size with the highest %yield was obtained using SDS at 1.5 phr and monomer concentration at 100 phr. The TEM micrograph of NR-g-PMMA latex produced using 1.5 phr of SDS and 100 phr of MMA monomer revealed that the NR core completely covered by PMMA shell. The powder has a good potential, where a powder-form NR is required. However, the application of the encapsulated NR powder as an impact modifier for PLA was not promising due to the fragile nature of PMMA. Further improvement is needed to reduce the amount of free PMMA. One of the potential approach is by using a tougher polymer as the wall material.

## 5. References

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