Reduction of Surface Friction of Natural Rubber Film Coated with PMMA Particle: Effect of Particle Size

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ABSTRACT: The friction coefficient of the sulphur-prevulcanized natural rubber (SPNR) film could be effectively reduced by deposition of poly(methyl methacrylate) (PMMA) particles. The nanoscale surface roughness of rubber, determined by atomic force microscope, was directly proportional to the particle size of PMMA particle at 12% surface coverage (Cs). The %Cs and surface roughness of the modified SPNR increased, while the friction coefficient decreased, with increasing PMMA latex concentration and immersion time. By using a mixture of latexes having both large and small sizes, the increase in the amount of small particles resulted in the better distribution of large particles deposited on the rubber surface. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 3680–3686, 2010

Key words: emulsion polymerization; films; rubber; self-assembly; surfaces

INTRODUCTION

Friction between skin and rubber is a crucial drawback in the application of gloves made of sulfur-prevulcanized natural rubber (SPNR) latex. In general, the friction coefficient of SPNR can be decreased with powder, grease or liquid. However, the use of lubricating powder such as talc or corn starch to dust the surgical gloves can cause contamination to the patient. Moreover, it is known that talc does not help the wound healing process and corn starch causes allergic reactions.[1] Recently, the mimetic behavior has been obtained by deposition of poly (methyl methacrylate) (PMMA) nanoparticles onto the SPNR film by using the simple and versatile Layer-by-Layer (LbL) technique.[2,3] The surface charge on SPNR sheet was derived from grafted polyacrylamide (PAAm), under UV, onto the rubber surface pretreated with Ar plasma. By the electrostatic interaction between the negative PMMA latex particles and the SPNR grafted with PAAm (SPNR-*g*-PAAm), the possible loss of coated particles is, therefore, overcome. This has been proven by the insignificant change of the amount of PMMA particles on the SPNR-*g*-PAAm film after applying 7 stretched cycles.[3] These particles caused an increase in surface roughness and effectively reduced the friction coefficient of rubber, which resulted from the decrease of contact area between the bodies.[4]

It was reported that the convenient and direct route for reducing real contact area (RCA) and, hence, friction between silicon surfaces was the deposition, followed by dry etching of microparticles having different sizes on the surface.[5] Analysis of the friction of the elastomer, carried out using a friction tribometer with different sizes of spherical steel indenter, confirmed that the friction coefficient decreases with increasing surface roughness directly linked to the decrease of RCA. The model, proposed by Bowden and Tabor, showed that the friction force due to adhesion force on rough surface was determined by the distribution of the number of asperities and asperity heights or shapes in contact.[6,7] Another source of the friction attributed to deformation depends also on the surface asperities of elastic, plastic or viscoelastic material.

As variation in the particle size of coated particles randomly adsorbed on SPNR would affect the hillocks and RCA, effect of the size of PMMA particles on the surface roughness and friction of SPNR-*g*-PAAm was investigated in this present work. The different sizes of PMMA latexes were synthesized by soap-free emulsion polymerization. As in the previous case on monodispersed PMMA, the modified

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rubber was characterized by using scanning electron microscope (SEM), atomic force microscope (AFM), and friction test machine.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) monomer (Fluka, Purum) was purified by passing through a column packed with neutral and basic aluminum oxide (Fluka, Purum). The purified monomer was stored at 4°C until use. Acrylamide (AAm) monomer (Fluka, Purum) and methanol (Merck, AR) were used as received.

Surface modification of SPNR sheet

A dried rubber sheet, casted from SPNR latex (Dr. Boo, Chonburi, Thailand), was pretreated with Ar plasma prior to surface grafting, under UV, with PAAm.[2] The SPNR-*g*-PAAm sheet was then immersed into PMMA latex synthesized by the soap-free emulsion polymerization using potassium persulphate (KPS) as initiator. To obtain anionic PMMA particles with the size of 162, 364, 480, or 626 nm, MMA concentration of 0.18, 1.46, 2.19, or 3.28*M*, respectively, was added in the aqueous solution of KPS (0.18 g) dissolved in deionized water (137 g) and the polymerization took place at 80°C for 2 h. The remaining steps and characterizations were carried out as explained elsewhere.[2] By varying immersion time, latex concentration and ionic strength, the surface coverage (Cs), determined from the ratio of the area of the deposited PMMA particles to the selected area under SEM image (15 × 21 μm^2), could be adjusted.[8]

Characterization of SPNR sheet coated with PMMA particles

Morphology of the modified SPNR sheet surface was examined by using a Multimode AFM (Digital Instrument, Nanoscope IIIa) equipped with Nanoscope IIIa controller in tapping mode with the scan size of 20 × 20 μm^2. Because of the fact that PMMA particles were deposited onto a smooth SPNR surface, the surface mean roughness (R_a) was calculated from Nanoscope software by applying the following equation previously used by Perrin et al.[9]:

$$R_a = \frac{1}{n}\sum_{j=1}^{n}|Z_j|$$

where Z_j is current difference between the height and the mean plane and n is number of points in the image.

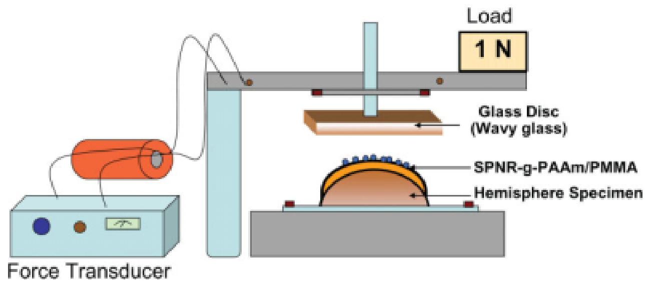

Figure 1 Schematic view of plate-on-hemisphere type friction test machine. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In tapping mode the cantilever is driven to oscillate at near its resonance frequency by a small piezoelectric element mounted on the AFM tip holder.[10] An electronic servo uses the piezoelectric actuator to control the height of the cantilever above the sample to maintain an oscillation amplitude while the cantilever is scanned over the sample. A height image is, therefore, produced by imaging the force of the oscillating contacts of the tip with the sample surface. The friction coefficient of the SPNR-*g*-PAAm coated with PMMA particles was then measured by using a friction test machine (TE 75R, Plint) as schematically shown in Figure 1.

The device consists of a wavy glass disc, fixed on the arm of counterbalance connected to the force transducer. Load was applied by a dead weight at 1*N* on a tip of counterbalance. The specimen (2.5 × 5.0 cm^2) was clamped on a rubber hemisphere. The friction coefficient was measured by moving the glass surface against the specimen with stroke length of 5 mm at a speed of 0.25 mm/s in six cycles and four directions.

RESULTS AND DISCUSSION

Effect of NaCl on %Cs

Because of the fact that the thickness of electrical double layer or Debye length (κ^{-1}) affects the hydrodynamic volume of charge particle, the effect of ionic strength of PMMA latex, with the smallest particle size (162 nm), on %Cs was investigated. Both the zeta potential of PMMA latex and %Cs values as a function of NaCl concentration are presented in Figure 2.

As expected, the Cs increased from 7.7 to 12.3% with increasing [NaCl] from 0 to 0.1*M* which correlated well with the decrease of the absolute value of zeta potential from −40 to −30 mV. It could be explained that the presence of NaCl compressed the electrical double layer and decreased the repulsion among the charged particles which, consequently, allowed the high number of particles to deposit onto

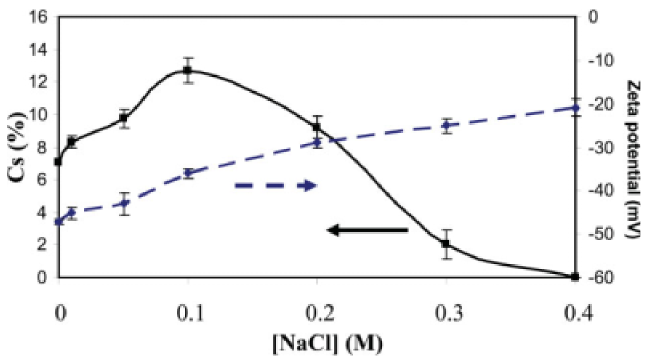

Figure 2 Effect of NaCl concentration on zeta potential of PMMA latex particle (162 nm) and on %Cs values of SPNR-*g*-PAAm sheet coated with the PMMA ([PMMA] = 3 mg/mL, pH 4, immersion time = 30 min). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the SPNR-*g*-PAAm surface.[11] However, with increasing [NaCl] greater than 0.1*M*, the Cs values suddenly decreased and coagulation visually appeared due to the instability of particles possibly caused by screening of the surface charge on the particles by Na^+ and Cl^-. The results also agreed well with the zeta potential value which illustrated that the charged colloidal particles are unstable in the range of −30 to + 30 mV.[12]

The higher Cs value when adding 0.1*M* NaCl (12.3%) compared to that in the absence of NaCl (7.7%) was clearly observed under SEM. The micrographs of the SPNR-*g*-PAAm film surfaces coated with PMMA latex particles without NaCl and with adding 0.1*M* NaCl are, respectively, shown in Figure 3(a,b).

It has been reported that the influence of electrical double layer of small particles on the surface coverage is more significant than that of large particles,[8,13] the maximum %Cs when depositing PMMA particles with the smallest size of 162 nm was selected for further investigation. In the study of the effect of PMMA particle size on the surface roughness and friction of the modified rubber, the Cs value of SPNR-*g*-PAAm sheets adsorbed with PMMA particles having sizes of 162, 364, 480, or 626 nm was fixed at 12% by varying the latex concentration and immersion time.

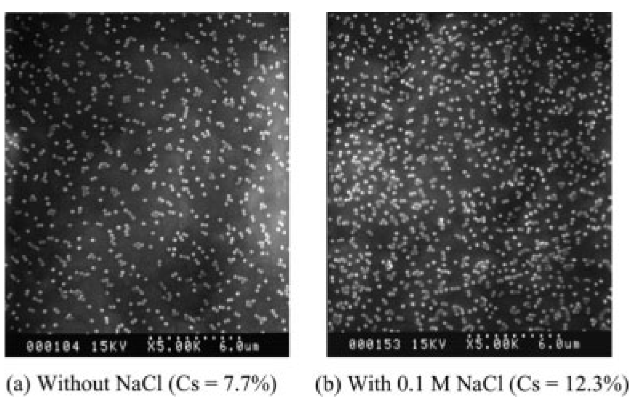

Figure 3 SEM micrographs of SPNR-*g*-PAAm surfaces adsorbed with PMMA particles; (a) without NaCl and (b) with adding 0.1*M* NaCl ([PMMA] = 3 mg/mL, pH 4, immersion time = 30 min).

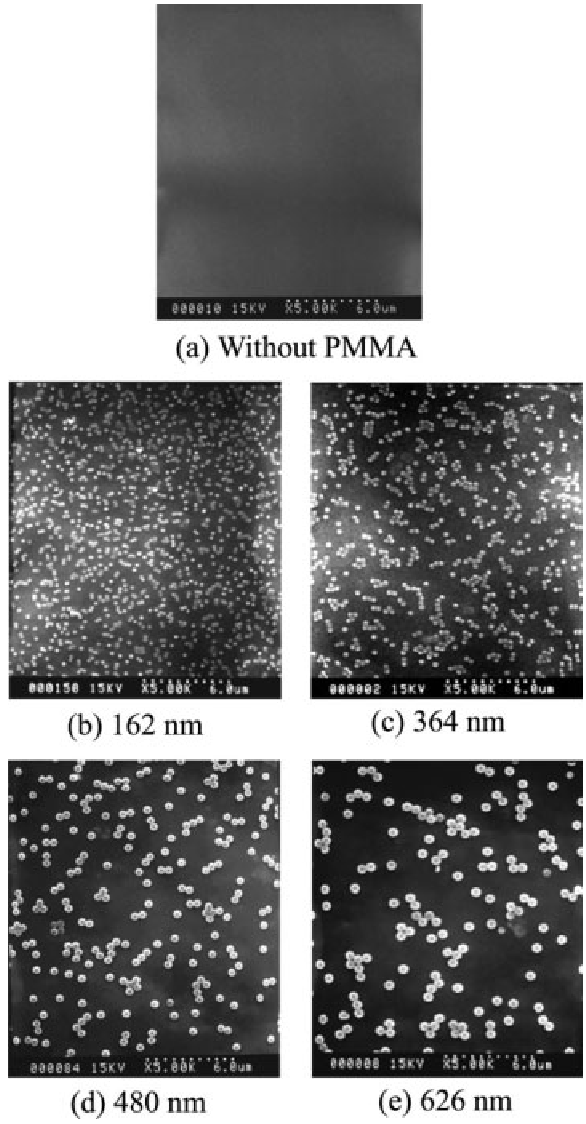

Figure 4 Surface morphology of (a) SPNR-*g*-PAAm and SPNR-*g*-PAAm surfaces coated with PMMA particles sizes of (b) 162, (c) 364, (d) 480, (e) 626 nm (Cs = 12%).

Effect of PMMA particle size

Figures 4 and 5 show the surface morphology, obtained from using SEM and AFM, of (a) SPNR-*g*-PAAm and SPNR-*g*-PAAm films after being deposited with PMMA particles having sizes of (b) 162, (c) 364 (d) 480 and (e) 626 nm at 12% Cs.

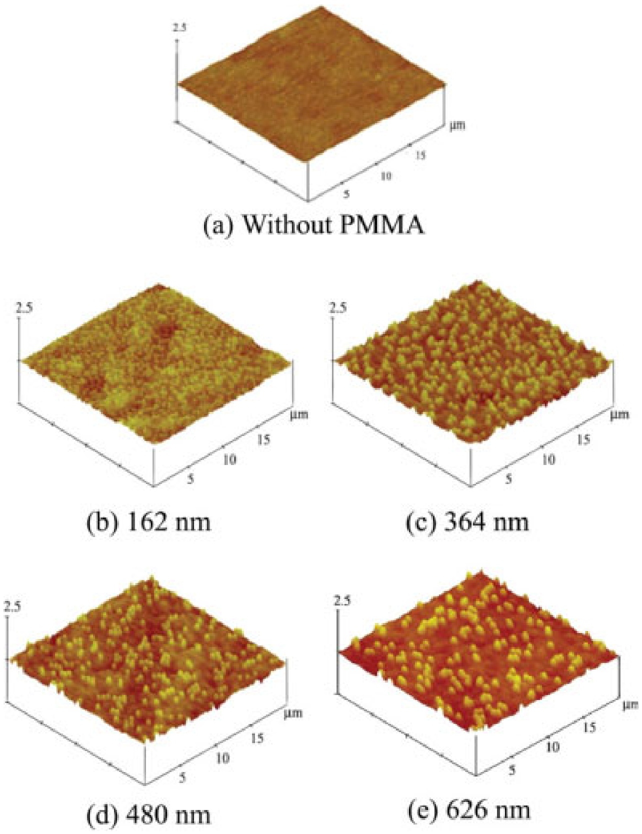

Figure 5 AFM images of (a) SPNR-*g*-PAAm and SPNR-*g*-PAAm surfaces coated with PMMA particles having sizes of (b) 162, (c) 364, (d) 480, (e) 626 nm (Cs = 12%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The micrographs in Figures 4 and 5 clearly showed that the PMMA particles adsorbed onto the rubber sheet in the form of monolayer possibly due to the strong repulsion between charge particles.[14] However, some aggregates were formed especially when using the large particles (626 nm). It can be explained by the effect of capillary force which is theoretically two order of magnitude higher than the electrostatic repulsive force of particles.[14,15] Moreover, the attractive capillary force between two particles during drying is proportional to the square of the diameter.

To obtain the surface mean roughness (R_a) value of the SPNR-*g*-PAAm sheets coated with PMMA particles, the AFM in tapping mode was used and the R_a values, obtained from the topographic images, plotted versus particle sizes are displayed in Figure 6.

The results clearly indicated that the R_a of SPNR-*g*-PAAm sheet coated with PMMA increased with increasing PMMA particle size at fixed *Cs*. It is likely that the decrease of contact area of the top surface of the sample is responsible for this observation. The presence of hard PMMA particles on the SPNR-*g*-PAAm surface resulted in the change in both surface chemical compositions and surface roughness. Consequently, the friction coefficient reduced from 2.2 for SPNR-*g*-PAAm (R_a = 29.7 nm) to 2.0 for SPNR-*g*-PAAm sheets coated with PMMA particles having particle size of 162 nm (R_a = 49.9 nm). However, for the rubber sheets coated with PMMA particles series, the %Cs was maintained at 12%, thus, friction force in this case is mainly dependent on the roughness, which directly linked to the real contact area. The increase in R_a from 49.9 to 72.6 nm corresponded to the decrease of the friction coefficient from 2.0 for SPNR-*g*-PAAm sheets coated with PMMA particles having particle size of 162 nm to 1.4 for the rubber sheet coated with PMMA having large particle size (626 nm) as shown in Figure 6.

Effect of %Cs

Because of the fact that the larger PMMA particle deposited onto the SPNR-*g*-PAAm provided the lower surface friction at fixed Cs, the largest PMMA particle size was selected for the study of the effect of %Cs on surface roughness and friction of the rubber. The SEM and AFM micrographs of the SPNR-*g*-PAAm surfaces coated with PMMA particles (626 nm) at various Cs values, obtained by varying dipping time and latex concentration, are presented in Figure 7.

As previously observed, the topographic images showed that these large PMMA particles, especially at high %Cs in Figure 7(e,f), arranged onto the SPNR-*g*-PAAm surface in aggregate form. Besides the capillary force, the bridging effect caused from the grafted PAAm chain which dangled into the solution and attached several latex particles might be responsible for the aggregation.[16] These aggregates

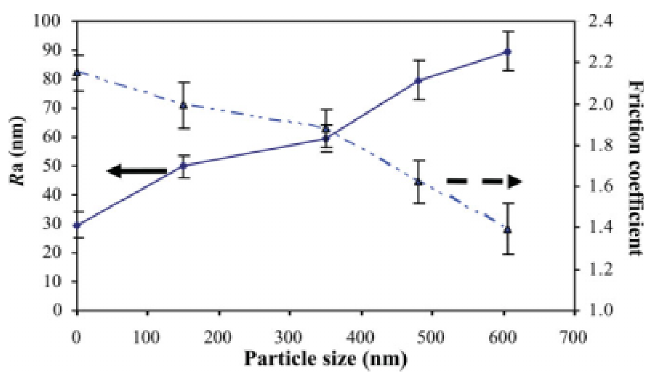

Figure 6 Surface mean roughness (R_a) and friction coefficient of SPNR-*g*-PAAm and SPNR-*g*-PAAm sheets coated with PMMA particles having various sizes (Cs = 12%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

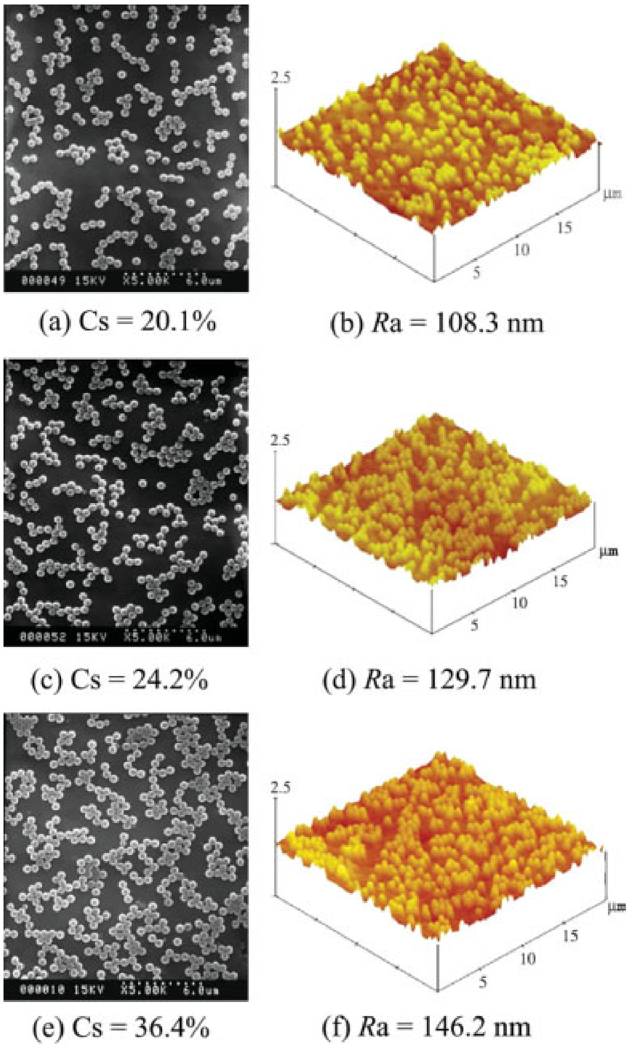

Figure 7 SEM and AFM micrographs of SPNR-*g*-PAAm surfaces coated with PMMA particles of 626 nm showing various %Cs and R_a. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

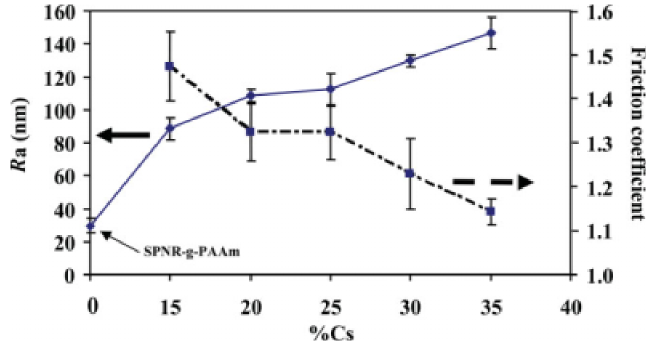

Figure 8 Effects of Cs value on R_a and friction coefficient of SPNR-*g*-PAAm surface coated with PMMA particles (626 nm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

could alter the surface asperities and, consequently, the R_a value was nonlinearly proportional to the %Cs as displayed in Figure 8.[17] An increase of R_a also led to a marked reduction in friction coefficient of the modified SPNR as also shown in Figure 8.

To confirm the stability of PMMA particles deposited onto the SPNR-*g*-PAAm surface, the SEM micrographs of the modified SPNR surface before and after rubbing for six cycles in four directions under the friction test machine are shown in Figure 9. The slightly change of %Cs from 36.4 to 33.4 might be due to the grafting PAAm chains which are able to increase the interfacial adhesion between particle and matrix.[18] It was, therefore, concluded that the SPNR-*g*-PAAm coated with PMMA particles was stable under the rubbing conditions.

Effect of polydispersity of PMMA particles

The highest Cs value of 36.4% obtained from using the largest size PMMA of 626 nm was still lower than that of the calculated value using the random sequential adsorption (RSA) model (54.7%) which indicated the SPNR-*g*-PAAm surface could not be completely covered. It should be noted that the presence of various complex particle-particle, particle-surface or hydrodynamic interactions is not considered in the RSA model.[18]

To increase the amount of PMMA particles on the surface, the deposition of a mixture of latexes having both large and small particle sizes of 162 and 626 nm on the rubber substrate was, therefore, attempted. It was believed that the small particles might adsorb into the interstices between large particles.[18] The %Cs values as a function of various number ratios of the large to small particles (N_L : N_S) are presented in Figure 10. The SEM micrographs of

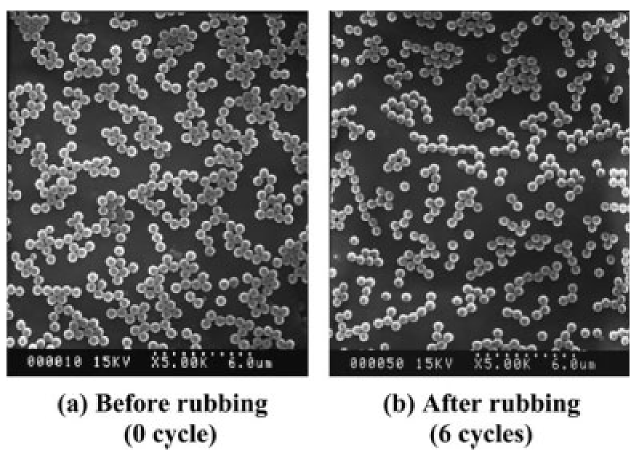

Figure 9 SEM micrographs of SPNR-*g*-PAAm surfaces coated with PMMA particles of 626 nm (a) before and (b) after rubbing for six cycles

the SPNR-*g*-PAAm surfaces at $N_L : N_S$ of 1 : 4, 1 : 12, and 1 : 17 are, respectively, displayed in Figure 11(a–c) while Figure 11(d) shows the AFM micrograph when $N_L : N_S$ was 1 : 17.

The results in Figure 10 revealed that the total Cs value decreased with increasing $N_L : N_S$ from 1 : 1 to 1 : 17. At a ratio greater than 1 : 17, the Cs approached a constant value of about 16% which might be explained by the selective deposition of the smaller particles resulting in smaller surface coverage as shown in Figure 11. The increasing number of N_S resulted in a decrease of %Cs. The reason for size selection is a combination of three mechanisms, i.e., (i) smaller particles diffuse faster to the surface from the bulk solution, (ii) small particles adsorbed on the surface may block a comparatively large area for adsorption of larger particles, and (iii) small particles can adsorb in the spaces between larger particles, not accessible for the large particles themselves.[19]

The better distribution of large particles with increasing the quantity of small particles was observed in Figure 11(c). This might be due to the high thickness of electrical double layer of the small particle which, consequently, increased the space between large particles and impeded their approach.[13,19] Similar effect of particle polydispersity on surface coverage was previously reported when a mixture of two silica particle sizes (100 and 500 nm) were adsorbed onto Si substrate having polyelectrolyte multilayer formation.[8] It should be noticed that at the Cs of 15%, the R_a obtained when using bimodal particle size in Figure 11(d) (105 nm) was greater than that obtained when using monodispersed PMMA particle (90 nm) as shown in Figure 8. The increase in R_a in the former case would increase RCA and, hence, potentially reduce the surface friction of rubber sheet.

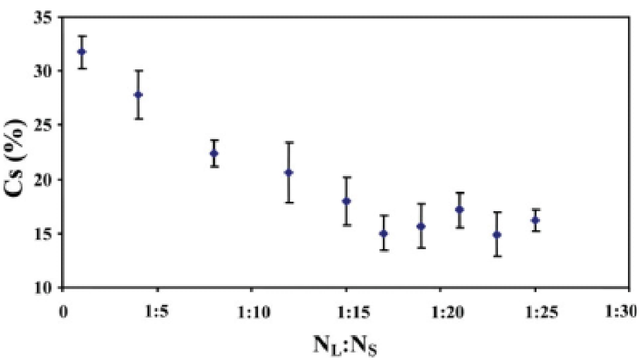

Figure 10 Effect of number ratios of the large (626 nm) to the small particles (162 nm) of PMMA latexes ($N_L : N_S$) on %Cs of the coated SPNR-*g*-PAAm surfaces. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

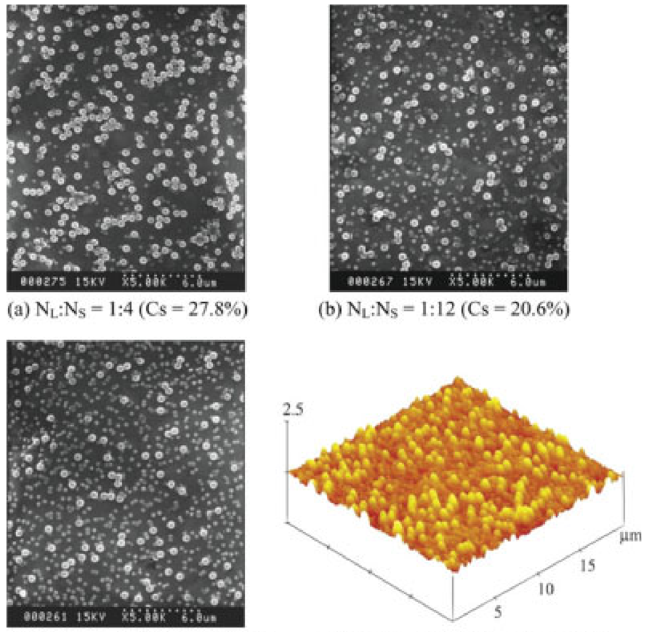

Figure 11 SEM micrographs of SPNR-*g*-PAAm surfaces deposited with a mixture of two PMMA latexes having number ratio of large (626 nm) to small (162 nm) particles ($N_L : N_S$) of (a) 1 : 4 (b) 1 : 12 and (c) 1 : 17 and (d) AFM micrograph at $N_L : N_S$ of 1 : 17. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

At the same %Cs value, the high surface roughness and, hence, low friction coefficient of the SPNR-*g*-PAAm sheet were obtained from coating with PMMA particle having large size (626 nm). By deposition of the large PMMA particles, both surface roughness and friction of the substrate could be further decreased with increasing %Cs. An attempt to cover the surface with the mixture of latex having both small (162 nm) and large particle sizes (626 nm) resulted in a better distribution of large particles which caused a slightly increase in R_a.

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