Grafting of Poly(vinyl alcohol) on Natural Rubber Latex Particles

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ABSTRACT: Poly(vinyl alcohol) (PVA) was grafted on natural rubber (NR) latex particles (NR-g-PVA) using potassium persulfate to generate active radicals on both NR particle surface as well as PVA molecules. ^{1}H- and ^{13}C-nuclear magnetic resonance spectroscopy suggested a possibly chemical attachment of PVA on the NR. The amount of graft-PVA expressed in term of grafting percentage (%G) increased almost linearly with the amount of PVA adding to the NR latex. Measuring by dynamic light scattering, the particle size of NR-g-PVA particles was larger than the size of unmodified NR, also it increased with the molecular weight and %G of PVA. Transmission electron microscopy images of the NR-g-PVA latex particles revealed that the size of PVA-grafted NR particle was enlarged by a layer of graft-PVA surrounding the NR particle. Given by the graft-PVA layer surrounding NR particles, the NR-g-PVA latex particles possessed better colloidal stability as lowering pH compared with the unmodified NR latex. Comparing with unmodified NR particles, the electrophoretic mobility of NR-g-PVA particles was lower due to the presence of graft-PVA that shifted the shear plane further away from the surface of the particles. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Concerns of the environment draw many attentions toward utilizations of the natural or natural-friendly materials in place of the synthetic ones. Among them is the natural rubber (NR), which is mostly obtained from *Hevea brasiliensis* tree in the latex form. The NR latex is natural polymer colloid consisting of *cis*-polyisoprene particles dispersed in aqueous medium (serum). The excellent elastomeric properties make NR among the highly utilized biosynthetic materials used mainly in the tires industry. Despite the extensive uses, there have been many efforts to modify the properties of NR to expand its applications. Besides blending with other polymers,[1-3] NR can be molecularly altered through the copolymerizations. The graft copolymerization has been used as a method for modifying NR both in solution[4] and latex[5-10] forms. The graft polymerization in NR latex is, nonetheless, more applicable because to completely dissolve NR is difficult due to the fact that it composes of very high molecular weight polyisoprene with varying amount of gel.[9] In addition, performing the grafting of hydrophilic polymers in NR latex is convenient because most hydrophilic monomers are readily soluble in water.

Naturally, NR latex particles are electrostatically stabilized by long-chain fatty acid soaps covering on the particle surfaces.[11-14] These indigenous stabilizers are the hydrolyzed product of phospholipids that, however, is susceptible to a change of pH in aqueous phase.[11] In all cases, a decrease of pH or, in many cases, an increase of electrolytes concentrations, will lead to the coagulation of NR latex particles. It is known that the grafted or adsorbed polymer layer provides the steric barrier for colloidal particles thus are capable of preventing the coagulation.[15,16] Accordingly, the grafting of hydrophilic polymer on NR particles is advantageous for the stability of NR latex. Generally, the graft copolymerization in NR latex involves the free-radical polymerization of vinyl-monomer at the active grafting-sites on the NR particle surfaces. Although the synthetic method is relatively simple with mild polymerization conditions, it is difficult to control the amount of grafted polymer and the occurrence of free homopolymer (no-grafting) is unavoidable.

Fortunately, it was possible to graft some hydrophilic polymers such as poly(vinyl alcohol) (PVA) directly on the NR latex particles.[17] PVA was widely used as the polymeric stabilizer to impart good colloidal stability in emulsion,[18-20] miniemulsion,[21,22] as well as dispersion[23-25] polymerizations. In the presence of active-

radicals, e.g., persulfate radicals, the hydrogen of the tertiary C—H bonds on PVA main-chains may be abstracted generating the PVA-radicals that is readily to react with other active radicals.[19,22] Also activated by the initiator, the active-radicals can be created at the isoprene units resided on NR particle surface by two possible ways, i.e., the abstraction of labile allylic hydrogen and the addition of radicals at the double bond of carbons.[9] Therefore, when the PVA-radicals reach the active sites on the NR particle surface, the grafting of PVA on the NR latex particles will achieve. Because the grafting takes place via polymer-radicals, it is expected that the amount and molecular weight of the PVA grafted on the NR particles is more controllable compared with a conventional grafting with monomers. Moreover, the stability of NR latex particles should improve because of the steric barrier provided by the graft-PVA layer surrounding the NR particles. In our previous study,[17] the grafting of PVA on NR latex particles was successfully performed and the NR-g-PVA latex was further prepared as the membranes. In this study, the grafting of PVA on the NR latex particles using the similar approach was investigated to study the effects of amounts of PVA and initiator as well as the colloidal properties of the NR-g-PVA latex particles.

EXPERIMENTAL

Materials

Concentrated NR latex with dry rubber content (DRC) of 60 wt % was purchased from Thai Hua Rubber (Udonthani, Thailand). The NR latex was cleaned twice by ultracentrifugation at 10,000 rpm for 20 min followed by dialysis in deionized water (DI) for a week to eliminate any insoluble and soluble impurities. PVA with 99% degree of hydrolysis was supplied by Sigma-Aldrich (St. Louis, USA). The weight-average molecular weights of PVA measured by gel permeation chromatography (GPC) were 17,300 g/mol for low MW PVA (LPVA) and 145,000 g/mol for high MW PVA (HPVA). Potassium persulfate (KPS) was obtained from BDH (UK) and used as received.

Grafting of PVA on NR Latex Particles (NR-g-PVA)

The desired amount of PVA was dissolved in DI water and stirred at 90°C until obtaining a clear solution. The initiator was prepared by dissolving KPS in DI water. The PVA solution was then mixed with the initiator prior to heating at 70°C for 30 min. The concentrated NR latex was diluted with DI water to approximately 10 wt % DRC after that the initiator was added. The latex-initiator was stirred thoroughly for 30 min at 70°C. The PVA-initiator solution and the NR-initiator latex were mixed together and stirred then allowed the grafting to proceed at 70°C for 3 h under nitrogen atmosphere. The amount of PVA adding to NR latex was expresses in term of weight ratio (%) of PVA to dry NR.

The amount of PVA grafting on NR latex particles was evaluated in term of the grafting percentage (%G) as expressed in eq. (1). To determine the weight of graft-PVA, the NR-g-PVA latex was coagulated by the acetic acid solution. The coagulum was then washed with DI water several times and dried at 60°C to a constant weight. The dried coagulum was weighted before it was subjected to extraction with DI water at 80°C for 48 h to eliminate the ungraft-PVA. Finally, the extracted NR-g-PVA was dried at 60°C until its weight was constant.

$$\%G = \frac{\text{Weight of graft} - \text{PVA}}{\text{Weight of dry NR}} \times 100 \qquad (1)$$

Nuclear Magnetic Resonance Spectroscopy

The samples were cut into small pieces and dissolved in CDCl$_3$ or DMSO-d$_6$. The ^{1}H- and ^{13}C-nuclear magnetic resonance spectroscopy (NMR) analyses were performed by Varian Mercury Plus 400.

Dynamic Light Scattering

The particle size of the latex particles was determined by dynamic light scattering (DLS) at 25°C using Brookhaven Instruments BI-200SM. The measurement was performed 10 times for each sample and the average particle size along with its deviation was calculated. All samples were diluted with DI water, and their pHs were adjusted by adding either 0.1M NaOH or 0.1M HCl solutions.

Transmission Electron Microscopy

The micrographs of NR and NR-g-PVA latex particles were obtained by the transmission electron microscopy (TEM) FEI Tecnai G^2 20 operating at 200 kV. To avoid the coalescence of the latex particles, the latex samples were diluted in DI water to a concentration of less than 1% DRC. Then the diluted latex samples were deposited on carbon-film coated 300-mesh copper grids prior to drying in a desiccator.

Electrophoretic Mobility (μ_e)

The μ_es of NR and NR-g-PVA latex particles were measured at 25°C by Malvern Instruments, DTS 1060 nanoseries using NaCl solutions as the electrolyte. The NaCl solution was also used for adjusting the ionic strength. The pH of the samples was adjusted by adding either 0.1M NaOH or 0.1M HCl solutions.

RESULTS AND DISCUSSION

Grafting of PVA on NR Latex Particles

^{1}H- and ^{13}C-NMR. The synthetic route to NR-g-PVA was demonstrated in Scheme 1. At 70°C, KPS was decomposed to persulfate radicals. The radicals would abstract the methine hydrogen on the PVA generating active radicals along the PVA main chain,[19] whereas the allylic hydrogen of isoprene unit was also abstracted giving active radicals on the NR particle surfaces.[9] A combination of surface-active NR particles and PVA-radicals yielded the NR-g-PVA as a product.

The synthesis of NR-g-PVA was confirmed by ^{1}H- and ^{13}C-NMR with the spectra shown in Figures 1 and 2, respectively. Because a complete dissolution of the graft polymer consisting of hydrophobic and hydrophilic parts may be difficult, two deuterated solvents of different polarities namely, CDCl$_3$ and DMSO-d$_6$, were used. It could be seen in Figure 1 that when a less polar solvent, CDCl$_3$, was used, only peaks corresponding to NR were observed, implying the complete collapse of the hydrophilic domain of the graft-PVA. The chemical shifts at δ 5.13 and δ 1.68 ppm could be assigned respectively to unsaturated methine proton (=CH—) and methyl protons (—CH$_3$) of NR. The methylene protons (—CH$_2$) peak was shown at δ 2.04 ppm.[7,9,26] When DMSO-d$_6$ as a nonselective solvent was used, peaks corresponding to both NR and PVA were evidenced. The chemical shifts at δ 1.41 and δ 3.82 ppm attributed respectively
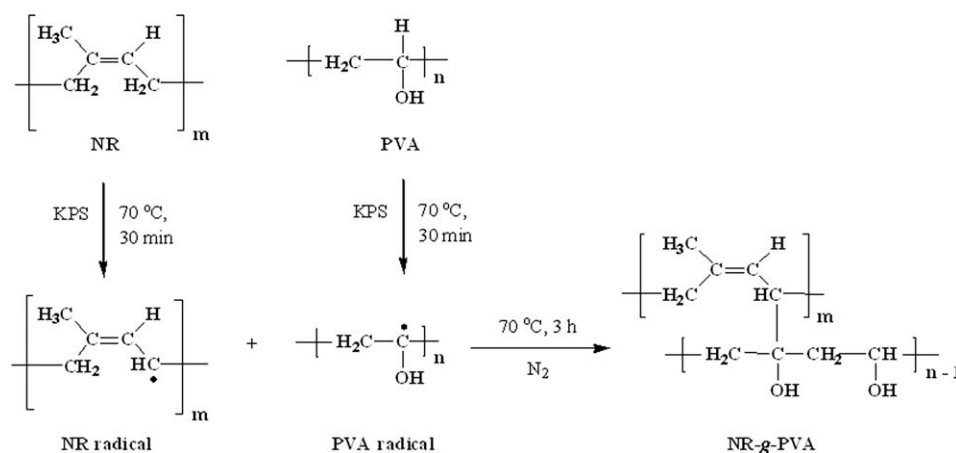
Scheme 1. Synthetic route to NR-*g*-PVA.

to methylene protons and methine proton on PVA backbone.[27,28] The hydroxyl protons (—OH) appeared as split peak centered at δ 4.55 ppm. The splitting was resulted from the difference in stereoisomeric positions of the hydroxyl groups.[29]

The ^{13}C-NMR spectra of the NR-*g*-HPVA in CDCl$_3$ and DMSO-d$_6$ are shown in Figure 2. All characteristic peaks of NR were observed when measuring in CDCl$_3$. The chemical shift at δ 23.41 ppm corresponded to primary carbon (—CH$_3$), while secondary carbons (—CH$_2$) were shown at δ 26.38 and δ 32.19 ppm. The chemical shifts at δ 125.00 and δ 135.18 ppm could be assigned to two olefinic carbons bonding with —H atom and —CH$_3$ group, respectively.[30] When DMSO-d$_6$ was used as an NMR solvent, the appearances of methane carbons of PVA at δ 64.28, 66.28, and 68.20 ppm were observed.[31] The peaks in the range of δ 45.09–46.60 ppm were assigned to methylene carbons.

Grafting Percentage (%G). The increase of %G with increasing PVA loading as observed in Figure 3 indicates that the grafting of PVA on the NR particles was enhanced with the amount of PVA dissolved in aqueous phase of NR latex. In the presence of the persulfate radicals, the number of PVA molecules being H-abstracted by the radicals and becoming the PVA-radicals will increase with the amount of PVA. Hence, increasing number of PVA-radical

gives a higher probability of PVA-radicals to react with surface-active NR particles. Moreover, an increase of PVA grafting was achieved not only by increasing numbers of PVA-radicals but also the molecular weight of PVA-radicals. This is also evidenced in Figure 3 as greater amount of graft-PVA was obtained for HPVA than LPVA particularly at high PVA/NR weight ratios.

Unlike the graft polymerization of monomers, the initiator concentration did not significantly affect the grafting of PVA as revealed in Figure 4. At the same PVA loading, %G was relatively constant regardless of the amount of KPS implying that the number of PVA-radicals did not increase but did the number of active-radicals on a main-chain PVA. The structure of PVA-radicals carrying many active-radicals along the main-chain suggests that the PVA chain forms multiple grafting points on NR particle and by increasing the initiator concentration, the number of grafting points per one PVA molecule will increase not the number of graft-PVA molecules.

Particle Size of NR-*g*-PVA Latex Particles by DLS

The effective diameters of NR and NR-*g*-PVA latex particles as determined by DLS are shown in Figure 5. The particle sizes
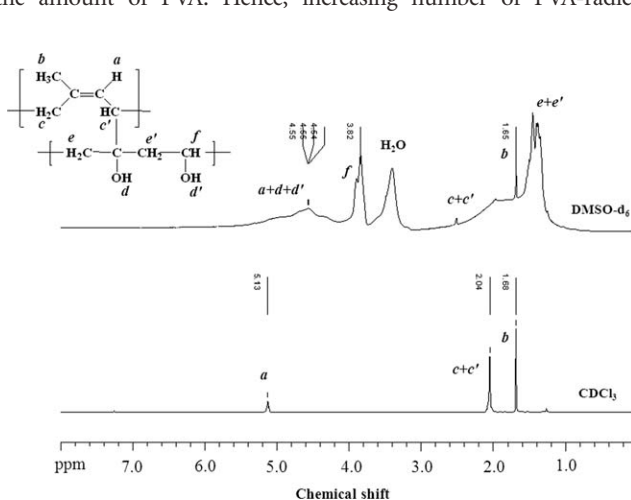

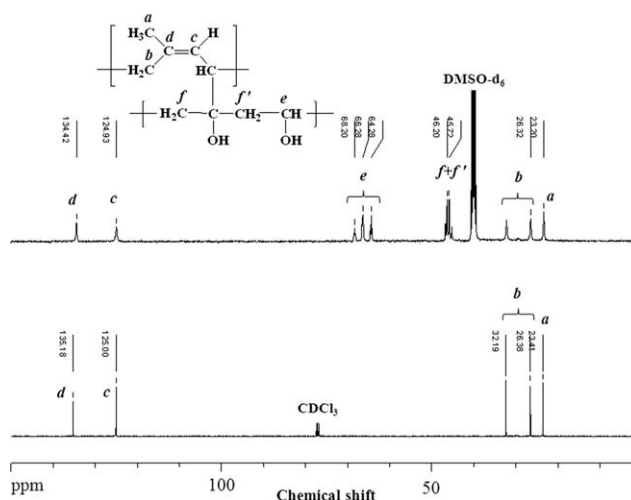**Figure 1.** ^{1}H-NMR spectra of NR and NR-*g*-HPVA at %G = 32.4.

Figure 2. ^{13}C-NMR spectra of NR and NR-*g*-HPVA at %G = 32.4.
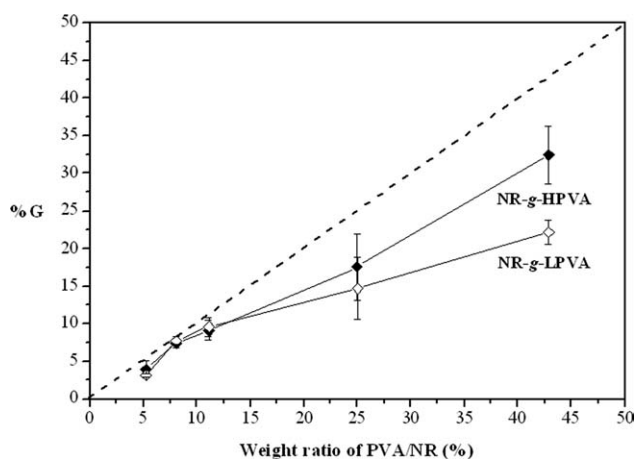
Figure 3. Effect of PVA/NR weight ratio (%) on %G of NR-g-PVA; [KPS] = 1 wt % of PVA.

Figure 5. Average effective diameter (D_{eff}) of NR-g-PVA latex particles at various PVA grafting amount (%G).

were measured at pH > 8.0 to ensure a colloidal stability therefore the coagulation was minimized. Obviously, the graft-PVA layer contributed to the enlargement of NR-g-PVA particles as evidenced by the increment of particle diameter with %G and the molecular weight of graft-PVA. For low grafting of PVA, the surface area of NR particles was mostly unoccupied and thus PVA could be grafted in a flat (train) conformation. As the grafting amount of PVA increased, the surface of NR particles was crowded with the grafted PVA chains; therefore, the PVA would be grafted in the extended forms, i.e., the conformation became more on the loops and tails.[32,33] At relatively the same %G, the particle size of NR-g-HPVA was higher than the size of NR-g-LPVA suggesting that HPVA was grafted on the NR particle surface with more tail conformations compared with grafting with LPVA.

Figure 6 shows the effect of pH on the particle size of NR and NR-g-PVA latex particles. The unmodified NR latex particles and the NR particles with PVA grafting responded differently to the change of pH. At pH > 6.0, the particle size of NR was relatively constant with narrow particle size deviation. For pH <

6.0, the sudden increase of NR particle size with a large deviation was observed indicating that NR latex started to loss its colloidal stability (the results at low pH were omitted but marked as unstable in Figure 6). The constant NR particle size at high pHs and the loss of colloidal stability at lower pHs suggests that the NR particles were stabilized by the electrostatic repulsions. The charges on the NR particle surface is negative which is originated from the hydrolysis of phospholipids resided on the surface of NR latex.[12,13] Unfortunately, the degree of hydrolysis substantially reduces as lowering the pH resulting in a decrease in number of negative charges and consequently, the surface potential. With the reduced surface charge density, the electrostatic repulsion is diminished and the NR latex particles are susceptible to the coagulation. For the NR-g-PVA particles, the particle size slightly changed regardless of a change of pH. This is because the graft-PVA layer provides additional stability to the NR-g-PVA latex particles. Although the electrostatic repulsion was ineffective that could draw NR particles to come into contact, the steric barrier given by the graft-PVA layer prevented the coalescence of NR particles that leading to the coagulation. Affirmatively, a better colloidal stability of NR-g-PVA particles is evidenced in Figure 7 where the particle size distribution (PSD) of NR and NR-g-PVA at pH = 4.0 are reported.
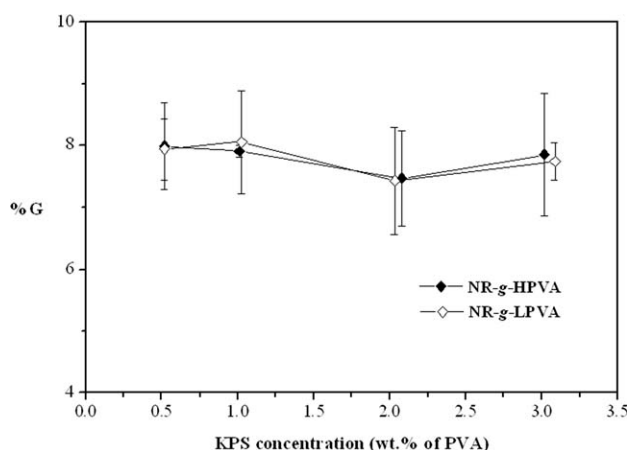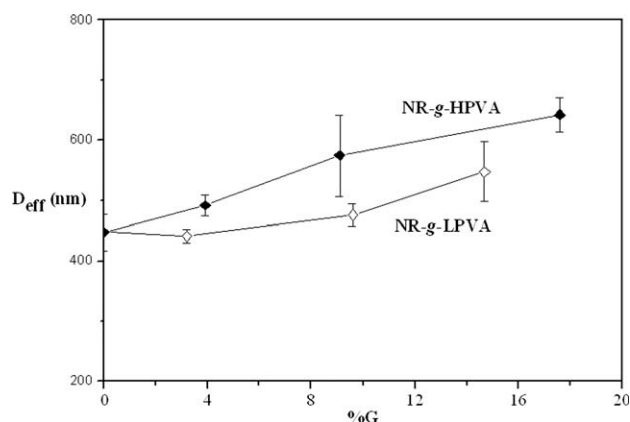

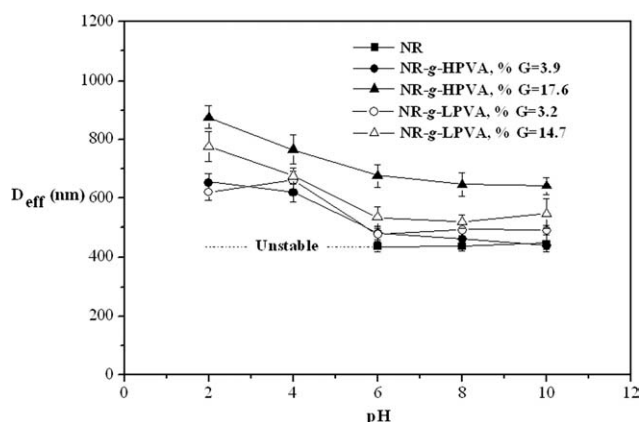**Figure 4.** Effect of initiator (KPS) concentration on %G of NR-g-PVA; PVA/NR weight ratio = 10%.

Figure 6. Average effective diameter (D_{eff}) of NR-g-PVA latex particles at different pHs.
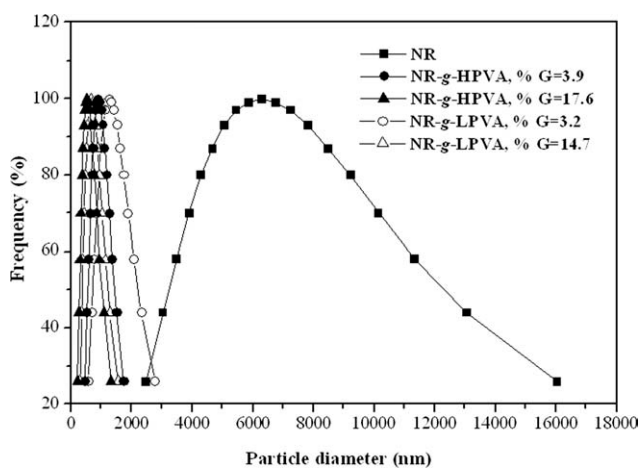
Figure 7. Particle size distribution (PSD) of NR and NR-*g*-PVA at pH = 4.0.

It can be seen that the PSD of NR latex particles was substantially broader than that of the NR-*g*-PVA particles. The broad PSD of NR latex particle indicates the coalescence of primary NR particles to form the multi-size coagulates.

Transmission Electron Microscopy

The transmission electron microscopy (TEM) images of NR, NR-*g*-LPVA, and NR-*g*-HPVA latex particles are displayed in Figure 8. As observed, the particle shape of the NR latex particles was spherical with a diameter of ~ 1 μm. Expectedly, the size of NR particle measured from TEM was larger than obtaining from DLS because of the elastomeric nature of NR that when dried on a TEM grid, NR particle was flattened out changing its shape from a spherical to a disc like. Alongside the single NR particle was coagulate of NR particles which caused an increase in the particle size and PSD when measured by DLS. The presence of the graft-PVA layers are evidenced for both NR-*g*-LPVA and NR-*g*-HPVA, which appear as pale-shade layers with ragged rim surrounding darker areas of NR latex particles. It is noticeable that the graft-layer of HPVA was thicker than the graft-layer of LPVA.
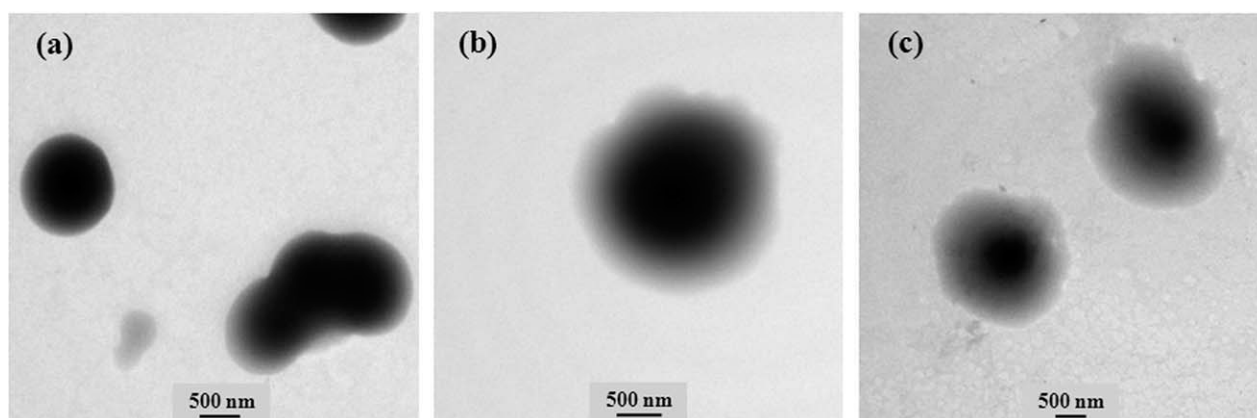

Figure 9. Effect of pH on the mobility (μ_e) of NR-*g*-HPVA latex particles (a) and NR-*g*-LPVA latex particles (b); [NaCl] = 1 mM.

Electrophoretic Mobility (μ_e) of NR-*g*-PVA Latex Particles

Effect of pH on the μ_e of NR and NR-*g*-PVA latex particles is revealed in Figure 9. For the NR latex particles, the μ_e was negative at high pHs and declining (less negative) as decreasing the pH until reaching the isoelectric point (IEP), where $\mu_e \approx 0$ at pH ~ 2.0–3.0. After the IEP, the μ_e became slightly positive. Although the NR latex was cleaned by centrifugation and dialysis, some polypeptides and phospholipids strongly bound on the surface of NR particles could not be completely removed.[13] A positive value of μ_e observed at pH = 2.0 is therefore due to the protonation of the polypeptides. At higher pHs, the phospholipids are hydrolyzed to long-chain carboxylated anions giving NR particles negatively charged. Lowering the pH decreases the hydrolyzed degree of the phospholipids and thus a number of negative-charges on the NR particle surfaces is reduced resulting in a decreasing of the μ_e.[11,13]

Figure 8. TEM images of NR latex particles (a), NR-*g*-LPVA latex particles at %G = 14.7 (b), and NR-*g*-HPVA latex particles at %G = 17.6 (c).
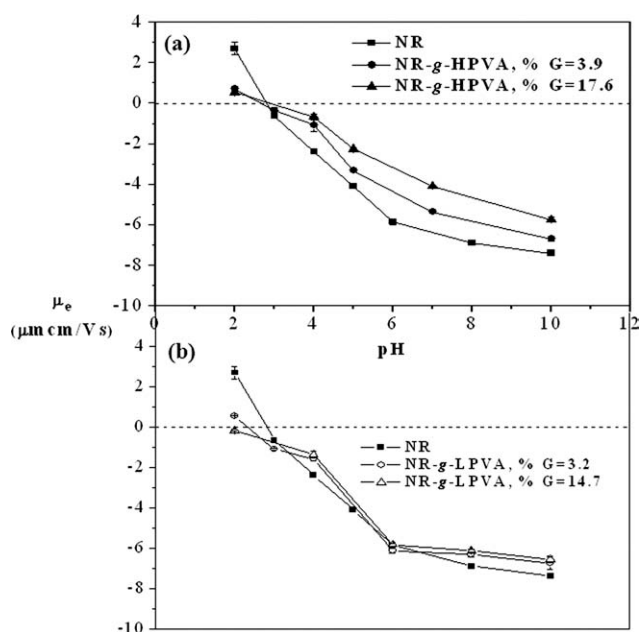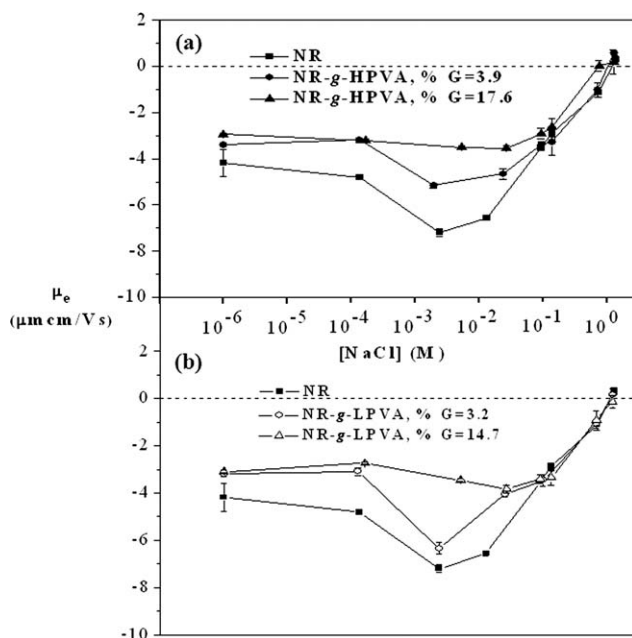
Figure 10. Effect of ionic strength (NaCl) on the mobility (μ_e) at pH = 10 of NR-g-HPVA latex particles (a) and NR-g-LPVA latex particles (b).

Upon grafting with PVA, the μ_es of the NR-g-PVA particles became lower indicating that the electrokinetic property of NR latex particles was altered by the presence of graft-PVA layer. An extent of μ_e reduction depended both on the molecular weight and %G of PVA and their effects were more pronounced for NR grafting with HPVA than LPVA. The decreased mobility upon grafting with PVA is possibly caused either by a decrease in the surface charge due to the neutralization of surface-ionized groups[34] or the moving of shear plane away from the particle surface owing to an alteration of ions atmosphere by the presence of graft-polymer layer.[35,36] Because the μ_e of NR-g-PVA particles was changed with pH in a similar manner to that of NR particles, it implies that the latter is responsible for a decrease in the mobility of NR-g-PVA particles. In view of the classical electrokinetic model, the μ_e depends on the potential at the hydrodynamic shear plane so called the zeta potential (ζ).[37] As the surface-charged particles moving through the fluid medium under the electric field, the fluid adhering on the particle surface forms a very thin hydrodynamic-stagnant layer which within this layer, the charges are immobile and at the boundary where the charges start to diffuse is the shear plane.[38] For a smooth-surface particle, the shear plane is very near the particle surface. The previous studies[11,14] have, however, revealed that the surface of NR latex particles is not smooth but covered with a mixed layer of phospholipids and proteins therefore the shear plane for the NR particles is somewhere within this mixed layer. The graft-PVA layer surrounding the NR particle impedes a moving of the grafted particle through fluid medium by exerting some friction as the fluid passing through the graft layer. With more resistance, the hydrodynamic-stagnant layer is expanded and the position of the shear plane for the NR-g-PVA particles is therefore shifted further out from the particle surface than that of unmodified NR particles. Consequently, the shifting of the shear plane causes the ζ to decrease resulting in a decrease in the μ_e of NR-g-PVA particles.

Figure 10 reveals the effect of electrolyte (NaCl) on the μ_e of NR and NR-g-PVA latex particles. The mobilities of both NR and NR-g-PVA particles showed similar changes with ionic strength in which they had the minima in μ_e at some intermediate ionic strength. The minimum in the mobility-ionic strength curves is not uncommon[36,39] and could be explained by the competing of three processes, for negatively charged particles they are as follows: (1) the neutralization of negative charge on the particle surface by adsorption of counter-ions causing a decrease in the μ_e (less negative); (2) the approach of co-ions to the particle surface which increases the μ_e (more negative); and (3) the compression of the electrical double layer (EDL) due to high bulk concentration of the electrolytes causing the μ_e to decrease (less negative).[40] The decreasing of μ_e upon grafting of PVA on the NR particles was obvious at low to intermediate ionic strength. However, the effect of grafting amount at low ionic strengths was not as noticeable as at the intermediate ones. At low electrolyte concentration, the EDL is extended to a comparable thickness with the graft-PVA layer and the potential slowly decays toward bulk solution. Therefore, under this condition, the effect of grafting amount on the μ_e may be concealed. As increasing the electrolyte concentration, the effect of grafting amount on the μ_e is witnessed because the EDL is compressed to a thickness thinner than the thickness of graft-PVA layer.[39]

CONCLUSIONS

PVA was successfully grafted on NR latex particles by introducing the initiator-KPS to NR latex particles as well as PVA solution. ^{1}H- and ^{13}C-NMR spectroscopy revealed the chemical attachment of PVA on NR particles. The grafting amount of PVA (%G) was found to increase almost linearly with the amount of added PVA but be indifferent to a change of KPS concentration. The particle size measurement by DLS showed the larger particle diameter of NR-g-PVA compared with that of unmodified NR by which the particle size increased with the molecular weight and %G of PVA. TEM images confirmed an enlargement of the NR-g-PVA latex particles by a layer of graft-PVA surrounding the NR particle. The NR-g-PVA possessed better colloidal stability as lowering pH while the NR particles lost the stability at pH < 6.0. The mobilities (μ_e) of NR-g-PVA latex particles were lower in magnitude than that of NR. The response of μ_e to the changes of pH and ionic strength were similar for NR and NR-g-PVA particles and the IEP of both particles located at almost the same pH and ionic strength. This suggests that the reduction of μ_e of NR latex particles upon grafting with PVA is caused by the moving of the shear plane away from the particle surface.

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