

Research Article

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Analysis of effect of modification of silica and carbon black co-filled rubber composite on mechanical properties

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Abstract: Silica and carbon black (CB) co-filled rubber composite was widely used for tire tread and other rubber products because of combined advantages of binary fillers, such as low hysteresis, good abrasion resistance, and reinforcement. Numerous studies have been focused on the filler–rubber interaction with the aim of obtaining optimum performances. To investigate the effect of modification on properties of rubber composite, modified silica and CB co-filled rubber composite was prepared with a multi-functional silane coupling agent, 2-aminoethyl-2-(3-triethoxysilylpropyl)aminoethyl disulfide (ATD). Such modification significantly enhanced the filler–rubber interaction and improved the filler dispersion. For the modified composites, the state of cure, hardness, tensile strength before and after aging, stress at 300% elongation, tear strength, abrasion resistance, rebound resilience, compression set, temperature rise, and the value of dynamic loss coefficient ranging from -20°C to 80°C were significantly improved, especially with low ATD dosage (3.0 phr). This modification provides an effective route to prepare silica and CB co-filled rubber composites with improved mechanical properties and dynamic mechanical properties.

Keywords: multi-functional silane coupling agent, silica/carbon black co-filled rubber composite, filler–rubber

interaction, mechanical properties, dynamic mechanical properties

1 Introduction

Silica and carbon black (CB) co-filled composite receives much attention because of its combined advantages of silica and CB, such as low hysteresis, good wet skid resistance, and reinforcement, especially suitable for tire tread (1–10). Because of poor compatibility between silica and hydrocarbon rubber (11–13), a great effort has been made to improve the filler–rubber interaction with the aim of obtaining optimum performances (14–21). Three main directions have been developed to enhance the interaction between filler and rubber, i.e., addition of coupling agent (22–29), surface modification of filler (30–39), and chemical modification of rubber (40,41).

Considerable research effort continues to be directed toward the enhancement of filler–rubber interaction in combination with silane coupling agent because of its suitability for industrial production. Previous research has been mostly focused on the effect of filler composition of silica and CB on the properties of rubber composites in the presence of bis(3-triethoxysilylpropyl)tetrakisulfane (Si69) (40,42–57). In addition, Hartomy and coworkers demonstrated the effect of silica/CB reinforcing filler upon the curing characteristics and mechanical and dynamic properties of natural rubber composites in the presence of bis(3-triethoxysilylpropyl)disulfane (58). Kim and Vander-Kooi investigated the moisture effects on styrene-butadiene rubber composites filled with silica and CB in the presence of bis(3-triethoxysilylpropyl)disulfane (59). Zhang et al. reported the effect of (3-aminopropyl)-triethoxysilane, γ -(2,3-epoxypropoxy)-propyltriethoxysilane, γ -methacryloxy-propyltrimethoxysilane, and Si69 on the dynamic properties and heat buildup of silica/CB filled natural rubber vulcanizates (60). However, the aforementioned silanes could not give rise to strong interactions between

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CB and rubber. This paper focuses on a multi-functional silane coupling agent, 2-aminoethyl-2-(3-triethoxysilylpropyl)aminoethyl disulfide (ATD), which bears ethoxysilyl group, amino group, and disulfide group (61). The ethoxysilyl group and amino group could interact with silanol group of silica surface and also with oxygen-containing functional groups of CB surface during mixing and vulcanization. It gives rise to the formation of covalent bonds, ionic bonds, and hydrogen bonds between ATD and silica as well as CB (61,62). The disulfide group could react with rubber during vulcanization and give rise to the formation of covalent bonds between ATD and rubber. Thus, strong interactions could be achieved not only between silica and rubber but also between CB and rubber. This would result in improvements in the dispersion of silica and CB and thus in the properties of such binary fillers-based rubber composites.

In this paper, we investigate the *in situ* modification of silica and CB co-filled isoprene rubber (IR) composite with ATD, and we further analyze the effect of such modification on mechanical properties and dynamic mechanical properties of vulcanized composites.

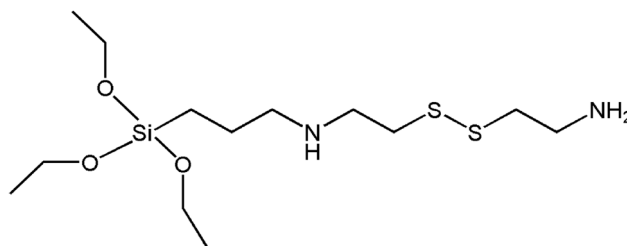
2 Materials and methods

2.1 Materials

Synthetic *cis*-IR (JSC Sterlitamak Petrochemical Plant, SKI-3), CB (China Carbon Black Institute, N330), and silica (Evonik Company, ULTRASIL VN3 GR) were used as received. ATD (Scheme 1) was synthesized using cystamine and 3-chloropropyltriethoxysilane (61). The other analytical reagents were purchased from Sinopharm Chemical Reagent Company and used as received.

2.2 Preparation of modified IR/silica/CB compounds and vulcanizates with ATD

Modified IR/silica/CB compounds and vulcanizates were prepared according to the formulation listed in Table 1. IR was masticated in a QINGDAO laboratory banbury mixer (1.5 L, 50–55 rpm) and then mixed with silica, CB, and ATD. The compounds were mixed at 145°C for 5 min, followed by cooling down to 70–80°C. Then the rest of reagents were added into the mixer and mixed with the aforementioned compounds at 90–100°C. The compounds obtained above were vulcanized by compression molding at 150°C for 20 min to prepare test pieces.



Scheme 1: Chemical structure of 2-aminoethyl-2-(3-triethoxysilylpropyl)aminoethyl disulfide.

2.3 Measurements

Vulcanization characteristic of modified silica/CB/IR compound was obtained using a GOTECH rotorless cure meter (frequency 1.7 Hz, amplitude $\pm 0.5^\circ$, vulcanization condition 150°C for 30 min) in accordance with ISO 6502. Bound rubber content was determined by extracting unbound rubber with toluene for 3 days and drying in a vacuum oven at room temperature to constant weight. Weights before extraction and after extraction were measured and bound rubber content was calculated (19).

Shore hardness of modified silica/CB/IR vulcanizate was determined using a BAREISS digital hardness tester based on ISO 7619. Tensile stress-strain, tear strength, and accelerated aging resistance were measured on a SUNS electron tensile tester (tensile rate 500 mm/min) according to ISO 37, ISO 34-1 (method B procedure (a)) and ISO 188, respectively. State of cure was determined by swelling in toluene at 30°C for 4 h, namely swelling test. Weights before and after swelling were measured and swelling index was calculated by weight ratios after swelling and before swelling based on HG/T 3870.

The dispersion of filler was examined using a scanning electronic microscopy (SEM, JEOL JSM-7500 F) at an acceleration voltage of 5 kV. Vulcanizate (2 mm in thickness) was fractured in liquid N_2 , and the fracture surface was covered with a layer of gold by sputtering treatment before SEM observation.

Abrasion resistances were measured on a MINGZHU rotating cylindrical drum device and a XINZHENWEI Akron abrasion machine in accordance with ISO 4649 and BS 903 A9, respectively. Compression set and rebound resilience were determined using a GOTECH compression machine (type A test piece, compressed to a 25% strain and maintained at 70°C for 72 h) and a GOTECH resiliometer (23°C) according to ISO 815 and ISO 4662, respectively.

Dynamic mechanical measurement was carried out on a GABO dynamic mechanical thermal analyzer EPLEXOR 500 N operating in tensile mode at the frequency of 2 Hz.

Table 1: Formulation (mass ratio) of modified IR/silica/CB compounds

Samples	SC-1	SC-2	SC-3	SC-4	SC-5	SC-6
IR	100	100	100	100	100	100
Silica	30	30	30	30	30	30
CB	20	20	20	20	20	20
ATD	0	1.5	3.0	4.5	6.0	7.5
Zinc oxide	4	4	4	4	4	4
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
<i>N</i> -(1,3-Dimethylbutyl)- <i>N'</i> -phenyl- <i>p</i> -phenylenediamine	1.5	1.5	1.5	1.5	1.5	1.5
<i>N</i> -Cyclohexyl-2-benzothiazole sulfenamide	1.3	1.3	1.3	1.3	1.3	1.3
Tetrabenzylthiuramdisulfide	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	1.4	1.4	1.4	1.4	1.4	1.4

The range of temperature sweep was −80°C to 80°C (heating rate 2°C/min) with 6% static load strain and 5% dynamic load strain. Temperature rise was tested using a YOUSHEN

compression flexometer at 55°C for 25 min (constant-strain type, pre-stress 1 MPa, cyclic strain amplitude 4.45 mm, frequency 30 Hz) according to ISO 4666-3.

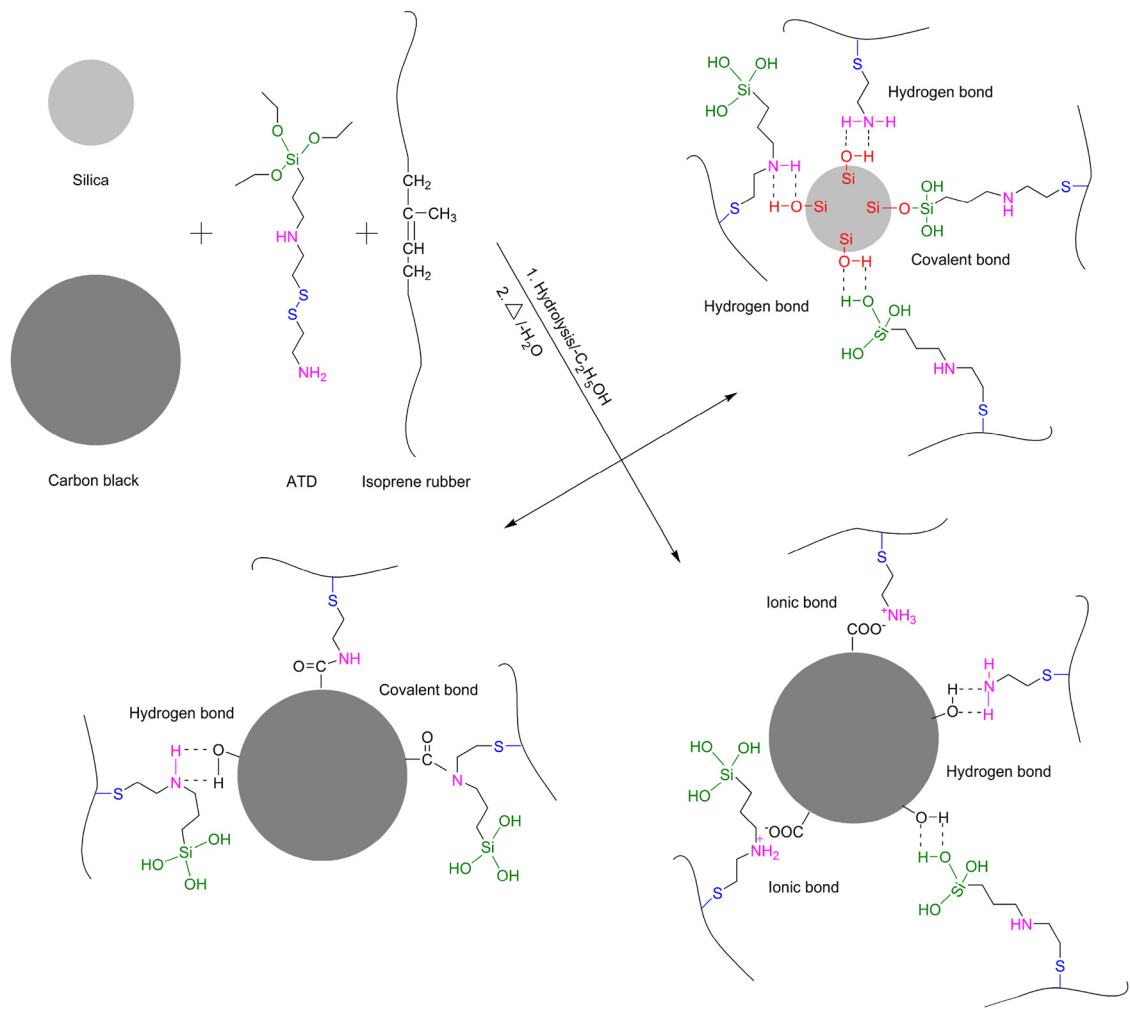


Figure 1: Postulated reactions of ATD toward rubber and fillers of silica and CB.

Table 2: Vulcanization characteristics and bound rubber content of modified IR/silica/CB compounds with ATD

Samples	t_{s2}^a (s)	$t_c(90)^b$ (s)	M_L^c (dNm)	M_H^d (dNm)	$M_H-M_L^e$ (dNm)	CRI ^f	Bound rubber content (g/g)
SC-1	239	983	2.99	28.64	25.6	7.72	0.216
SC-2	233	775	2.59	28.77	26.2	10.47	0.310
SC-3	192	658	2.48	30.03	27.6	12.17	0.391
SC-4	137	567	2.62	32.07	29.4	13.19	0.404
SC-5	94	497	2.50	33.36	30.9	14.20	0.424
SC-6	54	455	2.65	34.62	32.0	14.58	0.447

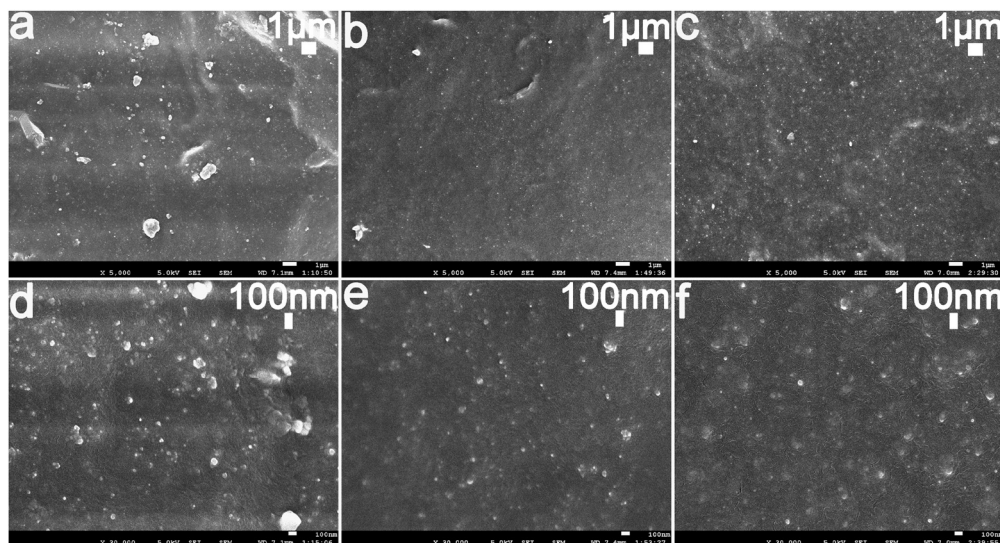
^a Scorch time denoting the time required for the torque to increase by 2 units from minimum torque. ^b Time to a percentage 90 of full cure from minimum torque denoting the optimum curing time. ^c Minimum torque. ^d Maximum torque attained after the specified time. ^e Torque denoting full cure at a specified time. ^f Cure rate index.

3 Results and discussion

3.1 Modification of IR/silica/CB composites with ATD

The results shown in Supplementary material indicate that the modification of IR and silica as well as CB with ATD as coupling agent took place. This modification gave

rise to the formation of ionic bonds, covalent bonds, and hydrogen bonds between IR and silica as well as CB, as illustrated in Figure 1. These bonds enhanced the filler–rubber interaction and improved the filler dispersion (63). It was also supported by the results of bound rubber contents of modified IR/silica/CB compounds (see Table 2) and the SEM images of modified IR/silica/CB vulcanizates (in Figure 2) (16,18).

**Figure 2:** SEM micrographs of IR/silica/CB vulcanizates: 0 phr ATD for SC-1 (a and d), 1.5 phr ATD for SC-2 (b and e), and 3.0 phr ATD for SC-3 (c and f).**Table 3:** Mechanical properties of modified IR/silica/CB vulcanizates with ATD

Samples	Hardness (Shore A)	Tensile strength (MPa)	Elongation at break (%)	Stress at 300% elongation (MPa)	Tear strength (kN/m)	Swelling index
SC-1	58	27.9	628	7.3	60	3.18
SC-2	59	30.3	485	13.2	67	2.86
SC-3	61	32.2	479	16.7	71	2.75
SC-4	63	28.9	405	17.5	72	2.64
SC-5	64	28.4	396	18.2	73	2.62
SC-6	66	28.1	384	18.4	73	2.60

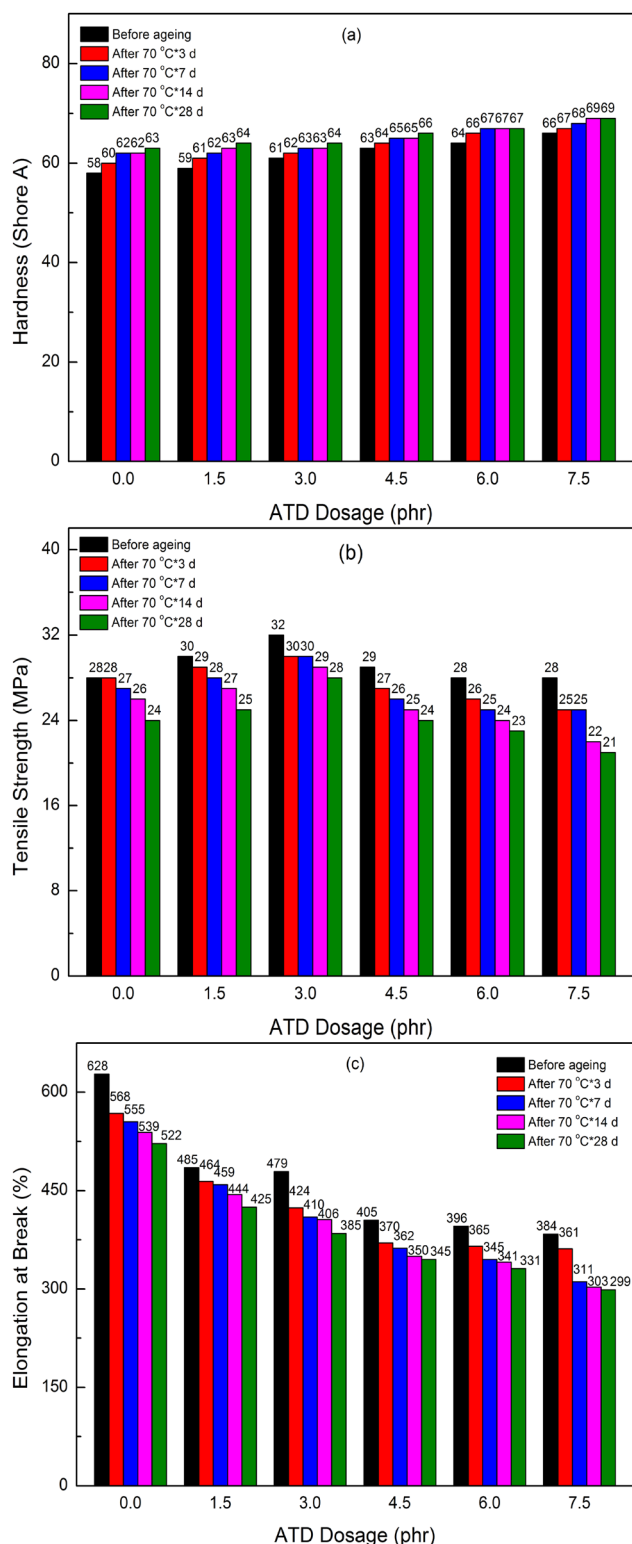


Figure 3: Variation of (a) hardness (Shore A), (b) tensile strength (MPa), and (c) elongation at break (%) with ATD dosage after accelerated aging at 70°C for different aging time for modified IR/silica/CB vulcanizates.

3.2 Effect on vulcanization characteristics

The effect of modification with ATD as coupling agent on vulcanization characteristics of modified IR/silica/CB compounds was investigated, as shown in Table 2. It demonstrates that this modification provides faster cure rate and enhanced state of cure (the difference between maximum torque and minimum torque). This general trend is consistent with Si69 system previously reported (42). With increasing ATD dosage, both scorch time t_{s2} and optimum curing time $t_c(90)$ decreased; while cure rate index and state of cure increased. These observations are probably attributed to the modification of filler with ATD. There are amounts of silanol groups on the silica surface and oxygen-containing functional groups on the CB surface (64). A portion of cure activator (Zn complex) and accelerators would be trapped by those reactive groups in the absence of silane coupling agent. The vulcanization is therefore somewhat retarded. With ATD as coupling agent, the ethoxysilyl group and amino group of ATD could interact with silanol group of silica surface and also with oxygen-containing functional groups of CB surface during mixing and vulcanization. It reduces the surface chemical reactivity of silica and CB. Thus, the amounts of Zn complex and accelerators adsorbed on the filler surface decrease. Therefore, shorter cure time and higher state of cure are obtained. In addition, the amine group and disulfide group of ATD might give rise to faster cure rate.

3.3 Effect on mechanical properties

The effect of such modification on mechanical properties of modified IR/silica/CB vulcanizates was investigated. The corresponding results are presented in Table 3. This modification imparts significant improvement in tensile strength at low ATD dosage (3.0 phr, SC-3, in Table 3). It might be because of enhanced filler–rubber interaction and better filler dispersion (18,65). At high ATD dosage (up to 7.5 phr), the tensile strength decreased, probably because of excessive cross-link density and softening action of ATD. The hardness, stress at 300% elongation, and tear strength increased with increasing ATD dosage, while elongation at break decreased. These results are in good agreement with the results of state of cure (see Table 2) and swelling index (see Table 3). These above trends are consistent with Si69 system (42).

3.4 Effect on aging resistance

The accelerated aging tests were designed to estimate the resistance of modified IR/silica/CB vulcanizates to deterioration with the passage of time, as shown in Figure 3. With increasing ATD dosage, the hardness after aging increased whereas elongation at break decreased continuously for modified IR/silica/CB vulcanizates, arising from further enhancement of state of cure after thermal aging (60). Tensile strength after aging increased with low ATD dosage (up to 3.0 phr). This observation is in contrast to that of Si69 system (66). Such improvement in tensile strength after aging is mainly attributed to the less effect of sulfur contribution of ATD. That is, ATD possesses two sulfur atoms per molecule, less than Si69 which bears four sulfur atoms. Therefore, ATD could contribute less sulfur atom to the matrix rubber to carry on sulfur vulcanization reaction during thermal aging, which would result in less increase in cross-link density.

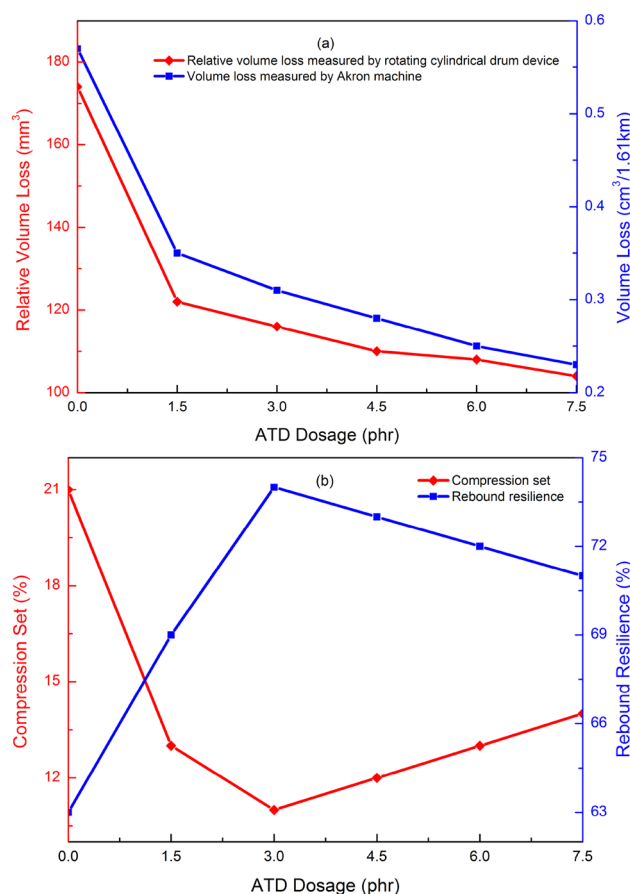


Figure 4: Variation of (a) abrasion resistance and (b) compression set and rebound resilience with ATD dosage for modified IR/silica/CB vulcanizates.

3.5 Effect on abrasion resistance, rebound resilience, and compression properties

The effects of modification on abrasion resistance, rebound resilience, and compression properties of modified IR/silica/CB vulcanizates were studied and the results are illustrated in Figure 4. As seen in Figure 4a, relative volume loss measured by rotating cylindrical drum device and volume loss measured by Akron machine both decreased pronouncedly as the ATD dosage increased (up to 3.0 phr) and tended to level off afterward (up to 7.5 phr). With

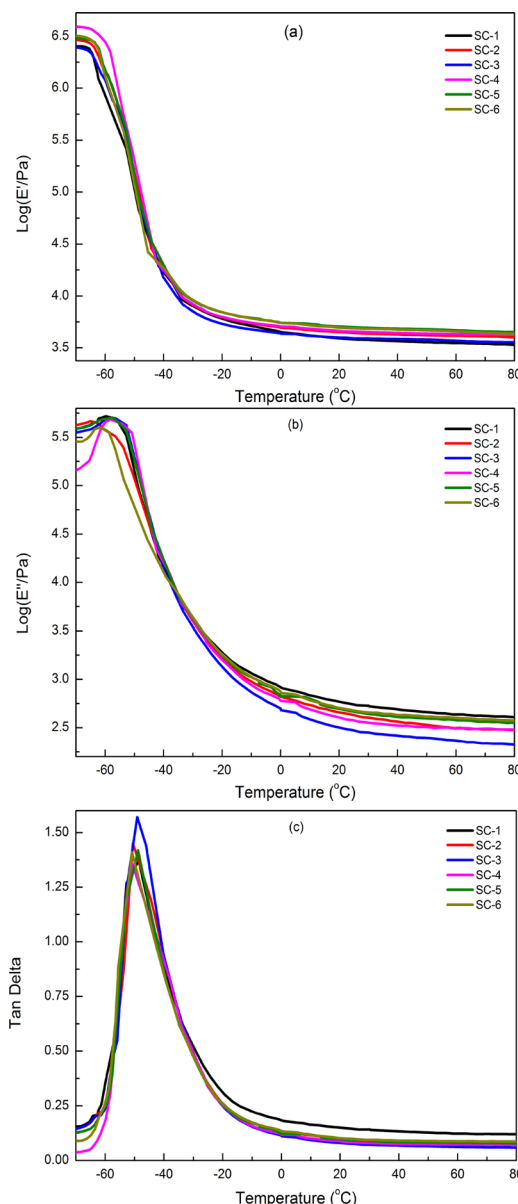


Figure 5: Variation of (a) storage modulus ($\log(E'/\text{Pa})$), (b) loss modulus ($\log(E''/\text{Pa})$), and (c) dynamic loss coefficient ($\tan \delta$) with temperature for modified IR/silica/CB vulcanizates with ATD.

Table 4: Dynamic mechanical properties of modified IR/silica/CB vulcanizates with ATD

Samples	tan δ						Temperature rise (°C)
	Maximum value	−20°C	0°C	23°C	60°C	80°C	
SC-1	1.35	0.312	0.183	0.145	0.122	0.119	22.7
SC-2	1.45	0.261	0.134	0.098	0.076	0.074	20.1
SC-3	1.57	0.250	0.114	0.077	0.062	0.059	18.8
SC-4	1.37	0.252	0.118	0.085	0.072	0.071	19.0
SC-5	1.42	0.256	0.123	0.094	0.080	0.079	19.4
SC-6	1.41	0.260	0.134	0.099	0.088	0.086	20.2

increasing ATD dosage, compression set decreased noticeably followed by a rise, whereas rebound resilience increased with a peak value (see Figure 4b). These observations are in good agreement with Si69 system (66) and probably because of the combined effects of strong filler–rubber interaction and thus better filler dispersion as well as enhanced state of cure (24). The rise of compression set at high ATD dosage might arise from the effect of sulfur contribution of ATD, resulting in the formation of polysulfidic bonds between rubber molecules. These polysulfidic bonds are weaker than mono- or disulfidic bonds and thus more susceptible to cleavage during thermal aging (66).

3.6 Effect on dynamic mechanical properties

DMA curves and relevant data of modified IR/silica/CB vulcanizates are shown in Figure 5 and Table 4. The modification resulted in an increase in storage modulus (E') and decreases both in loss modulus (E'') and dynamic loss coefficient (tan δ) in the range of −20°C to 80°C, consistent with the trend reported in literature (60). An increase in the maximum value of tan δ was also observed in the presence of ATD. With increasing ATD dosage up to 3.0 phr, the values of tan δ ranging from −20°C to 80°C significantly decreased. For the modified vulcanizate with 3.0 phr ATD (SC-3, in Table 4), the values of tan δ ranging from −20°C to 80°C reduced about 20–50% in comparison with that without ATD (SC-1, in Table 4). With further increasing ATD dosage up to 7.5 phr, the values of tan δ slightly increased. The DMA analysis was consistent with the results of temperature rise test (see Table 4). The temperature rise of modified vulcanizates gradually decreased with low ATD dosage (up to 3.0 phr) and slightly increased with high ATD dosage (up to 7.5 phr). These observations are probably because of strong interactions between filler and rubber

in the presence of ATD. Such strong interactions reduce the filler–filler interaction (24), improve the filler dispersion, and bound more rubber (see Figure 2 and Table 2). Therefore, the friction between filler and filler as well as the mobility of rubber molecular chains reduce, resulting in low hysteresis and less temperature rise; while the much more bound rubber contributes to the rebound in hysteresis (67,68).

4 Conclusion

In summary, multi-functional silane ATD could react with IR and silica as well as CB to prepare rubber composites containing finely dispersed filler. At low ATD dosage such as 3.0 phr, the resulting composites exhibited significant improvement in state of cure, hardness, tensile strength before and after aging, stress at 300% elongation, tear strength, abrasion resistance, rebound resilience, compression set, temperature rise, and the value of tan δ ranging from −20°C to 80°C. This modification with ATD as coupling agent imparts low hysteresis and improved mechanical properties, especially applicable for the preparation of high-performance tire tread and other rubber products as well as hybrid composites (69–82).

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