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A Study of Silica Reinforced Rubber Composites with Eco-Friendly Processing Aids for Pneumatic Tires

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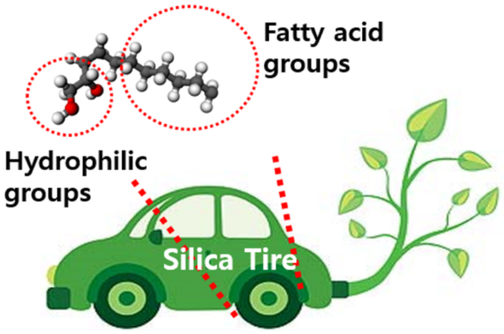
Abstract: The conventional carbon black filler, used in tread formulations, is being replaced with silica with the development of "green tires" in the tire industry. For this, the addition of a processing aid containing zinc ion was required as a dispersing agent and lubricant. However, zink being a heavy metal, zinc-free processing aids (ZFAs) are needed to satisfy global environmental issues. Therefore, this study presented a series of catalytically synthesized ZFAs and studied the effects of replacing zinc-containing processing aids (ZCAs) in a silica tread compounds. Interestingly, the rubber composite replacing ZCAs with ZFAs in 2 phr (parts per hundred rubber) improved both its tensile strength and elongation by as much as 31% and 20%, respectively. In addition, the rubber compounds with ZFAs exhibited a two-fold enhancement in fatigue properties over those with ZCAs. Furthermore, pneumatic tires were fabricated from the rubber compounds containing ZFAs and compared against tires with ZCAs. The tires containing ZFAs rubber composite showed enhanced dry and wet braking and rolling resistance due to enhanced dispersion of silica in the rubber matrix. These results show that rubber composites prepared with ZFAs may be promising in tire engineering applications.



Keywords: zinc-free processing aids, silica, tire, styrene butadiene rubber, mechanical properties.

1. Introduction

Carbon black is a conventional filler that improves the mechanical and physical properties, including abrasion resistance, hardness and tear strength in almost all industrial rubbers.[1-3] Recently, "green tires" made with silica fillers instead of carbon black have showed greater wet grip and abrasion resistance, as well as lower rolling resistance.[4-6] Silica with siloxane and silanol groups differs from carbon black in both chemical composition and method of manufacture.[7] Silanol groups are acidic[8] and interact with basic accelerators, thereby slowing cure rates and lowering the crosslink density in sulfur-cured systems [9]. The viscosity of a compound increases with the amount of silica particles, which tend to interact strongly with themselves due to their polar and hydrophilic nature.[10] Therefore, silica-containing compounds are more difficult to process because silica particles are relatively difficult to disperse in a rubber matrix.[11-14] It is necessary to use the silane coupling agents to enhance rubber-filler interactions. These include bis(triethoxysilypropyl)tetrasulfide (TESPT) and bis(triethoxysilylpropyl)disulfide (TESPD), which, due to their bi-functional characteristics, act as chemical bonding agents between the rubber matrix and silica during vulcanization.[15-17]

The processing agents used in the manufacture of tire rubbers are classified according to their chemical structure and include hydrocarbons, low molecular weight polymers, fatty acid derivatives, synthetic resins, and other organic compounds. Several additives, such as fatty acid esters, act as lubricants and/or dispersion agents. In particular, bi-functional silanes containing sulfur have been used to improve processability during mixing and the chemical bonding between silica and rubber. Currently, zinc soaps such as zinc stearate, zinc naphthenate, and zinc resinate are used as processing agents in rubber formulations. Most zinc soaps act as intermolecular lubricants because they are rubber-soluble. However, zinc consumption is a worldwide environmental concern and the automotive industry, as a main contributor, is under increasing pressure to decrease its share. Although large amounts of zinc-containing additives are used in the automotive industry, there are relatively few studies that address zinc-free processing aids (ZFAs).

The current study describes the catalytic fabrication of ZFAs bearing fatty acid and hydrophilic groups on opposite ends of the molecule. This structure serves to enhance the dispersion of silica in the rubber matrix. The hydrophilic group reacts with silanols on the silica surface via hydrolysis,[18,19] while the fatty acid group reacts with double bonds on the rubber chain.[20] This report also evaluates the effects of conventional and silica-based processing aids in styrene butadiene rubber (SBR) during mixing and after vulcanization. A master batch of SBR, made with typical processing aids and a silica filler, was used to improve their dispersion in a rubber latex matrix through latex co-coagulation. This process was a fast, inexpensive, scalable, versatile, and conve-

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nient means of enhancing the performance of rubber composites. Silica rubbers containing ZFAs exhibited more desirable mechanical, fatigue, and abrasion properties than those of zinc ion-containing processing aids (ZCAs). To demonstrate the potential of "green tires" featuring silica fillers, ZFAs were added directly to an SBR-based tread formulation used to manufacture a pneumatic tire. This tire boasted a low rolling resistance and highly improved grip in both dry and wet conditions. This research shows the advantages and potential of silica-based fillers for tire engineering.

2. Experimental

2.1. Materials

An SBR (SBR 1500, Kumho Petrochem Co. Ltd., Korea), consisting of 23% styrene and 77% butadiene, was selected as the matrix material. Carbon black (N-330) was obtained from OCI Co. Ltd., Korea. N-tert-butyl-benzothiazole sulfonamide (TBBS) was obtained from Shangdong Shanxian Co. Ltd., China. Zinc oxide (ZnO), stearic acid (S/A) and sulfur were purchased from Sigma-Aldrich. The silica and coupling agent used in this study were supplied by Rhodia Silicas and zinc ion processing aids were obtained from Struktol Co., USA.

2.2. Preparation of ZFAs

Glycerol was prepared from the catalytic reaction of a metal catalyst (KOH and NaOH) and triglycerides in methanol. Glycerol and fatty acid (mole ratio 2:1) were mixed with a metal catalyst (KOH) and stirred at 400 rpm at 200 °C for 5 h in an inert atmosphere until the acid value was zero.

2.3. Preparation of rubber composites

SBR composites were prepared by following the standard procedures detailed in Tables S2 and S3. First, as given in Table S2, an SBR latex of 20 parts per hundred rubber by weight (phr) containing 20 phr silica with ZFAs and ZCAs was mixed by vigorous stirring for 24 h. An SBR latex (20 phr) was also prepared with silica (20, 40 and 60 phr) and contained ZFAs and ZCAs at 2 phr (Table S3). This mixture was also mixed for 24 h. During coagulation, a relatively small amount of butadiene-styrene-vinyl-pyridine rubber (VPR) was added to each mixture. VPR not only plays a key role in the prevention of silica aggregation, but also acts as an interface or bridge material between silica and the SBR matrix. The processing aid/silica-SBR emulsions were then coagulated with a 1.0-phr sulfuric acid solution. The coagulated composites were rinsed with water until the pH of the rinsate was 6~7 and then dried in an oven at 50 °C for 24 h. Then, master batches were prepared from SBR (80 phr) and silica (20 phr)/SBR (20 phr) emulsion and various additives in a Banbury mixer at a rotor speed of 60 rpm. The additives and vulcanization agents were added at the end of mixing to initiate the curing process. The resulting materials were placed in an aluminum mold and cured at 160 °C for T_{90} as determined by a rheometer under pressure. The formulations of the SBR composites are summarized in Tables S2 and S3.

2.4. Characterization

Scanning electron microscopy (SEM; JEOL JSM-6490LV) was used to observe the morphology of fractured surfaces of rubber composites. Prior to SEM analyses, specimens were fractured after freezing in liquid nitrogen and the resulting cross sectional surface was coated with gold using a sputtering process. Modulus and tensile tests were carried out on an Instron tensile machine (Instron Co., UK) at a crosshead speed of 300 mm/min. Dumbbell-shaped samples were 100 mm in thickness and 5 mm in width. At least four tests were carried out for each type of sample. Dynamic tests were conducted in a dynamic mechanical analyzer (DMA

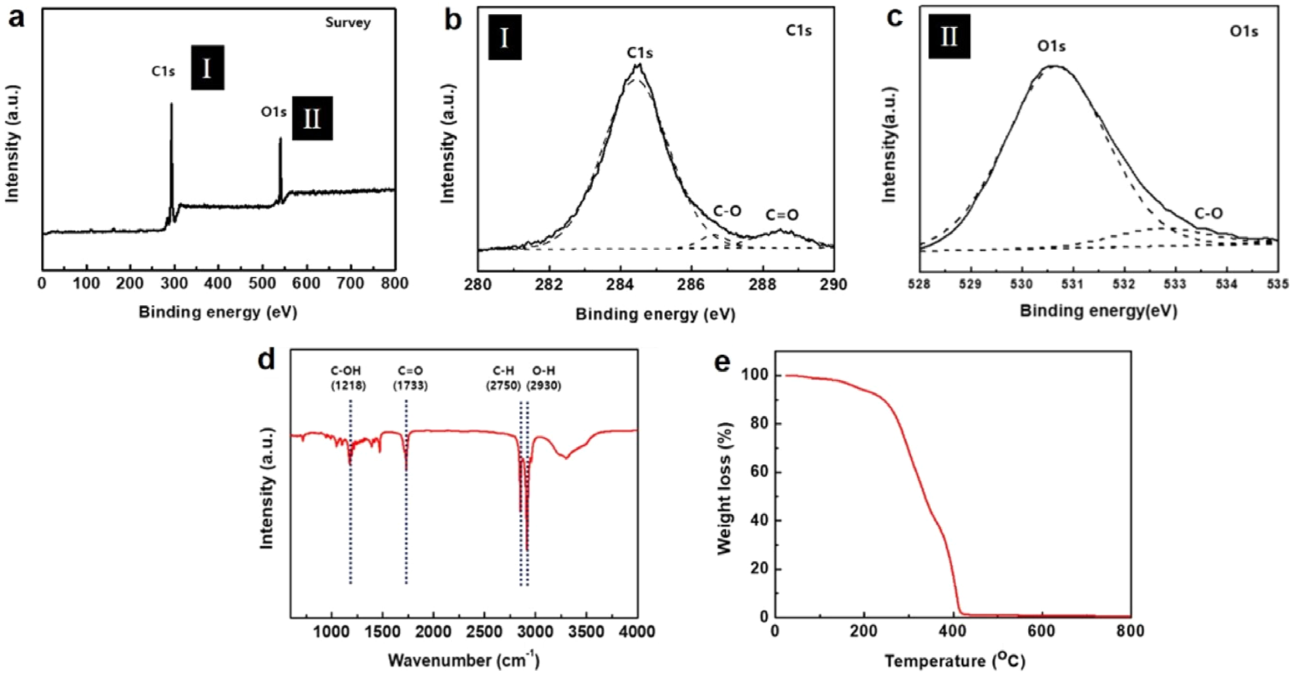

Figure 1. Characterization of as-prepared ZFAs.

50N01Db-METRAVIB) in tensile mode. The temperature dependence (temperature sweep) of the loss factor (tan delta) and the storage modulus were measured from 20 °C to 120 °C, at a heating rate of 3 °C/min and a frequency of 10 Hz. A thermogravimetric analysis (TGA) was performed using a G 209 F3 at a heating rate of 10 °C/min under Ar atmosphere. The surface functional groups of the samples were measured by X-ray photoelectron spectroscopy (Sigma Probe, Thermo VG Scientic, AlKα). Hakke torque rheometer (Thermo Scientific HAAKE PolyLab QC System) was used to monitor the sheet forming and extrusion behavior of the SBR composites.

4. Results and discussion

We present herein, for the first time, a series of ZFAs fabricated by the catalytic reaction shown in Figure S1. Figure S1 shows the preparation of glycerol using a metal catalyst and triglycerides in methanol. This process afforded ZFAs bearing both hydrophilic and hydrophobic groups in large quantities. The properties of ZFAs is confirmed by the spectroscopic analysis and thermogravimetirc analysis (TGA) in Figure 1. In Figure 1(a), the chemical bonding state of the ZFAs was analyzed by X-ray photoelectron spectroscopy (XPS). The Cis consisted of the C-C bond (284.5 eV), C-O (286.6eV) and C=O (288.2 eV) of the carbonyl groups in Figure 1(b). The peaks of O1s (530.5 eV) and C=O peaks (532.8 eV) were observed in the ZFAs from the O1s narrow scan in Figure 1(c). In the FT-IR spectra, ZFAs two characteristic peaks related to C-H stretching and C-OH stretching in carbonyl moieties and carboxylic acid are shown in Figure 1(d). Furthermore, TGA were performed on the ZFAs in a TGA instrument to 800 °C at heating rate 5 °C/min under N_2 in Figure 1(e). It was observed that ZFAs is thermal unstable and starts to lose mass upon heating even 100 °C, and there are significant drops in mass between around 200 °C and 400 °C. The melting points of the ZFAs were lower than those of the corresponding ZCAs, as shown in Table S1, due to the absence of zinc in the former. The ZFAs were pelletized so that they were more easily incorporated into tire engineering applications.

Figure 2(a)-(b) show a comparison of the modulus, tensile strength and elongation of SBR composites as a function of increasing ZFA or ZCA content. Modulus and tensile strength decreased with increasing amounts of processing aid, while elongation increased due to increasing viscosity. The modulus and tensile strength of composites containing ZFAs (2 phr) were as much as 11% and 31% greater than those containing ZCAs, respectively. This performance enhancement was due to the amphoteric nature of ZFAs and the resulting strong interfacial bonding and improved dispersion of silica within the elastomer matrix, and the restriction of segmental elastomer chain motion. Figure 2(b) shows that the elongation at break of ZFA/SBR composites (490%) was greater than that of ZCA composites (410%). The increased reinforcement can be attributed to the large contact area between silica and the elastomer matrix. Figure 2(c) shows the abrasion properties of SBR composites containing ZFAs or ZCAs. The amount of abrasion loss, on the whole, increased with the amount of processing aid due to the increasing viscosity of the composites. Note that the ZFA/SBR composites exhibited greater wear resistance (William wear 4.03%) due to enhanced silica disper-

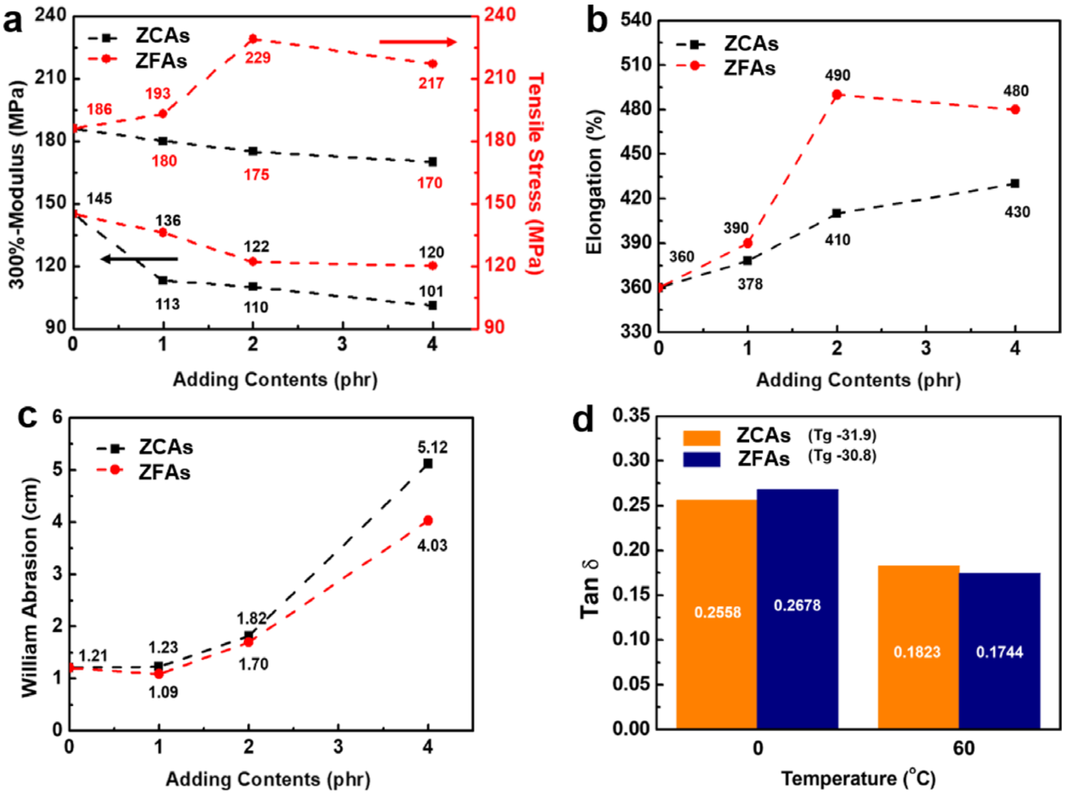

Figure 2. (a) Modulus and tensile strength, (b) elongation, (c) William abrasion, and (d) dynamic properties (tan δ) of rubber composites with zinc ion-containing processing aids (ZCAs) and ZFAs.

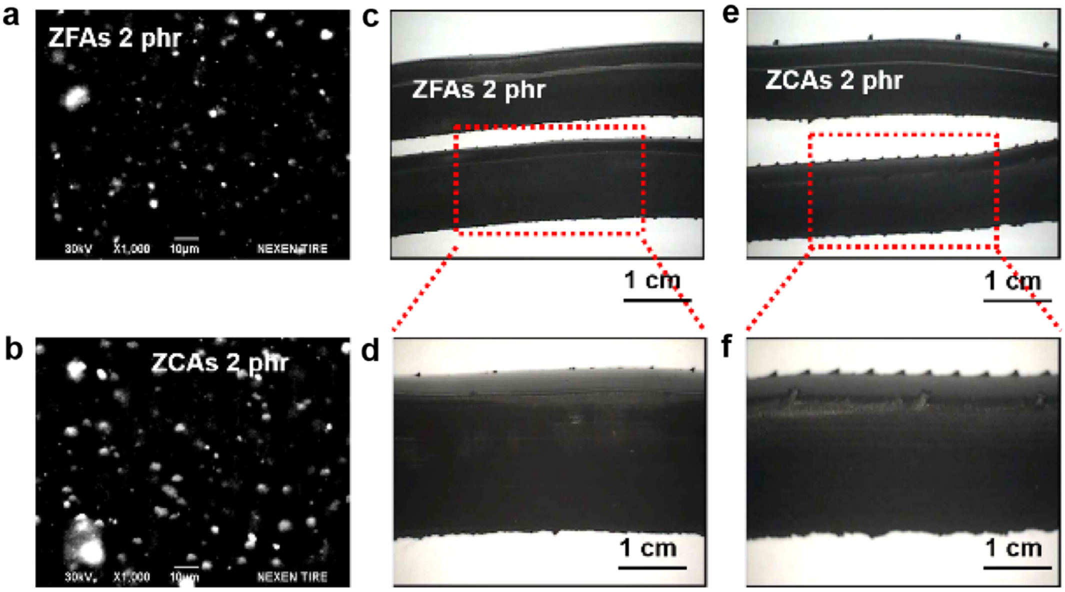

Figure 3. Scanning electron microscopy (SEM) micrograph of rubber composites made with (a) ZFAs and (b) ZCAs. (c) Images of Gravey die extrusions of rubber composites made with (c) ZFAs (enlarged image in (d)), and (e) ZCAs (enlarged image in (f)).

sion and crosslinking density. The dynamic mechanical properties (DMA), such as tanδ and the ratio of loss modulus to storage modulus of SBR composites containing ZFAs and ZCAs are shown as a function of temperature in Figure 2(d). DMA tests can be used to predict both wet traction and rolling resistance.[21] With the addition of ZFAs, the tanδ of 0 °C was about 5% higher than that of SBR composites containing ZCAs. This implies that pneumatic tires incorporating ZFAs have the potential for improved wet grip tire performance. Furthermore, the 60 °C tanδ of the ZFA/SBR composites was about 5% lower than that of the ZCA/SBR composites, indicating a potentially lower rolling resistance of the former.[22,23]

The SEM micrographs in Figure 3(a)-(b) and S2 show that silica (20 phr) disperses evenly throughout ZFA/SBR compos-

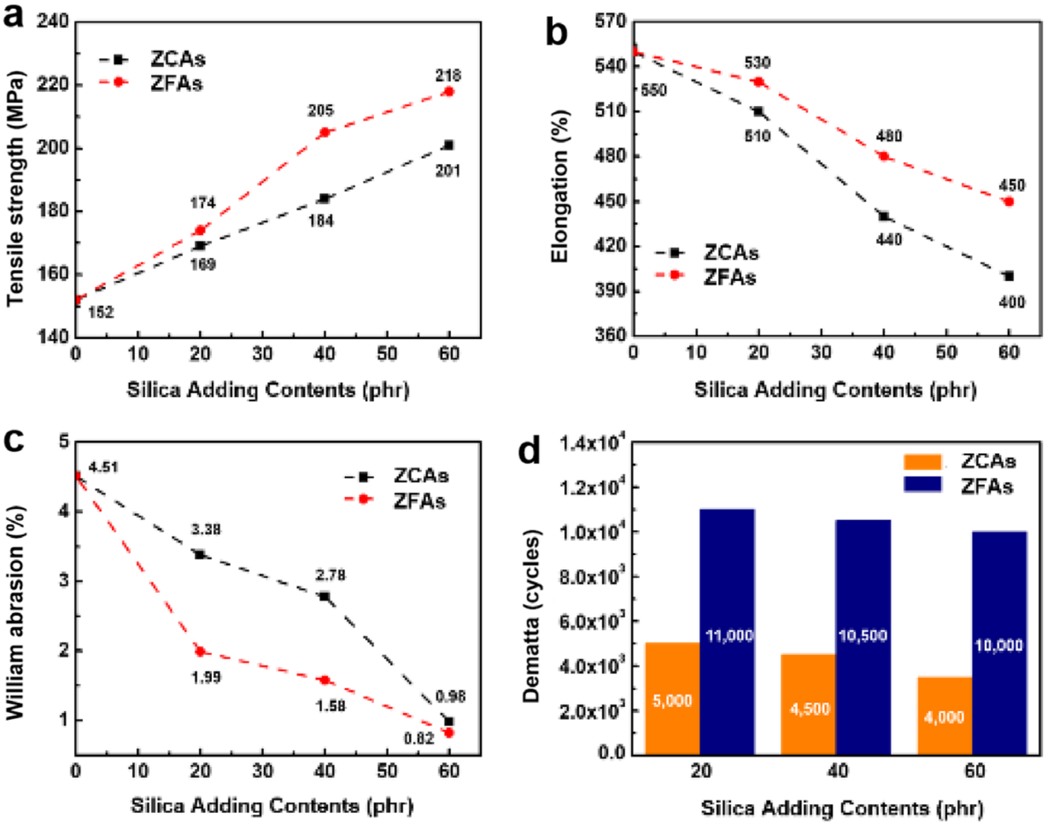

Figure 4. (a) Tensile strength, (b) elongation, (c) William abrasion, and (d) fatigue properties (fatigue crack generation) of rubber composites containing ZCAs or ZFAs with varying degrees of silica loading.

ites without coagulation. Figure S2 also shows that increasing the proportion of ZFA decreased the number of coagulated particles in the rubber matrix. This result supports the Garvey Die Extrusion tests. A Garvey die in a Hakke torque rheometer was used to monitor the sheet forming and extrusion behavior of the SBR composites. Figure 3(c)-(f) show extrusion quality as a function of the type of processing aid. Figure 3(c)-(d) and S3 show that rubber extrusions containing a high loading of ZFA exhibited smoother and more stable edges. This effect was likely due to the relatively high viscosity of the ZFA formulations. Figure 3(e)-(f) show that extrusions made with the ZCA/SBR composites had rough surfaces and unstable edges.

Tensile strength and elongation of SBR composites are shown as a function of silica loading in Figure 4(a)-(b). While the addition of silica resulted in significant increases in tensile strength (Figure 4(a)), it also resulted in decreased elongation (Figure 4(b)). Compared to ZCA/SBR composites, the tensile strength and elongation of ZFA/SBR composites containing 60 phr silica increased to 218 MPa and 450%, corresponding to enhancements of 8% and 12.5%, respectively, while the modulus remained unchanged (Figure S4). Figure 4(c) shows that abrasion resistance also increased with increasing silica content. The William abrasion of ZFA rubber composites was lower than that of ZCA composites, implying improved dispersion of silica in the rubber matrix. The fatigue properties of SBR composites with various processing aids are shown in Figure 4(d). In general, reductions in fatigue life were observed with increasing silica content. However, the fatigue life of ZFA/SBR composites was more than twice that of ZCA/SBR composites. This is likely due to the more uniform dispersion of ZFAs in the rubber matrix.

SEM micrographs of silica (60 phr)/SBR composites containing 2 phr of processing aids show that the silica was evenly dispersed in the ZFA/SBR composites without coagulation (Figure 5(a)-(b) and S5). Furthermore, Figure S5 shows that both the degree of dispersion and the uniformity of distribution of silica were enhanced with the use of ZFAs. This result is also supported by the fatigue properties of silica treads shown in Figure S6. After 10,000 cycles, the crack length in silica treads made with ZFA/SBR composite was approximately 26% greater than that of treads made with ZCA/SBR. Figure 5(c)-(f) show that ZFA (2 phr)/SBR composites yielded smoother extrusions with more stable edges compared to those made with ZCA/SBR composites.

Pneumatic tires were made with each composite to confirm the superior performance of the ZFA/SBR composites. The results of mechanical tests are given in Figure 6. Figure 6(a) compares the physical properties of SBR composites made with different processing aids. The modulus and tensile strength of tread compounds made with ZFA/SBR was as much as 3% and 12% greater than those of the control, respectively. In addition, the elongation of ZFA/SBR treads was significantly greater than that of ZCA/SBR treads. The elongation of ZFA/SBR treads increased by 8%. As discussed above, this enhancement was due to strong interfacial bonding and improved dispersion of silica within the rubber matrix.

The DMA of a particular rubber formulation is important because rubber composites are frequently subjected to dynamic loading. Figure 6(b) shows the DMA of pneumatic tires, including tanδ of the control and ZFA/SBR composite tires, as a function of temperature. While the tanδ of 0 °C for ZFA/SBR treads was about 5% higher than that of control, the tanδ of 60 °C was about 11% lower than that of control. These data demonstrate the potential of pneumatic tires incorporating ZFAs for improved wet grip and rolling resistance.[22,23] The abrasion and rebound properties of silica tread compounds are shown in Figure 6(c). The William abrasion of pneumatic tires made with ZFAs was more than two orders of magnitude higher than that of the control. This is attributed to filler-filler interactions among ZFA particles. The effect of ZFA loading on rebound resilience at room temperatures is given in Figure 6(c). The percent rebound resilience of ZFA/SBR composites was about 9% greater than that of ZCA/SBR

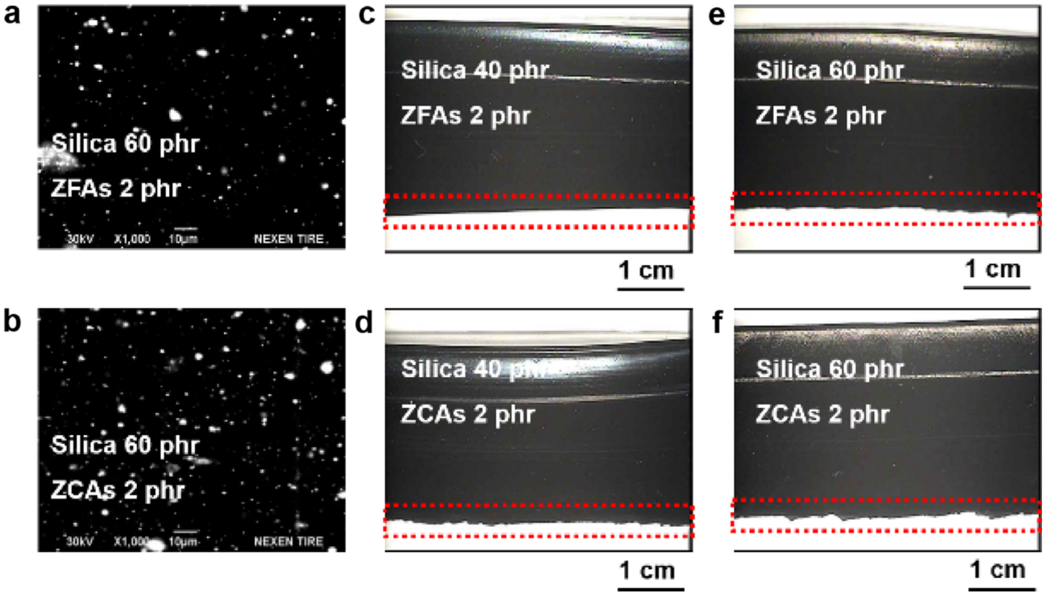

Figure 5. SEM micrographs of (a) ZFA- and (b) ZCA-rubber composites with 60 parts per hundred rubber (phr) silica. (c) Garvey die extrusion images of (c) ZFA (2 phr)- and (d) ZCA (2 phr)-rubber composites with 40 phr silica, (e) ZFA (2 phr)- and (f) ZCA (2 phr)-rubber composites with 60 phr silica.

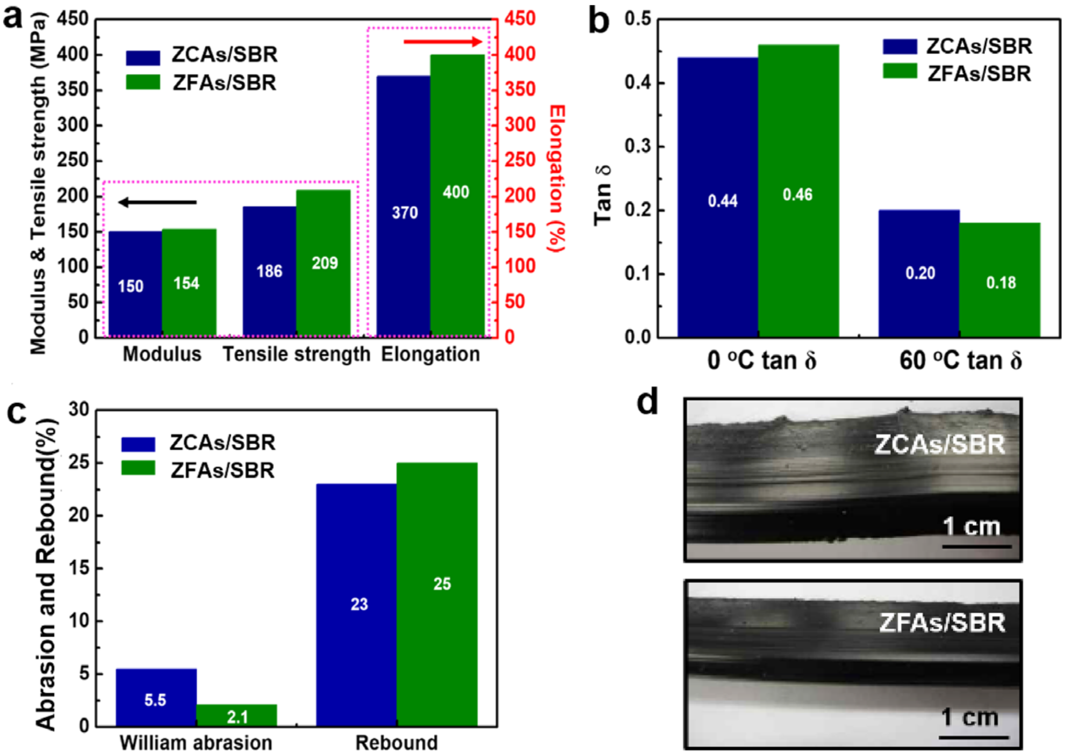

Figure 6. (a) Modulus, tensile strength and elongation, (b) dynamic properties (tan *δ*), (c) abrasion and rebound, and (d) Garvey die extrusion images of tire tread compounds made with ZCA/styrene butadiene rubber (SBR) or ZFA/SBR composite.

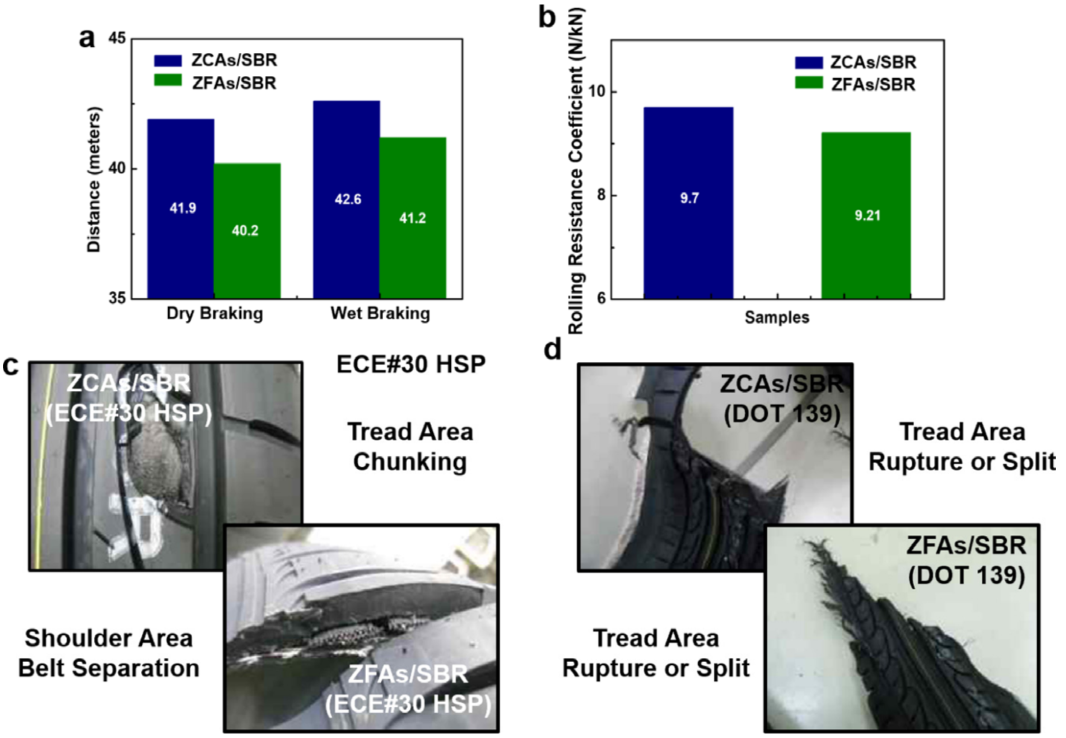

Figure 7. (a) Dry and wet braking properties, (b) rolling resistance coefficients, (c) high-speed durability (ECE#30 HSP), and (d) high-speed durability (DOT 139) of pneumatic tires made with ZCA/SBR or ZFAs/SBR composite.

composites. This result indicates that the presence of ZFAs improves the elasticity of rubber composites due to increased cross-link density between silica and the rubber matrix. This agrees with the results of Garvey die extrusion tests shown in Figure 6(d). Due to the higher viscosity of the ZFA formulations, extrusions made with ZFA/SBR composites exhibited stable edges and a smoother shape than those made with the control composite.

Finally, virtual tests were performed using a vehicle-mounted pneumatic tire made with ZFA/SBR or ZCR/SBR composite rubbers. The results are shown in Figure 7. The tire is an important subsystem of the total vehicle dynamics system, which also comprises the suspension, brakes, and steering apparatus. Under high braking, the rolling resistance and high-speed durability of the tires play particularly important roles in determining vehicle dynamics.[24,25] The data in Figure 7(a)-(b) show that treads made with ZFA/SBR composites exhibited lower rolling resistance with increased grip under braking in both wet and dry conditions. The dry and wet braking abilities of ZFA/SBR pneumatic tires were about 4% and 3% greater than those of the control, respectively. Furthermore, the rolling resistance coefficient of a pneumatic tire made with the ZFA/SBR composite (9.21 N/kN) was lower than that of the control (9.7 N/kN), as shown in Figure 7(b). These results indicate that strong interfacial interactions between silica and the rubber matrix in ZFA/SBR composites resulted in improved viscoelastic properties. Finally, Figure 7(c)-(d) show the results of high speed endurance tests in accordance with guidelines set by the ECE (Economic Commission for Europe) #30 HSP, and DOT 139 (US Department of Transportation). The DOT guidelines ensure that a tire meets or exceeds the safety requirements of the US Department of Transportation, and ECE#30 is a European guideline that sets requirements for tire size, rolling resistance, braking, and high speed durability. Generally, in high speed tests, tire failure is caused by belt separation due to the heat generated from movement and external impact. In high-speed tests, the pneumatic tire tread made with ZCA/SBR composite came apart in chunks because of its decreased durability. In contrast, tires made with ZFA/SBR composite exhibited belt separation, as shown in Figure 7(c). Figure 7(d) shows that similar results were obtained in DOT tests. The closer the silica filler aggregates are to each other, the greater the desorption and heat concentration, which means that polymer chains can more easily break away from the silica particles, resulting in a drop in mechanical properties.[26,27]

Pneumatic tires made with ZFA/SBR composite showed significantly improved abrasion resistance, rolling resistance, and high-speed durability. Therefore, the approach described herein has demonstrated potential applicability to new scalable and commercial rubber engineering projects.

4. Conclusion

In summary, for the first time, ZFAs were synthesized using a catalytic reaction and evaluated in rubber compositions used for tire treads. The incorporation of ZFAs into SBR rubber matrices resulted in remarkable improvements in modulus, tensile strength, elongation, and dynamic properties. These enhancements were attributed to uniform dispersion of silica particles, and enhanced interfacial bonding between these particles and the SBR, in the rubber matrix. This study also demonstrates the ease with which ZFAs/SBR composites can be integrated into a rubber matrix using a new, versatile, and simple approach based on latex technology. Furthermore, ZFAs/SBR composites were employed directly as additives in the tread of a pneumatic tire. Tires fabricated with the ZFAs/SBR composite exhibited significantly improved dry and wet braking, rolling resistance, and high-speed durability due to enhanced dispersion of silica in the rubber matrix. These results also demonstrate the effectiveness of ZFA processing aids in the production of elastomer composites for use at low loading levels. Rubber composites prepared with ZFAs provide significant new opportunities for future tire engineering applications.

Supporting Information: Information is available regarding the experimental procedure of the preparation of rubber composite with ZFAs and rubber composite characterization: formation recipe of rubber composites, schematic diagram of ZFAs, modulus data, fatigue properties, SEM and gravey die extrusion images. The materials are available *via* the Internet at http://www.springer.com/13233.

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