From Natural Rubber to Smart Surfaces

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ABSTRACT

Surface oxidation of crosslinked natural rubber provided a hydrophilic substrate that reconstructed under nitrogen atmosphere at room temperature to become more hydrophobic. Subsequent equilibration against water at room temperature returned its original hydrophilicity. This behavior may arise from the minimization of interfacial free energy of the system by the migration of hydrophilic functional groups away from or to the interface. The change in surface moieties, influences tackiness at the rubber surface – it is tackier when functional groups are at the interface rather than when they migrate away. The magnitudes and kinetics of this surface reconstruction depends on the molecular weight between crosslinks (M_c) and temperature. The results reported here provide information for further development of smart surfaces from crosslinked natural rubber.

Key words: Smart surfaces - Surface oxidation - Natural rubber - Surface energy - Surface reconstruction - Crosslink density

INTRODUCTION

Using cheap, simple raw materials to create materials that could provide benefits to our daily life has been a major focus of research in material science and engineering. For example, there is literature reporting that simple polymers have been used as anti-fouling film barriers (1) or that researchers are able to synthesize artificial skin from shrimp and crab shells (2,3). These innovations would also provide an opportunity to add value to these simple raw materials.

For Thailand, a country recovering from the recent economy crisis, using local raw materials, especially those from agriculture, to supply industry instead of imported materials would greatly benefit the sustainable development to the country. Natural rubber is one of the most important agricultural materials of Thailand. About 40% of raw natural rubber consumed worldwide comes from Thailand (4). This makes Thailand the number one in the world for the export of raw natural rubber (4). However the export of raw rubber, which is just a cheap basic agricultural material, can not sustain the economy of the country. The attempt to use natural rubber for new innovations has recently become an active research topic in Thailand.

This paper illustrates the design of natural rubber in order to make its surface energy automatically respond to external stimuli, i.e. surface energy of the contacted substrates, temperature. The surface of solid rubber against air or water is used as a model to study interfacial properties relevant to the interaction between the rubber surface and other substrates. Organic chemistry at the surface is used to introduce

functional groups to the rubber interphase in order to provide the means for monitoring composition and dynamics on the surface. The modified surfaces of crosslinked rubber provide lower surface energy or less sticky surfaces when equilibrated against air and provide higher surface energy or stickier surfaces when equilibrated against water (5). This paper also reports that magnitudes and kinetics of the changes in tackiness at this rubber surface can be simply controlled just by raising/lowering the temperature as well as by designing the right amount of crosslinking to the bulk rubber. This may provide an opportunity to develop a prototype of a smart floor from natural rubber, a floor that would automatically provide stronger grip when wet; and, on the other hand, it would hardly be stuck when dry.

MATERIALS AND METHODS

General. Dicumyl peroxide (98%; Aldrich), toluene (99%; E.M. Science), potassium permanganate (99+%; Fisher), potassium carbonate (99+%, Fisher), and hydrochloric acid (36.5%, Mallinckrodt) were used as received.

All water equilibration experiments were done by floating rubber plaques on de-aerated water prepared by bubbling nitrogen gas into 20 ml of distilled water for 1 min.

Crosslinking and Film Formation. Five grams of natural rubber (STR 5L) was dissolved in ~100 ml of toluene and stirred overnight, normally within 16 h. Dicumyl peroxide (Dicup) was pre-dissolved separately in 10 ml of toluene, and then added to the rubber solution and stirred for an additional 4 h. The rubber was then dried under vacuum to a constant mass. These compound mixtures were stored at room temperature until pressing, normally within 24 h.

Two polished aluminum plates (10×10 cm^2) were cleaned by soaking in toluene for 20 min and wiped with cotton balls. A cardboard frame with a thickness of ~1 mm was cut to the dimensions of the plates, and a window (~5×5 cm^2) cut in the frame to serve as a mold. A hot press was used to cure the rubber at 150°C for 84 min (8 half-lives of Dicup) (6). After cooling to room temperature, the plaques were peeled from the aluminum plates using tweezers and cut into small pieces (~0.7×2.5 cm^2). Each of these pieces was swelled in a separate vial with 20 ml of toluene for at least 36 h to extract any unbound polymer chains that were not part of the crosslinked network and to measure the molecular weight between crosslinks (M_c). The optimum swelling time was determined by following the loss of mass of the swelled samples until it reached a constant value. Swelling for 36 h was generally sufficient to reach a constant mass for the plaques with the lightest degree of crosslinking (M_c = 107,000 g/mol). These samples were then dried under vacuum at room temperature to constant mass.

Surface Oxidation of Rubber. Sample surfaces were oxidized with an aqueous solution of $KMnO_4$ (0.045 M) and K_2CO_3 (0.017 M) as described else where for other elastomers (7,8,9).

Analysis of Oxidation Products by Infrared Spectroscopy. One of the broad sides of a crosslinked polyisoprene plaque (M_c = 20,000 g/mol) with dimensions of ~1×3 cm^2 was oxidized by floating on an aqueous solution of $KMnO_4/K_2CO_3$ for 45 min. The oxidized plaque was placed on both sides of a 50-mm×20-mm×2-mm (60° angle of incidence) KRS-5 crystal. Attenuated total reflectance infrared (ATR-IR)

spectra were then collected using a Perkin-Elmer 1650 Spectrometer. For comparison, plaques that had not been oxidized were analyzed in the same way.

Measurement of Contact Angles. All advancing contact angles (θ_a) of water were recorded at room temperature and ambient humidity using a Rame-Hart Model 100 contact angle goniometer and a Tantec Model: CPM 09 contact angle meter. Water, pH 1 was used unless other wise stated in order to avoid the pH-dependent behavior of the oxidized surfaces (10,11). Before determining θ_a on samples that had been heated under a nitrogen atmosphere, they were immediately cooled to room temperature under a stream of nitrogen for 1 min. Likewise, samples that had been heated with water were also immediately cooled in room temperature water for 1 min to slow the surface reconstruction during the measurements. Each of the reported values of θ_a is an average of at least eight different measurements taken within 10-20 s of applying the drop of water.

RESULTS AND DISCUSSION

Crosslinking and Surface Oxidation

To form a smooth and stable surface of rubber plaques, it is necessary to introduce crosslinking into the rubber bulk. Dycumyl peroxide (Dicup) was used as a crosslinking agent, instead of a sulfur vulcanizing system, in order to minimize the complexity of the systems (12). After plaque formation, they were swelled in toluene for at least 36 h to extract the unbound chains (the fraction which is not part of the crosslinked network) to ensure that the surface reconstruction observed in this study is associated only to the movement of chains in the crosslinked network. The rubber plaques were then deswelled under vacuum until reaching a stable weight before use. During this swelling process, the molecular weight between crosslinks (M_c) was measured using the Flory-Rehner method (13). **Figure 1** displays the variation of M_c against the amount of Dicup added to the rubber. The value of M_c in rubber plaques fell sharply from 107,000 to 17,000 g/mol when the amount of crosslinking agent added was raised from 0.05 to 0.5 parts per hundred of rubber (phr) (14) and then fell further to 3,000 g/mol when the amount of crosslinking agent was raised to 4.0 phr. This method provides the means to vary the amount of crosslink density systematically in the rubber plaques; thereby, allowing the study of the dependence of surface reconstruction on crosslink density. The greatest value of M_c shown in this plot ($M_c =$ 107,000 g/mol) also had the lowest crosslink density. The plaques containing lower crosslink density than this could not maintain their shape after swelling and deswelling process, and were not observed.

Oxidation of the rubber surface with basic, aqueous $KMnO_4$ (0.045 M) introduces a range of functional groups, including, carboxylic acids, ketones, and diols, thus providing a hydrophilic surface (7,10,15). The decrease in contact angles on the rubber surface after oxidation is consistent with the presence of these functional groups. As shown in **Figure 2** the value of advancing contact angles (water, pH 1) dropped from 96°, which is the value of unoxidized rubber surfaces, to 68° after oxidation for 45 min. Longer oxidation times than 45 min did not result in a significant decrease in contact angles. As a result, the oxidation time for all of the rubber plaques in this study was 45 min. Carboxylic acids at the surface are known to be ionizable by basic water (11). Thus, the lower contact angle values of water pH at

13 on the rubber surface **(Figure 2)** were consistent with these carboxylic acids introduced by oxidation. To ensure the presence of these hydrophilic functional groups, infrared spectra of crosslinked synthetic polyisoprene (97% cis, M_c = 30,000 g/mol) were taken instead of using natural rubber to avoid the interference of the C=O peak from lipids contained in the rubber particles (16). θ_a on polyisoprene surface after oxidation for 45 minutes is about 70°. Thus, about the same degree of surface oxidation as introduced to natural rubber was also expected on polyisoprene surface. Infrared spectra of rubber in **Figure 3** also confirmed the presence of oxidized functional groups. The new peak at 1718 cm^{-1} in the spectrum of the oxidized sample may be assigned to C=O stretching in carboxylic acids and ketones (15,16).
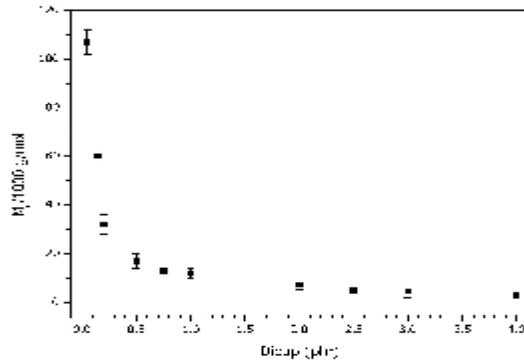

Figure 1. Average molecular weight between crosslinks (M_c) for crosslinked natural rubber plaques. The error bar indicates the values within one standard deviation of the average for that plot.
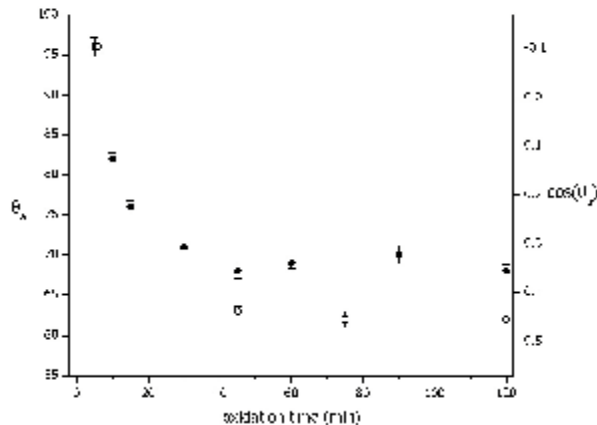

Figure 2. The change in advancing contact angles (θ_a) of water (pH 1, ~) on the surface of crosslinked natural rubber oxidized as a function of time in an aqueous solution of KMnO$_4$/K$_2$CO$_3$. The symbols ($\circ$) represent values of θ_a on these surfaces using water at pH 13. Each symbol is a separate sample and the error bar indicates the values within one standard deviation of the average on that sample, in θ_a.
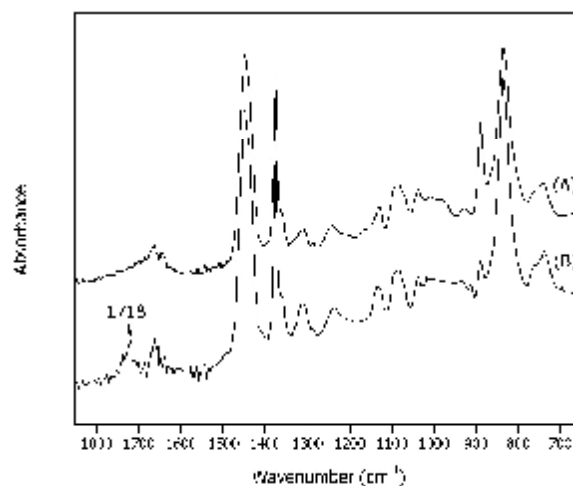
Figure 3. Attenuated total reflectance infrared spectra of (A) unmodified *cis*-1,4-polyisoprene, and (B) oxidized *cis*-1,4-polyisoprene after 45 min in an aqueous solution of $KMnO_4/K_2CO_3$.

Surface Reconstruction of Oxidized Natural Rubber

It is expected on the basis of the need of the rubber surface to minimize its interfacial free energy that when the oxidized surface is equilibrated against air, hydrophilic functional groups on the surface migrate to the bulk and hence lower surface energy (tackiness) (17,18,19). On the other hand, when this air-treated sample is equilibrated against water, hydrophilic groups would migrate back to the surface again leading to stronger tackiness at the surface as illustrated in **Figure 4**. To test this hypothesis, just oxidized surfaces of crosslinked rubber plaques were equilibrated against a nitrogen atmosphere. This atmosphere was used instead of the ambient air to minimize any autoxidation that might happen to the rubber surfaces. The kinetics of surface reconstruction on the plaques with different degrees of crosslink density were monitored by contact angle measurement. As shown in **Figure 5**, initially, the rate of increase in hydrophobicity of the oxidized surfaces is fast; then, it becomes slower as surface hydrophobicity approaches almost constant values. The kinetics for samples with different values of M_c, however, were different – rubber plaques with the greatest degree of crosslinking ($M_c = 5,000$ g/mol) display the slowest rate of surface reconstruction. The kinetics of surface reconstruction for this sample approaches equilibrium within 24 h while the plaques with two other degrees of crosslink density ($M_c = 107,000$ and $32,000$ g/mol) do so faster – within 4 and 8 h, respectively. This result likely reflects limiting chain motion by large numbers of branch points in highly crosslinked samples compared to more free chains in lighter crosslinked samples (see **Figure 4**). The highly crosslinked samples also show a tendency towards lower hydrophobicity at the plateau indicating that some hydrophilic functional groups are pinned on the surface by a tremendous amount of branch points. Moreover, the values of contact angles at the plateau measured on the plaques with $M_c = 107,000$ g/mol are close to the values of contact angles of unoxidized rubber surfaces. This result infers that, mostly, the hydrophilic functional groups at this surface migrate deeply away

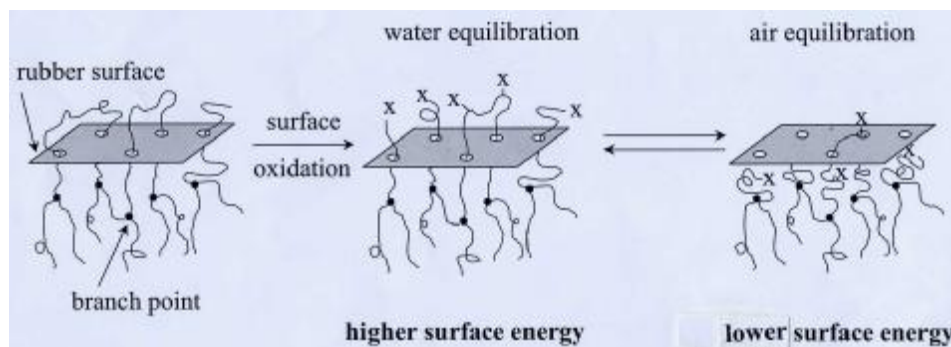from the interface (at least 5-10 Å deep[11]) when equilibrated under a nitrogen atmosphere.

Figure 4.   Schematic illustration of mechanism leading to changes in surface compositions. The symbol "x" represents the hydrophilic functional groups introduced by oxidation.

To further test the central hypothesis, these annealed samples were then exposed to water at room temperature. As expected, after taking contact angles at various intervals, hydrophilicity of the annealed plaques increased with different kinetics depending on the level of crosslink density as well. The same tendency as shown in **Figure 5** are also observed here, the plaques containing the lowest amount of crosslink density (M_c = 107,000 g/mol) show the fastest kinetics of increasing in hydrophilicity **(Figure 6)**. The level of hydrophilicity for this sample reached equilibrium after ~6 h with room temperature water, while that of the plaques with an intermediate level of crosslinking (M_c = 32,000 g/mol) reach equilibrium slower, within 8 h. The samples with the greatest crosslink density (M_c = 5,000 g/mol) show the slowest kinetics during equilibration with room temperature water, it reaches equilibrium after 24 h. Again, slower kinetics observed here for the plaques with a greater amount of branch points is due to limiting chain motion. The kinetics of surface reconstruction observed in **Figures 5 and 6** are consistent with each other even though the direction of surface rearrangement is opposite. These results indicate that surface tackiness of the oxidized rubber plaques can be switched on and off reversibly. They also reflect the relationship between the kinetics of surface reconstruction, which is an interfacial property, and the degree of crosslinking, which is a bulk property of rubber.

To monitor the effect of temperature on the changes in surface energy of the oxidized plaques, different temperatures of nitrogen and water were applied. Rubber plaques with an intermediate level of crosslinking, M_c = 32,000 g/mol, were used as representative samples. Oxidized surfaces of rubber plaques were equilibrated under a nitrogen atmosphere at 50 and 70ºC as shown in **Figure 7**. It was found that the kinetics of every sample reached the plateau faster than those at room temperature and the kinetics for samples equilibrated at 70ºC were faster than that for samples equilibrated at 50ºC, as expected. Moreover, the hydrophobicity at the plateau after equilibration against nitrogen at elevated temperatures is significantly greater than that of the same samples equilibrated at room temperature and is close to the values of the

unoxidized rubber surfaces. These results indicate that greater chain motion can be achieved at higher temperatures. To test the kinetics of the reverse direction of this surface reconstruction, these samples were then immediately equilibrated against water at elevated temperatures. The same tendency is observed (see **Figure 8**), the increase in hydrophilicity for samples treated at higher temperature is faster. The kinetics for this experiment were also faster than that performed previously at room temperature. The results observed here are consistent with a mechanism controlling changes in surface energy of oxidized rubber surfaces in order to rearrange surface compositions to minimize the interfacial free energy of the system.
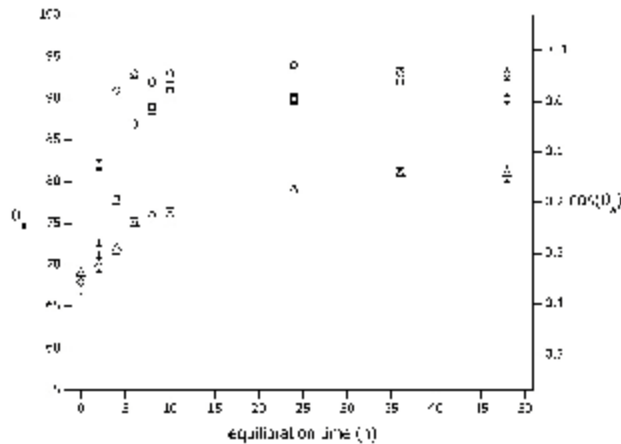

Figure 5. Magnitude of the change in advancing contact angles (θ_a) of water on surface-oxidized plaques as a function of equilibration time under a nitrogen atmosphere at room temperature: (A) crosslinked plaque with M_c=107,000 g/mol $\left(\bigcirc\right)$; (B) M_c=32,000g/mol ($\mathbf{\mathcal{E}}$); (C) M_c=5,000 g/mol (ρ). The error bar in each plot indicates the value within one standard deviation of the average for that plot, in θ_a.
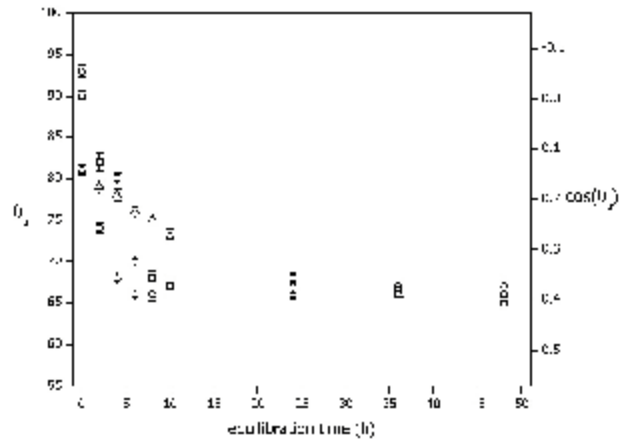
Figure 6. Magnitude of the change in advancing contact angles (θ_a) of water on surface-oxidized plaques that had been already equilibrated under nitrogen for 48 h, as a function of equilibration time with de-aerated water at room temperature: (A) crosslinked plaque with M_c=107,000 g/mol (○); (B) M_c=32,000 g/mol (𝓢); (C) M=5,000 g/mol (ρ). The error bar in each plot indicates the value within one standard deviation of the average for that plot, in θ_a.
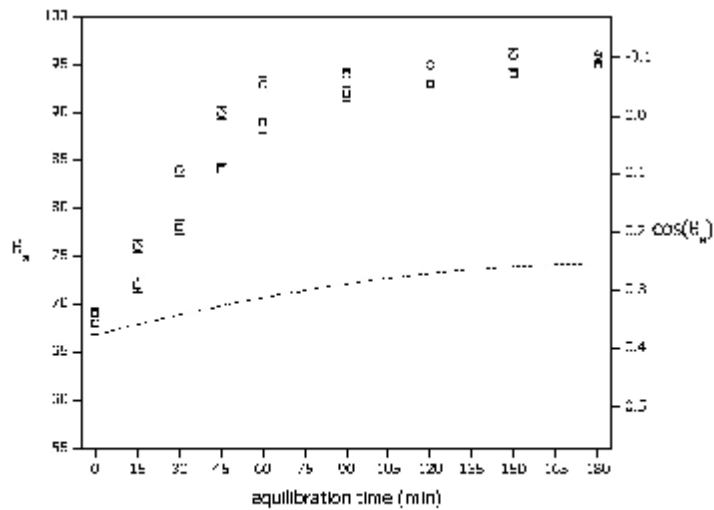

Figure 7. Magnitude of the change in advancing contact angles (θ_a) of water on surface-oxidized plaques as a function of equilibration time against a nitrogen atmosphere at different temperatures : (A) 70ºC (○) ; (B) 50ºC (𝓢). For comparison, the result for equilibration against a nitrogen atmosphere at room temperature is also provided (dashed line). The error bar in each plot indicates the value within one standard deviation of the average for that plot, in θ_a.
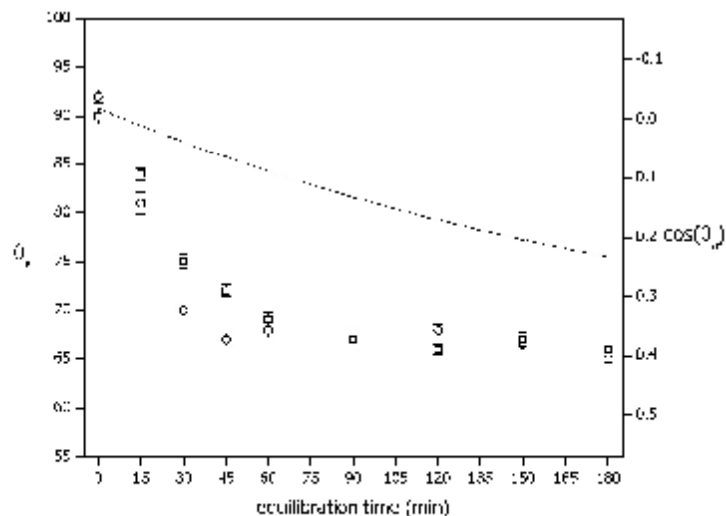
Figure 8. Magnitude of the change in advancing contact angles (θ_a) of water on surface-oxidized plaques, that had been already equilibrated against nitrogen for 180 min, at 70 and 50°C, as a function of equilibration time against de-aerated H_2O at different temperatures of (A) 70°C $\left(\bigcirc\right)$; (B) 50°C (**£**). For comparison, the result for equilibration with de-aerated water at room temperature is also provided (dashed line). The error bar in each plot indicates the value within one standard deviation of the average for that plot, in θ_a.

CONCLUSIONS

An oxidized surface of crosslinked natural rubber can respond to contacted substrates and temperature by itself. It provides lower surface energy (less sticky) when exposed to a hydrophobic substrate (ie nitrogen atmosphere) and higher surface energy (stickier) when exposed to a hydrophilic substrate (ie water), reversibly. The kinetics are faster and the magnitude is greater, for this surface reconstruction, at higher temperatures. The results reported in this paper also reflect the relationship between interfacial properties (ie changes in surface energy) and bulk properties (ie crosslink density) of crosslinked natural rubber. They also confirm the importance of treating natural rubber as an integrated system by comprising bulk (ie the optimal level of crosslink density) and interfacial properties (surface reconstruction) to provide an opportunity for inventing a smart rubber surface.

ACKNOWLEDGEMENTS

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บทคัดย่อ

สุฤกษ์ คงทอง
จากยางธรรมชาติ สู่พื้นผิวที่มีการปรับตัวโดยอัตโนมัติ

    การปรับปรุงพื้นผิวของยางธรรมชาติโดยการเติมกลุ่มจำเพาะที่ชอบน้ำบนพื้นผิวยางจะ
ทำให้ยางมีพลังงานที่พื้นผิวเพิ่มขึ้น นั่นคือผิวยางจะมีความเหนียวมากขึ้น   ซึ่งผลการวิจัยพบว่า
พลังงานที่พื้นผิวยางธรรมชาติที่คงรูปแล้วนี้ (crosslinked rubber)   สามารถเกิดการเปลี่ยนแปลง
ได้เอง โดยหากพื้นผิวของยางนี้มีการสัมผัสกับอากาศ พลังงานที่ผิวจะลดลง นั่นคือความเหนียว
ที่ผิวของยางจะลดลง และหากผิวของยางนี้มีการสัมผัสกับน้ำอีกครั้ง พลังงานที่ผิวก็จะเพิ่มขึ้นจน
กลับมาเท่ากับระดับเดิมได้อีก   นั่นคือความเหนียวที่ผิวของยางจะเพิ่มขึ้นเหมือนเดิมอีกครั้ง การ
เปลี่ยนแปลงนี้เกิดขึ้นจากคุณสมบัติทางเทอร์โมไดนามิกส์ของพื้นผิวที่พยายามลดค่าพลังงาน
อิสระของพื้นผิวให้มากที่สุด เช่น โดยการจำกัดจำนวนของกลุ่มจำเพาะที่ชอบน้ำบนพื้นผิวของ
ยาง (เมื่อยางสัมผัสกับอากาศ) ในสภาวะนี้กลุ่มจำเพาะที่ชอบน้ำจึงต้องหนีลึกลงไปอยู่ในเนื้อของ
ยาง และเมื่อการจำกัดจำนวนของกลุ่มจำเพาะที่ชอบน้ำบนพื้นผิวของยางหมดไป (เมื่อยางสัมผัส
กับน้ำ) กลุ่มจำเพาะที่ชอบน้ำก็จะกลับขึ้นมาอยู่ที่พื้นผิวของยางได้อีก   อย่างไรก็ตามกลุ่มจำเพาะ
เหล่านี้เชื่อมต่ออยู่กับสายโซ่โมเลกุลของยาง   ดังนั้นความหนาแน่นที่สูงเกินไปของเครือข่ายของ
สายโซ่โมเลกุลในเนื้อยางจึงมีอิทธิพลทำให้การเคลื่อนที่ของกลุ่มจำเพาะที่ชอบน้ำ ระหว่างพื้นผิว
กับเนื้อระดับลึกของยางธรรมชาติเกิดขึ้นได้ช้าลง   นอกจากนั้นอุณหภูมิที่สูงขึ้นก็ยังมีผลให้ความ
สามารถในการเคลื่อนที่ของกลุ่มจำเพาะที่ชอบน้ำเหล่านี้สูงขึ้นด้วย   ผลงานวิจัยนี้เป็นแนวทางที่
จะสามารถนำไปพัฒนาเป็นพื้นผิวยางธรรมชาติที่คงรูปแล้วให้สามารถปรับเพิ่ม-ลดสัมประสิทธิ์
ความเสียดทานได้ด้วยตัวเอง

สำนักวิชาวิศวกรรมศาสตร์และทรัพยากร มหาวิทยาลัยวลัยลักษณ์ อำเภอท่าศาลา จังหวัดนครศรีธรรมราช