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Preparation and Characterization of Natural Rubber/Poly [styrene-co-2-(methacryloyloxy) ethyl trimethylammonium chloride] Nanocomposites by Heterocoagulation

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Abstract

The simple technique as heterocoagulation was used to prepare natural rubber (NR) with poly[styrene-co-2-(methacryloyloxy) ethyl trimethylammonium chloride] (P(S-QDM)) nanocomposites (NR/P(S-QDM)). P(S-QDM) particle was prepared by emulsion polymerization at 80°C using azobisisobutylamide dihydrochloride as initiator. Under the alkaline condition, NR latex (NRL) surface represents negative charge deriving from protein adsorbed on its surface while strong positive charge of P(S-QDM) surface deriving from QDM structure is obtained. The assembly via electrostatic interaction between NRL and P(S-QDM) particles in the emulsion state is then taken place with pH adjustable from 2 to 8. The particle surface, particle size and charge of the polymer nanocomposites were measured by scanning electron microscope, dynamic light scattering and zeta potential, respectively, to compare those with the original NR properties.

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Keywords: Natural Rubber; Nanoparticle; Nanocomposite; Electrostatic interaction; Heterocoagulation

1. Introduction

Natural rubber latex (NRL) is one of the most important economic products. Because it is able to comfortably improve the properties with the addition of an appropriate amount of fillers to benefit the

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application concerned [1], it is widely used in various applications such as medical glove and tubing [2-4]. Polymer nanocomposites as only small amount of the nanometer size filler dispersed inside the polymer exhibit markedly improved properties compared to the original or their traditional composites. They represent an alternative and a powerful technique to improve various polymer properties including increased modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability [5]. To improve natural rubber (NR) properties, various techniques have been done as adding inorganic and organic materials such as carbon black [6] ultra-fine calcium carbonate [7] and modified montmorillonite [8]. The heterocoagulation is a simple and interesting technique to prepare the composite materials. The materials as the small and large particles in the emulsion state are blended by various forces such as electrostatic and hydrophobic interactions. It can be used to prepare various composite materials such as inorganic-inorganic [9], inorganic-organic [10] and organic-organic [11-15] composites.

In our previous work [16], NR/poly(styrene-methacrylic acid) (P(S-MAA)) and NR/polystyrene (PS) nanocomposites were successfully prepared by heterocoagulation using electrostatic interaction. NRL and vinyl polymer (PS and P(S-MAA)) particles were blended in the emulsion state at pH of 1 where the opposite charges between those polymers were obtained. P(S-MAA) and PS represent negative charge mainly derived from potassium persulfate initiator on their surfaces while NRL surface showed the positive charge. The mechanical properties of the obtained polymer nanocomposites are dramatically improved. However, less positive charge of NRL (+17.1 mV) leading to less dynamic to interact with the negative charge of the polymer nanoparticles resulting in the formation of unstable polymer nanocomposites. To overcome this problem, pH of the blending condition was changed from the acidic (pH of 1) to the alkaline (pH of 8) condition to introduce highly negative charge on the NRL surface. In addition, poly[styrene-co-2-(methacryloyloxy) ethyl trimethylammonium chloride] (P(S-QDM)) particle having strong positive charge was used instead of PS and P(S-MAA) particles [17]. The obtained NRL/P(S-QDM) nanocomposite represents good colloidal property with long term storage. In this work, the extension study including NRL and P(S-QDM) ratios and pH of pre-blending in the heterocoagulation step were optimized.

2. Experimental

2.1. Materials

High ammonia NR latex (ca. 60% dry rubber content; donated from Thai Rubber Latex Co., Ltd., Bangkok, Thailand) was used as received. Styrene (S; Aldrich; purity, 99%) was purified by pass through the column packed with basic aluminium oxide. 2-(methacryloyloxy) ethyl trimethylammonium chloride (QDM; Aldrich) was used as received. Azo-bisisobutylamide dihydrochloride (AIBA; Wako) was used as received. The chemical structures of QDM and AIBA are shown in Fig. 1. Analytical grade of sodium-hydroxide (NaOH; BDH Prolabo), hydrochloric acid (HCl; Ajax Finechem), polyoxyethylene (20) sorbitan monooleate (Tween 80; Aldrich) and cetyltrimethyl ammonium bromide (CTAB; Fluka) were used as received.

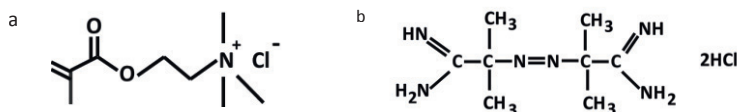


Fig. 1. The chemical structures of QDM (a) and AIBA (b)

2.2. Preparation of polymer nanoparticles

P(S-QDM) nanoparticles were prepared by emulsion polymerization under the conditions listed in Table 1. The water (129 g) containing surfactant (1 g of Tween80) was charged into the reactor. After the addition of monomers (15 g of S and QDM), the reaction was purged with N₂ for 30 min. Consequently, the polymerization was initiated by the addition (5 g) of AIBA aqueous solution (1.2 wt % of monomer) and carried out at 80°C with a stirring rate of 200 rpm for 8 hours.

Table 1. Recipe for the preparation of P(S-QDM) nanoparticles by emulsion polymerization

Ingredients	
Styrene (g)	13.50
QDM (g)	1.50
AIBA (mg)	60.00
Tween80 (g)	1.00
H ₂ O (g)	134.00

200 rpm, 80°C, 8 hr., purged by N₂

2.3. Preparation of NRL/P(S-QDM) nanocomposites

The nanocomposites of NR/P(S-QDM) were prepared using electrostatically driven heterocoagulation technique (Fig. 2.) according to the following procedures. The pH of NRL aqueous dispersion (solid content about 10 %wt) containing Tween 80 emulsifier (6 %wt of NR) was firstly adjusted from approximately 10 to 2 with 0.3 M HCl. The P(S-QDM) nanoparticle aqueous dispersion (10 %wt solid content at pH of 2) was gradually dropped into the NR dispersion with mechanical stirring rate of 200 rpm. The polymer composites of NR/P(S-QDM) were obtained when the pH of the mixture dispersion were gradually adjusted to 8 by the addition of 0.3 M NaOH. The blending ratio was determined relating to the theoretical number (N_{max}) which is the maximum number of small particle [P(S-QDM)] to form a closely packed particulate in a monolayer on a large particle (NRL) as given by Equation (1) shown below [18].

$$N_{\max} = \frac{2\pi}{3} \cdot \left[\frac{R_L + R_S}{R_S} \right]^2 \dots\dots\dots (1)$$

R_L radius of large particle

R_S radius of small particle

2.4. Characterizations

pH were measured by pH meter multi parameter analyser (pH meter; Consort C831, Belgium). Particle diameters and zeta potential were measured by dynamic light scattering (DLS; Delsa nanoC, Beckman, USA) at 25 °C. Polymer emulsion samples (approximately 10 %wt) withdrawn from the reactor were

directly measured by dilution mode of DLS. Scanning electron microscope (SEM; JSM-6340, Jeol Ltd., Japan) was used to investigate the morphology of the P(S-QDM) and NR/P(S-QDM) nanocomposite. For SEM observation, one drop of the polymer dispersion was placed on a nickel SEM stub and dried before Au-coating.

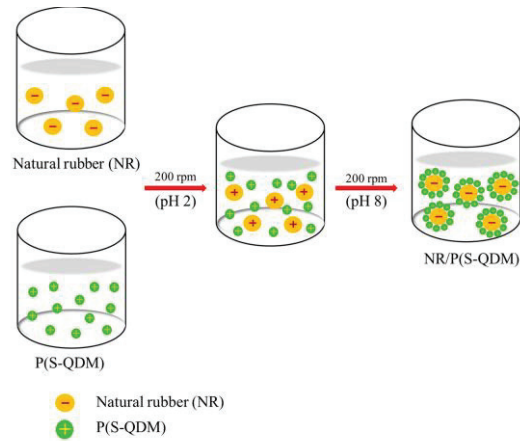


Fig. 2. The schematic of the nanocomposite preparation using electrostatically driven heterocoagulation

3. Results and discussion

P(S-QDM) nanoparticles were selected to be the small particles having positive charge on their surfaces at the alkaline condition (pH of 8). Generally, the obtained positive charge was derived from initiator as AIBA (weak positive charge) and QDM monomer (strong positive charge). However, at the alkaline condition amino group in polymer chain derived from AIBA would be deprotonated. Therefore, the main positive charge represented at the blending condition caused only from QDM monomer. It accords to the above assumption that the prepared P(S-QDM) gives positive charge ($> +30$ mV) throughout the pH range (1-14) as shown in Fig. 3b. A few additional charges at acidic condition would derive from the protonation of amino group of AIBA. P(S-QDM) nanoparticles (76 nm as shown in Table 2) with narrow particle size distribution (Fig. 4) prepared by emulsion polymerization were the spherical particles as SEM micrograph shown in Fig. 5.

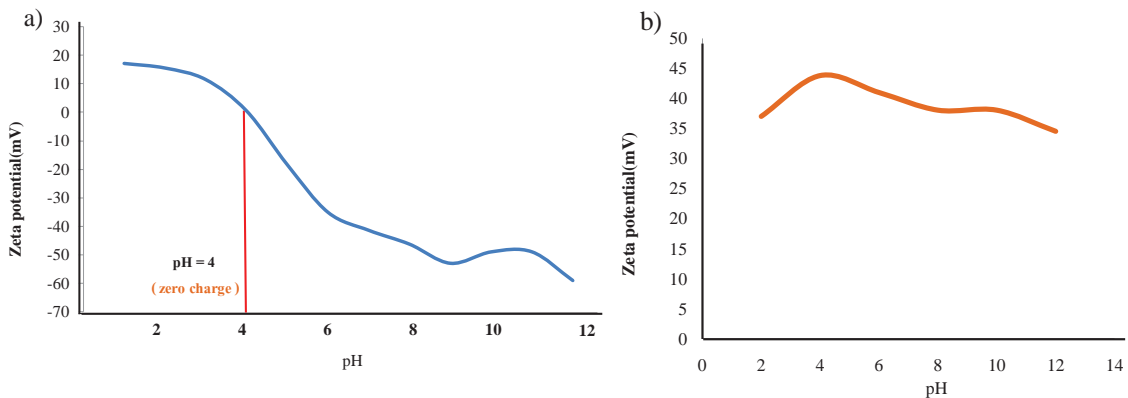


Fig. 3. Zeta potential of NRL adsorbed with nonionic emulsifier (a) and P(S-QDM) (b) at various pHs

Table 2. Particle size distributions and Zeta potential of P(S-QDM) nanoparticle prepared by emulsion polymerization and NRL

	Particle size (nm)	Zeta potential (mV)
P(S-QDM)	75.80	52.10
NR-Tween80	142.30	-49.93

The particles are usually maintain colloidal stability via their surface charges having either lower than -30 or higher than +30 mV [17]. To successfully prepare NR/P(S-QDM) nanocomposites, NRL (particle size of 142 nm as shown in the Table 2) surface should present negative charge in the alkaline condition. Therefore, NRL surface charge was measured at various pHs in order to obtain the information of charge behavior with pH. Before charge measurement, nonionic emulsifier (Tween 80) was added to NRL emulsion to maintain the colloidal stability of NRL throughout the experiment [16, 17]. The charges on its surface varied with the pH from positive to negative charges at acidic to alkaline conditions, respectively as shown in Fig. 3a. Generally, the surface of the NRL was covered with protein molecules. They contain both carboxyl and amino groups showing different charges depending on the pH. At the pH of 8, the negative charge seems to be stable and reached to the maximum (approximately -57 mV). On the other hand, at the same pH, strong positive charge (approximately +40 mV) still obtained on the P(S-QDM) surface. Therefore, pH 8 is selected for the blending condition of both polymer particles. At this condition, it is able to avoid the self-coagulation while the dynamic for the opposite charges interaction is sufficient. However, in the step of pre-blending, both polymer particles should represent the same (positive) charge to avoid large coalescence of both polymers as mentioned in the previous works [14-16]. Therefore, pH of the system is firstly adjusted to the acidic condition in order to gain positive charge on NRL surface. It is well known that NRL is easily to coagulate and precipitate in the acidic condition. Although, NRL was pre-adsorbed by nonionic emulsifier as Tween 80 to protect the coalescence, some of larger particles or precipitation of NRL with long term storage were still found. The main reason is that the amount of Tween 80 is limited to avoid the obstruction of electrostatic interaction of both NRL and P(S-QDM). To successfully prepare NR/P(S-QDM) nanocomposites pH of pre-blending is an important parameter. Therefore, it is further optimized.

Pre-blending condition was studied at various pHs (1-4). The size of NR/P(S-QDM) nanocomposites was increased with the pH as shown in Fig. 6. In the case of pH of 3 and 4, much larger particles (299 and 2,766 nm, for pH of 3 and 4, respectively) were obtained. This seems that the occurrence of NRL self coagulation during the blending compete to electrostatic interaction between NRL and P(S-QDM). In contrast, the size of polymer nanocomposites (175 and 229 nm, for pH of 1 and 2, respectively) is reasonable according to the original polymer particles. Because of less acid, pH of 2 is selected to use for the further study.

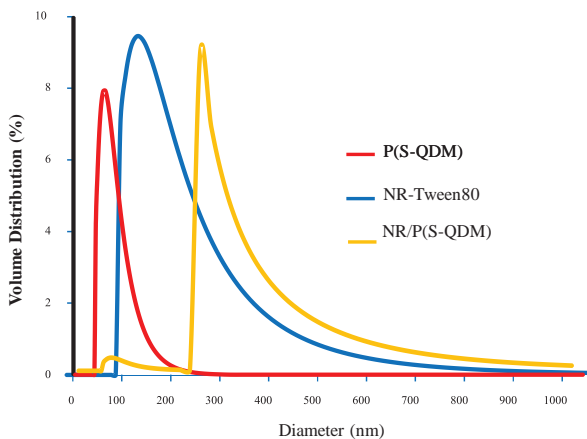


Fig. 4. Particle size distributions of (red) P(S-QDM) nanoparticle prepared by emulsion polymerization (blue) NR-Tween80 and (yellow) NR/P(S-QDM) prepared by heterocoagulation

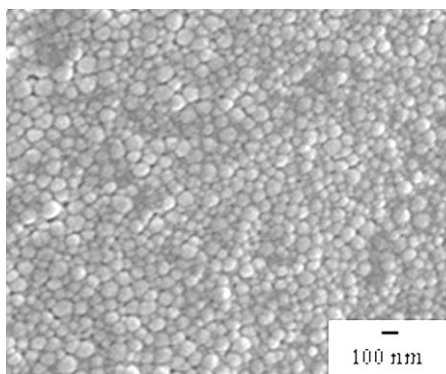


Fig. 5. SEM micrograph of P(S-QDM) nanoparticle prepared by emulsion polymerization

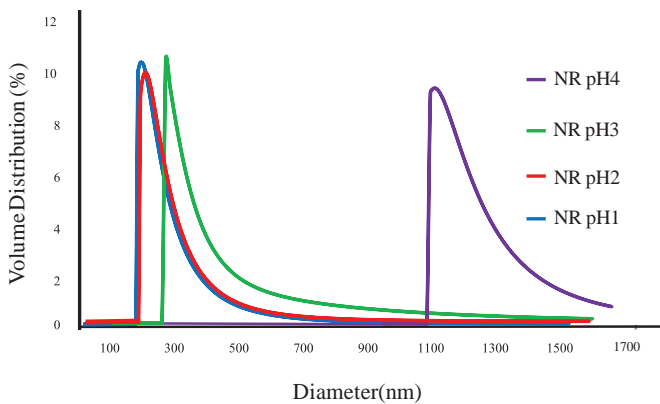


Fig. 6. Particle size distributions of polymer nanocomposites at various pHs

To obtain the appropriate amount of P(S-QDM) to form a close-packed monolayer covering the NRL, the ratios of both polymer particles base on N_{\max} were studied. Table 3 represents the particle size and zeta potential of NR/P(S-QDM) nanocomposites at the different ratios of both polymers. The size of the NR/P(S-QDM) nanocomposites increased with amount of P(S-QDM) particle from $N_{\max}/2$ (163.9 nm) to N_{\max} (228.7 nm) and then decreased at $2N_{\max}$ (93.9 nm). This result may accord to the theory that at the N_{\max} , the size of NR/P(S-QDM) nanocomposites is the largest where P(S-QDM) completely covered NRL by monolayer. In contrast, some of free P(S-QDM) particles were remained in the case of $2N_{\max}$ resulting in the reduction of the average particle size of the nanocomposites. Moreover, the zeta potentials of the NR/P(S-QDM) nanocomposites at various blending ratios ($N_{\max}/2$, N_{\max} and, $2N_{\max}$) were also measured. It increased with the amount of P(S-QDM) particles. In the case of the lowest amount of P(S-QDM), the lowest net positive charge (8.74 nV) was obtained because the NRL surface was incompletely covered by P(S-QDM) particles resulting in low colloidal stability. The zeta potential of 23.60 mV was obtained at N_{\max} giving more colloidal stability. Because free P(S-QDM) particles were presented in the case of $2N_{\max}$, the much more positive charge (33.74 mV) was represented. Moreover, NR/P(S-QDM) nanocomposites as nano-cluster in all ratios were found in the SEM micrographs (Fig. 7). The smallest amount of nano-cluster was found in the case of $N_{\max}/2$ (Fig. 7a) due to the insufficient amount of P(S-QDM) particle to envelope the NRL while the others were more observed. The closed-pack monolayer seemed to be formed for N_{\max} without any free P(S-QDM) particles (Fig. 7b). Some of free P(S-QDM) particles were observed in the case of the twice of N_{\max} (Fig. 7c) according to the particle size and zeta potential data. These results indicated that NR/P(S-QDM) nanocomposites were successfully prepared by heterocoagulation technique.

Table 3. Particle size distributions of polymer composites at various blending ratios

	Particle size (nm)	zeta potential (mV)
$N_{\max}/2$	163.9	8.74
N_{\max}	228.7	23.60
$2N_{\max}$	93.9	33.74

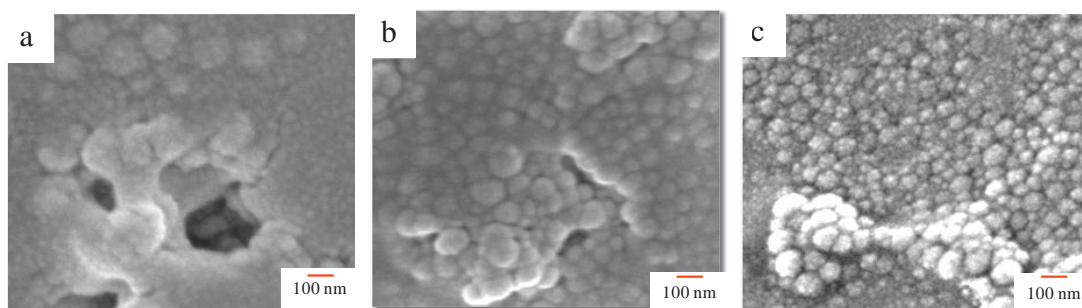


Fig. 7. SEM micrographs of NR/P(S-QDM) nanocomposites prepared by heterocoagulation $N_{\max}/2$ (a) N_{\max} (b) and $2N_{\max}$ (c)

4. Conclusions

The NR/P(S-QDM) nanocomposites was successfully prepared with a simply blending as heterocoagulation via electrostatics interaction. pH of 2 was selected as the pre-blending condition where both NRL and P(S-QDM) represented positive charge. The P(S-QDM) particles were gradually adsorbed on the NRL when pH changed from 2 to 8 resulting in the formation of nanocomposite of NR/P(S-QDM). The nanocomposite seemed to be more stable in the case of N_{\max} than $N_{\max}/2$ relative to much more positive charge. The additional positive charge of the $2N_{\max}$ would derive from free P(S-QDM) particles. Nano-clusters were observed in all cases of NRL and P(S-QDM) ratio. The smallest amount of nano-cluster was observed in the case of $N_{\max}/2$ while it seemed to be similar in the others. However, more amount of free P(S-QDM) particles was found in the $2N_{\max}$ than in the N_{\max} .

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