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Notes

Improved Adhesive Strength of Vulcanized Rubber upon Laser Treatments

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Abstract: Surface treatment using an excimer pulse laser beam has been conducted in order to increase the adhesive strength of vulcanized rubber. The adhesive strength increased with increasing the number of irradiation time with laser pulses and reached to 1,500 N/m after 100 cycles of irradiation. Increased in energy density was directly proportional to the improvement of the adhesive strength. Maximum value of the adhesive strength of 1,500 N/m obtained at the energy density of 176 mJ/cm^2. We conclude that an increased energy density improves in both the surface area and adhesive strength.

Keywords: vulcanized rubber, surface treatment, ArF excimer laser, adhesion.

Introduction

For perfect adhesion to occur between two layers there must be sufficient cohesion between the layers and the adhesive. During adhesion, a solid adhesive is transformed into a liquid having a high viscosity by either melting with heat or adding it to a solvent. When pasting an adhesive, it is spread on the surface of the adhering material to make it wet. When both sides of the adhering material are overlapped, adhesion occurs when the adhesive transforms into a solid. If the adhesive is a solution, the solvent can be removed by volatilizing it upon heating, and then the molten adhesive can be solidified upon cooling. The adhesion of vulcanized rubber does not take place in the same manner as that of unvulcanized rubber, which can be applied merely by wiping a solvent on the adhesion surface. Vulcanized rubber consists is of a three-dimensional polymer that is cross-linked with such things as sulfur and metallic oxides. Therefore, it is impossible to compare its properties with those of unvulcanized rubber, or to expect chemical fusion. In addition, the surface of vulcanized rubber contains many reversers, softeners, and waxes, which must be removed for adhering purposes. Moreover, for improved adhesion, appropriate surface treatment or reforming of the adhesive must be undertaken. Methods for improving adhesiveness include scratching,[1] oxidizing the surface,[2,3] and introducing a functional group to the surface.[4,5]

The surface treatment of the chemical compounds in silicon rubber or vulcanized rubber is usually performed by using a glow discharge or a corona discharge.[2,6,7] Modifying a polymer surface of a low-temperature plasma through glow discharge or corona discharge does not directly influence the characteristics of the polymer material itself; only the modification of the surface layer is capable of having that effect. The use of an excimer laser is a dry process, compared to the others that are generally wet, and it not only simplifies the surface modification process but it also saves water resources that are used largely for cleaning the surface. There is no need to expend energy on sewage treatment and drying, and there is no need to worry about atmospheric diffusion of organic solvents. In experiments performed to date, almost none of the procedures above have been undertaken.

In this study, we examined the surface treatment of vulcanized rubber using an ArF excimer laser. Herein, we discuss arguments in favor of this process and examine the mechanism that results in improvements in adhesion between the vulcanized rubber and the urethane adhesive.

Experimental

Figure 1 displays the excimer pulse laser equipment used in this experiment. The light source was a Lambda Physik LPX-100ArF excimer laser (wavelength: 193 nm). We examined the experimental material by concentrating the pulse laser rays (pulses in 20 nm intervals) through a lens. Because the location of the lens affects the degree of concentration, the concentration lens was controlled by attaching x-y-z microseism equipment, which includes storing equipment; this set-up allowed compensation to be induced regularly. As indicated in Table I, the sample material we used was a vulcanized rubber of 2 mm width, a chemical compound of natural rubber, and styrene butadiene rubber that had been vulcanized for 30 min at 140 °C using a heat press. The surface

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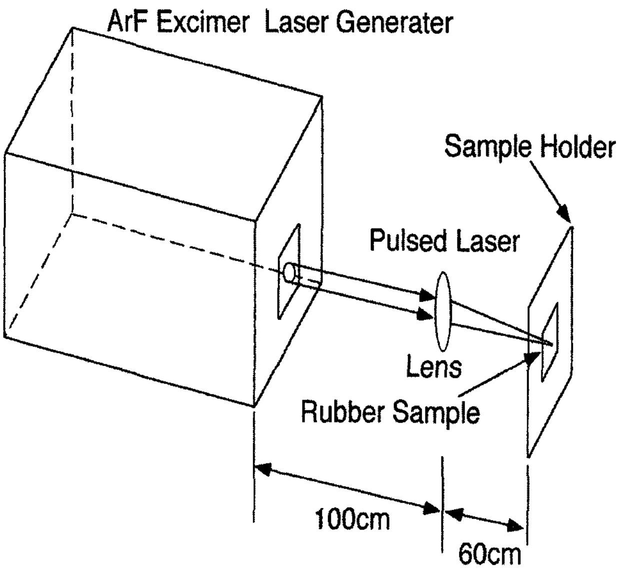
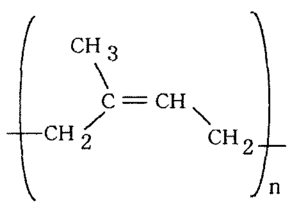


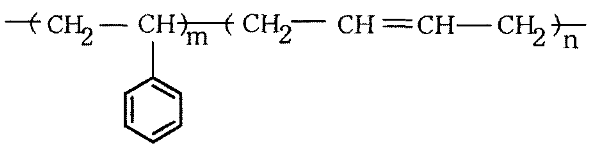
Figure 1. Schematic diagram of the excimer laser system.

Table I. Ingredients of the Vulcanized Rubber Used in This Study

cis 1.4 — Polyisoprene Rubber:IR



Emulsion Polymerized Styrene -Butadiene Rubber:E-SBR



Vulcanization agent	Sulfur
Vulcanization accelerater	Sulfenamide Thiazole
Assistant of vulcanization Accelerater	ZnO Stearic Acid
Filler	Carbon Black $CaCO_3$

of the vulcanized rubber sample was wiped with acetone and toluene and then positioned 60 cm from the concentration lens, which was located 100 cm from the exit point of the laser light. We observed the surface of the vulcanized rubber through a scanning electronic microscope (HITACHI: FE-SEM S-4000). As indicated in Figure 2, the adhesive strength was measured using a tensile tester (SHIMADZU AGS-100D, Japan) at a crosshead speed of 10 mm/min at room temperature. The polyurethane adhesive was first applied between the vulcanized rubber and rubber that had been treated with chlorine (used as a reference) and then it was fixed with a clip and left for 2 days at room temperature. Finally, the adhesive strength was measured by pulling each end of the two sides in opposite directions.

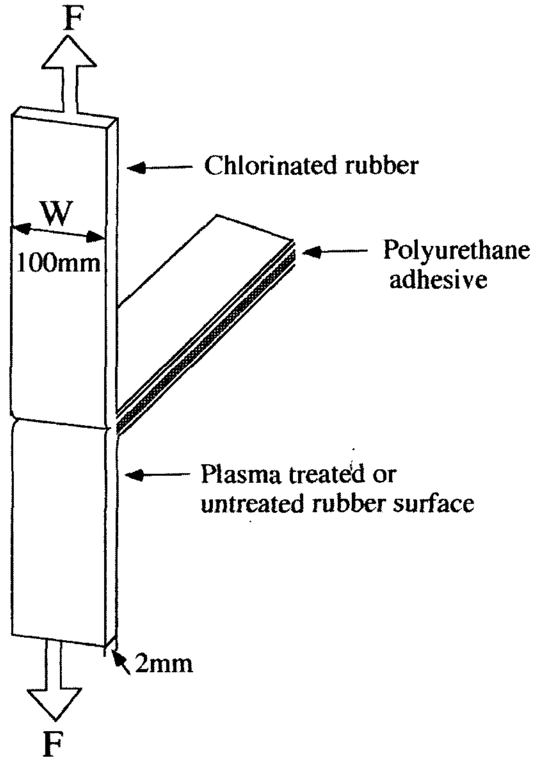


Figure 2. T-Peel test geometry.

Results and Discussion

The excimer pulse laser equipment is displayed in Figure 1. The sample was examined by concentrating the excimer pulse laser rays through a lens. Therefore, one pulse peak creates a large energy density on the surface; if a material absorbs the laser rays, then it is eradicated from the sample by easily causing an instantaneous separation from the polar layers.

Figure 3 illustrates the dependency of adhesive strength on the number of laser rays emitted. In these experiments, the energy density was 179 mJ/cm^2 at a laser pulse rate of 1 Hz. There was a large increase in the adhesive strength (originally 1,200 N/m) as the number of laser pulses increased. After ten pulses, the adhesive strength was 1,350 N/m; after 55, it was 1,440 N/m; after 100, the largest adhesive

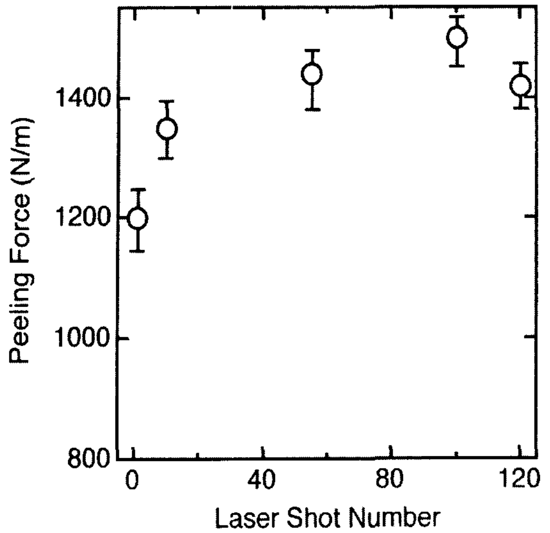


Figure 3. The peeling force as a function of the number of laser pulses. The peeling force of untreated rubber was 280 N/m.

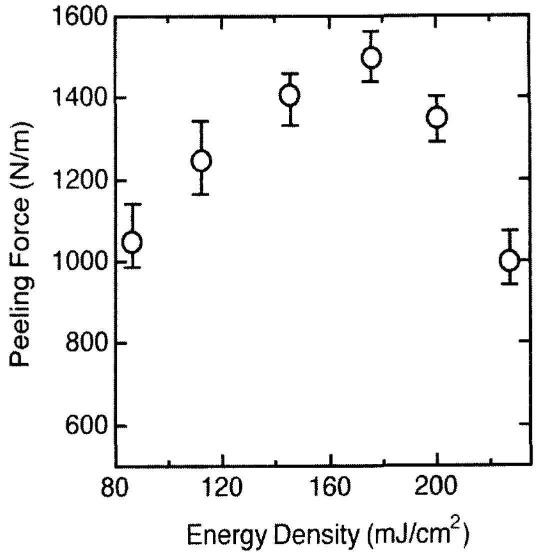


Figure 4. The peeling force as a function of laser energy density. The peeling force of untreated rubber was 280 N/m.

strength was obtained: 1,500 N/m. After irradiation with the 120th pulse, however, the adhesive strength decreased to 1,420 N/m. We observed that up to the 100th laser pulse, separation from the surface occurs causing the roughness of the surface to change (an increase in the surface area) and an anchor effect takes place (i.e., a collection of the adhesive in the rough parts so that they become hard to separate). Upon further irradiation, however, not only does separation occur on the surface but metamorphism also occurs through the temperature change; even though adhesion occurs, the adhering sides separate easily.

Figure 4 presents the dependency of the adhesive strength on the laser energy density. The conditions of this experiment were such that the number of laser pulses at 1 Hz totaled 100. As we observe in this Figure, the adhesive strength was 280 N/m before the experiment began, but as the energy density increased, the adhesive strength increased proportionally: to 1,050 N/m at 86 mJ/cm^2, 1,250 N/m at 112 mJ/cm^2, 1,410 N/m at 145 mJ/cm^2, and at 176 mJ/cm^2, the highest adhesive strength (1500 N/m) was achieved. When the energy density was increased further, however, to 200 mJ/cm^2, the adhesive strength was 1,350 N/m; at 227 mJ/cm^2, there was a further decrease to 1,000 N/m. This observation indicates that not only does separation from the surface occur with successive increases in energy density but also metamorphism occurs through the rise in temperature; even though adhesion occurs, the adhering sides come apart easily.

Figure 5 displays SEM images of the surface of the rubber before and after laser irradiation. Before irradiation, as indicated in Figure 5(a), there was almost no change on the surface. After laser irradiation, however, at an energy density of 176 mJ/cm^2 (Figure 5(b)), the sizes of the particles become larger and rough sections became visible, which implies an

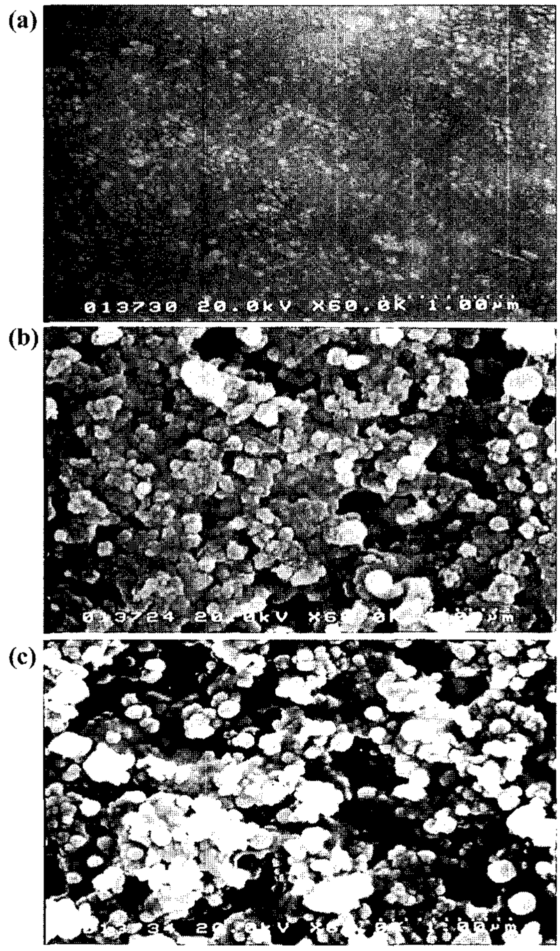


Figure 5. SEM images of treated and untreated rubber surfaces. (a) untreated; (b) treated at a laser energy density of 176 mJ/cm^2; (c) treated at a laser energy density of 227 mJ/cm^2.

increase in surface area. Therefore, the adhesive appears in the dented areas such that the layers became difficult to separate, which resulted in the enhanced adhesive strength. When the energy density was increased to 227 mJ/cm^2, however, as in Figure 5(c), the particle combination was sparse, which led to an increase in the number of dented regions and the adhesive strength decreased accordingly.

Before laser irradiation, rough zones were scarce on the surface, but they were uniform, and so the adhesive strength was small (280 N/m). Increasing the energy density, however, led to the increase of not only the surface area but also the number of dented regions, and so the adhesive collected in these places and increased the adhesive strength. An increase in the energy density caused the particles to combine inconsistently and resulted in more dented areas. Through combustion of the surface as a result of the increased laser energy, metamorphism of the rubber occurred and, thus, the adhesive strength decreased.

Conclusions

The adhesive strength of vulcanized rubber was improved upon surface treatment using excimer pulse laser rays that were concentrated through a lens. Upon increasing the energy density, the adhesive strength increased; the highest adhesive strength, 1,500 N/m, was achieved at an energy density of 176 mJ/cm^2. By increasing the number of irradiation pulses, the adhesive strength increased 100-fold: and the highest adhesive strength was 1,500 N/m. Upon further irradiation, however, the adhesive strength decreased to 1,420 N/m because of changes in the roughness of the surface as a result of separation on the surface. When the energy density was increased further, a decreased in adhesive strength also occurred. Increased energy density not only brings about an increase in surface area due to an increase in the number of dented regions but it also increases the adhesive strength through a gathering of the adhesive in these regions.

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