



Material properties

Comparison of coupling effectiveness among amino-, chloro-, and mercapto silanes in chloroprene rubber

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ABSTRACT

Organoalkoxysilane was grafted onto the surface of precipitated silica (PSi), and the modified PSi was characterized by particle size analysis, DRIFT and ²⁹Si NMR spectroscopy. There were 3 types of organoalkoxysilane used in this work, namely, 3-aminopropyl triethoxysilane (APTES), 3-chloropropyl triethoxysilane (CPTES) and bis (3-triethoxysilylpropyl) tetrasulfide (TESPT). The magnitude of the Payne effect, bound rubber content and mechanical properties of chloroprene rubber (CR) filled with unmodified and silane-modified PSi were investigated. Results reveal that the type of silane coupling agent (SCA) affects not only compound processability, but also mechanical properties of the CR vulcanizates. Among the 3 SCAs, it is evident that APTES and TESPT are capable of reducing the filler-filler interaction more efficiently than CPTES, as evidenced by Payne effect results, leading to superior compound processability. Mechanical properties of the CR vulcanizates filled with APTES-modified and TESPT-modified PSi are also greater than those filled with CPTES-modified PSi. This might be ascribed to the combined effects of enhanced rubber-filler interaction and improved filler dispersion.

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1. Introduction

The use of particulate fillers to achieve desirable reinforcement has been widely accepted by the rubber industry. Generally, carbon black (CB) and precipitated silica (PSi) are used as reinforcing fillers. The latter is typically used in light-colored products. The magnitude of PSi reinforcement is greatly influenced by its specific surface area [1]. The surface chemistry of PSi is dramatically different

from that of CB, due mainly to the presence of silanol groups. Thus, the interactions between PSi and rubber matrix must be taken into consideration to obtain maximum reinforcement efficiency [2]. The surface of PSi is polar and hydrophilic due to the abundance of silanol groups, resulting in strong filler-filler interaction via hydrogen bonds. This in turn causes poor filler dispersion in the rubber matrix [3]. Moreover, the silanol groups on the PSi surface are reactive to both cure activator (soluble zinc) and alkaline accelerators, causing detrimental effects on cure efficiency, such as undesirably long cure time in association with slow cure rate, as well as low crosslink density in sulfur-cured compounds [4,5]. Bi-functional silane coupling agents (SCAs) are commonly used to chemically modify the silica surfaces in order to enhance

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the interaction with hydrocarbon rubbers. The presence of silane not only leads to enhancement in silica dispersion, but also prevents adsorption of curatives on the silica surface [6]. Remarkable improvements in mechanical properties such as tensile strength [7], tear strength [8] and abrasion resistance [7] of silica-reinforced rubber vulcanizates can, therefore, result. Reductions of rolling resistance [9] and heat build-up [10] are also reported. Currently, there are many types of organosilane commercially available. So far, mercapto or polysulfide silane, namely bis(3-triethoxysilylpropyl) tetrasulfide (TESPT or Si-69), is still one of the most widely used general purpose silanes in the rubber industry [11]. The presence of sulfur atoms in TESPT is beneficial, particularly in a system cured by sulfur vulcanization, due to a co-vulcanization phenomenon. However, there are still some other silanes including bis(3-triethoxysilylpropyl) disulfide (TESPD), 3-thiocyanatopropyl triethoxysilane (Si-264), 3-methacryloxypropyl trimethoxysilane (MPTMS), and 3-mercaptopropyl trimethoxysilane (MPS) being used in the rubber industry for improving the performance of PSi in rubber compounds [12–14].

Many attempts have been made to study the role of silane coupling agent in improving the reinforcement efficiency of silica, and most of the published works have been carried out on the sulfur-curable rubbers such as NR and SBR [15,16]. Little attention has been given to the role of silane coupling agent in a functionally active rubber such as polychloroprene (CR). Recently, it has been reported that Si-69 is capable of improving the mechanical properties of silica-filled CR by the sulfur contribution effect [7]. It is, therefore, interesting to intensively investigate the role of silane coupling agent in silica-filled CR. In this work, 3 types of silanes (i.e., 3-aminopropyl triethoxysilane (APTES), 3-chloropropyl triethoxysilane (CPTES) and bis (3-triethoxysilylpropyl) tetrasulfide (TESPT) were used to modify silica surface. The coupling efficiency and the effect of each silane on viscoelastic and mechanical properties of PSi-filled CR vulcanizates were investigated.

2. Material and methods

2.1. Materials

Polychloroprene (Neoprene; CR grade W) was purchased from DuPont Dow Elastomer Co., Ltd., USA. Precipitated silica (PSi, Tokusil 233) was manufactured by Tokuyama Siam Silica Co., Ltd., Thailand. Silane coupling agents (SCAs), i.e., 3-aminopropyl triethoxysilane (APTES), 3-chloropropyl triethoxysilane (CPTES) and bis (3-triethoxysilylpropyl) tetrasulfide (TESPT) were supplied by Evonik Co., Ltd., Germany. Magnesium oxide (MgO), N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6-PPD), zinc oxide (ZnO), ethylene thiourea (ETU), stearic acid and sulfur (S₈) were purchased from local suppliers. All chemicals were used as received without further purification.

2.2. Silanization of PSi surfaces

Approximately 25 g of PSi was dispersed in 1:4 water:ethanol mixture under continuous stirring for 1

hour, and pH of the dispersion was adjusted to 2 by 1.0 M hydrochloric acid (HCl). 1.5 g of silane (APTES, CPTES or TESPT) was added, and the mixture was refluxed at 80 °C for 5 hours to allow the silanization reaction on PSi surfaces. The modified PSi was then separated by centrifugation technique (30 min at 6,000 rpm), and washed 3 times with toluene. Finally, the modified PSi was dried in an oven at 80 °C for 15 hours. Surface chemistry of the unmodified and modified PSi was characterized by Fourier Transform Infrared spectroscopy (FTIR; Bruker, Bruker Equinox55, Germany) using the diffuse reflectance mode under a wavenumber of 4,000–400 cm⁻¹ with a resolution of 4 cm⁻¹. ²⁹Si solid-state nuclear magnetic resonance, (²⁹Si-NMR, Bruker; DPX-300, Germany) was also used to study changes in chemical structure of silanes on the PSi surface. The test was performed at room temperature, and the spectra were acquired in the cross 3-polarization mode using a contact time of 10 ms and high power dipolar decoupling to reduce line broadening. Spectra were recorded at a frequency of 60 MHz and scanning rate of 4,000 ns⁻¹. A pulse repetition time of 5 s over 10,000–30,000 scans was used to gain sufficiently high signal to noise (S/N) ratio.

Measurement of agglomerate size was carried out by a particle size analyzer (Malvern Mastersizer 2000, Malvern Instruments Ltd., UK). Approximately 1 g of the sample was dispersed in 20 ml of distilled water and the suspension was sonicated in a water bath for 30 min prior to being measured.

2.3. Preparation and testing of rubber compounds and rubber vulcanizates

Rubber compounds were prepared using a laboratory-scale internal mixer (Haake Rheomix 90, Germany) equipped with roller rotors. The mixing conditions used were as follows; fill factor = 0.8, chamber temperature = 50 °C, rotor speed = 40 rpm and mixing time = 20 min. The compound recipe is given in Table 1. Loading of precipitated silica (PSi) was kept constant at 40 phr. A 2-stage mixing technique was used for preparing the compounds. In the first mixing stage, MgO, unmodified (or modified PSi), stearic acid and 6-PPD were incorporated sequentially into raw CR with total mixing time of 20 min. In the second stage, ZnO, ETU and sulfur were charged into the rubber mix, and further mixed for 7 min in order to achieve good dispersion and distribution of all ingredients.

Table 1
Compounding recipe.

Ingredient	Loading (phr ^a)	Function
CR	100	Raw rubber
MgO	4	Curative/Acid acceptor
PSi	40	Reinforcing filler
Stearic acid	2	Cure activator/Softener
6-PPD	2	Antioxidant
ZnO	5	Curative
ETU	0.5	Cure accelerator
Sulfur	0.5	Curative

^a Parts per hundred of rubber.

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