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Reducing friction with Al_2O_3/SiO_2-nanoparticles in NBR

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ABSTRACT

Friction is a phenomenon that is sometimes desired and sometimes to be avoided. In the past, material development grants have not focused on this task. In this article, we present a new and alternative method of reducing elastomer friction when sliding on different kinds of substrates by inducing hard alumina/silica nanostructures on the elastomer surface. The formation of Al_2O_3/SiO_2 nanostructures is based on an in situ sol–gel process of a dispersion of spherical aluminum oxide nanoparticles in a silica liquid precursor polymer – hyperbranched polyalkoxysiloxane (PAOS) – in an elastomer mixture. The influence of variable amounts of Al_2O_3/PAOS dispersion, variable amounts of carbon black fillers and annealing time on the friction coefficient is studied for a large velocity range. Experiments were conducted with and without lubricant and discussed with regard to material and surface properties of the samples. It is found that sufficient PAOS concentrations significantly decrease friction for all systems and prevent stick-slip phenomena.

1. Introduction

Our goal is to reduce friction for elastomers sliding over solid surfaces such as granite, steel and glass, which can be either dry or wet. Fillers such as PU precursors, organomodified nanoclays and carbon nanofibers have been used by previous authors to produce elastomer nanocomposites containing HNBR or NR [1,2]. Latest investigations have shown that inorganic fullerene like materials (IFLM) can be used as nanomaterials for reduction of friction [3].

In this article, we focus on NBR samples (acrylnitril butadiene copolymers) because of their stability against oil, heat and abrasion, which offers broad usage as gaskets, hoses and rubberized fabric with small friction coefficients.

A model developed at the DIK [4–10] has shown that two effects contribute to friction: The first is a hysteresis part that is due to the energy loss when the rubber is squeezed into the substrate surface and deformed by the lateral movement according to its viscoelastic properties. Consequently, temperature is important for friction behavior [11]. Neglecting internal heating effects, hysteresis friction increases with sliding velocity.

The other effect is caused by molecular forces of the direct contact of elastomer and substrate in the absence of lubricant (dry friction) [12]. The adhesion occurring in this case is directly related also to the real area of contact, which cannot be established accurately when sliding fast, and which depends on the surface tensions of rubber and substrate [13,14]. To achieve minimal friction, it is useful to minimize the real area of contact [15–18], which plays a major role, especially for dry friction, thus reducing abrasion effects [19]. In every system, friction is increased when the elastomer is forced into substrate cavities. Hard structures with small cavities will hinder this process, and reduce the total friction coefficient. In nature, this is shown by surface nano structures of the Sandfish (scincus scincus) [20].

To produce such a sample, hard spherical nanoparticles were formed at the surface of the rubber matrix. These particles consist of silica that arises from the silica liquid precursor hyperbranched polyalkoxysiloxane in an in situ sol–gel process and aluminum oxide.

Compared to the monomeric sol–gel precursor tetraethoxysilane (TEOS) PAOS is a well defined precursor polymer (Fig. 1) with preferable properties [21]: A high resistance to hydrolysis due to the absence of OH groups. Completely covered by organic end groups, PAOS shows hydrophobic properties combined with solubility in most organic solvents. It can easily be modified for a better compatibility to different polymers. For example, incorporation of long alkyl chains, i.e. hexadecyl alkyl chains, increases the hydrophobicity of such modified PAOS.

Recently, PAOS was employed in thermoplastic processing aimed at the development of a solvent-free sol–gel technology for the in situ formation of nanoscale filler particles in polypropylene [22,23]. Applied as an additive without addition of a catalyst for conversion to silica, PAOS being throughout the sample is surface active and enriches at polymer surfaces after processing. There it is converted to silica by atmospheric moisture. PAOS is also a suitable dispersant for silica or alumina nanoparticles.

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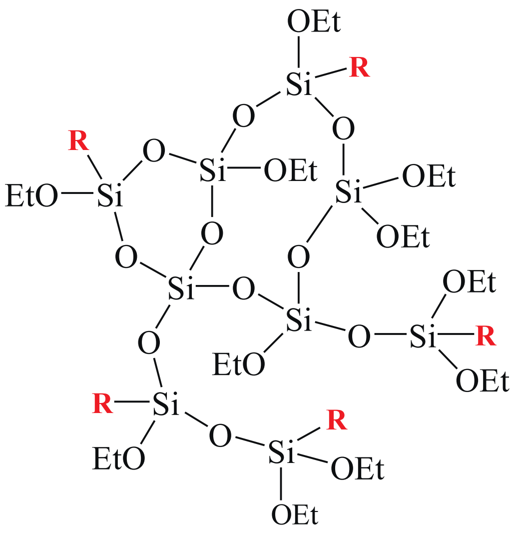

Fig. 1. Structure of hyper branched polyalkoxysiloxane (PAOS), with R: $-C_{16}H_{33}$.

2. Preparation, material and surface properties

2.1. Preparation

To form alumina/silica nanostructures on an elastomer surface, hydrophobically modified Al_2O_3 particles (diameter: 100–120 nm, 10 wt. % in relation to PAOS) dispersed in a hexadecyl-modified PAOS (Fig. 1) were added to the mixing process. We will abbreviate this dispersion here simply as “PAOS”. The nanostructures were formed when the sample surface was treated with a heated humid atmosphere, which will be called annealing in this article. The NBR sample composition is made of 100 phr (“per hundred rubber”) Perbunan NT 2870F, 5 phr ZnO, 1 phr stearic acid, 1.5 phr sulphur, 2 phr N-cyclohexyl-2-benzthiazylsulfenamide (CBS) and 0.5 phr diphenylguanidine (DPG) for unfilled samples, or additionally 50 phr carbon black N 330 for filled samples. Both filled and unfilled samples were prepared at 50 °C in an industrial type mixer either without PAOS, with 10 phr or with 20 phr PAOS, which had been produced at the DWI Aachen.

The following steps were carried out to prepare the samples:

1. mixing of an NBR batch, including various parts of PAOS and carbon black;
2. vulcanization until t_{90} time;
3. if annealing is indicated, the sample was exposed to a 90% humid atmosphere at 60 °C for 24 h to ensure a complete process of silica building on the surface.

When not in use, samples were kept in a desiccator to prevent further silica formation. To protect the surface, clean conditions were applied to vulcanization and further handling.

2.2. Material properties

First, the influence of PAOS and of annealing on the material properties was investigated. Increasing amounts of PAOS prolonged the vulcanization time. They also increased the shear moduli G' and G'' in the high temperature range, as shown by DMA measurements (dynamic mechanical analysis). Consequently, the maximum of the loss angle $\tan\delta = G''/G'$ is diminished without changing the associated temperature of the maximum (see Fig. 2)—PAOS behaves like a non-active filler without coupling to the polymer. As expected, carbon black filled samples show higher shear moduli with a decreased maximum of $\tan\delta$. Annealing had only minor effects on the viscoelasticity.

Mechanical properties were determined by PAOS amount, carbon black amount and annealing (Table 1). The combination of

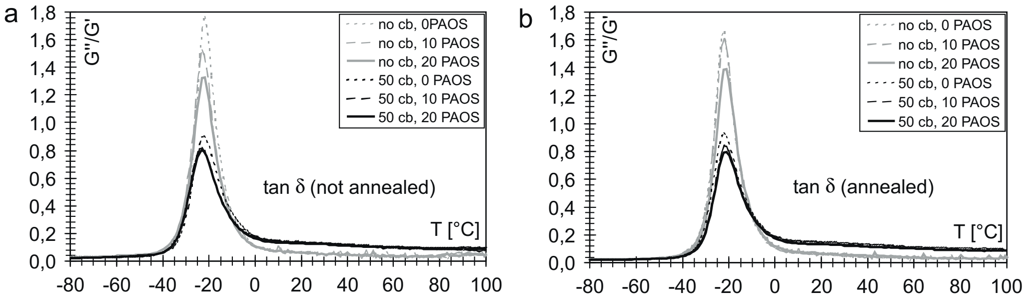

Fig. 2. Viscoelastic properties (shown as $\tan\delta$) of unfilled and filled samples with different amounts of PAOS before (left) and after annealing (right).

Table 1
Mechanical properties.

Carbon black [phr]	PAOS [phr]	Anneal time [h]	IRHD hardness	Rebound [%]	Tensile strength	Elongation at break [%]	Stress 200% [MPa]	DIN abrasion [mm^3]	Density [g/cm^3]
0	0	0	54	53	5.0	344	2.3	67	1.01
0	10	0	55	53	3.8	347	2.2	100	1.02
0	20	0	56	54	2.2	336	1.4	143	1.03
0	0	24	54	55	4.3	357	2.2	65	1.01
0	10	24	58	56	5.7	381	2.5	151	1.02
0	20	24	64	56	2.7	385	1.7	263	1.03
50	0	0	75	33	27.9	294	16.8	71	1.17
50	10	0	76	36	23.3	272	14.9	87	1.17
50	20	0	75	39	18.6	248	13.4	141	1.16
50	0	24	74	33	24.7	262	16.7	77	1.17
50	10	24	78	36	24.7	268	16.1	105	1.17
50	20	24	80	38	17.8	231	14.4	174	1.17