

실란 커플링제를 이용한 실리카/고무 복합재료의 기계적 계면 물성의 향상

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Improvement of Mechanical Interfacial Properties of Silica/Rubber Composites by Silane Coupling Agent Treatment

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KEY WORDS : Silica, Silane coupling agent, Surface properties, Mechanical properties, Butadiene rubber

ABSTRACT

Surface-modified silica holds considerable promise in the development of advanced materials for good mechanical properties and stability. In this work, the surface and mechanical interfacial properties of silicas treated with silane coupling agents, such as γ -methacryloxy propyl trimethoxy silane (MPS), γ -glycidoxy propyl trimethoxy silane (GPS), and γ -mercapto propyl trimethoxy silane (MCPS), are investigated. The effect of silane surface treatments of silica on the surface properties and surface energetics are studied in terms of surface functional values and contact angle measurements. And their mechanical interfacial properties of the silica/rubber composites are studied by the composite tearing energy (G_{IIIc}). As a result, the mechanical interfacial properties are improved in the case of silane-treated composites compared with untreated one. It reveals that the functional groups on silica surface by silane surface treatments play an important role in improving the degree of adhesion at interfaces in a silica-filled rubber system.

1. INTRODUCTION

The commercial applications of elastomers often require the use of particulate fillers to obtain the desired reinforcement. In the rubber industry, besides carbon black, silica is the other reinforcing filler used impart specific properties to rubber compounds.¹ It is well known that the carbon black filled rubber composite have multiphase systems depending on the mobility of rubber molecules, which influence the reinforcement of the composites. Extensive works have also been carried out for the structural development in the silica filled rubber composites.²

The surface functional environment of silica particle is quite different from that of carbon black due to the

existence of silanol groups in the particles. Thus, the primary discussion on the structural development in the silica filled rubber systems is focused on the interactions between silica particles and rubber molecules. Wolff and Wang³ studied the effects of surface energies of fillers on rubber reinforcement, and reported that the surface energies of silica were characterized by a lower London dispersive component and a higher polar component. The higher polar component led to strong interactions among silica particles; on the other hand, the lower London dispersive component caused weak filler-rubber interactions, leading to the lower moduli of the vulcanizate at a high elongation. Therefore, surface treatments are needed to improve the reinforcement of the composites by increasing London dispersive component of surface free energetics.

Silane coupling agents have been used in the rubber industry for the last three decades to improve the performance of silica and other mineral fillers in rubber compounds. A silane coupling agent contains functional

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groups that can react with the rubber and the silica. In this way, the rubber-silica adhesion is increased and consequently the reinforcing effect of silica is enhanced.⁴⁻⁶

In the light of these studies, the effect of silane surface treatments on silica surfaces are to introduce surface functional groups onto silica surfaces to increase the specific polar or London dispersive components of surface free energy. Also the mechanical tearing results obtained from the rubber compound composites are discussed.

2. EXPERIMENTAL

Materials and Sample Preparation

Virginal silicas denoted in VS (product name: VN2000) were supplied by Degusa Co. of Korea. The samples denoted in MPS, APS, MCPS were, respectively, prepared in the VS treated with silane coupling agents. The silane coupling agents used in this study, γ -methacryloxy propyl trimethoxy silane (MPS), γ -glycidoxy propyl trimethoxy silane (GPS), and γ -mercapto propyl trimethoxy silane (MCPS), were supplied by Shinetsu Co. of Korea. The chemical structures of the various silane-coupling agents are given in Fig. 1.

In this work, all of the silane coupling agents studied were prepared under constant conditions in order to treat silica surfaces. In these solutions, a co-solvent of methanol (95 wt% in total solvent) and distilled water (5 wt% in total solvent) was used, and the silane concentration was fixed at 0.4 wt%. After the silane coupling agents were hydrolyzed at pH 4.0 for 1 h with acetic acid solution, the silica was dipped in the hydrolyzed silane solution for 1 h and was filtered. The samples washed with distilled water and dried at 60°C for 24 h.⁶⁻⁹

The compounding formulations are reported in Table 1. For the measurement of mechanical properties of filled vulcanized, the compounds were cured at 1.5 MPa and 160°C for 60 min.

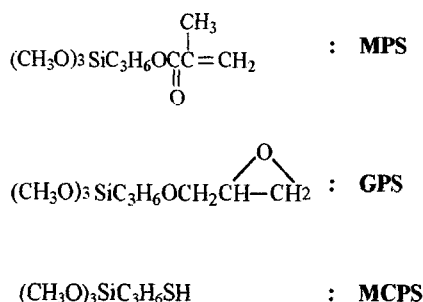


Fig. 1. Chemical structures of the silane-coupling agents studied.

Table 1. Compounding formulations

Ingredients	Loading (phr)
Rubber ^a	100
Silica ^b	40
Zinc oxide	5
Stearic acid	2
Dispersive agent ^c	3
Silane coupling agent ^d	5
Accelerator ^e	1
Sulfur	2

a: Butadiene rubber

b: VN 2000

c: EF44

d: SCA 98

e: N-oxydiethylene-2-benzothiazole sulfenamide

Table 2. Surface tension components and parameters of liquids, measured at 20°C

	γ_L^L (mJ/m ²)	γ_L^{SP} (mJ/m ²)	γ_L (mJ/m ²)	γ_L^+ (mJ/m ²)	γ_L^- (mJ/m ²)
Water	21.8	51.01	72.8	25.5	25.5
Diiodomethane	50.42	0.38	50.8	0.0	0.0
Ethylene glycol	29.0	19.0	48.0	1.92	47.0

Surface properties and Surface free energy

The pH of the silica was measured according to ASTM D3838. In this procedure, about 1 g of the samples were added to 20 ml of freshly distilled water. A few drops pure acetone were used to facilitate wetting. The solutions were shaken for 12 h and its PH was measured with a glass PH electrode.

The acid-base values of the silica surfaces were determined by Boehm's titration method. In the case of acid value measurement, about 0.1 g of the samples were added to 100 ml of 0.1 N NaOH solutions and shaken for 24 h. The solutions were then filtered through membrane paper ($\Phi = 0.45 \mu\text{m}$, nylon) and titrated with 0.1 N HCl solutions. Likewise, the base value was determined by converse titration.

The surface free energy γ_s of a solid can be obtained by measuring the contact angle formed between the solid and liquid of known surface free energy characteristics. In this work, the surface free energy of silica was determined at $20 \pm 1^\circ\text{C}$ using a sessile drop method (Rame-Hart Goniometer). Three different wetting liquids, distilled water, diiodomethane, and ethylene glycol were selected. The basic characteristics of surface free energy of the liquids are given in Table 2.

Mechanical interfacial properties

The tearing energy (G_{TC}) which is one of the critical strain energy release rate (G_C) was characterized by split cantilever beam (SCB) tests for the mechanical behaviors of rubber compound composites. Rectangular specimens with dimensions of about 70 mm long, 50 mm width, and

2 mm thick was cut from a sheet that was manufactured by a two-roll mill technique. All tests were conducted at a crosshead displacement rate of 5 mm/min

3. RESULTS AND DISCUSSION

Surface analysis

Table 3 shows the results of pH and acid-base values of silica surfaces during the silane surface treatments. As results, pH and base surface values of the MPS, GPS, and MCPS samples are decreased and acid surface values of the all samples are increased in these properties as compared with VS, respectively. The result indicates that introduction of silane coupling agent leads to an decrease the hydroxy groups on silica surfaces through siloxane or hydrogen bonding at the interfaces between silica and silane coupling agent.

Surface free energy

The surface free energy (γ_s) of the silicas studied is determined by measuring the contact angles of three test liquids with known London dispersive (or apolar), γ_L^L and polar component, γ_L^{SP} of surface free energy, as seen in Table 2, as follows

$$\gamma_{SL}^L = \gamma_s^L + \gamma_L^L - 2\sqrt{\gamma_s^L \cdot \gamma_L^L} \quad (1)$$

$$\gamma_{SL}^{SP} = 2\left(\sqrt{\gamma_s^+ \cdot \gamma_L^-} + \sqrt{\gamma_s^- \cdot \gamma_L^+} - \sqrt{\gamma_s^+ \cdot \gamma_s^-} - \sqrt{\gamma_L^+ \cdot \gamma_L^-}\right) \quad (2)$$

where subscripts S and L, respectively, represent solid and liquid.

Fig. 2. shows the surface free energy of the silicas modified by silane surface treatment. The results are indicated that introduction of silane coupling agent resulted in increase both the polar and London dispersive component of surface free energy compared to VS. Also, MPS-treated silica show the maximum surface free energy which is mainly due to its highest London dispersive component, even though the polar component of MPS is lower than GPS, as shown in Fig. 2. This is due to the fact that the silane surface treatments on silicas are to introduce stable organic functional groups on silica surfaces.¹¹⁻¹²

Table 3. Results of pH and acid-base values of the silica studied

	pH	Acid value (meq/g)	Base value (meq/g)
VS	6.65	280	40
MPS	5.77	400	10
GPS	6.19	340	20
MCPS	5.90	360	20

Mechanical interfacial properties

The tearing energy, G_{MC} was calculated using the following equation:

$$G_{MC} = \frac{2F}{t} \quad (3)$$

where, F is the applied force and t the width of the tear path, measured on the torn trip after tearing was completed.

Fig. 3 shows the tearing energies measured in a trouser beam test. The results are revealed that the silica/rubber composites by silane surface treatment, as MPS, GPS, MCPS, are increased the tearing energy (G_{MC}) compared to VS. And the MPS, which is higher London dispersive component than GPS and MCPS, is higher tearing energy (G_{MC}) than those of rubber composites made GPS, MCPS. It is found that the London dispersive component of surface free energy of silicas leads to an increase of the tearing energy (G_{MC}) of rubber compound composites, as seen in Fig. 2. Therefore, it is recognized that an increase of γ_s^L of silicas improves the degree of adhesion at interfaces between silicas and rubber matrix.¹¹⁻¹³

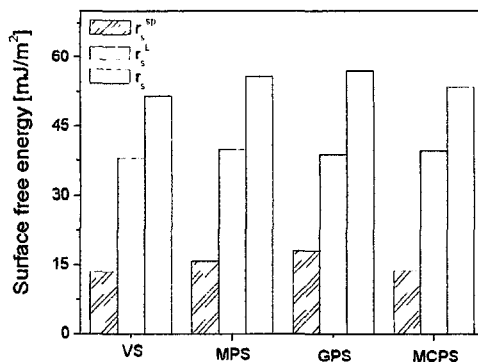


Fig. 2. Surface free energies and their components of the silicas studied.

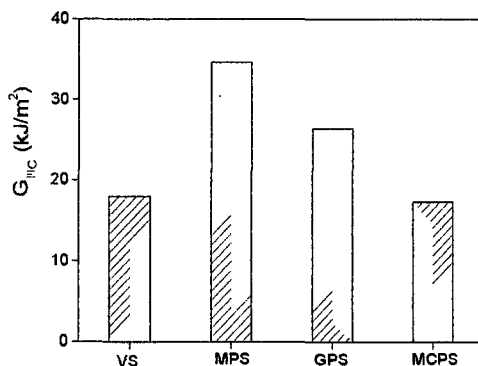


Fig. 3. Tearing energy of silica/rubber composites studied.

4. CONCLUSION

In this work, rubber compound composites systems reinforced with silicas modified by silane surface treatments were studied in terms of acid-base values and surface free energy for improved mechanical properties of the composites.

The treatments of silicas appear to considerably increase both the London dispersive and polar component of surface free energy of silica surfaces. Also, the tearing energy in composites by silane surface treatments, such as MPS, GPS, and MCPS, are increased according to the degree of the increasing of the London dispersive component compared to VS.

It is then concluded that an increase of London dispersive component of surface free energy plays a major role in determining the degree of adhesion at interfaces between modified silicas and hydrocarbon-based rubber in a composite system.

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