

A smart surface from natural rubber: the mechanism of entropic control at the surface monitored by contact angle measurement

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Abstract

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Surface oxidation of crosslinked natural rubber provided a hydrophilic substrate (sticky surface) that became more hydrophobic (less sticky) when equilibrated against hot water. This unusual temperature-dependent surface reconstruction is interpreted as the result of recoiling of entropic unfavorable uncoiled chains induced when rubber surface was oxidized. Subsequent equilibration of these annealed samples against water at room temperature returned their original hydrophilicity. The degree of this surface reconstruction and its kinetics are also dependent on the amounts of crosslinking of the samples.

Key words : natural rubber, smart materials, polymer surface, surface reconstruction

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บทคัดย่อ

สุฤกษ์ คงทอง

พื้นผิวที่ฉลาดจากยางธรรมชาติ: ผิวที่มีเอนโทรปีเป็นกลไกควบคุม
ศึกษาโดยใช้การวัดมุมสัมผัส

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ผิวของยางธรรมชาติที่ผ่านการออกซิเดชันเพื่อเติมหมู่จำเพาะจะเป็นผิวที่มีความชอบน้ำสูง (ความสามารถในการติดกับพื้นผิวอื่นสูง) ซึ่งหากพื้นผิวนี้มีการสัมผัสกับน้ำร้อน ความชอบน้ำที่ผิวจะลดลง (ความสามารถในการติดกับพื้นผิวอื่นลดลง หรือสามารถป้องกันไม่ให้วัสดุอื่นมาติดผิวยางได้ดีขึ้น) การเปลี่ยนแปลงนี้เกิดขึ้นในทิศทางที่ตรงข้ามกับทิศทางปกติ ดังนั้นคาดว่ากลไกที่ทำให้เกิดการเปลี่ยนแปลงนี้ขึ้นคือ การคลายตัวของสายโซ่พอลิเมอร์ที่บริเวณพื้นผิวของยางซึ่งเกิดขึ้นในขณะที่ผิวยางถูกออกซิเดชัน การคลายตัวของสายโซ่นี้ทำให้ค่าเอนโทรปีลดลง ส่งผลให้สายโซ่พยายามม้วนพับคืนสู่สภาพเดิม ดังนั้นเมื่อสายโซ่เหล่านี้ได้รับแรงกระตุ้นจากอุณหภูมิของน้ำร้อน สายโซ่ดังกล่าวจึงสามารถม้วนพับคืนสู่สภาพเดิมได้ และในขณะเดียวกันได้ดึงเอาหมู่จำเพาะที่ชอบน้ำลงไปใต้พื้นผิวของยางด้วยทำให้ความชอบน้ำของผิวลดลง และหากผิวยางนี้ได้สัมผัสกับน้ำที่อุณหภูมิห้องอีกครั้ง ความชอบน้ำที่ผิวยางก็จะกลับมาเหมือนเดิมได้อีกเนื่องจากหมู่จำเพาะที่ชอบน้ำสามารถเคลื่อนที่กลับขึ้นมาที่พื้นผิวได้อีกครั้ง นอกจากนี้ ระดับการเปลี่ยนแปลงความชอบน้ำที่ผิวยางและความเร็วของการเปลี่ยนแปลงนี้ยังขึ้นอยู่กับความหนาแน่นของเครือข่ายในชั้นยางด้วย

สำนักวิชาวิศวกรรมศาสตร์และทรัพยากร มหาวิทยาลัยวลัยลักษณ์ อำเภอท่าศาลา จังหวัดนครศรีธรรมราช 80160

Using of simple raw materials to create things widely provide benefit to our daily life has been a focus of researches in materials science and technology. Natural rubber, the cheap simple agricultural product, is the raw material we are interested in. Although natural rubber could create almost 50,000 million baht annually to Thailand, the exporting of Thai natural rubber has been in the fashion of fundamental products, i.e., concentrated latex, smoked sheets (Jumpasut, 2004). Surprisingly, Thailand also imports rubber products for 16,000 million baht a year and most of them are industrial rubber products and specific-propose rubber parts (Jumpasut, 2004). This may imply that Thailand urgently needs to develop a knowledge in rubber science and technology in order to use natural rubber to create these products.

As a result, our research group has been tried to develop a smart surface, the surface that could respond to the external stimuli by itself, from natural rubber. This surface could adjust its surface energy (tackiness) automatically when brought into contact with different substrates, i.e., water

and air. In our research, we used contact angle measurement to investigate changes at rubber surface since this is the method that is sensitive to changes in surface compositions and surface dynamics happening at the very outermost layer (few angstroms depth) of the surface. Using of other techniques, e.g., x-ray photoelectron spectroscopy (XPS) or attenuated total reflectance infrared spectroscopy (ATR-IR), to investigate this surface may not give any useful information because of too deep interphase ranges of them (50-100 angstroms for XPS and over 10^4 angstroms for ATR-IR) (Ferguson and Whitesides, 1992). We reported previously that the oxidized surface of natural rubber - the surface containing polar functional groups - became more hydrophobic (less sticky) when contacted with air and became more hydrophilic (stickier) when contacted with water (Khongtong, 2004). The kinetics of this change was faster at higher temperatures. The mechanism involved this change was the minimization of interfacial free energy at oxidized rubber surfaces - polar functional groups migrated deeply away

from the surface when equilibrated against air and migrated back to the surface again when equilibrated against water (Ferguson and Whitesides, 1992; Wong *et al.*, 1997; Valint *et al.*, 1997; Rouse *et al.*, 1999; Chen and McCarthy, 1999).

In this paper, we reported the behavior at oxidized surfaces of natural rubber more deeply. We oxidized rubber surface using procedures mentioned previously to introduce hydrophilic functional groups to all samples used in this study (Khongtong and Ferguson, 2001; Khongtong and Ferguson, 2002; Khongtong and Ferguson, 2004). Functionalized rubber plaques were then floated on hot water immediately and we observed the unusual change at the surfaces - they became *more hydrophobic* or *less sticky*! This behavior occurred in the opposite direction, generally, according to the surfaces to minimize their interfacial free energy (Ferguson and Whitesides, 1992; Rouse *et al.*, 1999; Chen and McCarthy, 1999; Wong *et al.*, 1997). We also found the relationships between the magnitude of this unusual surface reconstruction and the temperatures of water as well as the degrees of crosslinking in rubber plaques. In addition, the hydrophobicity at these annealed surfaces declined while they were equilibrated against water at room temperature. We hypothesized that the entropic unfavorable conditions of the uncoiled interfacial chains occurred during surface oxidation playing a role on this unusual phenomenon (Gent, 1978; Flory, 1989; Sperling, 1992). During surface oxidation, polymer chains - in random coil conformations at an unperturbed state - were pulled out of their interfacial holes leading to uncoiling. As a result, these uncoiled chains tended to recoil in order to increase entropy of the system; hence, when exposed to hot water, they recoiled and pulled functional groups away from the surface due to the dominance of entropy. Thus, functionalized surfaces become more hydrophobic or less sticky. Subsequently, when this sample was placed into contact with water at room temperature, enthalpically favorable hydrogen bonding brought the buried functional groups back to rubber surface again. As a result, the compositions at functionalized rubber surfaces are determined by the balance

of entropic and enthalpic driving forces. The results reported here and reported previously illustrate that functionalized rubber surfaces could respond to the external stimuli in more than one way depending on the direction approached and may lead to the development of a smart barrier film and a smart adhesive from natural rubber.

Materials and Methods

General Methods

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. Water equilibration at 100°C was performed in pressure tube containing distilled water submerged in an oil bath.

Crosslinking and Film Formation

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

Two polished aluminum plates (10 x 10 cm²) were cleaned by soaking in toluene for 20 min and wiped with cotton balls. A cardboard frame with thickness of ~ 1 mm was cut to the dimensions of the plates, and a window (~5 x 5 cm²) 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). After cooling to room temperature, the plaques were peeled from the aluminum plates using tweezers and cut into small pieces (~ 0.7 x 2.5 cm²). Each of these pieces was swelled in a separate vial with 20 mL of toluene for at least 36 h to extract any unbound fractions that were

not part of the crosslinked network and to measure the molecular weight between crosslinks (M_c) (Sperling, 1992). The optimum swelling time was determined by following the loss of mass of the swelled samples until it reached the 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 in 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) by floating one of the broad sides in this solution for 45 min at room temperature. After oxidation, the samples were rinsed with water, floated on an aqueous NaHSO_3 for 3 min, rinsed with water, and then blown by N_2 until dry.

Measurement of Contact Angle

A solid-liquid contact angle measurement is used to measure the compositions at the interphase of samples since the motions of the oxidized interfacial chains occur at the outer most few angstroms of the interphase (Rouse *et al.*, 1999; Khongtong and Ferguson, 2001; Khongtong and Ferguson, 2002). All contact angles (θ) of water were taken at dry sample surfaces at room temperature and ambient humidity using a Tantec Model: CPM 09 contact angle meter. Water pH 1 (aqueous 0.1M HCl) was used in order to avoid the pH-dependent behavior of the oxidized surfaces (Ferguson and Whitesides, 1992). Before determining θ on samples that had been heated against water, they were immediately cooled in room temperature water for 1 min to slow the surface reconstruction during the measurements. Each of the reported values of θ is an average of at least eight different measurements taken within 20 s of applying the drop of water.

Results and Discussion

Temperature-dependent surface reconstruction

Dicumyl peroxide (Dicup) was used to

crosslink all samples in this study instead of sulfur vulcanizing agents in order to minimize the complexity of bulk structure. All crosslinked samples were swelled in toluene and then deswelled in order to extract the unbound fraction from rubber plaques as described previously to ensure that the surface reconstruction observed in this study is due to the chain motions of crosslinked networks only (Khongtong, 2004). Molecular weight between crosslinks (M_c) would be also determined during this swelling and deswelling processes using Flory-Rehner equation (Sperling, 1992). After deswelling, crosslinked plaques were oxidized to introduce hydrophilic functional groups - maybe carboxylic acids, ketones, and diols - to the surface (Carey and Ferguson, 1994; Khongtong and Ferguson, 2001; Khongtong and Ferguson, 2002; Khongtong and Ferguson, 2004; Khongtong, 2004). Contact angles of water pH 13 (aqueous 0.1M NaOH) and ATR-IR spectra confirmed the presence of carboxylic acids and ketones at the oxidized surfaces as described previously.

These oxidized surfaces were now ready for the further treatments. We then floated these oxidized samples ($M_c = 32,000$ g/mol) in 70°C water and the contact angles of these surfaces were taken. Figure 1 shows the change of contact angles at the surface of these oxidized samples as a function of equilibration time. When equilibrate against hot water, rubber surfaces likely become more *hydrophobic* (or less sticky) instead of maintaining or elevating its hydrophilicity. However, the samples equilibrated against water at room temperature still maintain the hydrophilicity of the surfaces. This behavior is contrary to the phenomena observed at other functionalized polymer surfaces in order to minimize the interfacial free energy (Ferguson and Whitesides, 1992; Wong *et al.*, 1997; Valint *et al.*, 1997; Rouse *et al.*, 1999; Chen and McCarthy, 1999). As a result, there must be other mechanisms responsible for this unusual surface reconstruction and we have hypothesized that entropic unfavorable conditions of the oxidized interfacial chains plays a major role on this strange behavior. During surface oxidation in an aqueous solution of potassium permanganate,

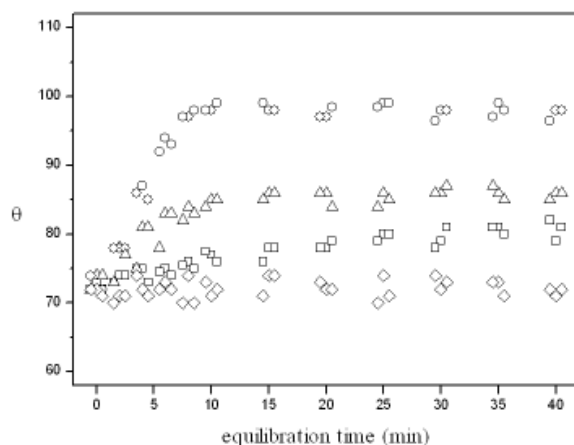


Figure 1. The change in contact angles (θ) of water on surface-oxidized rubber plaques as a function of equilibration time against water at room temperature (\diamond), 50°C (\square), 70°C (\triangle) and 100°C (\circ). Each data point indicates the average values of contact angles taken on separate samples.

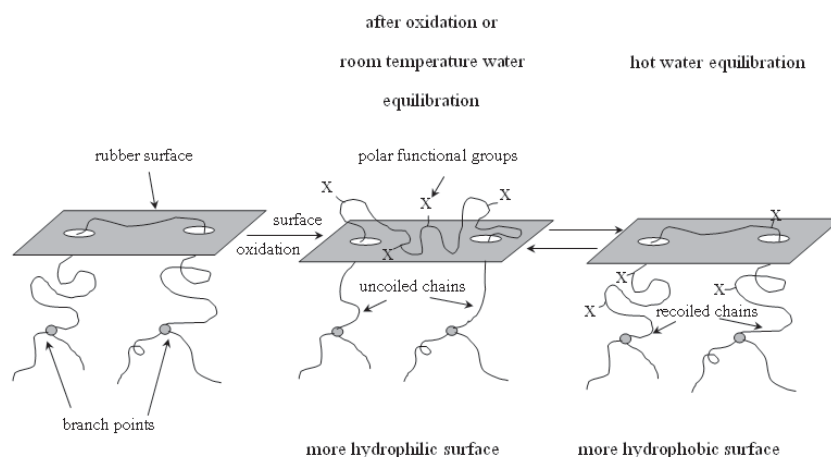


Figure 2. Schematic illustration of the mechanism leading to entropic unfavorable conditions of the interfacial chains.

polar functional groups are introduced to rubber surface. They, at the same time, pull interfacial chains out of their random coil conformations due to the interaction between these functional groups and water molecules leading to uncoiling of interfacial chains (Figure 2). Under this condition, interfacial chains tend to recoil in order to increase their entropy. When samples are equilibrated against hot water, the uncoiled chains could recoil and take polar functional groups deeply away from the interface for at least 5-10 Å deep (Sperling,

1992; Ferguson and Whitesides, 1992; Rouse *et al.*, 1999; Khongtong and Ferguson, 2001; Khongtong and Ferguson, 2002). The longer samples are exposed to hot water, the greater amounts of functional groups are removed from the interface; hence, greater hydrophobicity at surfaces is observed as the equilibration time increased as showed for samples equilibrated against 70°C water in Figure 1.

To ensure that an entropy is playing a major role on the surface reconstruction observed here,

rubber plaques with the same degree of crosslinking ($M_c = 32,000$ g/mol) were oxidized and equilibrated against two more temperatures of water, 50 and 100°C. In Figure 1, the directions of surface reconstruction of samples heated against these two temperatures of water are consistent each other and consistent to that equilibrated against 70°C water - surfaces become more hydrophobic as a function of equilibration time and then reach the steady state. Moreover, the higher the temperature of water applied to the samples, the greater the hydrophobicity at steady state observed. The results reported here likely reflect the restoring force of the uncoiled chains to recoil and carry functional groups away from the interface. This restoring force is proportional to temperature of the system as described using freely jointed chain model of an extended single polymer chain (Gent, 1978; Flory, 1989). Thus, the restoring force has more advantage over the interaction between polar functional groups and water molecules when the oxidized samples exposed to higher temperatures of water. In addition, the kinetics of entropic surface reconstruction when equilibrated against water at higher temperatures is faster. This result also supports our hypothesis according to the mechanism of this surface reconstruction - greater entropic driving force at higher temperatures.

The effect of segmental chain length on surface reconstruction

As mentioned previously that the uncoiling of polymer chains during surface oxidation is a trigger leading to this unusual surface reconstruction, we also expected that if longer segments of interfacial chains were uncoiled, greater entropic restoring force would be built up and cause greater magnitude of surface reconstruction. This mechanism is likely the same as a stretched rubber band - the bigger extension is applied to it, the greater restoring force is built up. To test this hypothesis, we equilibrated oxidized rubber plaques containing different degrees of crosslinking against water at 70°C. The samples with greater value of M_c was expected to have longer chain segments to be uncoiled during oxidation; hence, greater

restoring force would be built up. As expected, after equilibration against 70°C water, the samples with greater values of M_c displayed bigger magnitude of entropic surface reconstruction, and higher hydrophobicity at the steady state is observed (Figure 3). The values of contact angles at the steady state of rubber plaques with $M_c = 107,000$ g/mol, which shows the greatest entropic effect, are still below the unoxidized rubber surfaces ($\theta \sim 100-110^\circ$). This may infer that some functional groups still remain at the interface after equilibration against 70°C water and these functional groups are the result of the competition between entropic restoring force and enthalpic H-bonding at the interface. Additionally, the kinetics of this surface reconstruction is slower for rubber plaques with greater values of M_c . This may imply that longer interfacial chain segments required longer period of time to change conformations (Gent, 1978; Flory, 1989). Thus, the results stated here also support our central hypothesis - chain uncoiling leading to this unusual surface reconstruction.

The reversibility of surface reconstruction

As mentioned at the beginning that the application of this study is to develop a smart rubber surface; thus, we need to ensure that this behavior is reversible. We used the annealed rubber plaques ($M_c = 32,000$ g/mol), the samples that had been already equilibrated against hot water at 50, 70, and 100°C (the treatment mentioned in Figure 1), in this experiment. These samples were, then, immediately floated in water at room temperature for 30 h and the contact angles were taken at different periods of time. Figure 4 displays the decreasing of surface hydrophobicity as a function of equilibration time against room temperature water. At equilibrium, all samples reach about the same level of hydrophilicity and the values of contact angles observed here are consistent with that of these surfaces before annealing (just after oxidation surfaces). This may reflect that all hydrophilic functional groups, buried deeply away from the interface during hot water equilibration, could migrate back to the interface again to form H-bonding with water molecules. In the same

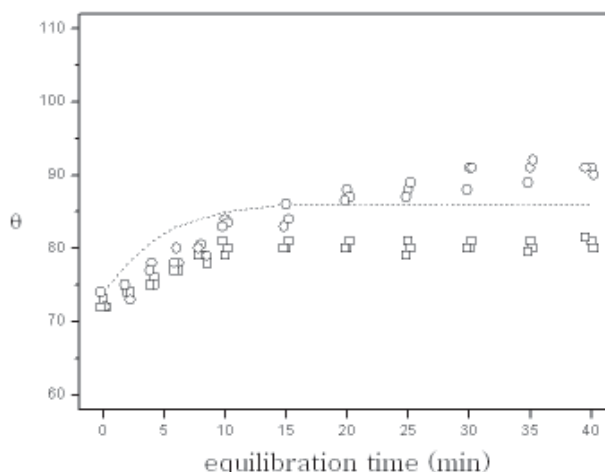


Figure 3. The changes in contact angles (θ) of water on surface-oxidized rubber plaques as a function of equilibration time against water at 70°C for the rubber plaques with $M_c = 5,000$ g/mol (\square), 107,000 g/mol (\circ). The results for rubber plaques with $M_c = 32,000$ g/mol (dashed line) are also provided, for comparison. Each data point indicates the average values of contact angles taken on separate samples.

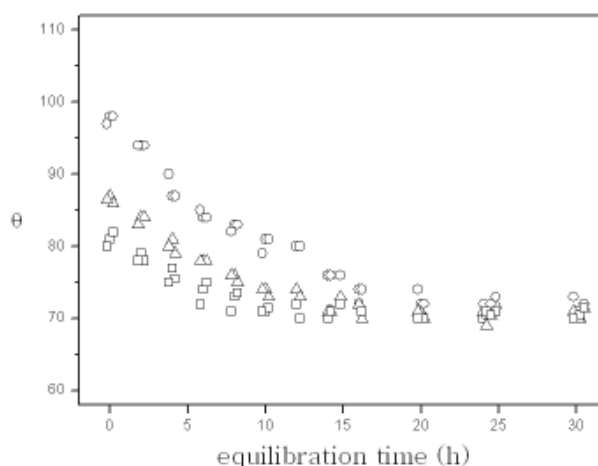


Figure 4. The changes in contact angles (θ) of water as a function of equilibration time against water at room temperature for the samples that had been equilibrated against water at 50°C (\square), 70°C (\triangle), and 100°C (\circ). The data points at time equal to zero indicate the values of contact angles right after equilibration against each temperature of hot water. Each data point indicates the average values of contact angles taken on separate samples.

experiment, we also found that the samples that had been equilibrated against higher temperature of water shows slower kinetics of the reversible surface reconstruction when equilibrated against water at room temperature. Slower kinetics

observed here may infer that the functional groups on these surfaces were pulled more deeply away from the interface, during equilibration against higher temperatures of water, due to greater restoring force. Thus, when this sample was

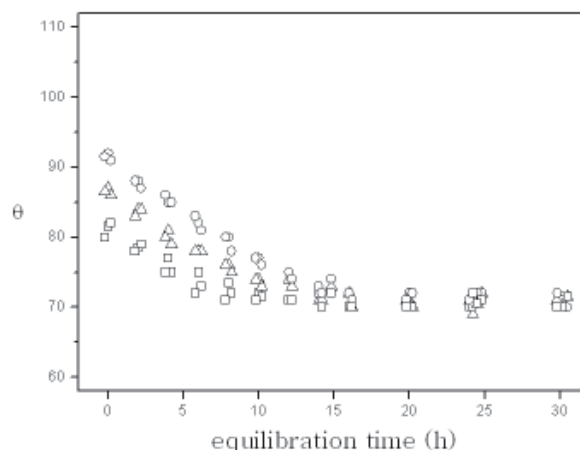


Figure 5. The changes in contact angles (θ) of water as a function of equilibration time against water at room temperature for the samples with different degrees of crosslinking: $M_c = 5,000$ g/mol (\square), $M_c = 32,000$ g/mol (\triangle), and $M_c = 107,000$ g/mol (\circ). The data points at time equal to zero indicate the values of contact angles right after equilibration against water at 70°C . Each data point indicates the average of values of contact angles taken on separate samples.

brought into contact with water at room temperature, these buried functional groups need longer time to migrate back to the interface.

To confirm the result observed in Figure 4, we conducted the parallel experiment using the annealed rubber plaques - the samples that had been treated by the procedures mentioned in Figure 3. These samples were floated in water at room temperature for 30 h and the contact angles were taken at different periods of time. Figure 5 shows that after equilibration against water at room temperature, the surfaces of all samples also return to their original hydrophilicity, the level of contact angles right after oxidation, at the equilibrium. Moreover, the samples with longer chain segments (greater values of M_c) display slower kinetics of surface reconstruction here. This result is analogously consistent with that mentioned in Figure 4 and confirms that chain recoiling is the mechanism leading to entropic surface reconstruction observed in this research.

Conclusion

The oxidized surfaces of crosslinked rubber respond to hot water in the opposite direction base

on the minimization of interfacial free energy, they become more hydrophobic. The magnitudes of this surface reconstruction are greater and the kinetics is faster when equilibrated against higher temperatures of water. The uncoiling of interfacial chains during surface oxidation are expected to play a major role on this unusual change. We also demonstrated that the samples with different degrees of crosslinking show the analogous results. Moreover, this change is reversible and the kinetics of the reversibility also confirms the mechanism of this surface reconstruction. These results illustrate that the oxidized surface of crosslinked rubber could show different ways of change in surface energy that could be used to develop a smart rubber surface. They also illustrate the importance of treating polymeric materials as an integrated system by comprising interfacial properties (i.e., surface reconstruction) and bulk properties (i.e., entropic unfavorable condition of uncoil chains, crosslink density) together.

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