Heterocoagulation of Natural Rubber Latex and Poly[Styrene-co-2-(Methacryloyloxy) Ethyl Trimethylammonium Chloride] Nanoparticles

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Keywords: Heterocoagulation, Natural Rubber, Polymer Nanocomposite

Abstract
In this work, the heterocoagulation of natural rubber latex (NRL) with polymer nanoparticles having positive change on their surfaces was studied to prepare polymer nanocomposites. Firstly, poly(styrene-co-2-(methacryloyloxy)ethyl trimethylammonium chloride) (PS-QDM) nanoparticles were prepared by emulsion-free emulsion polymerization at 80 °C for 8 hours using azobisobutyronitrile dihydrochloride (AIBA) as initiators. The size (211 nm) of PS-QDM particles was measured by dynamic light scattering (DLS). Secondly, the PS-QDM emulsion was mixed with NRL at the pH of 9 where the PS-QDM and NRL surfaces presented positive (+77.6 mV) and negative (-43.2 mV) charges, respectively. The polymer nanocomposite where PS-QDM adsorbed on the NRL surface by electrostatic interaction was characterized with scanning electron microscope, thermogravimetric analyzer and DLS.

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Introduction
Polymer composite particles having heterogeneous structure such as core-shell can be produced by heterocoagulation technique. This technique is the common interaction of small and large particles having different sizes upon collision. The small particles adsorb onto the larger particle surface with various forces such as electrostatic, hydrophobic and secondary molecular interactions as hydrogen bond. It is well known that the conventional blending such as melt process and the reinforcement materials needed more energy and time because of the preparation of pre-greded polymer for use as a compatibilizer. Thus, the heterocoagulation is useful to prepare polymer composite because the polymers are directly blended in the emulsion state which would consume less energy and time without grinding. Generally, it can be used to prepare various polymer composites such as inorganic-inorganic, inorganic-organic and organic-organic composites. Moreover, to improve NR properties (oil and ozone-resistance and mechanical properties), nanocomposites including NR and inorganic or polymer nanoparticles have also been prepared by this technique. It is simple and appropriate to control the good properties of both polymers by adding small amount of nanoparticle to NRL. In the previous work, it is increased NRL film strength, we have successfully used Poly(styrene-methacrylic acid) (PSMMA) and Poly(styrene) (PS) having negative charge (mainly derived from potassium persulfate initiator) on their surfaces to blend with NRL in the emulsion state at acidic condition (pH 1) where NRL surface showed positive charge derived from protein-lipid. At pH 10, the NRL surface was firstly adsorbed with isoelectric emulsifier (TWEEN 60) and blended with vinyl polymer particles before adding.
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Abstract. In this work, the heterocoagulation of natural rubber latex (NRL) with polymer nanoparticles having positive charge on their surfaces was studied to prepare polymer nanocomposite. Firstly, poly(styrene-co-2-(methacryloxyloxy) ethyl trimethylammonium chloride) (P(S-QDM)) nanoparticles were prepared by emulsifier-free emulsion polymerization at 80 °C for 8 hours using azobisisobutyramid dihydrochloride (AIBA) as initiator. The size (211 nm) of P(S-QDM) particles was measured by dynamic light scattering (DLS). Secondly, the P(S-QDM) emulsion was mixed with NRL at the pH of 9 where the P(S-QDM) and NRL surfaces presented positive (77.6 mV) and negative (49.3 mV) charges, respectively. The polymer nanocomposite where P(S-QDM) adsorbed on the NRL surface by electrostatic interaction was characterized with scanning electron microscope, thermogravimetric analyzer and DLS.

Introduction

Polymer composite particles having heterogeneous structure such as core-shell can be produced by heterocoagulation technique. This technique is the common interaction of small and large particles having different nature upon collision. The small particles adsorb onto the larger particle surface with various forces such as electrostatic, hydrophobic and secondary molecular interactions as hydrogen bond[1]. It is well known that the conventional blending such as melting process and the reinforcement materials needed more energy and time because of the preparation of pre-grafted polymer for use as a compatibilizer. Thus the heterocoagulation is useful to prepare polymer composite because the polymers were directly blended in the emulsion state which would consume less energy and time without grinding. Generally, it can be used to prepare various polymer composites such as inorganic-inorganic [2], inorganic-organic [3] and organic-organic [4] composites. Moreover, to improve NR properties (oil and ozone-resistance and mechanical properties), nanocomposites including NR and inorganic or polymer nanoparticles have also been prepared by this technique. It is simple and appropriate to control the good properties of both polymers by adding small amount of nanoparticle to NRL. In the previous work [5], to increase NRL film strength, we have successfully used Poly(strene-methacrylic acid) [P(S-MAA)] and Polystyrene (PS) having negative charge (mainly derived from potassium persulfate initiator) on their surfaces to blend with NRL in the emulsion state at acidic condition (pH 1) where NRL surface showed positive charge derived from protein-lipid. At pH of 10, the NRL surface was firstly adsorbed with nonionic emulsifier (Tween 80) and blended with vinyl polymer particles before
gradually decrease the pH (10) to acidic condition (pH 1). However, the colloidal property of the obtained polymer nanocomposite seems to be unstable and some of polymer nanoparticles precipitated with long term storage. The positive charge (dissociation of weak base as amino group) of NRL at pH of 1 was only +17.1 where NRL could not maintained the colloidal property and have less dynamic to interact with the negative charge of the polymer nanoparticles. Consequently, some of polymer nanoparticles desorbed from the nanocomposite and NRL thus seemed to be aggregated.

To overcome this problem, in this work, the polymer nanocomposite was prepared by blending of NRL and P(S-QDM) at the alkaline condition where they have strongly negative and positive charges, respectively. The obtained polymer nanocomposite was expected to be good colloidal property with long term storage.

**Experimental Procedure**

The polymer nanoparticles were prepared by emulsifier-free emulsion polymerization as the condition listed in Table 1. The polymerization was carried out at 80 °C with stirring rate at 200 rpm. The monomer (30 g of S and QDM) and water (250 g) were charged into the reactor and then purged with N₂ for 30 min. The polymerization was initiated by the addition (20 g) of AIBA aqueous solution (1.2 wt % of monomer). The nanocomposites of NR/P(S-QDM) were prepared with heterocoagulation technique according to the following procedures. The pH of NRL aqueous dispersion (solid content of about 10 %wt) containing Tween 80 emulsifier (6 %wt of NR) was adjusted from approximately 11 to 2 with 0.3 M HCl. The P(S-QDM) nanoparticle aqueous dispersion (10 %wt at pH 2) was gradually dropped to the NR solution with gentle mechanical stir. The polymer composites of NR/P(S-QDM) were obtained when the pH of the mixture solutions were adjusted to 9 by the addition of 0.3 M NaOH. The blending ratio was determined relating to the theoretical number (\(N_{\text{max}}\)) which is the maximum number of small particle [P(G-QDM)] to form a close-packed in a monolayer on a large particle (NRL) as given by Equation (1) shown below.

\[
N_{\text{max}} = \frac{(2\pi/3) \times [(R_L + R_S)/R_S]^2}{R_L: \text{radius of the large particle; } R_S: \text{radius of the small particle}}
\]

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

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>P(S-QDM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S (g)</td>
<td>13.5</td>
</tr>
<tr>
<td>QDM (g)</td>
<td>1.5</td>
</tr>
<tr>
<td>AIBA (mg)</td>
<td>60.0</td>
</tr>
<tr>
<td>H₂O (g)</td>
<td>135.0</td>
</tr>
</tbody>
</table>

200 rpm, 80°C, 8 hr., purged by N₂

**Results and Discussion**

**Polymer nanoparticles.** P(S-QDM) nanoparticles with a diameter of 211 nm prepared by emulsifier-free emulsion polymerization were spherical particles as shown in Fig. 3a. Narrow particle size distribution (Fig. 2a) was obtained which is the characteristic of polymer particle obtained from emulsifier-free emulsion polymerization whereas emulsifier-present give broader distribution. The quite small polymer particle was obtained because the particle is not only stabilized with electrostatic repulsion of amino group generated from AIBA initiator but also with quaternary ammonium cation existed in QDM molecules. Then, the positive charge (pH 3) about +77.6 mV was presented on their surface.
Polymer nanocomposites. To prepare composite polymer with heterocoagulation technique where the smaller particle was adsorbed on the larger particle using the electrostatic interaction, both particle surfaces should have the opposite charge. This technique required the larger particle as core and smaller particle as shell. As measured by DLS, the size of NRL is approximately 388 nm whereas the P(S-QDM) particle is about 211 nm. Therefore, NRL and P(S-QDM) were expected to be a core and a shell, respectively. Due to the presence of the positive charge of smaller particles derived from both ammonium ion existed in QDM molecules and amino group of AIBA, NRL surface should contain the negative charge in order to achieve the blending.

![Zeta potential of NRL adsorbed with nonionic emulsifier at various pH](image)

**Fig. 1** Zeta potential of NRL adsorbed with nonionic emulsifier at various pH

Generally, NRL surface is covered by protein molecules containing carboxyl and amino groups showing different charges depending on its pH. The result obtained from Fig. 1 (NRL surface charge at various pH) showed that at the pH 2.95, named isoelectric point, there is no ionization of the functional groups where the charge of NRL is zero. The negative charge will be obtained by carboxyl group ionization when the pH is higher than the isoelectric point. Before charge measurement, nonionic emulsifier (Tween 80) was added to NRL emulsion to maintain the colloidal stability of NRL throughout the experiment especially at the pH giving less charge or neutral. It was found that pH higher than 8 reached the maximum negative charge (-57.0 mV). The particles usually can maintain colloidal property via their surface charges having either lower of -30 or higher of +30 mV. Therefore, in this work pH of 9 was selected for the further blending condition.

![Particle size distributions of P(S-QDM) nanoparticle prepared by emulsifier-free emulsion polymerization](image)

**Fig. 2** Particle size distributions of P(S-QDM) nanoparticle prepared by emulsifier-free emulsion polymerization (a); NRL (b) and NR/P(S-QDM) prepared by heterocoagulation (c)

For the blending of NRL and P(S-QDM), they were mixed at the pH where their surfaces gave the same charge and then change the pH to the optimum condition where both polymers show the opposite charge to prevent the aggregation. Therefore, firstly, the emulsion of P (S-QDM) at pH 1...
was added to NRL emulsion (pH 1). Secondly, the pH of the mixing emulsion was adjusted to 9 where NRL and nanoparticle surfaces show negative and positive charges, respectively. The nanoparticle would gradually adsorb on NRL particles during the increasing of the pH with good control. Finally, the composite polymer (NR/P(S-QDM) where NRL particle is core and nanoparticle is shell dispersed in aqueous medium was formed. The composite polymer of NR/P(S-QDM) was successfully prepared by heterocoagulation as the particle size distribution of the blending dispersions of NRL and polymer nanoparticles is larger than those of the host NRL and P(S-QDM) as shown in Fig 2. The prepared composite polymer was observed with SEM as shown in Fig. 3b. SEM micrograph of the prepared composite polymer showed that the P(S-QDM) particles are adsorbed on NRL surface as nano-cluster. This confirms that NR/P(S-QDM) nanocomposite was successfully prepared by the heterocoagulation technique.

![SEM micrographs of P(S-QDM) nanoparticles prepared by emulsifier-free emulsion polymerization (a) and NR/P(S-QDM) nano-cluster prepared by heterocoagulation (b)](image)

**Fig. 3** SEM micrographs of P(S-QDM) nanoparticles prepared by emulsifier-free emulsion polymerization (a) and NR/P(S-QDM) nano-cluster prepared by heterocoagulation (b)

**Conclusions**

The NR/P(S-QDM) nanocomposite was successfully prepared with a simply blending as heterocoagulation. The polymers were mixed in aqueous dispersed phase at pH of 9 where the NRL and P(S-QDM) surfaces gave strongly negative and positive charges, respectively. The adsorption of polymer nanoparticles on NRL'surface was taken place via electrostatic interaction resulting in the formation of the composite polymer of NR/P(S-QDM). The obtained nanocomposite was confirmed by DLS measurement where the particle size of polymer nanocomposite was higher than those of the original NRL and P(S-QDM). In addition, the adsorption of P(S-QDM) on NRL surface as nano-cluster was observed by SEM.

**Acknowledgement**

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**References**