

EFFECTS OF SURFACE TREATMENTS WITH FLAME PLASMA AND SILANE ON MECHANICAL PROPERTIES OF SILICA REINFORCED ELASTOMERIC COMPOSITES

Jun-Man Lee, Sang-Ryeoul Ryu, Dong-Joo Lee*

School of Mechanical Engineering, Yeungnam University, Gyungsan, Korea

* Corresponding author (djlee@yu.ac.kr)

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1 Introduction

Particle-reinforced composites have been studied extensively because of their technological and scientific importance. The strength and stiffness can be readily improved by adding either micro or nano particles since rigid inorganic particles generally have a much higher stiffness than polymer matrices. [1-4] The mechanical properties of polymeric composites containing various particles depend strongly on their size, particle-matrix interface adhesion and particulate content. Especially, the particle size and strong adhesive bonding with the rubber matrix have an obvious effect on mechanical properties of elastomeric composites.[5]

In this paper, the effect of surface treatments with the atmospheric pressure flame plasma (APFP) and epoxy silane (ES) is experimentally investigated as a function of silica mean diameter to yield the best mechanical properties of reinforced elastomeric composites.

2 Experimental Procedure

The matrix for experimental works was a RTV (room temperature vulcanization) type silicone KE-12 (viscosity: 100poise at 25 °C) from Shin-Etsu chemical Co., Ltd. The reinforcing silica size is 2.2, 12.4, 26.6 and 110 (μm), and the volume fraction is 10, 20 and 40 (%) from SAC Co., Ltd. The silica surface was treated with two kinds of method; the physical treatment of silica with an APFP treatment apparatus (Super Flame 100® Center) [6] and the chemical treatment with an epoxy silane coupling agent. The tensile properties were measured using an Autograph (Model AG-5000E) of the Shimadzu machine with a testing speed of 50mm/min. The

specimen geometry was a dumbbell shape (60mm \times 10mm \times 1mm) and cut from the cured plate as shown in Fig. 1-(a) The tearing test was performed using the same machine with a testing speed of 10mm/min. The specimen geometry was 60mm in length and 10mm in width with a crack at the center of one side as shown in Fig. 1-(b) Typically, five specimens were used for a single evaluation.

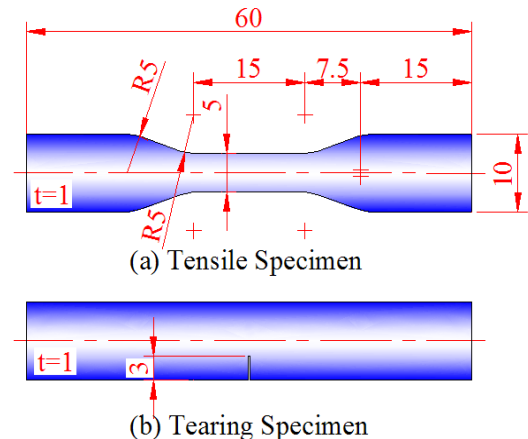


Fig. 1. Specimen geometry.

3 Results and Discussion

3-1 Effects of Particle Size and Volume Fraction

Figs. 2-3 show tensile properties of the matrix and the reinforced rubber as functions of the particle mean diameter and volume fraction. The tensile strength of the matrix is 2.52MPa. The tensile strength of composites increases with the volume fraction and decreases with the mean diameter. When the mean diameter is 110 μm , the tensile strength is lower than the matrix for all volume fraction. The tensile modulus (Young's modulus) was calculated from the initial slope ($\epsilon=0.1\sim0.25$) of

the stress-strain curve. The tensile modulus of matrix is 0.88MPa. That of composites increases with the volume fraction, and indicates the maximum when the mean diameter is $26.6\ \mu\text{m}$. For the size larger than $26.6\ \mu\text{m}$, the tensile modulus decreases slightly. Fig. 4 shows the result of tearing test. The tear energy of elastomeric composites is calculated by integrating the area of the load-displacement curve. The tear energy of the matrix is 6.84N-mm, and the composites with silica increase with the volume fraction and mean diameter. However, the cases for 2.2 and $12.4\ \mu\text{m}$ with the volume fraction of 10% show a lower value in comparison with the matrix.

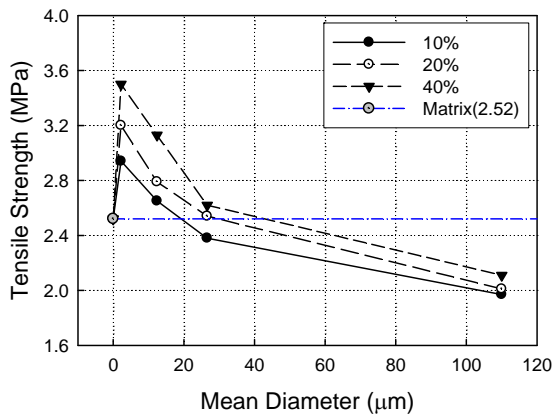


Fig. 2. Effects of mean diameter and volume fraction on the tensile strength of reinforced rubbers.

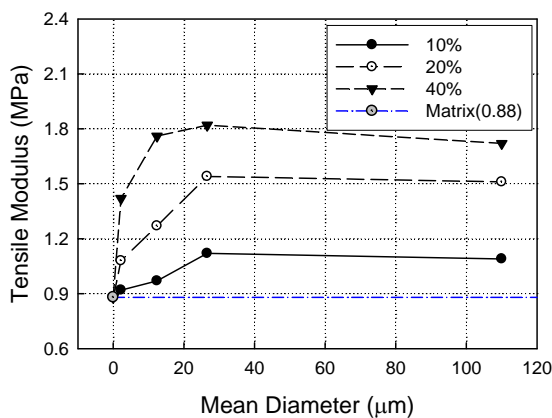


Fig. 3. Effects of mean diameter and volume fraction on the tensile modulus of reinforced rubbers.

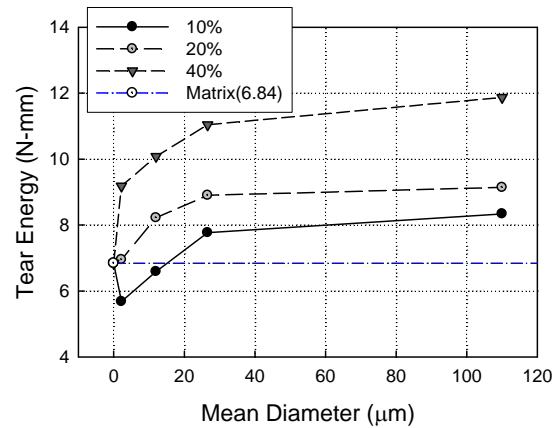


Fig. 4. Effects of mean diameter and volume fraction on the tear energy of reinforced rubbers.

3-2 Effects of Surface Treatments

Fig. 5 shows tensile stress-strain curves of the matrix and silica ($26.6\ \mu\text{m}$, 40%) reinforced rubbers. The rupture strain of composites is greatly reduced, and the stress of those is significantly increased at low strain region when it compared to the matrix. Also, the mechanical properties with APFP ('P') or epoxy silane ('ES') treatment tend to increase compared to the untreated. Figs. 6-7 show the tensile strength and tensile modulus with different the mean diameters at the volume fraction of 40%. The tensile strength of composites shows the maximum value when the mean diameter is $2.2\ \mu\text{m}$, and that of composites decreases with increasing the mean diameter. Also, the tensile strength of composites with APFP and ES treated silica is higher in the order of 5~9% and 10~12%, respectively. The tensile modulus of composite increases with increasing the mean diameter and shows the maximum value at $26.6\ \mu\text{m}$. The tensile modulus of silica reinforced composites with APFP and ES treated is increased 14~22% and 21~26%, respectively. Fig. 8 shows the result of the tear energy as a function of the mean diameter. The tear energy of composites increases with increasing mean diameter compared with the matrix, because of the crack bias of around particles and the increasing energy loss in the cracked region. The tearing energy of silica reinforced composites with APFP and ES treated is increased 11~13% and 12~15%, respectively.

The mechanical properties of silica reinforced composites with the surface treatment greatly improved. Especially, the tensile modulus which is mostly affected by interface adhesion increased significantly. Fig. 9 reveals the rate of the tensile modulus increase as functions of mean diameter and surface treatments. The rate of that for both APFP and ES treatments is increased with increasing mean diameter. It seems that the case for a large mean diameter has a good dispersion in the matrix. During the APFP treatment, the support plate was shaken automatically for better treatment. The particle with the large diameter was easy to shake. However, the smaller one was difficult to shake uniformly. Therefore, it is believed that it is necessary to review the amplitude and frequency of the shaker for the further improvement of mechanical properties.

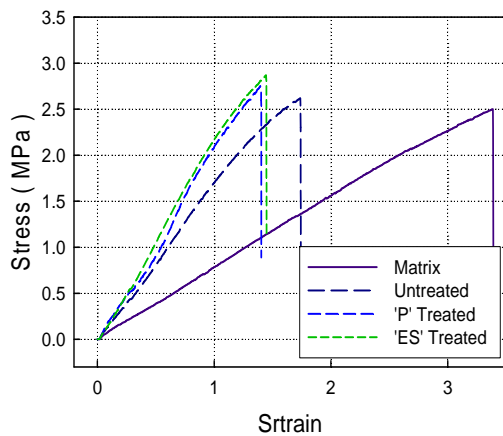


Fig. 5. Stress-strain curves of the matrix and silica reinforced rubbers.

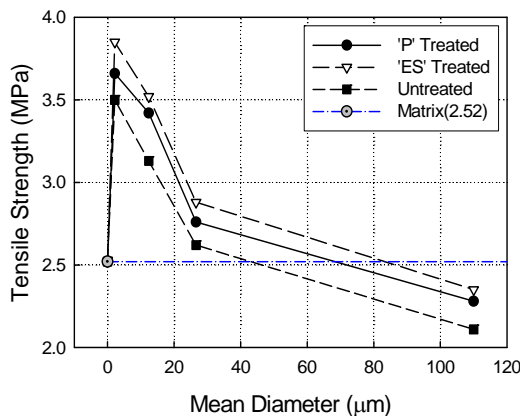


Fig. 6. Effects of mean diameter and surface treatments on the tensile strength of reinforced rubbers.

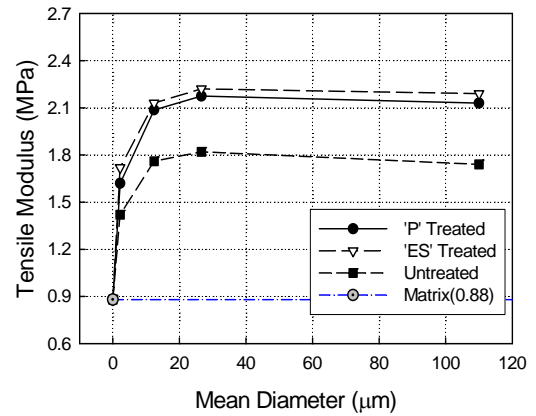


Fig. 7. Effects of mean diameter and surface treatments on the tensile modulus of reinforced rubbers.

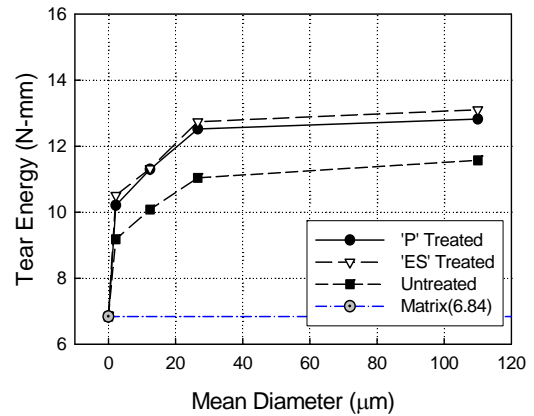


Fig. 8. Effects of mean diameter and surface treatments on the tear energy of reinforced rubbers.

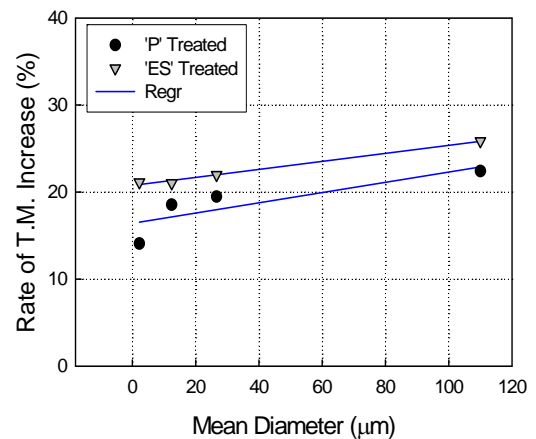


Fig. 9. Effects of mean diameter and surface treatments on the rate of tensile modulus increase.

The major factors in determining mechanical characteristics of silica particles include the size, the volume fraction, structure and silanol (Si-OH) content. In particular, the silanol is known to be mostly affected. Due to the silanol groups on the surface, the silica indicates hydrophilic by adsorbing the water. Accordingly, the dispersion will not be easy and assemble among silica particles in non-polar rubber such as silicon.[7-8] Most of the current plasma treatments require a low pressure or high vacuum, which is a limitation for industrial applications such as the footwear and construction industries. Also, they are too expensive. The APFP treatment is an environmentally-friendly technology and can be incorporated in on-line production. It does not require a vacuum and its effectiveness has been demonstrated in the treatment of several materials with different shapes and sizes.[9-10] Effects of the plasma treatment include improved wettability, adhesion[11], and dyeability because the treatment can be incorporated with large variety of chemically active functional groups as well as roughen the surface of materials.

3.3 Comparisons of Fractured Surface

Figs. 10-11 display the fracture surfaces of untreated and APFP treated silica reinforced rubber. After the APFP treatment, the silica shape is deformed slightly, and the rubber particles are attached on the its surface. Fig. 12 shows the flame plasma from the burner port (85×12.5mm). The primary zone is incomplete combustion and low temperature region of the flame plasma. However, the secondary zone contains a lot of gas and has the highest temperature (about 1000°C) by flame plasma. This temperature is close to the silica glass transition temperature (about 1140°C). Therefore, it is believed that the deformation of silica occurs due to high temperature depending on processing time and shaking condition. Fig. 13 displays the SEM photograph of 'EP' treated silica reinforced rubber. The rubber particles can be seen on the surface, and the boundary between silica surface and matrix is different when compared to the untreated case (Fig. 10).

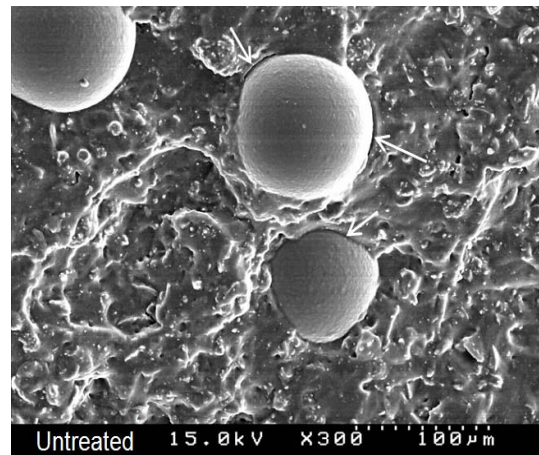


Fig. 10. SEM photograph of untreated silica reinforced rubber.

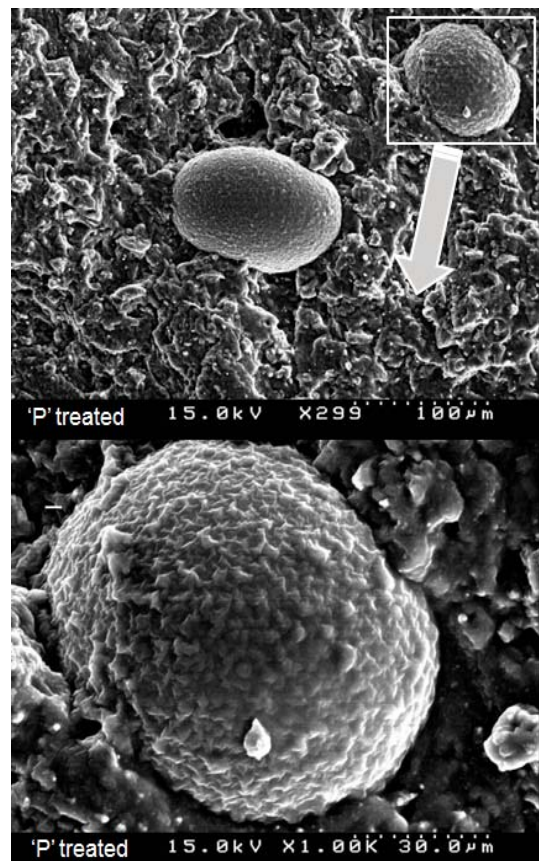


Fig. 11. SEM photograph of APFP treated silica reinforced rubber.

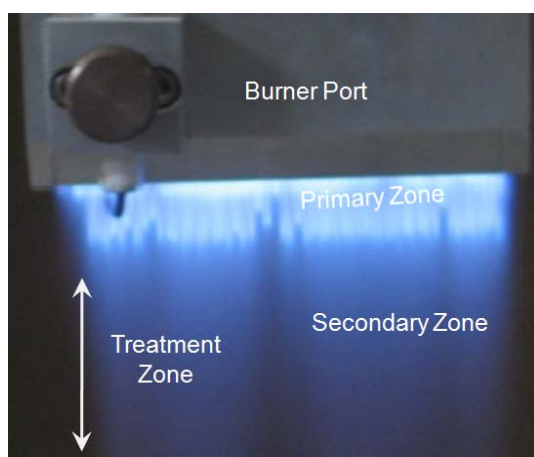


Fig. 12. A flame plasma from the burner port.

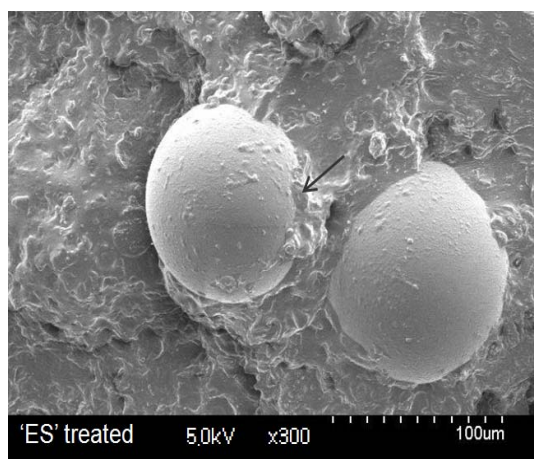


Fig. 13. SEM photograph of epoxy silane treated silica reinforced rubber.

4 Conclusions

The following conclusions can be drawn from this study.

(1) The tensile strength of composites increased significantly with decreasing mean diameter. When the diameter is $2.2\ \mu\text{m}$ and volume fraction of 40%, that of the composite increased about 1.4 times compared to the matrix (2.52MPa). Also, the tensile strength of silica reinforced composites with APFP and ES treatments increased by 5~9% and 10~12%, respectively.

(2) When the diameter is $26.6\ \mu\text{m}$ and volume fraction of 40%, the tensile modulus of the composite increased about 2 times compared to the

matrix (0.88MPa), and the tensile modulus of silica reinforced composites with APFP and ES treatments increased by 14~22% and 21~26%, respectively.

(3) The APFP treatment is a fast, economic and environmental friendly method to improve the mechanical properties of silica reinforced elastomeric composites.

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