Physico-Mechanical Properties of Natural Rubber Sheets Coated by Polyethyleneimine-Functionalized Poly(methyl methacrylate) Nanoparticles

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ABSTRACT: The surface modification of sulfur-prevulcanized natural rubber (SPNR) sheets by the polyethyleneimine-functionalized-poly(methyl methacrylate) (PMMA/PEI) nanoparticles was successfully performed via a simple dipping method. The percentage of surface coverage (C_s) of the nanoparticles on SPNR sheets was found to be affected by a variation of nanoparticle latex concentrations and immersion times. The adsorption isotherm of PMMA/PEI nanoparticles on SPNR sheets was analyzed and found to fit well to the Freundlich model. After coating, it can be observed that the presence of PMMA/PEI nanoparticles on SPNR surface had no effects over the SPNR mechanical properties e.g., tensile strength, elongation at break, and hardness. On the other hand, the coated SPNR sheets showed a reduction of surface friction coefficients and interfacial adhesion up to 45 and 59%, respectively. Furthermore, PMMA/PEI nanoparticles adsorbed on the SPNR surface was subjected to stretching and wearing conditions, and found to be stable for at least seven stretching and wearing cycles. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 49–57, 2012

Key words: surface modification; core-shell polymer; adsorption; PMMA/PEI nanoparticle; natural rubber sheet

INTRODUCTION

Natural rubber (NR) from *Hevea brasiliensis* is a naturally occurring polymer that has been utilized in a large and increasing amount in recent years. NR is widely used in many applications such as tubing, balloons, condoms, tires, and gloves. For utilizing NR in the forms of thin articles, even though it has excellent elasticity and flexibility, the relatively high tack and surface friction limit its uses in some applications.[1] Thus, to diminish such limitation, several approaches on surface modification of NR without influencing its bulk properties have extensively investigated. For example, powder talc or corn starch was applied on the surface of NR gloves to reduce friction when in contact with human skin. Unfortunately, such additives may be immunogenic itself.[2–4] The powder-free gloves were also developed by using a halogenation treatment. However, the halogenated NR gloves become hard and brittle, and their color turns dark while their surface is very slippery after using for a period of time.[5,6] Interestingly, there was a report showing that the presence of functionalized hard particles chemically bonded to the glove surface can decrease the overall friction coefficient of its surface and permit the glove to be donned more readily.[7] In the similar purpose, Sruanganurak et al. reported on a deposition of hard PMMA latex particles onto the polyacrylamide (PAAm) grafted NR sheets via layer-by-layer (LbL) technique.[8]

Previously, we are the first to report a convenient surface modification of SPNR sheet by polyethyleneimine-functionalized poly(methyl methacrylate) (PMMA/PEI) nanoparticles. The modification was successful without pretreatment steps of the SPNR sheet.[9] The SPNR sheet was simply immersed into the latex dispersion of such nanoparticles. It is hypothesized that PEI located on the PMMA/PEI particles' surface becomes positively charged due to the protonation of amine groups on its chemical backbone.[10] These positively charged groups could physically interact with negatively charged nonrubber

components (e.g., long chain fatty acid soaps, and polypeptides) on SPNR sheets via electrostatic interaction in aqueous media, leading to an adsorption of the particles on the surface of SPNR sheet. The presence of PMMA/PEI nanoparticles on SPNR sheet was revealed by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). This leads to the changes in surface roughness, adhesion force, and relative surface stiffness determined using atomic force microscopy (AFM) analysis.

To continue our study on this simple surface modification of NR sheet, further indispensable investigation was described herein. The in-depth analysis for the adsorption behavior of PMMA/PEI nanoparticles on SPNR sheets was investigated. The effect of PMMA/PEI nanoparticle coating on physicomechanical properties of SPNR sheet, including tensile strength, elongation at break, and hardness were also investigated. The interfacial adhesion and surface friction as a variation of surface coverage (C_s) values were examined by a peel test and a friction test, respectively. Finally, the physical stability of the PMMA/PEI coating layers on SPNR sheet was determined by SEM and AFM after subjected to several simulated stretching and wearing cycles.

EXPERIMENTAL

Materials

High ammonia-preserved NR (HA-NR) latex was obtained from Bangkok Rubber, Rayong, Thailand. Sulfur, zinc oxide (ZnO), zinc diethyldithiocarbamate (ZDEC), and Lovenox used were purchased from Lucky Four, Nonthaburi, Thailand. Methyl methacrylate (MMA) monomer (Fluka, Purum), was purified by passing through a column packed with neutral and basic aluminum oxide adsorbents (Fluka, Purum). PEI, MW of 750,000 (Aldrich, 50 wt % aqueous solution) was diluted by distilled water to 10 wt % before subjected to polymerization. Other reagents, e.g., t-butyl hydroperoxide (TBHP) (Fluka, 70%), potassium hydroxide (KOH) (AnalaR, pellets), potassium laurate (Fluka, Purum), or methanol (Fisher, AR) were used without prior treatment.

Synthesis and characterization of PMMA/PEI nanoparticles

The general synthesis procedure of PMMA/PEI nanoparticles and their characterization techniques used in this work were fully described in Ref. 9.

Preparation and characterization of SPNR sheets

Preparation of SPNR sheets

The detailed formulation used for preparing SPNR latex was reported in Ref. 9. Briefly, a concentrated NR

latex, having $\sim$ 60% dry rubber content (DRC), was transferred into a reaction vessel. After adding the stabilizers, i.e., KOH, potassium laurate solution, Lovenox, and vulcanizing reagents, i.e., sulfur, ZDEC, and ZnO, into NR latex, the mixture was stirred at 70°C with a speed of 150 rpm for 90 min. At the end of reaction, the prevulcanized latex was obtained and rapidly cooled to room temperature to prevent further vulcanization.

SPNR was casted onto a glass plate and allowed to dry at room temperature. Afterward, dried SPNR sheets were placed in an oven at 70°C for 60 min. The dried SPNR sheets (0.1 $\times$ 1.5 $\times$ 4 cm^3) was subsequently adhered on a poly(ethylene terephthalate) (PET) sheet to maintain their dimension. The SPNR surface was cleaned by immersing in methanol and then water for about 15 min in each step, and sonicating in an ultrasonic bath. Then, the SPNR sheets were allowed to dry in air, and kept in a desiccator for further use.

Determination of swelling ratio and crosslink density of SPNR sheets

The crosslink density of rubber sheets casted from SPNR latex was determined by using the swelling method. The dried rubber sheet was cut into small pieces ($\approx$ 0.2 g) and immersed in toluene (40 mL) at room temperature for seven days. The swollen specimen was removed from the toluene, and the excess of toluene was blotted with towel paper. Then, the sample was placed in a weighing bottle and weighed accurately. The swelling ratio (Q) of crosslinked rubber sheet was calculated as follows:

$$\text{Swelling ratio}(Q)(\%) = \frac{W_2 - W_1}{W_1} \times 100, \quad (1)$$

where W_1 = weight of dried rubber before swelling (g), and W_2 = weight of swollen rubber after equilibrium swelling (g).

Density of matrix network chains (v_c) was determined from the Flory-Rehner equation[11]:

$$-[\ln(1 - v_2) + v_2 + \chi_1 v_2^2] = V_1 v_c \left[v_2^{1/3} - \frac{v_2}{2} \right] \quad (2)$$

where v_2 is the volume fraction of polymer in the swollen mass, V_1 is the molar volume of the solvent (106.3 cm^3/mol for toluene), v_c represents the number of active network chains per unit volume, and χ_1 is Flory-Huggins polymer–solvent dimensionless interaction term (0.39 for the NR-toluene system).

The volume fraction of a rubber network in the swollen phase is calculated from equilibrium swelling data as[12]:

$$v_2 = \frac{\left(\frac{W_2}{d_2} \right)}{\left(\frac{W_1}{d_1} \right) + \left(\frac{W_2}{d_2} \right)} \quad (3)$$

where W_1 is the weight fraction of solvent, d_1 is the density of solvent (toluene = 0.8662 g/cm^3), W_2 is the weight fraction of the polymer in swollen specimen, and d_2 is the density of polymer (rubber hydrocarbon = 0.92 g/cm^3).

Adsorption of PMMA/PEI nanoparticles on SPNR sheets and determination of C_s values

The SPNR sheets were dipped in a glassware ($r = 1$ cm, $h = 10$ cm), containing 1.25–15.00% TSC of PMMA/PEI latex. The immersion time was varied from 10 to 60 min. The excess of latex was removed by washing through a series of three rinsing water baths. The immersion and withdrawal times were at 5, 20, and 60 s in those three rinsing baths 1, 2, and 3, respectively.

The surfaces of coated SPNR sheet were clarified by SEM (SEM 2300s, Hitachi), and AFM (Model Ns3a, Digital Instrument) equipped with Nanoscope IIIa controller via the tapping mode with a scan size of 10×10 μm^2 at six different locations. The surface coverage (C_s) values, indicating the amount of PMMA/PEI nanoparticles adsorbed per unit area of the sheet surface, were determined by the image analysis of SEM and AFM micrographs. C_s values were then calculated by the following equation[13]:

$$\text{Surface coverage(Cs)}(\%) = \frac{N}{N_{\max}} \times 100, \quad (4)$$

where N is the number of nanoparticles per unit area; $N_{\max}$ is the maximum number of nanoparticles on the same area assuming a hexagonal dense packing of particles.[14]

Adsorption isotherms were attained using two typical adsorption isotherms: Langmuir and Freundlich models. The parameters used in fitting these isotherms are C_e and q. The C_e values (particles/L) were assumed to be equal to the initial concentration of PMMA/PEI latex calculated from % TSCs. The q values (particles/m^2) was converted from C_s (%) values. The Langmuir model is represented by the following equation[15]:

$$q = \frac{q_m b C_e}{1 + b C_c} \quad \text{or} \quad \frac{C_e}{q} = \frac{1}{b q_m} + \frac{C_e}{q_m}, \quad (5)$$

where C_e = equilibrium concentration of the PMMA/PEI latex; q = surface coverage; q_m = maximum surface coverage; b = Langmuir constant.

The plot of $\frac{C_e}{q}$ against C_e will yield a straight line with a slope of $\frac{1}{q_m}$ and intercept of $\frac{1}{b q_m}$. While, the Freundlich isotherm is described by eq. (6)[16]:

$$q = K_f C_e^{1/n} \quad \text{or} \quad \log q = \log K_f + \frac{1}{n} \log C_e, \quad (6)$$

where the additional parameters K_f = Freundlich constant and n = the numerical value of Freundlich constant

A linear of $\log q$ versus $\log C_e$ gives a slope of $1/n$ and intercept of $\log K_f$.

Physical–mechanical property measurement of surface-modified SPNR sheets

Tensile properties of modified rubber sheets

Tensile strength and elongation at break of the modified rubber were measured according to ASTM D412-98a, using an Instron tensile tester (model 5566) at a crosshead speed of 500 mm/min with the load cell of 1000N. Dumbbell specimens were stamped out from the casted SPNR sheet using a sharp die. At least five specimens were used for a measurement.

Hardness (shore A)

The hardness of modified SPNR sheets was measured by following the ASTM D2240-97. The square specimen having 6 mm in thickness and smooth surface was placed on the platform of hardness tester (Wallace H17A Hardness tester). Then, measurements were made at different positions on the specimen. An average of 10 positions was taken as the hardness value of the tested sample.

Determination of friction coefficient of SPNR sheets

The coefficient of friction of SPNR sheets was determined by measuring the friction at extremely low speed.[17] A circular rubber specimen ($d = 4.50$ cm) fixed to a polyethylene (PE) capped by a double-sided sticky tape on a smooth TEFLON board was used. The string was treaded through the PE cap, passed through the pulley at the other end of the TEFLON board, and attached to a weight bottle. The experimental setup is available in the supporting materials.

A weight of 100 g was placed on the sample to provide a normal load. The weight was added to the weight bottle until the cap just started to move at the average speed of 0.2 cm/min. The required load was recorded. The experiment was again repeated, commencing with the cap at the same position. The friction could be calculated according to the following equation:

$$F = \mu N \quad (7)$$

where F = frictional force (N), μ = coefficient of friction, and N = normal force (N).

Measurement of peel strength

To measure the adhesion force between the rubber sheets when they are adhered together, the T-peel test was carried out. Two dried rubber sheets having dimension of $0.1 \times 2.5 \times 15$ cm^3 were adhered together. Then, the roller with a weight of 2 kg was passed over the samples at the approximate rate of 300 mm/min without an application of additional pressure. After 20 min, the strength of interfacial adhesion between the rubber sheets was determined by using the Instron testing machine (Model 5569). The measurement was carried out at a crosshead speed of 50 mm/min with the load cell of 10N. Five specimens were tested for each sample. Then, peel strength was determined by using the following equation:

$$\text{Peel strength} = \frac{2F}{W} (\text{J/m}^2) \qquad (8)$$

where F = Force required to separate the rubber sample (N), and W = Width of the specimen (m).

Physical stability of PMMA/PEI nanoparticle monolayer coated on SPNR sheets

The physical stability of PMMA/PEI nanoparticle coating layers on the SPNR sheets was investigated through the changes of C_s values as a result of stretching and wearing conditions.

Stretching test

The sample was stretched to 300% strain by the tensile tester and then allowed to recover to the original position at a rate of 50 mm/min. Consequently, the surface of stretched SPNR sheet was characterized by SEM.

Wearing test

The equipment used in this test was the same as that used for determining the friction coefficient. A weight of 100 g was placed on the sample to provide a normal load. The weight was added to the weight bottle until the cap just started to move at the average speed of 10.0 cm/min for 5 cm. Subsequently, the surface of the sample was characterized by SEM.

RESULTS AND DISCUSSION

Adsorption of PMMA/PEI nanoparticles on SPNR sheets and C_s values

The PMMA/PEI nanoparticle latex, synthesized by the soap-free emulsion polymerization, was subjected to size and zeta potential measurements. The

TABLE I
C_s (%) of PMMA/PEI Nanoparticles at Various % TSC and Immersion Times

Immersion time (min)	C_s (%)			
	1.25% TSC	5.00% TSC	10.00% TSC	15.00% TSC
10	0.85 ± 0.66	5.31 ± 1.03	19.77 ± 3.95	25.21 ± 5.43
20	1.18 ± 0.35	8.24 ± 2.28	21.21 ± 0.68	24.87 ± 2.07
30	1.64 ± 0.53	9.18 ± 2.90	19.77 ± 2.24	27.44 ± 5.98
40	2.08 ± 1.56	10.88 ± 3.30	19.69 ± 4.58	28.14 ± 1.70
50	2.22 ± 2.57	10.64 ± 3.10	21.90 ± 4.17	29.35 ± 4.37
60	2.97 ± 0.95	9.87 ± 3.75	26.92 ± 2.99	28.16 ± 1.58

data from the Master Sizer showed that the average diameter of PMMA/PEI nanoparticle was 130 ± 4 nm with narrow size distribution. The zeta potential was + 56 mV, indicating the presence of amine groups in their protonated states on the nanoparticle surfaces. These protonated groups are hypothesized to play a significant role in the electrostatic interaction with non-rubber negative species (e.g., long-chain fatty acid soaps, and polypeptides), existing on the SPNR surface. Before conducting the surface modification process, the swelling ratio, and the crosslink density of SPNR sheets were evaluated. The % swelling ratio of rubber sheets can be used to approximately indicate its crosslinking density.[11] After the samples were immersed in toluene, the calculated results showed that the % swelling ratio was approximately 568.54%. In addition, the calculated volume fraction (v_2) of 0.168 was also obtained. Finally, the network chain density (v_c) relating to the crosslink density of rubber was derived as 9.88×10^{-5} mol/cm^3. These values indicated that the SPNR sheets fabricated in this present condition were not fully crosslinked.[8,11] However, its mechanical properties were in an acceptable range, as confirmed by the evidence in section Properties of PMMA/PEI-coated SPNR sheets.

In the adsorption process by a simple dipping method, two process parameters: the %TSC of PMMA/PEI latex and immersion times, were varied. The PMMA/PEI-coated SPNR sheets were then characterized by SEM and AFM, and C_s values were determined from those micrographs. The effect of %TSC of PMMA/PEI latex and immersion times on the C_s values of PMMA/PEI nanoparticles adsorbed on SPNR sheets is shown in Table I. From Table I, it can be seen that the C_s values increased with immersion time in the immersion periods of 10–40 min for all latex concentration levels and became slowly increased after 40 min. The slightly change of C_s values at the time longer than 40 min implied that the deposition-detachment process might reach the equilibrium state where the rates of deposition and detachment of the particles are equal. Moreover, the

TABLE II
q Values of PMMA/PEI Nanoparticles at Various C_e and Immersion Times

Immersion time (min)	q (10^{16} particle /m^2)			
	2.89 (10^{19} particles /L)	11.53 (10^{19} particles/L)	23.00 (10^{19} particles/L)	34.59 (10^{19} particles/L)
10	0.77	4.83	17.99	22.94
20	1.07	7.50	19.30	22.63
30	1.49	8.35	17.99	24.97
40	1.89	9.9	17.92	25.61
50	2.02	9.68	19.93	26.71
60	2.70	8.98	24.50	25.63

TABLE III
Freundlich Constants For the Adsorption of PMMA/PEI Nanoparticles on SPNR Sheets at Various Immersion Times

Immersion time (min)	Freundlich constants		
	K_f (10^{16} particles/m^2)	N	Correlation coefficient R^2
10	0.1679	0.7037	0.989
20	0.2963	0.7818	0.986
30	0.4581	0.8668	0.995
40	0.6540	0.9470	0.993
50	0.6823	0.9449	0.996
60	0.9592	1.0396	0.976

results showed that the higher concentrations provided the higher C_s values for all immersion times.

On the effect of latex concentration, the fitting of experimental data for all immersion times to two typical adsorption isotherms: Langmuir and Fruendlich models, was also attempted. The concentration levels of PMMA/PEI latex were assumed to be at equilibrium and represented as C_e (particles/L), and the C_s values were represented as q (particles/m^2) as illustrated in Table II. It was observed that the linear regressions were obtained only with the Freundlich model (Fig. 1) (the nonlinear plots obtained from Langmuir model were shown in supporting materials). Freundlich constants (K_f and n) for the adsorption of PMMA/PEI nanoparticles on SPNR sheets were shown in Table III. This leads to the summary that the adsorption behavior of PMMA/PEI nanoparticles on SPNR sheets is more likely following the Freundlich adsorption, assuming the SPNR sheet has a heterogeneous surface or a surface with active sites of various affinities.

Properties of PMMA/PEI-coated SPNR sheets

Hardness and tensile properties

Because of the concern that properties of SPNR sheets may be affected by coating of PMMA/PEI nanoparticles, the hardness and tensile properties of SPNR sheets coated with PMMA/PEI nanopar-
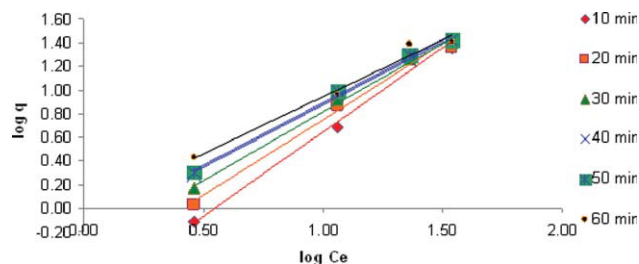
ticles were acquired. Figure 2 presents the effect of C_s values of PMMA/PEI nanoparticles on the hardness of PMMA/PEI-coated SPNR sheets. It can be seen that by varying the C_s values from 0 to 37%, the hardness levels were around 41–43 Shore A. The similar values of hardness upon changing the C_s values could assure that the presence of PMMA/PEI nanoparticles did not affect the property of the SPNR sheets.

The tensile strength and elongation at break of SPNR sheets plotted against the C_s values are displayed in Figures 3 and 4, respectively. The tensile strengths of the uncoated and coated SPNR sheets by varying the C_s values from 0 to 28% were not much different and in a range of 24.5–26.7 MPa. Similarly, the elongations at break of both uncoated and coated SPNR sheets were not much different and in a range of 830–890%. These properties could evidently confirm that the coating of PMMA/PEI nanoparticles on the SPNR sheet did not significantly affect its bulk properties. Moreover, it was found that both tensile strength and elongation at break values of SPNR sheets coated with PMMA/PEI nanoparticles were in an acceptable range according to the standard gloves test (ASTM D 3577).
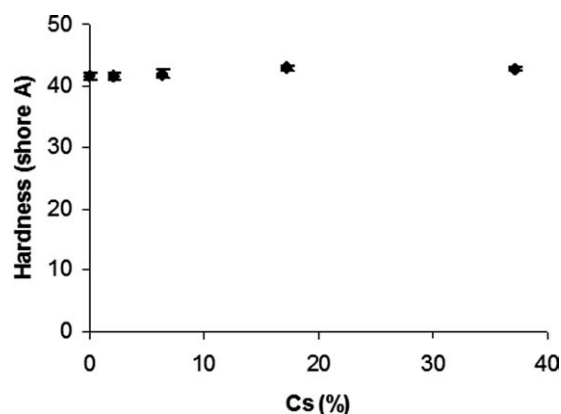

Figure 1 Freundlich adsorption isotherms of PMMA/PEI nanoparticles on SPNR sheets at various immersion times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

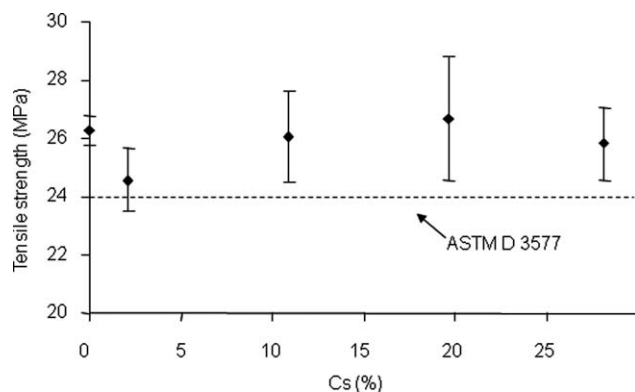**Figure 2** Hardness of SPNR and modified SPNR sheets containing various C_s values.

Figure 3 Effect of C_s values on tensile strength of SPNR sheets.

Coefficient of friction of PMMA/PEI-coated SPNR sheets

From Figure 5, it can be seen that the coefficient of friction decreased from 3.09 to 1.69 when increasing the C_s from 0.00 to 49.48%. The decrease of coefficient of friction clarified that the presence of PMMA/PEI nanoparticles on the SPNR surface would potentially reduce the friction force of the rubber sheet. Anancharungsuk et al.[18] found that the friction coefficient of SPNR-*g*-PAAm sheets coated with lean PMMA particles decreased with the size of PMMA particles and C_s values. At 626 nm of PMMA particles and the C_s value of 36.4%, the friction coefficient can be reduced to $\sim$ 1.2 or 45% reduction. In our work, the lowest friction coefficient obtained was 1.7 (at 130 nm of PMMA/PEI particles and C_s value of 49.5%). The difference in friction coefficient values would be from the differences in the size of hard particles used and % C_s values. In addition, it was found that the % reduction of friction coefficient were similar (45% reduction) for both cases. However, the presence of soft PEI layers on the PMMA/PEI particles' surface in our work has proven a more convenience for modification of SPNR sheets. This result indicated that
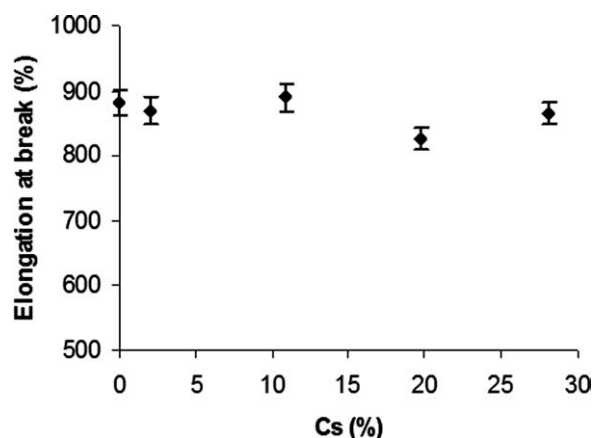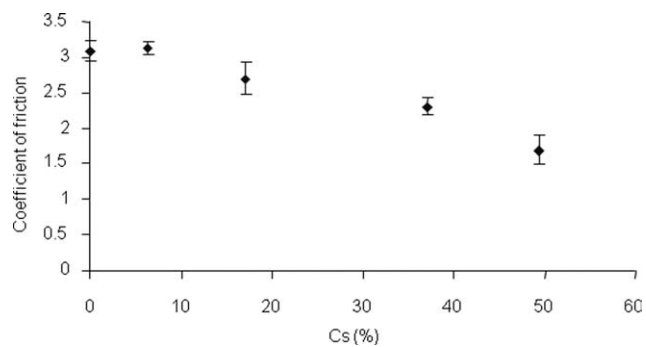

Figure 5 Effect of C_s values on coefficient of friction of SPNR sheets.

this treatment can be an alternative method for making the rubber products (e.g., medical gloves) with lower surface friction, which are donned more easily and convenient for users.

Peel strength of PMMA/PEI-coated SPNR sheets

A peel test was used to illustrate the peel strength between PMMA/PEI-coated SPNR surfaces. The peel strength of the coated SPNR sheets having different C_s values is illustrated in Figure 6. It was clearly seen that the peel strength rapidly decreased from 37.67 to 21.97 J/m^2, when the C_s values increased from 0.00% to 7.61%. These results suggest that the presence of PMMA/PEI nanoparticles on SPNR surface could decrease their adhesion force between each other. Furthermore, the peel strength continuously decreased when C_s was increased, indicating that the adhesion force between the PMMA/PEI-coated SPNR sheets decreased as a function of PMMA/PEI nanoparticles' surface coverage.

Physical stability of PMMA/PEI nanoparticle coating layers

In fact, the rubber products such as the latex glove might be stretched and abraded when it is being
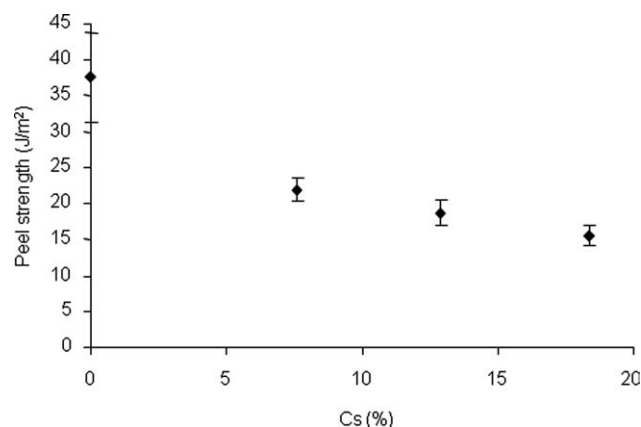

Figure 4 Effect of C_s values on elongation at break of SPNR sheets.

Figure 6 Effect of C_s values on peel strength of SPNR sheets.
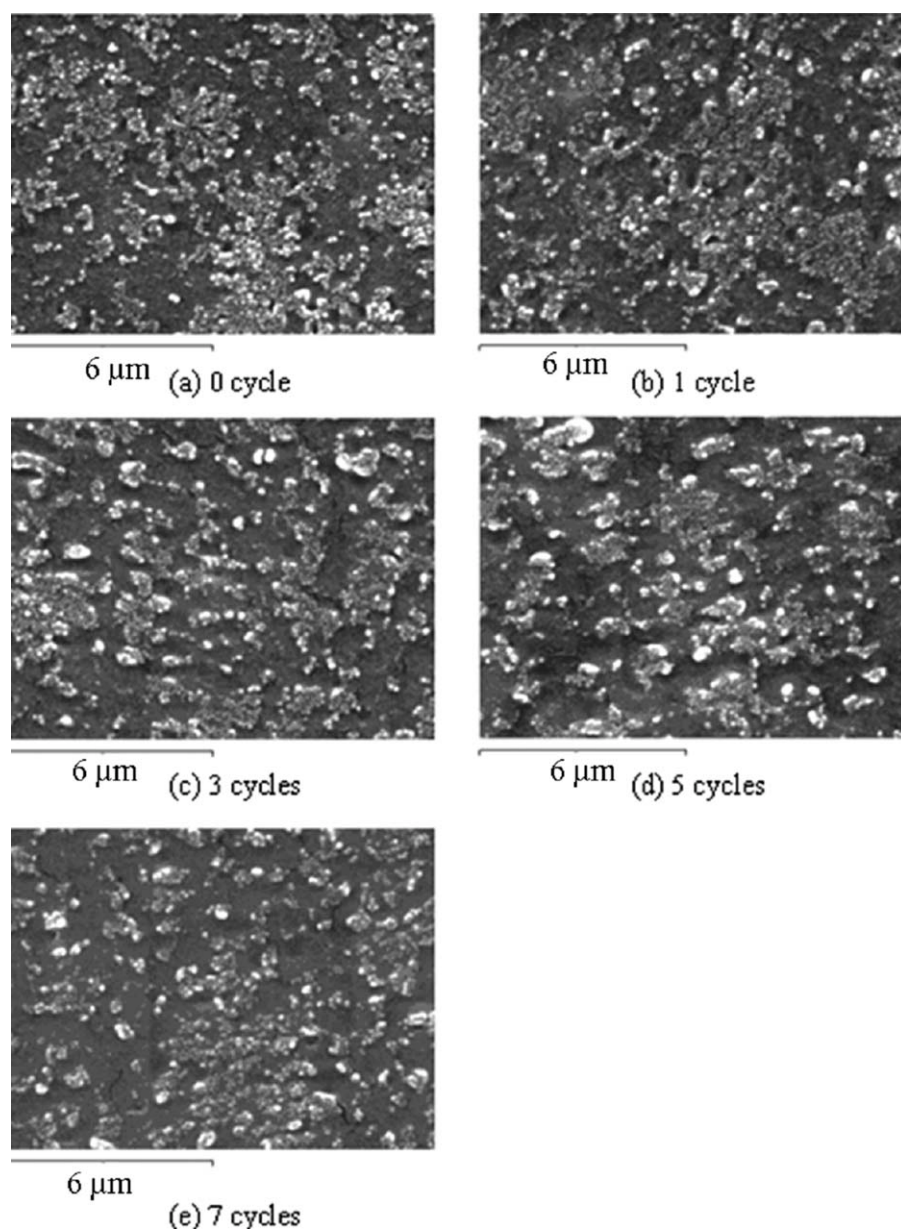
Figure 7 SEM micrographs of SPNR sheets adsorbed with PMMA/PEI particles as a function of stretched cycle numbers: (a) 0, (b) 1, (c) 3, (d) 5, and (e) 7 cycles at 15% TSC for 40 min.

used, especially during hand insertion. Therefore, the physical stability of PMMA/PEI nanoparticle coating layers on the SPNR surface was evaluated by applying contraction–extension forces. Then, the surface morphology of the samples treated with various stretching cycles was traced by SEM, and is shown in Figure 7. SEM micrographs apparently show that the PMMA/PEI nanoparticles still existed even under stretching up to seven cycles. From the plot of stretching cycles against C_s values in Figure 8, the C_s values decreased from 30 to 24% when increasing the stretching cycles from 0 to 7. This may lead to two possibilities for the decrease in C_s
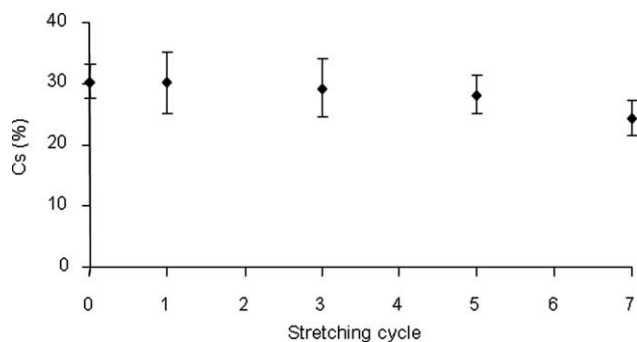

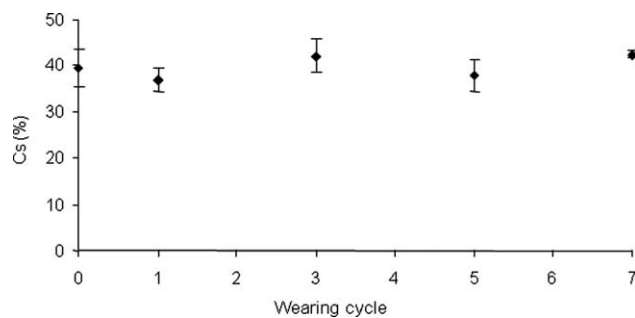**Figure 8** Effect of stretching cycle on C_s values of SPNR sheets at 15% TSC for 40 min.

Figure 9 Effect of wearing cycle on C_s values of SPNR sheets at 15% TSC for 40 min.

values. The first one is a hypothesis that the PMMA/PEI nanoparticles might come off from the SPNR's surface after stretching. The second is based on the fact that the SPNR sheet did not fully recover after subjecting to many stretching cycles. This incomplete recovery would certainly lead to the increase in the surface area of PMMA/PEI-coated SPNR specimen. Therefore, the lowered C_s values could be observed, even though the number of PMMA/PEI nanoparticles was considered almost the same. The incomplete recovery, which is related to the permanent set, is a general characteristic of most elastomers. It depends not only on the type of
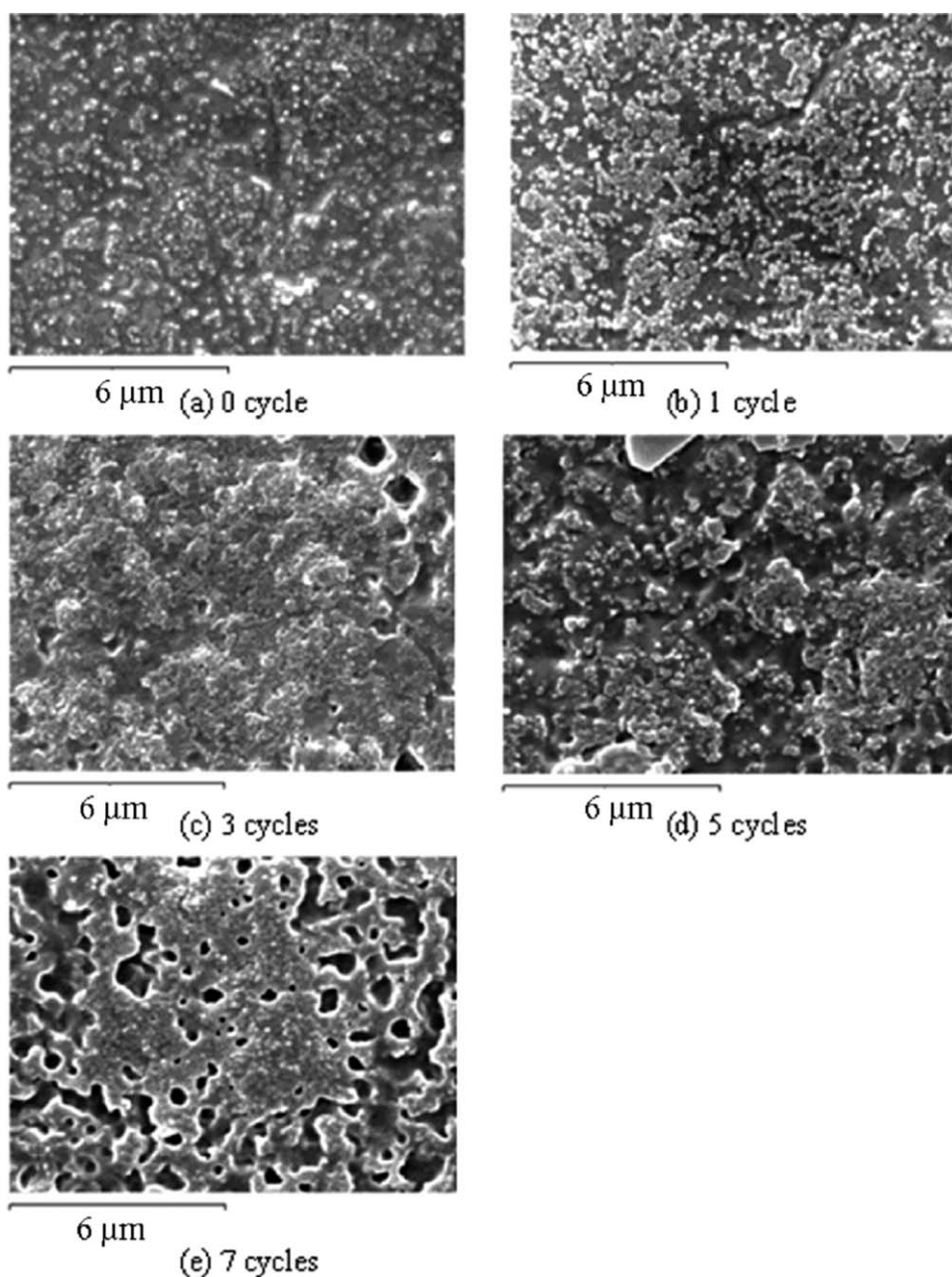

Figure 10 SEM micrographs of SPNR sheets adsorbed with PMMA/PEI nanoparticles as a function of wearing cycle : (a) 0, (b) 1, (c) 3, (d) 5, and (e) 7 cycles at 15% TSC for 40 min.

elastomer but also other compounding ingredients.[19] Further investigation revealed that the permanent set of the SPNR specimen without nanoparticle deposition, determined after stretching for seven cycles and leaving at room temperature for 1 h, was about 5.6%. Therefore, it could be said that the adsorbed PMMA/PEI nanoparticles was quite stable under the stretching conditions.

Not only stretching, but also wearing can influence the surface properties of the gloves when they are used. Thus, the surfaces of PMMA/PEI-coated SPNR specimens, which were rubbed against the surface of friction equipment, were examined. Figure 9 illustrates the SEM micrographs of sample surfaces subjected to various wearing cycles. The SEM micrographs showed that the PMMA/PEI nanoparticles still existed even after wearing test up to seven cycles. In addition, the C_s values of worn SPNR specimens were not significantly different from the unworn sample as shown in Figure 10. This result could confirm the slightly effect of wearing process on the surface coverage of samples. From both stretching and wearing tests, it can be stated that there was the interaction between PEI on the PMMA/PEI nanoparticles and the surface of SPNR sheets, which could enhance the adsorption.

CONCLUSIONS

The PMMA/PEI core-shell nanoparticles can be adsorbed on SPNR sheets via a convenient dipping method. The C_s values were found to be affected by the PMMA/PEI latex concentration and immersion time. The adsorption behavior was found to fit well with the Freundlich isotherm. The increase in C_s values led to the decrease of interfacial adhesion and surface friction while hardness and the bulk proper-ties such as tensile strength, and elongation at break of SPNR sheets were not affected by the coating. In addition, the adsorbed PMMA/PEI nanoparticles on SPNR sheet were sufficiently stable under stretching and wearing conditions at least seven cycles.

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