



Effect of silica particle size on chain dynamics and frictional properties of styrene butadiene rubber nano and micro composites



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ABSTRACT

Size and curvature of filler particles affect dynamics of polymer chains in composites. In this work, effects of filler particle size, in two scales of nano- and micro-meters, on dynamics of rubbery chains and frictional properties of composites were studied. Surface modification of nano- and micro-fumed silica by grafting low molecular weight hydroxyl-terminated polybutadiene (HTPB) guaranteed similar surface energy for fillers as measured by their surface tension. Nano- and micro-composites of styrene butadiene rubber were prepared by solvent assisted mixing and progressively increasing volume fraction of fillers. Achievement of nano and micro-composites was confirmed by the scanning electron microscopy. Effect of silica aggregate size on the dynamics of rubber chains was measured by dynamic-mechanical-thermal analyzer and compared through calculation of the activation energy for mobilization of slow-dynamic chains in the rubbery region. It was shown that nano-silica immobilizes the rubber chains more than micro-silica even at equal total interfacial area between filler aggregates and rubber matrix, especially above the percolation limit. Similar trend was seen for the coefficient of friction of composites against rough surfaces, showing the strong effect of chain dynamics on friction properties of rubber vulcanizates.

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1. Introduction

It has been proven that friction of rubber on hard surfaces is related to the internal friction of rubber and is mainly a bulk property [1]. Extended experimental works of Grosch showed that dependency of rubber friction on speed follows the same temperature dependency as other viscoelastic properties of rubber [2]. Therefore, a master-curve for coefficient of friction against speed can be formed which resembles the one for dynamic loss factor of rubber against frequency. Although the source of soft rubber friction on hard substrates was distinguished to be the internal hysteresis of rubber as well as the interfacial adhesion between the two bodies, Person argued that even surface adhesion has hysteric nature due to very small scale deformation of rubber resulting from attachment and detachment into nano-metric scale of surface roughness by electrostatic forces [3]. Heinrich and Kluppel adopted this view of rubber friction and developed a physical model based on the viscoelastic nature of rubber and the fractal nature of rough surfaces using Greenwood–Williamson's theory for self-affine surfaces [4]. They demonstrated applicability of the model for

rubber vulcanizates filled with large amounts of carbon black or silica [5].

Reinforcing fillers modify mechanical properties and viscoelastic behavior of rubber vulcanizates to a great extent. This bulk modification has been correlated to changes in the density profile, conformation, and relaxation dynamics of the polymer chains in the vicinity of impermeable filler particles evaluated by molecular simulations and/or experimental studies [6–10]. Majority of these studies compared their results to the observations obtained from modifications in properties of polymer thin films on flat surfaces [11–13]. Important role of immobilized rubber and gradient of glass transition temperature in the vicinity of filler particles have been described as the source of reduction in modulus of polymer composites by temperature in the rubbery region [13–15]. Temperature and frequency dependent dynamic-mechanical analyses are proven to be useful for assessing the filler effects on rubber chain dynamics and related apparent mechanical and fracture properties of such composites [16,17]. Reinforcing fillers extend the glass transition region to higher temperatures and broaden the distribution of relaxation times in the rubbery region. Mobilization of slow-dynamic chains along with Arrhenius-like decrease of the storage modulus by temperature in the rubbery region is a characteristic of the highly-filled polymer composites, and the corresponding activation energy has been interpreted as the required

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energy for mobilization of the shell as well as glass-like chains bridging filler particles [16]. Also, strong immobilization of styrene butadiene rubber (SBR) chains in the vicinity of silica particles at high loadings has been shown to result in the appearance of a second peak in the loss factor, in addition to the major peak for the unfilled rubber [18]. Application of different surface modifiers for silica and positive effects of bi-functional silanes in optimizing the elastic and viscoelastic behavior of SBR vulcanizates has been discussed [19–21].

Although dynamics of polymer chains around spherical particles has been resembled to those next to planar rigid surfaces, contact of a polymer chain to multiple particles and curvature of the spherical particles differentiate the former from the latter [6,7]. In this regard, the size as well as energetic and geometrical heterogeneity of particles is important parameters for reinforcement. The density of highly energetic adsorbing sites on the surface of filler increases as the particle size decreases [22]. Also, the size and size distribution of filler will define the packing of particles and confinement of rubber in the filler network [23]. Effect of increase in the interfacial area between rubber and carbon black by increasing filler loading or increasing surface area of this filler has been studied, and the activation energy of chain mobilization has been estimated [16]. However, the effect of silica aggregates size on dynamics of rubber chains, viscoelastic behavior of rubber composites, and related properties such as friction on rough surfaces are rarely studied [24,25].

The current research work focuses on the effect of silica particle size, in nanometer and micrometer scales, on dynamics of rubber chains in vulcanizates filled with fumed silica below and above the percolation limit. In order to differentiate particle size effect from the effect of surface area, measured properties are also reported against total interfacial area between filler aggregates and rubber matrix as well as the volume fraction of fillers [15]. Activation energy for mobilization of rubber chains in the vicinity of filler is used to study effects of silica particle size on dynamics of rubber chains and frictional behavior of the vulcanizates.

2. Experimental

2.1. Materials

Emulsion polymerized styrene butadiene rubber (E-SBR) of type 1502 was obtained from Bandar Imam Petrochemical Company (BIPC) of Iran. Two types of fumed silica with the trade names of Aerosil OX50 and Aerosil 200 from Evonic Industries were used as fillers. The main difference between these two products is the average primary particle size, which are 40 nm and 12 nm, respectively. Detail specifications of these products are given in Table 1. Aerosil OX50 is considered as the micro-silica because of a large average primary particle size and low specific surface area with respect to Aerosil 200, which is considered as a nano-silica [26]. Other compound ingredients include sulfur (2.5 phr) and N-Tert-Butylbenzothiazole-2-Sulphenamide (TBBS) (3 phr) from Solutia, Inc, stearic acid (0.5 phr) from Acidchem, and zinc oxide

(0.5 phr) from Rangine-Pars. Dispersion of the modified silica in rubber was assisted by toluene from Merck.

2.2. Methods

In order to reduce silica particle interactions and agglomeration, Aerosil OX50 and Aerosil 200 were modified by grafting low-molecular-weight hydroxyl-terminated polybutadiene (HTPB) onto the silica surface. This novel modification method was fully explained in our previous work [27]. This method provides a thorough coverage of silica particles by polymeric chains to guarantee similar surface energy for particles of both sizes. Similar surface energy provides similar effect of fillers on chemical cross-link density of rubber matrix. This modification method also provides the mean for covalent links between silica particles and rubber matrix through double bonds of HTPB during the vulcanization process. These advantages will allow the study of just particle size on the dynamic properties of rubber chains around filler aggregates.

Surface tension of the un-modified and modified silica powders was measured by contact angles in the drop-shape method and using Girifalco–Good–Fowkes (GGF) model according to ASTM D 724.

Mixing of modified silica with rubber was performed in toluene, and compounding with other ingredients was performed on a two-roll-mill as explained in our previous work [27]. Loading of micro-silica, Aerosil OX50, was varied as 5, 10, 20, 30, 40, 50, and 60 parts per hundred rubber (phr). The nano-silica, Aerosil 200, was added as 2, 4, 6, 8, 10, 15, and 20 phr. These loading levels guaranteed similar ranges of total interfacial area between filler aggregates and the rubber matrix in micro- and nano-composites. Geometric specific surface area (GSSA) of fillers was estimated using geometric characteristics of filler aggregates, assuming spherical particles, as follow [28]:

$$GSSA = \frac{A}{m} = \frac{A}{\rho V} = \frac{6}{\rho d} \quad (1)$$

In this equation, 'A' is the surface area of an equivalent spherical aggregate, and 'm', 'ρ', 'V', 'd' are mass, density, volume, and average diameter of aggregates, respectively. The average diameter of the aggregates was estimated based on the in-rubber microstructure of filler obtained from Scanning Electron Microscopy (SEM). The reason for using geometric-SSA rather than BET-SSA is that the latter is measured by nitrogen which penetrates into pores of silica particles and over-predicts the surface area accessible to rubber chains. Unlike nitrogen, rubber chains partially diffuse into pores of silica and interact mostly with the surface of particles.

Cure characteristics and optimum cure time were obtained by a Rheometer type Hiwa 900. Rubber sheets were cured in a Collin hot press and used for further study. Dynamic-Mechanical-Thermal Analysis (DMTA) was performed to access the effect of filler particles on the dynamics of rubber chains. For this purpose DMA-8000 from Perkin–Elmer was used by sweeping temperature between –100 °C and 100 °C, frequency of 1 Hz, and strain of 0.2% in the bending mode. Finally, frictional properties of the samples against P360 sandpaper were measured by an in-house friction tester as explained in our previous publication [29]. The friction tester allows for measurement of the coefficient of friction for rubber rings as a measure of rotational velocity and load on variety of flat surfaces. Linear velocity and contact pressure were chosen as 361 mm/s and 0.5 MPa, respectively. This condition is similar to the average slip rate and contact pressure in the footprint of passenger car tires in partial breaking. The rubber rings were vulcanized by the compression molding.

Table 1
Characteristics of the un-modified fumed silicas.

Property	Unit	Aerosil 200	Aerosil OX50
Type	–	Nano silica	Micro silica
Specific surface area (N ₂ absorption)	m ² /g	200 ± 25	50 ± 15
Primary particle size	nm	12	40
Moisture	wt%	1.5 ≤	1.5 ≤
Powder density	g/lit	50	130
Hydroxyl density	nm ⁻²	4.4–4.6	2.0–3.3
Surface tension	mJ/m ²	80	44

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