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Dry rolling and sliding friction and wear of organophilic layered silicate/hydrogenated nitrile rubber nanocomposite

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Abstract Dry rolling and sliding tribological behaviors of hydrogenated nitrile rubber (HNBR) and its compound, containing 10 parts per hundred rubber (phr) organophilic layered silicates (OLS), were evaluated. As OLS modifier a quaternary amine with hydroxyl and double bonds was selected to support the intercalation/exfoliation by triggering possible interactions with HNBR. According to X-ray diffraction results the OLS was intercalated. Network-related parameters were deduced from dynamic-mechanical thermal analysis (DMTA). The tribological parameters, i.e., coefficient of friction (COF) and specific wear rate (W_s), were determined in various home-made test configurations. The OLS reinforcement of HNBR affected the COF and improved the resistance to rolling and sliding wear (except fretting) compared to the pure HNBR. The worn surfaces of the rubber compounds were inspected in scanning electron microscope (SEM) and the dominant wear mechanisms concluded.

Introduction

Hydrogenated nitrile rubber (HNBR), being a saturated rubber, has excellent resistance to oils, heat aging, ozone attack, and many chemicals. In addition, it exhibits good resistance to wear, and remarkable dynamic properties in a broad temperature range. Its properties can be tailored upon requests by different modifiers, fillers. As a consequence HNBR is often used in demanding automotive and oilfield applications.

Rubbers become preferred materials to be modified by novel platy-shaped nanofillers, such as layered silicates, clays [1, 2]. Note that a distinction between layered silicate and clay has been made depending whether the corresponding mineral is of synthetic or natural origin. Their organophilic versions are easily intercalated and exfoliated in rubbers due to favored chemical interactions with the rubber and/or curatives, and high shear forces acting during mixing [1]. Modification with layered silicates/clays strongly improves the mechanical performance, barrier behavior, flame retardance, and selected other properties of rubbers [1, 2]. HNBR was already the target of this kind of nanomodification (e.g., [3–7]). Researchers focused, however, on the curing, mechanical, and barrier properties of the related nanocomposites. Friction and wear behaviors of layered silicate/clay modified rubbers were scarcely studied. Few papers addressed the tribological performance under sliding [8, 9] and rolling [10] conditions of such rubber nanocomposites. The related tribological results are, however, scattering. Organoclay modification of rubbers was reported to both improve and deteriorate the wear resistance. It can thus hardly be concluded whether layered silicate/clay modification of rubbers is the right way to improve their tribological performance. It is well known that the original intercalant (organophilic modifier) of the layered silicate has a great impact on the intercalation/exfoliation behavior, and this statement holds for HNBR, as well, as reported (e.g., [1, 3, 11]). Therefore, we have selected an organophilic layered silicate the intercalant of which can interact with the HNBR chains (creating

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H-bonds) and also participate in the curing reaction (co-curing due to the presence of double bonds). This organophilic layered silicate (OLS) has already been successfully applied for the nanomodification of unsaturated vinyl ester resins [12].

In the present work, the filler OLS was added in the HNBR and its influence on the dry rolling and sliding wear against steel was evaluated in various test rigs. OLS was made organophilic by a quaternary amine bearing both hydroxyl and double bonds, in order to favor the intercalation/exfoliation with HNBR. The coefficient of friction (COF) and specific wear rate (W_s) were determined. The worn surfaces were investigated in scanning electron microscope (SEM) and the wear mechanisms analyzed. The intercalation of OLS was checked by X-ray diffraction (XRD) tests. The network-related characteristics of unfilled and OLS filled HNBR compounds were deduced from dynamic-mechanical thermal analysis (DMTA).

Experimental

Materials

The formulation of the peroxide curable HNBR was described in Refs. [13, 14].

The pristine layered silicate was a synthetic sodium fluorohectorite (Somasif® ME-100 of Co-opChemicals, Tokyo, Japan) that was made organophilic by octadecylamine-*N*,*N*-bis[allyl(2-hydroxypropyl)ether] (OAE) via cation exchange. The intergallery distance and silicate content of the OAE-modified OLS were 2.85 nm and 65 wt%, according to X-ray diffraction (XRD) and thermogravimetric analysis (TGA) data, respectively.

The mixing of this peroxide curable HNBR with 10 part per hundred rubber (phr) OLS and follow-up curing to 2 mm thick sheets were done as disclosed earlier [13, 14]. The compounds are referred to as HNBR-PURE, HNBR-10OLS, respectively. Intercalation of the OLS was assessed by XRD. The related spectra were recorded in reflection mode by a D500 X-ray diffractometer from Siemens (Munich, Germany). Ni-filtered Cu K_α radiation ($\lambda = 0.1542$ nm) was adopted and the diffractometer operated at 40 kV and 30 mA. The samples were scanned in step mode (5 s/step, step increment: 0.05°) in the scattered angle (2θ (theta)) range from 1° to 10°. XRD spectra indicated that the OLS has been intercalated: the initial intergallery distance was expanded from 2.85 to 3.33 nm—cf. Fig. 1.

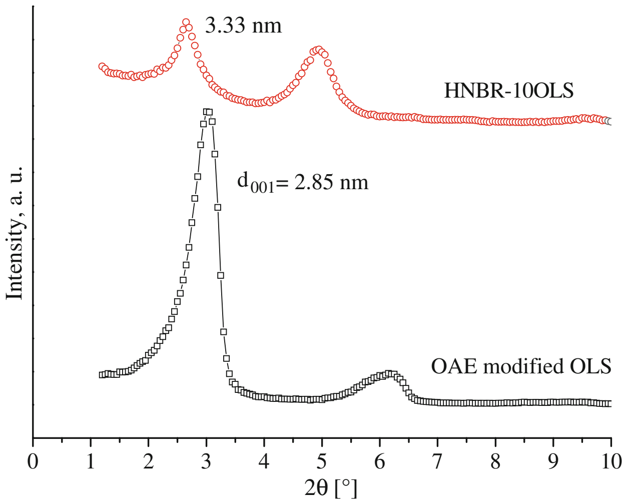

Fig. 1 XRD spectra of the OAE modified fluorohectorite (OLS) and HNBR-10OLS compound

This intercalation is most likely owing to the combined action of hydrogen bonding (between the hydroxyl groups of the modifier and the acrylonitrile groups of the HNBR) and peroxide-induced co-curing (between the modifier and HNBR matrix). The density and hardness (Shore A) of the compounds were determined according to ISO 1183 and ISO 868, respectively.

Testing

Dynamic-mechanical thermal analysis (DMTA)

DMTA spectra were measured with rectangular specimens in tensile mode at a static preload 0.01 N with a superimposed sinusoidal 0.01% strain (frequency: 10 Hz) in a Q800 device of TA Instruments (New Castle, DE, USA). The temperature ranged from −100 to +100 °C. From −100 °C, the temperature was increased by 5 °C/step and for each step the temperature was stabilized for 3 min.

Rolling and sliding friction and wear testing

An orbital rolling ball-on-plate (Orbital-RBOP) home-made test configuration was used to determine the rolling friction and wear of the HNBR compounds. In the testing rig, a steel ball (100Cr6, diameter: 14 mm, arithmetical roughness R_a: 1 μm) rolled along a circular path under a defined normal load on the rubber sheet. The experimental parameters were: normal load 90 N, revolution 280 rpm, duration 3 hours (h).

Sliding friction and wear behaviors of the composites were determined in pin-on-plate (POP), roller-on-plate (ROP), and oscillating cylinder-on-plate (fretting) tribotests. Note that the pin/roller/cylinder and the plate were made of steel and rubber, respectively.

In POP, a steel pin (100Cr6, R_a: less than 1 μm) with a hemispherical head (diameter: 10 mm) was driven to rotate along a circular path with a given load against the rubber plate. This set-up was fixed in a Wazau tribometer (Berlin, Germany). The experimental conditions were: normal load 2 N, sliding speed 250 mm/s, duration 1.5 h.

In ROP, a rotating steel roller (9SMnPb28k, diameter: 10 mm, width: 20 mm, $R_a \approx 0.9$ μm) was pressed against a rubber strip of ca. 9 mm width in a SOP 3000 tribotester (Dr. Tillwich GmbH, Horb-Ahldorf, Germany). Test parameters were: load 2 N, sliding speed 250 mm/s, duration 1.5 h.

In the fretting tribotest a steel cylinder (diameter: 15 mm, contact length: <12 mm, $R_a \approx 0.9$ μm) rubbed the surface of the rubber specimen via an oscillation movement at a frequency of 10 Hz under a defined normal load. The applied experimental parameters were: normal load 10 N, stroke < 3 mm (varied), duration < 3 h (varied).

The specific wear rate was calculated according to:

$$W_s = \frac{\Delta V}{F \cdot L} \qquad (1)$$

where ΔV (mm^3) is the volume loss, F (N) is the normal load, and L (m) is the overall rolling/sliding distance. The loss volume (ΔV) was calculated by measuring the depth and width of the wear tracks by a white light profilometer (see later). All above devices allowed recording the COF as a function of time. Test set-up of the above testing facilities is depicted schematically in Fig. 2.

The above test conditions were selected by considering rubber seals in reciprocating duties and high-frequency oscillating wear (fretting). So the sliding speeds and apparent contact pressures were usually below 250 mm/s and 5 MPa (cf. Ref. [13]), respectively. As to rolling wear, a rather high normal load was chosen to produce measurable wear. The duration of the experiments in the four machines could promise the measurable volume loss and at the same time, not wear the samples out.

The wear tracks were scanned in a MicroProf white light profilometer (Fries Research & Technology, Bergisch Gladbach, Germany) and in SEM (Zeiss Supra$^{\text{TM}}$ 40VP, Oberkochen, Germany). Prior to SEM investigations the specimens were sputtered with an Au/Pd alloy.

Results and discussion

DMTA

The measured storage modulus (E') and loss factor (tan δ) of the compounds as a function of the temperature are displayed in Fig. 3. Note that the incorporation of OLS did not affect the position of the glass transition temperature of the HNBR composites ($T_g \approx -25$ °C). Introducing OLS in HNBR increased the stiffness (E') of the corresponding composite, but only in the rubbery stage. Lacking reinforcement in the glassy state suggests that OAE was involved in the HNBR crosslinking process, in fact. The apparent network-related parameters, such as apparent mean molecular mass between crosslinks (M_c) and apparent network density (ν_c) of the studied compounds were

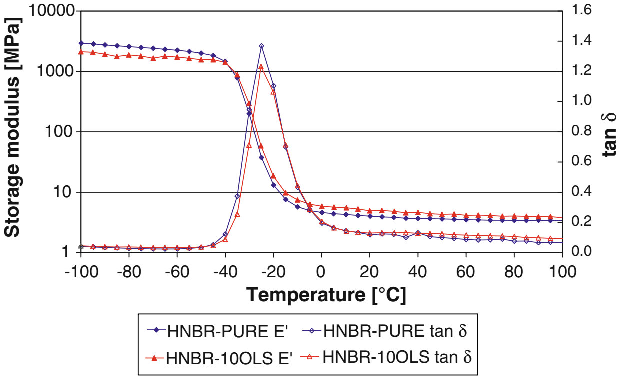

Fig. 3 Storage modulus E' and loss factor tan δ as a function of temperature for the HNBR compounds

Fig. 2 Schemes of the test configurations of Orbital-RBOP, POP, ROP, and fretting. Top right picture reflects the division of the wear track for SEM "sampling" after Orbital-RBOP test

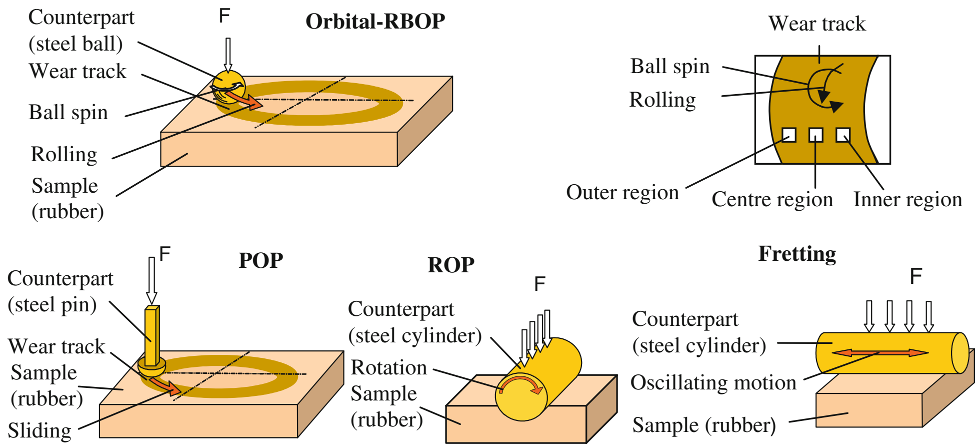

Table 1 Structural and wear properties of the HNBR compounds

	HNBR-PURE	HNBR-10OLS
Shore A (°)	42	52
Density (g/cm^3)	1.057	1.050
M_c (g/mol)	2013	1564
ν_c (mol/dm^3)	0.52	0.67
tan δ at T_g	1.37	1.23
Orbital-RBOP		
COF	4.23×10^{-2}	5.36×10^{-2}
W_s (mm^3/N m)	2.95×10^{-4}	1.34×10^{-4}
POP		
COF	1.14	1.24
W_s (mm^3/N m)	1.13×10^{-1}	3.68×10^{-2}
ROP		
COF	3.00	1.89
W_s (mm^3/N m)	3.79×10^{-2}	7.83×10^{-3}
Fretting		
COF	0.90	1.00
W_s (mm^3/N m)	1.50×10^{-3}	3.56×10^{-3}

calculated as described in Refs. [13, 14], and summarized in Table 1.

Friction and wear

Table 1 lists the COF and W_s of the HNBR compounds measured in Orbital-RBOP, POP, ROP, and fretting rigs. One can recognize that the effect of OLS strongly depends on the tribological test set-up. This is in accordance with the claim that COF and W_s are "system parameters," i.e., their actual values are not controlled solely by material properties but they depend markedly on many other variables, like test configuration, material and roughness of the counterpart, test parameters including the testing environment. Incorporation of OLS lowered the W_s but increased the COF in rolling tests. In sliding experiments, the OLS filled HNBR exhibited reduced W_s under POP and ROP conditions, but experienced increased W_s in fretting compared to HNBR-PURE. The improvement in the resistance to wear under POP and ROP is significant especially when considering the low amount of the added OLS. Incorporation of OLS in HNBR reduced the COF dramatically in ROP but slightly enhanced this value in POP and fretting.

Rolling and sliding wear mechanisms

Rolling wear

Figure 4 displays SEM photos taken from the wear track of HNBR-PURE after Orbital-RBOP test. As explained in Ref. [13] and depicted in Fig. 1 (top right), the wear track was divided into three regions: outer region-with additional forward spin of the ball, inner region-with additional backward spin of the ball, and the center region-between the outer and inner regions. The worn surfaces of HNBR-PURE and HNBR-10OLS are quite similar (cf. Figs. 4, 5). Both outer and inner regions show surface waves, i.e., Schallamach-type pattern [15] with roll heads which is the result of elastic instability caused by the tangential force in the contact region between the rubber and the steel counterpart (cf. Figs. 4a, c, 5a, b). The adverse directions of the waves in the two regions for HNBR without and with OLS reflect the rubbing speeds in the outer and inner regions are reverse to each other. Incorporation of OLS decreased the width of the Schallamach pattern and the distance between the neighboring waves, which may be the reason for the lower W_s of the filled compound. Large agglomerates appeared in the center regions for both the pure and reinforced HNBR (cf. Figs. 4b, 5a). This finding suggests that the debris were not swept away from this region.

Sliding wear

Figure 6 collects SEM photos of the worn surfaces of the both researched HNBR compounds after POP, ROP, and fretting tests. HNBR-PURE failed by crater formation after POP (cf. Fig. 6a). By contrast, HNBR-10OLS shows

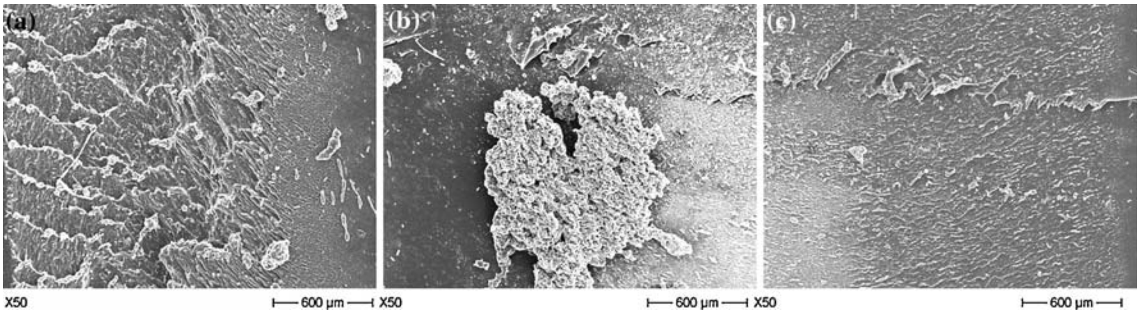

Fig. 4 SEM photos taken from the rolling wear track of HNBR-PURE after Orbital-RBOP test. Designation: **a** outer region, **b** center region, and **c** inner region. *Note*: rolling direction is downward

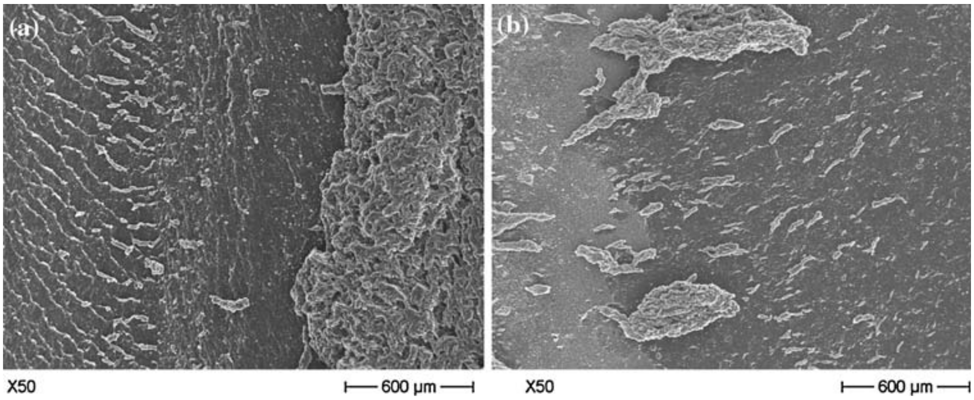

Fig. 5 SEM photos taken from the rolling wear track of HNBR-10OLS after Orbital-RBOP test. Designation: **a** outer and center regions, and **b** inner region. *Note*: rolling direction is downward

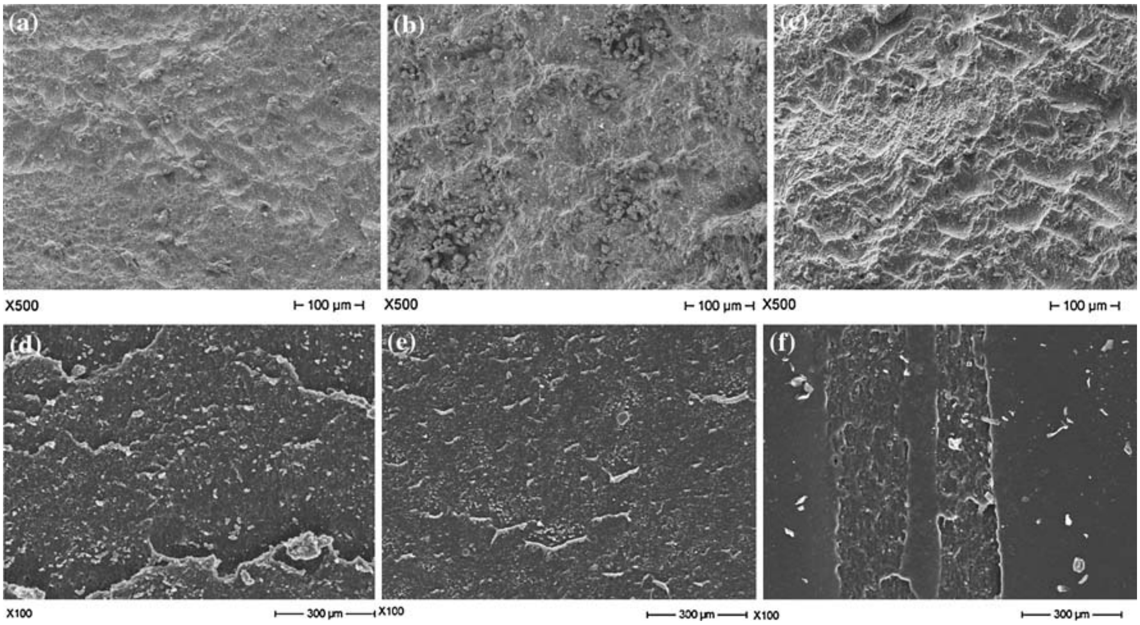

Fig. 6 SEM photos taken from the sliding wear tracks of HNBR-PURE (*up*) and -10OLS (*down*) after POP (**a** and **d**), ROP (**b** and **e**), and fretting (**c** and **f**) tests. *Note*: sliding direction is downward (for POP and ROP) or vertical (for fretting)

abrasion type pattern with ironed roll debris and particles (cf. Fig. 6d). Those particles may account for the higher COF of HNBR-10OLS compared to the unfilled HNBR. After ROP test spherical debris were observed in the unfilled HNBR (cf. Fig. 6b), which is likely linked with the much higher COF compared to all other sliding tests of the rubber compounds. OLS reinforcement of HNBR produced slightly extended and “ironed” rolling stripes (cf. Fig. 6e). The changes in the wear mechanism reflect well that W_s of HNBR-10OLS was markedly reduced compared to HNBR-PURE in POP and ROP. In fretting tests, cratering and local peeling are recognizable for pure and OLS filled HNBR, respectively (cf. Figs. 6c, f). The peeled rubber surface layer may stick to the steel ball (acting as a “transfer film”) and thus enhancing both the W_s and COF compared to those of HNBR-PURE.

Conclusion

Based on this work devoted to study the dry friction and wear performance of an organophilic layered silicate (being intercalated) modified hydrogenated nitrile rubber (HNBR) in different rolling and sliding tribometers, the following conclusions can be drawn:

- Under rolling the COF was enhanced while the specific wear rate (W_s) reduced by OLS incorporation. This was attributed to the debris enrichment in the center region of the wear track and reinforcing effect of the OLS in HNBR, respectively.
- Under sliding the COF was less affected in POP and fretting, and markedly reduced under ROP. W_s was reduced for POP and ROP whereas the opposite

occurred under fretting condition. This was explained by significant changes in the wear mechanisms. By OLS addition an “ironed” wavy pattern appeared instead of crater formation. The increased COF and W_s under fretting was traced to the appearance of a rubber transfer film.

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