

Tunable Glue : Rubber Elasticity Control of Adhesion at Polymer/Metal Interface

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ABSTRACT

The adhesion at this interface could be switched on and off just by lowering and raising temperature. A treated surface of 1,4-polybutadiene provides strong adhesion to aluminum at room temperature due to the interaction between hydrophilic functional groups, introduced by surface oxidation, and Al_2O_3 —native oxide on aluminum surface. This interaction also acts as an enthalpic driving force to stretch chains at the interfacial region of an elastomer to entropically unfavorable condition. Increasing temperature, in turn, induces these stretched interfacial chains to recoil in order to increase entropy of the system, thereby functional groups are pulled away from the elastomer/aluminum interface leading to the weakening of adhesion.

Key words: Tunable adhesion - Smart surface - Polymer interface - Rubber elasticity

INTRODUCTION

Designing material surfaces so that their adhesion could respond automatically to environmental changes (e.g. temperature) has been a focus of attention in the research field of smart surfaces. This would provide active control solution of adhesion over time such as antifouling, barrier films, or cell adhesion (1,2). We report here an interface of polymer/metal that could achieve greater temperature-dependent adhesion at low temperature and weaker adhesion at high temperature.

METHODS

We used 1,4-polybutadiene ($M_w=420,000$ g/mol; 36% *cis*, 55% *trans*, and 9%-1,2; Aldrich), the elastomer the oxidized surface of which became more water repellent when heated and less water repellent when cooled in different temperatures of water to ensure that the system of 1,4-polybutadiene/aluminum interface would behave analogously the same (3-5). Before using this polymer, we formed it into a film by adding ~ 50 ml of toluene (99 %; E.M. Science) to five grams of 1,4-polybutadiene to make polymer solution to which was added 0.02 phr of dicumyl peroxide (DCP; 98 %; Aldrich) as a crosslinker (3). After overnight stirring, the solvent was removed under vacuum until the polymer was completely dry. This dry polymer was then molded into a film with thickness of ~1 mm by compression

S KHONGTONG AND GS FERGUSON

molding at 150°C for 84 min which is eight half-lives of DCP (3,4). The crosslinked films were cut into 1 cm x 10 cm strips. Then one of the board surfaces was oxidized by floating on an aqueous solution of KMnO_4 (0.045 M) and K_2CO_3 (0.017 M) at room temperature for 50 min to introduce adhesion promoting groups, carboxylic acid, and other hydrophilic functional groups on the surface (3-5). In order to test the adhesion at the surface of this polymer, aluminum sheet (99.5%, thickness of 0.007 mm; A.J. Oster Foils) was chosen because of the well established interaction between the adhesion promoting groups and the Al_2O_3 , native oxide which is produced as soon as aluminum comes into contact with air (6,7). The aluminum sheet was cut into strips of the same dimensions as those of the elastomer strips. Aluminum and elastomer strips were then placed into contact. An expected mechanism controlling the tunable adhesion is illustrated in **Figure 1**. When the oxidized elastomer surface is placed against aluminum, adhesion promoting groups migrate to the interface to interact with Al_2O_3 and provide a strong adhesive joint (3-6). The migration of these adhesion promoting groups requires interfacial chains that connect to crosslinked points to extend out of their random coil conformations, and this mechanism induces restoring force in each extended single chain due to rubber elasticity (3-5,8,9). When temperature increases, those extended interfacial chains are driven to recoil and pull the adhesion promoting groups away from the interface resulting in a weaker adhesive joint.

RESULTS AND DISCUSSION

To test the hypothesis illustrated in **Figure 1**, we equilibrated elastomer/aluminum interface under ~50 psi of pressure at room temperature for 12 h to enhance strong adhesive joint. We found in separated experiments that 12 h is long enough to maximize adhesion at this interface. The data point at 0 min of heating time indicates the level of adhesion for samples after this treatment (**Figure 2**). T-peel test (ASTM D1876-95) was performed to monitor this adhesion using an Instron 5567 tensile testing machine with a 500-N loadcell). All samples were tested at room temperature with the slow constant peeling rate of 20 mm/min. In order to test the adhesion at higher temperature, the room temperature-treated samples were then heated at 80°C, which is the temperature expected to lead interfacial chains to reach the upper limit of rubber elasticity effect (3,4), under the same pressure for different periods of time to introduce interfacial chain recoiling. After quick cooling to room temperature under a stream of nitrogen to slow chain reptation at the interfacial region, adhesion at these interfaces was monitored. As shown in **Figure 2**, adhesion drops from its room temperature level until it reaches the steady state after about 10 min of heating and stabilizes roughly at that level. Adhesion at unoxidized elastomer/aluminum interface, which is treated in the same way for comparison, is independent of temperature. These results suggest that deterioration in adhesion at the oxidized elastomer/aluminum interface is due to migration of adhesion promoting groups away from the interface while the atomic contact between elastomer and aluminum at the interface remains nearly unchanged during heating process (7). The stable adhesion at unoxidized elastomer/aluminum interface also strongly argues against the possibility of reduction in adhesion upon heating due to rubber elasticity being formed at the elastomer surface when it penetrates into micro-roughness of aluminum (10-13). In addition, the higher level of adhesion at oxidized

elastomer/aluminum interface after heating, compared to the unoxidized system, reflects the necessary adhesion promoting groups remaining at the interface. These results confirm the hypothesis illustrated in **Figure 1** and are consistent with the behavior at elastomers/water interfaces.

To examine this tunable adhesion further, oxidized elastomer/aluminum strips were equilibrated under ~ 50 psi of pressure at room temperature for 12 h to enhance strong adhesion. They were heated at 80°C under the same pressure for 30 min to weaken the adhesion and were then equilibrated under ~ 50 psi of pressure again at room temperature. On the second room temperature equilibration, the adhesion slowly increased and reached its original level within 24 h (**Figure 3**). The reversibility of adhesion found here is also consistent with the result at polymers/water interfaces reported elsewhere (3,4). The slower increase of adhesion observed here, compared to the 12 h that it took on the first room temperature equilibration, suggests that adhesion promoting groups may be buried deep below the interface due to the effect of rubbery elasticity. In addition, we found in separated experiments that this reversibility of adhesion extended through several cycles of heating at 80°C and cooling to room temperature.

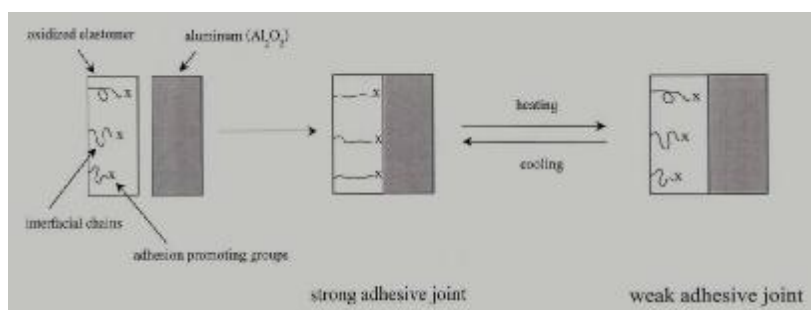


Figure 1. An illustration of the mechanism leading to temperature-dependent adhesion at the interface of oxidized elastomer and aluminum (Al_2O_3)

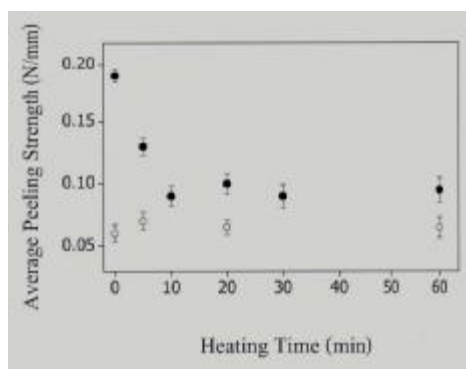


Figure 2. Adhesion during heating at 80°C under ~ 50 psi for 1,4-polybutadiene/aluminum interface. The symbol (●) represents the data for oxidized samples. The symbols (○) represents the data for unoxidized samples. The points represent the average values of peeling strength in the plateau of force-displacement

plots from T-peel tests measured on separate samples, and the error bars indicate the standard deviation of peeling strength on the same plot for that sample

In summary, oxidized 1,4-polybutadiene/aluminum interface provides a tunable adhesion that becomes strongly adhesive at room temperature and less adhesive at 80°C. We hypothesize on the basis of the behavior at elastomer/water interface that, during room temperature equilibration, adhesion promoting groups migrate to the interface to interact with Al_2O_3 . These chemical groups are connected to the floppy interfacial chains linking to crosslinked points. As a result, this migration causes them to extend out of their random coil conformations and to lose their entropy, the condition that produces elastic restoring force. During high temperature equilibration, these extended interfacial chains recoil and subsequently cause the withdrawal of those chemical groups from the interface. The results described in this paper also illustrate the importance of treating polymers as integrated systems comprising the interfacial properties (e.g., adhesion) and their known bulk properties (e.g., rubber elasticity).

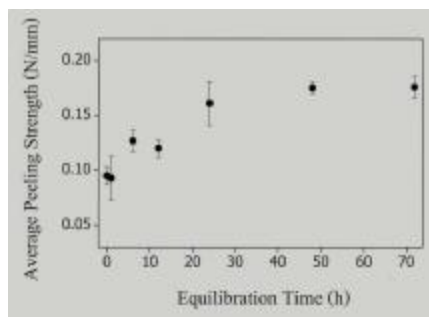


Figure 3. The kinetics of adhesion recovery when the samples that had been heated at 80 °C were subsequently equilibrated at room temperature. The points indicate the average values of peeling strength in the plateau region of force-displacement plots (T-peel tests) measured on separate samples, and the error bars indicate values within one standard deviation of the average

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บทคัดย่อ

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กาวที่ปรับสภาพได้โดยใช้สมบัติความยืดหยุ่น

ผิวสัมผัสระหว่าง oxidized 1,4-polybutadiene/aluminum ให้ความเป็น “กาว” ที่สามารถตอบสนองต่อสิ่งเร้าภายนอก เช่น อุณหภูมิ ได้ด้วยตัวเอง กล่าวคือ ความแข็งแรงของผิวสัมผัส (adhesion) จะลดลงเมื่ออุณหภูมิของสิ่งแวดล้อมเพิ่มขึ้นและความแข็งแรงของผิวสัมผัสสามารถกลับมาสูงเหมือนเดิมได้อีกครั้ง เมื่ออุณหภูมิของสิ่งแวดล้อมลดลง สำหรับกลไกที่ควบคุมเป็นกาวที่ผิวสัมผัสนี้คาดว่าเนื่องมาจาก rubber elasticity ของสายโซ่พอลิเมอร์ที่อยู่บริเวณผิวสัมผัสของพอลิเมอร์ โดยกลไกนี้เกิดขึ้นจาก adhesion promoting groups ซึ่งติดอยู่กับสายโซ่พอลิเมอร์ จะทำหน้าที่เหมือนกระสวยทอผ้าที่วิ่งไป-มา ระหว่าง bulk และรอยต่อระหว่างผิวสัมผัส (interface) เมื่อขึ้นทดสอบอยู่ในสภาวะแวดล้อมที่มีอุณหภูมิต่ำ adhesion promoting groups จะวิ่งไปอยู่ที่รอยต่อระหว่างผิวสัมผัส เพื่อให้เกิด interaction กับ Al_2O_3 ซึ่งเป็น native oxide ที่ผิวของ aluminum ส่งผลให้รอยต่อระหว่างผิวสัมผัสมีความแข็งแรงเพิ่มขึ้น และในขณะเดียวกันนั้น เมื่อ adhesion promoting groups อยู่ที่ยูที่รอยต่อระหว่างผิวสัมผัส สายโซ่พอลิเมอร์ก็จะถูกยืดออก สายโซ่ของพอลิเมอร์ที่ถูกยืดออกกันจะมีสภาวะเช่นเดียวกับหนังสดึงที่ถูกยืดคือจะเกิดแรงที่พยายามหดตัว (restoring force) เนื่องจากคุณสมบัติของ rubber elasticity ดังนั้นเมื่ออุณหภูมิของสภาวะแวดล้อมเพิ่มขึ้น สายโซ่พอลิเมอร์เกิดการหดตัวและดึงเอา adhesion promoting groups กลับไปสู่ bulk ส่งผลให้ความแข็งแรงของผิวสัมผัสลดลง

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