Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology
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Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology published online 15 November 2012
DOI: 10.1177/1350650112464613

Special Issue Article

Institution of MECHANICAL ENGINEERS

Journal of ENGINEERING TRIBOLOGY

Proc IMechE Part J:
J Engineering Tribology
0(0) 1–8

DOI: 10.1177/1350650112464613
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Tribologically modified surfaces on elastomeric materials

NV Rodríguez[1,2], MA Masen[1] and D-J Schipper[1]

Abstract

As the result of tribological loading, the properties of the surface of elastomeric materials will alter. This effect has been observed using SEM and EDS analysis of the tread of a used car tyre, where differences in structure between the substrate and the area near the surface were found. To study the effects of tribological loading on the surface properties of elastomers in a more reproducible manner, a pin-on-disk tribometer was employed, using EPDM disks and spherical pins made of 100Cr6 steel. In the tribologically loaded area, a modification of the surface with a thickness ranging between 4 and 8 μm was observed, whilst in the unloaded area such a surface modification was not observed. The mechanical and tribological properties of the modified and unmodified surfaces were analysed using micro-indentations and friction experiments on a nano-tribometer, showing a reduction of the stiffness of the tribo-modified surface as well as altered time-dependent behaviour and a 60% reduction in the coefficient of friction when sliding against steel.

Keywords

Elastomers, tribology, friction, surface modification, sliding contact

Date received: 18 July 2012; accepted: 24 September 2012

Introduction

It is well known that, during sliding contact, materials such as ceramics and metals develop an interfacial layer, see for instance the work of Czichos[1] or Bhushan.[2] The interfacial layer is a modification of the surface of the material due to stresses, strains and/or strain rates that are the result of the normal and tangential loads. Such a layer can have a thickness ranging from several nanometres to tens of micrometres and may influence the tribological behaviour of the tribo-system because the properties, such as hardness and shear strength, are different from the original material in contact. For polymeric materials, such an alteration of surface properties as the result of tribological loading has also been observed. Toney et al.,[3] for instance, attributed the changed mechanical properties of rubbed polyamide to the near-surface alignment of the molecules. Molecular orientation is also known to occur in other polymers, such as PTFE and UHMWPE.[4,5] Studies on the mechanical properties of polymeric surfaces commonly focus on polymeric coatings for use on more rigid substrates; in such cases there is a substantial difference between the properties of the layer and the substrate, which often forms the basis of the used methods to characterize the elastic properties of such films.[6,7] It has been suggested[8–10] that the various environments encountered by atoms and molecules at the surface and in the bulk cause chemical and topological changes. Lei et al.[11] found chemical and morphological differences between the surface and the bulk in polymer blends. Additionally, Schwab and Dhinojwala[12] found differences between the viscoelastic relaxation times of a rubbed polystyrene surface and its bulk, indicating improved mobility at the free surface of glassy polymers.

For elastomeric materials, early investigations into the sliding friction behaviour showed an important influence of the interface of the contact.[13–15] Boonstra et al.[16] discussed the occurrence of a ‘sticky layer’ on SBR material under mild conditions and attributed this to a combination of rupture of molecular chains and thermal degradation. Smith and Veith[17] used TEM to show a layered structure that has developed in a worn tyre tread. Ghatak et al.[18] and She et al.[19] pointed out that adhesion, friction and fracture can be described by the kinetics occurring in the interface of a tribo-system formed by

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an elastomer. Recently, a number of authors[20–24] have explained their obtained tribological results by suggesting the possibility of changed surface properties. Examples are Lorentz, Persson and co-workers[20] who extended a theoretical model for rubber contact and friction with a 'surface film shear component' and Deladi[21] who showed that a surface layer had developed during tribological testing of polyurethane samples.

Even though there is a substantial amount of literature describing both theoretical and experimental studies of the contact and friction behaviour of elastomers and rubber materials, they often utilise the bulk properties of the materials to describe the mechanical and tribological behaviour. The existence of tribologically induced surface modifications on elastomers was already mentioned in the early seventies, but the properties of these surfaces have not been quantified in literature. The current work aims to confirm the development of a modified surface on an elastomeric material as the result of a sliding contact and to show its effects on friction. By employing a pin-on-disk contact between an Ethylene Propylene Diene polyMethylene (EPDM) model material sliding against a steel counter surface, a surface modification is induced under controlled conditions and the mechanical and tribological properties of the created modified surface are analysed.

Surface analysis of a used automotive tyre

Techniques such as Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) have been used in literature to show differences between the surface and the bulk for a wide range of materials. In the present work, these techniques are employed to analyse the rubber surface. Cubical samples of 5 mm sides were cut out of the thread of the used car tyre with a surgical scalpel at ambient temperature. Special attention was given to keep the surface of the tread unaffected in preparation and no coating was applied prior the analysis in the SEM. Figure 1(a) and (b) shows the resulting SEM images of the cross sections of the samples.

At a low magnification, Figure 1(a), it is possible to distinguish a bright line indicating the surface, which slightly differs from the bulk. Figure 1(b) shows the surface at a higher magnification. In the bulk of the material, clusters of randomly distributed particles (carbon black) can be seen, whilst towards the surface the distribution of these particles becomes more compact, apparently merging until no individual particles can be observed anymore. An EDS analysis showed an increased concentration of oxygen when compared to the bulk, which agrees with the findings of Zhang et al.[22] The increase of oxygen in the surface suggests

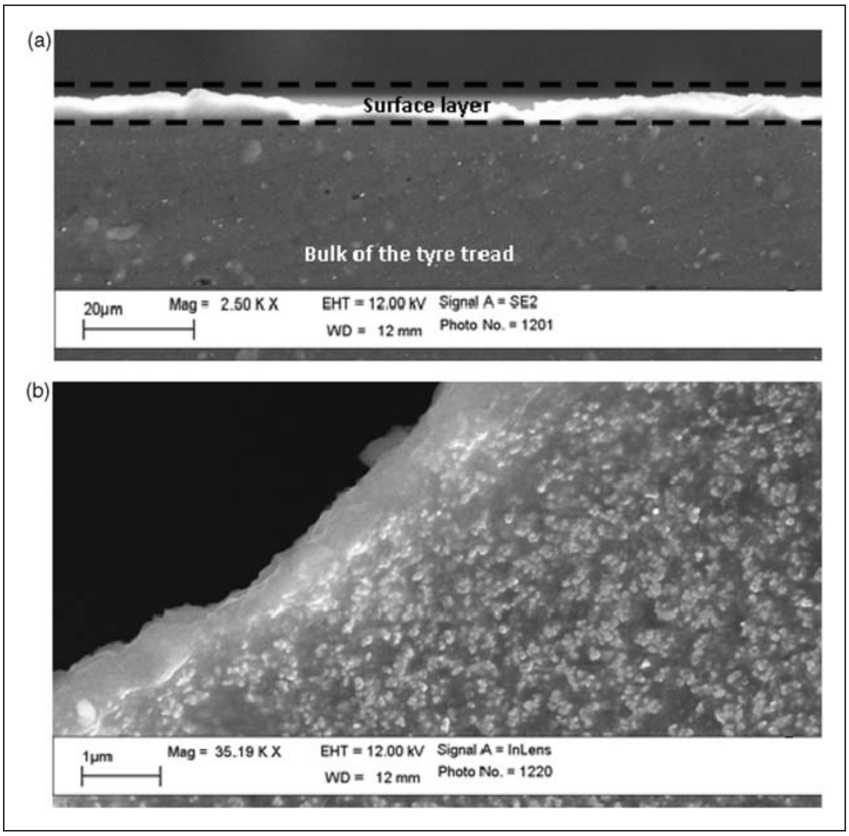

Figure 1. SEM analysis of the tread of a car tyre: (a) at low magnification, (b) at a higher magnification.

that the rubber reacts chemically with the environment and is undergoing an oxidation process during sliding. These findings using SEM and EDS show the existence of a modified surface layer in the tread of a car tyre.

Controlled tribo-generation of surface layers

To study the mechanisms behind the development of the observed surface modification on elastomeric materials in a more reproducible and controlled manner, EPDM disks (DSM Elastomers, the Netherlands, Keltan® 8340A with 5.5 wt% ENB, 55 wt% ethylene and 39.8 wt% propylene contents, see Table 1) were tribologically loaded under controlled and reproducible conditions. This type of EPDM has a high homogeneity and consistency of properties, enabling repeatable material properties during the experiments.

The EPDM was moulded and vulcanised in the shape of discs with a diameter of 59 mm and a thickness of 10 mm. The generation of modified surfaces on these EPDM samples was done by applying a tribological load using a pin-on-disc tribometer, with a 100Cr6 steel ball with a diameter of 25 mm as the pin, under a controlled environment at a temperature of 23°C and a relative humidity of 60%. The applied load of 2 N and a sliding velocity of 0.2 m/s are chosen to result in a contact pressure and sliding velocity that are of the same order of magnitude as in an automotive tyre. After a sliding distance of 500 meters a clear track is seen on the disks, as schematically illustrated in Figure 2(a).

Subsequently, these EPDM disks were analysed using SEM and EDS following the same procedure as used to analyse the tread of the car tyre. As shown in Figure 2(b), a change in the structure of the material can be observed that is similar to that found in the car tyre: in the bulk clusters of particles are visible and towards the surface these particles are more closely packed until no individual particles can be distinguished anymore. The depth of the modification into the surface is approximately 4 μm. The EDS analysis showed a slight increase in the amount of oxygen in the modified surface, agreeing with the results as found for the used car tyre. The analysis of both the car tyre tread and the EPDM disks confirm that the surfaces have modified properties after having been tribologically loaded.

Mechanical properties of the tribo-generated of surfaces

To study the mechanical properties of the tribo-generated surfaces and to compare them to the original, unmodified surface, micro-indentation measurements and friction measurements were done.

Indentation tests

To analyse the mechanical properties of both surfaces, indentation experiments were performed using a Shimadzu Micro Hardness Tester. It is known that a high surface roughness of the test specimens will result in a large variation of the measured load-indentation curves. Thus, for surfaces with thin layers, selecting the appropriate measurement conditions to determine the mechanical properties is a balance between reducing the effects of the surface roughness on the measured result and being able to accurately determine the mechanical properties of the single layer or of the layer-substrate combination. To minimise effects of roughness, Fisher-Cripps[25] recommends to perform indentations at a depth of at least twenty times the surface roughness: $\delta > 20\,R_a$. The roughness of the tribo-generated surface was measured using a Keyence Color 3D Laser Confocal Microscope using a cut-off length of 120 μm, i.e. the same as the contact size. The measured surface roughness R_a equals 0.19 μm, indicating that the indentation depth should be at least 3.8 μm. This minimum recommended indentation depth is of the same order of magnitude as the thickness of the observed layer, meaning that the obtained load-indentation curves will represent the mechanical properties of the combination of layer and substrate. To obtain the material properties of only the surface layer the maximum indentation depth should be less than approximately 10% of the thickness of the layer. As seen in Figure 2, the thickness of the tribo-generated surface layer is 4 μm, hence the maximum depth indentation should be around 0.4 μm. Due to the roughness of the surface, at these indentation depths the uncertainty of the indentation results would be very high.

Tweedie and Van Vliet[26] studied the nano-indentation of viscoelastic materials and concluded that linear viscoelastic theory cannot be used to interpret the results of indentation experiments performed with sharp indenters. For spherical indenters with a sufficiently large radius, the maximum contact pressure is

Table 1. Recipe of the used EPDM.

	Keltan 8340A	Stearic acid	FEF N550	Sunpar 2280	TMQ	PEG 2000	Perkadox 14/40	TRIM 50
Phr	100	1	105	60	1.25	2.5	7.5	4

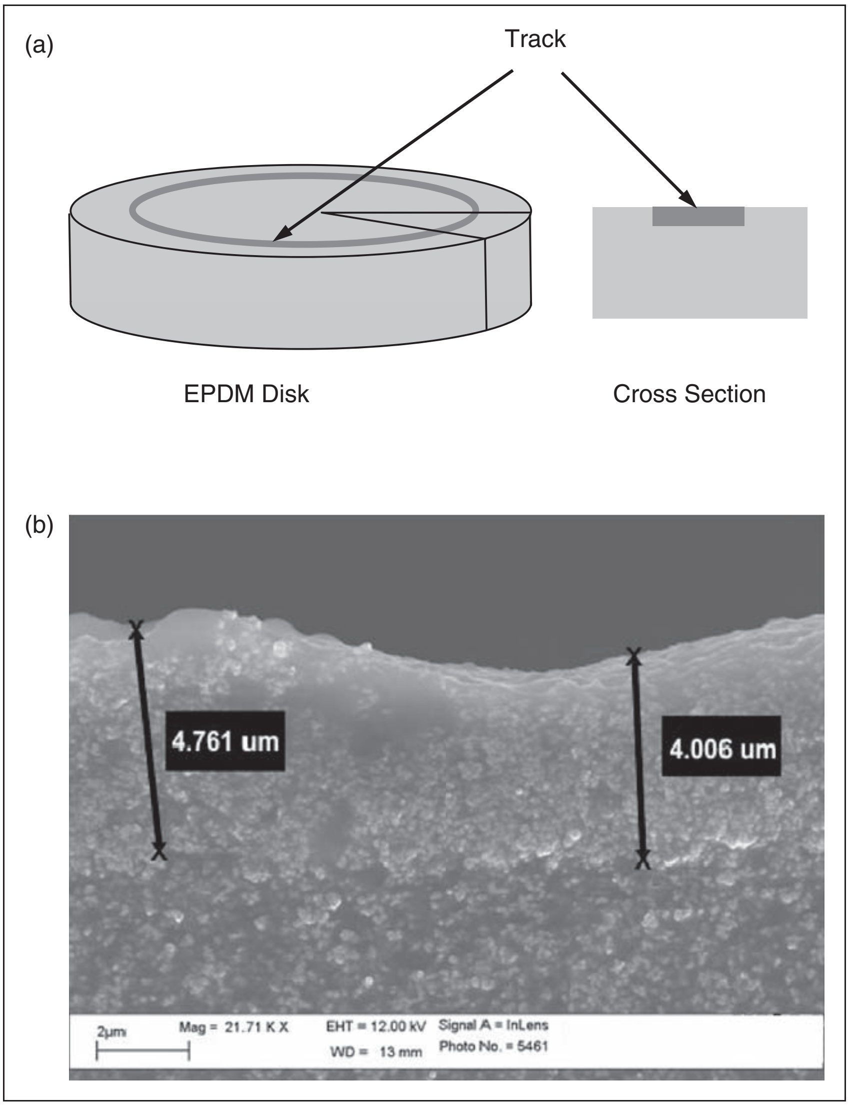

Figure 2. Cross-section of the surface of the EPDM track: (a) schematic illustration of the modified surface on the EPDM disc, (b) SEM analysis of the cross section of the EPDM disc.

lower than the elastic strain limit, enabling the use of linear viscoelastic theory to describe indentation. In Figure 3 the resulting load-displacement curves obtained using a spherical indenter with a diameter of 2 mm, at three different loads are shown for the original (unmodified) surface in black and for the tribo-generated surface in grey. Each curve represents the average of three measurements and is composed of a loading phase, a 500 ms holding-load phase and an unloading phase. To minimise the energy dissipation through viscous response of the elastomer, the maximum loading rate allowed by the instrument was used.[26] It can be seen that the measurements obtained on the surface layer show a significantly higher indentation depth than those on the original surface, meaning that the surface layer has a lower stiffness.

Oliver and Pharr[27] showed that an estimate of the Young modulus can be obtained from the slope of the unloading curve. In Figure 4, these are indicated by the segmented lines. For the original surface, each unloading curve gives a similar slope. For the surface layer this same slope is obtained only at the highest normal load, whilst at lower normal loads the unloading curve has a lower slope. From this it can be concluded that the observed surface layer has different material properties than the bulk.

Visco-elastic properties

The creep compliance of the surfaces can be calculated using the measured load-indentation data. From the measured change in the indentation depth during the 500 ms holding time, h(t), Ting's[28] solution for the contact between a viscoelastic half space and a rigid indenter and the relation between indentation and creep of Tweedie,[26] the creep compliance in shear under spherical indentation is given by

$$\phi(t) = \frac{8\sqrt{R}}{3F_N}[h(t)]^{3/2} \tag{1}$$

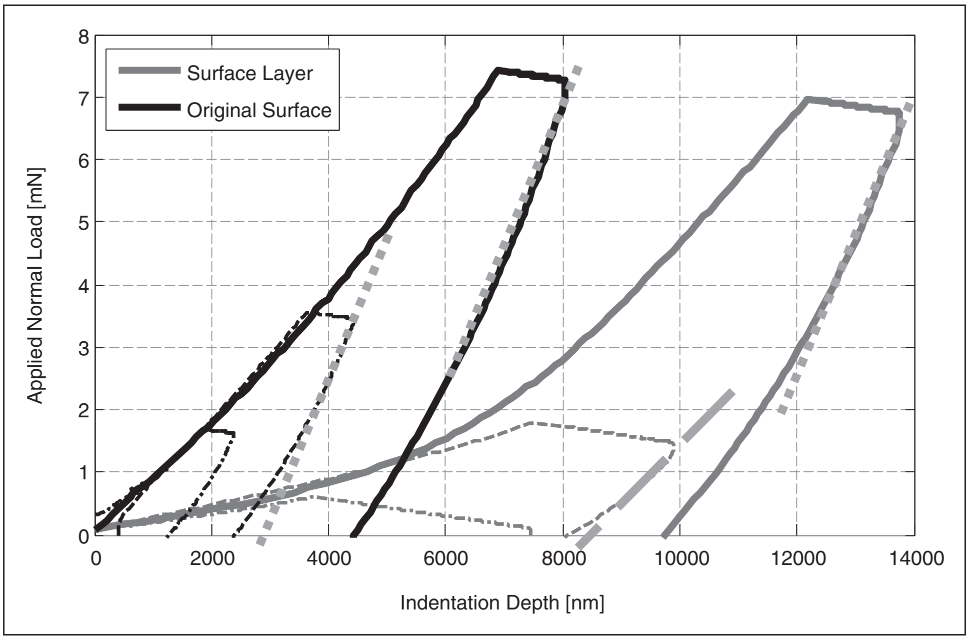

Figure 3. Load-indentation curves inside and outside of the track. The dotted line represents the slope of the unloading curve.

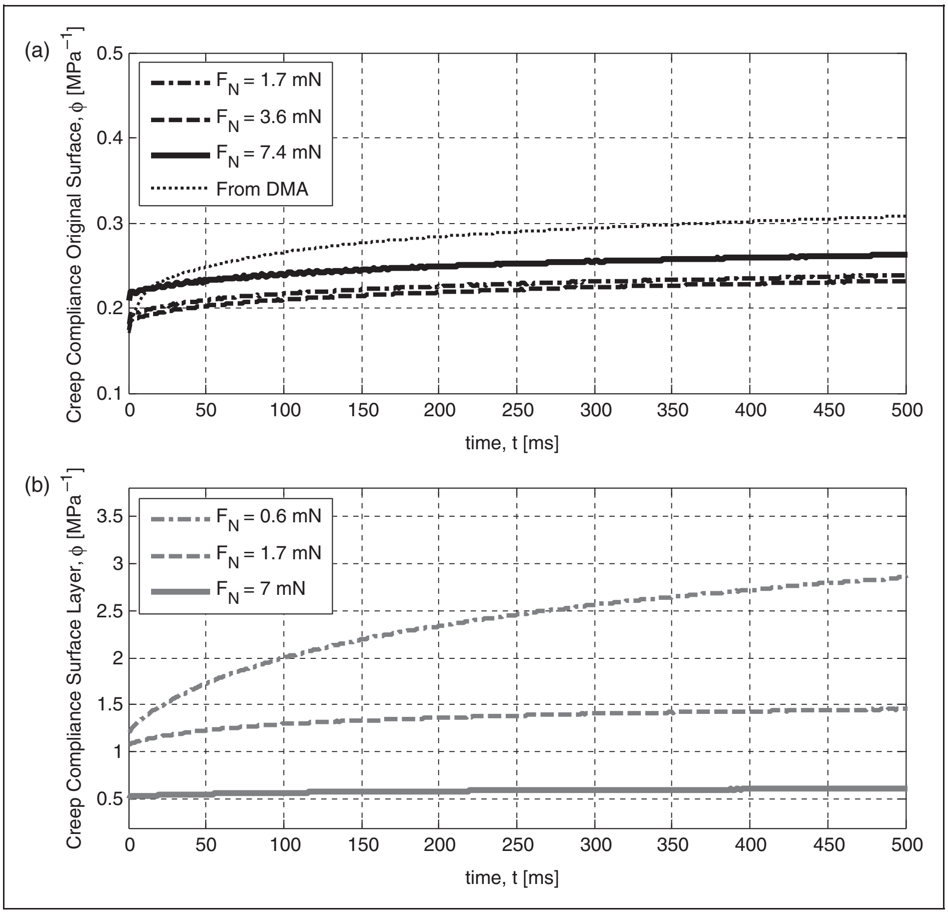

Figure 4. Creep compliance at different normal loads: (a) original surface, (b) tribo-generated surface layer.

The resulting creep compliances at the different indentation depths are shown in Figure 4(a) and (b) for the original surface and the tribo-generated surface respectively. The various creep compliances obtained for the original surface are also compared with the creep compliance for the bulk material, as determined using DMA measurements. In Figure 4(a) it can be seen that the creep functions obtained by indenting the original surface at different loads are rather similar. There is a small difference between the curves obtained at different loads, but this variation falls within the range usually observed for mechanical measurements on elastomers. In Figure 4(b) the creep compliance functions obtained from the indentations on the tribo-generated surface are shown. It can be seen that at low normal loads the creep compliance is much larger than at high loads. This shows that the surface layer has rather poor material properties in comparison with the bulk.

In order to quantify the differences between the properties of the EPDM bulk and the properties of the surface layer, the creep compliance function obtained for the indentations at the lowest load of 0.6 mN was fitted using a series of exponential terms, similar to Prony series in a stress relaxation measurement. The results are given in Table 2. The relaxed creep compliance, Φ_r, of the tribo-generated surface layer is three orders of magnitude higher than that of the original surface, and its visco-elastic behaviour is much slower.

From these results it can be concluded that the material properties of the surface layer are significantly reduced in comparison with the properties of the original EPDM surface and bulk.

Table 2. Compliance coefficients and retardation times of the EPDM Bulk and of the tribo-generated surface layer.

	Bulk EPDM		Surface layer	
i	Φ_i (MPa^{-1})	τ_i (s)	Φ_i (MPa^{-1})	τ_i (s)
Φ_r	3.49E-01		6.40E + 02	
1	4.69E-02	0.0064	1.82E-01	0.0073
2	4.90E-02	0.0713	9.16E-01	0.108
3	8.23E-02	0.7284	6.34E + 02	499.7

Friction

The differences in tribological performance between the original material and the samples with a tribo-generated surface layer are studied in more detail at low loads; executing the experiments at lower loads and lower indentation depths ensures that the sliding contact will be more influenced by the tribo-generated surface layer and less by the bulk. Employing a nano-tribometer (CSM Instruments, Switzerland) allows this. The contact geometry was a ball on flat configuration using a 100Cr6 steel ball with a diameter of 2 mm, a sliding velocity of 10 μm/s, a reciprocating amplitude of 640 μm and a normal load of 2 mN. At this load the indentation of the ball into the EPDM will be several micrometres and hence the friction will be influenced by the properties of both the surface layer and the bulk material.

Results of these friction experiments are shown in Figure 5; the black line corresponds to friction experiments performed on the original surface and the grey line corresponds to friction experiments performed on the tribo-generated surface layer.

The coefficient of friction measured on the original surface is $\mu = 6.0 \pm 0.4$ and on the tribo-generated surface layer $\mu = 1.7 \pm 0.6$. These expressed coefficients of friction are the average of five repeated measurements and for each measurement the friction was calculated as the average value measured in the final three reciprocating cycles. The coefficient of friction obtained on the tribo-generated surface layer is much lower than the coefficient of friction obtained on the original surface, meaning that the tribo-generated

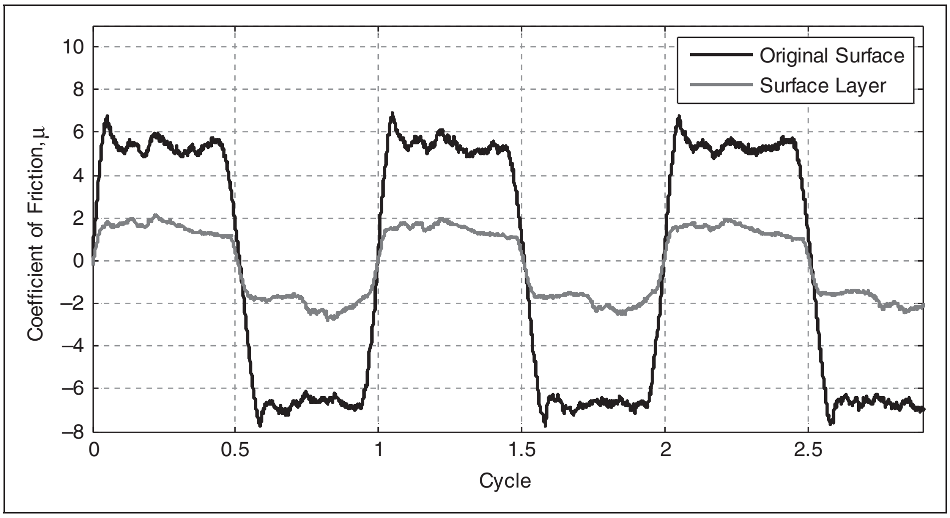

Figure 5. Nano-tribometer experiments. Measured coefficient of friction for the original surface, black line, and the tribo-generated surface layer, grey line, as a function of the number of cycles.

surface layer has a substantial influence on the friction behaviour of the EPDM material.

Discussion

Quantitative differences were found between the properties of the tribo-generated surface layer and the original surface. The measured material properties and the coefficient of friction on the tribo-generated surface layer are significantly lower than those measured on the original EPDM surface.

Friction is commonly modelled as the superposition of a deformation component and an interfacial adhesion component. For visco-elastic contacts it is not uncommon that the adhesion component dominates the friction behaviour and, particularly for elastomeric materials, depending on the contact conditions, sometimes the deformation component may even be ignored. An expression for the deformation component to the coefficient of friction was given by Greenwood and Tabor[29]

$$\mu_{def} = 0.17 \cdot \beta \cdot \left(R^2 \cdot E^*\right)^{-\frac{1}{3}} \cdot F_N^{\frac{1}{3}} \qquad (2)$$

in which β represents the visco-elastic loss fraction and E^* the equivalent Young's modulus or contact modulus. An upper estimate of the deformation component of the coefficient of friction for the nanotribology experiments ($R = 1$ mm, $F_N = 2$ mN) is obtained by taking $\beta = 1$. Inserting these parameters in equation (2) shows that for practically relevant values of E^*, μ_{def} does not exceed 0.1, whilst the total measured coefficient of friction is 1.7 for the tribo-generated layer and even higher for the original surface. This indicates that in the current situation, the friction behaviour is dominated by the adhesion component. Bowden and Tabor[30] expressed the friction due to adhesion as the product of the real contact area A and the shear strength in the interface τ. Because the contact area is inversely proportional to the Young's modulus to the power $^2/_3$, the coefficient of friction due to adhesion follows the shear strength and Young's modulus according to

$$\mu_{adhesion} \sim \tau \cdot E^{-\frac{2}{3}} \qquad (2)$$

This proportionality means that, for a constant shear strength in the interface, a decrease of the elastic modulus would result in an increase of the coefficient of friction. In contrast, the obtained experimental results show that the coefficient of friction in the tribo-generated surface layer is lower than in the original surface, even though the tribo-generated surface has a reduced stiffness. This reduced friction can be caused by a reduced shear strength of the tribo-generated surface layer, meaning that its functioning could be compared to a "solid lubricant".

Figure 6 shows a tribo-modified surface layer that was created at an increased sliding velocity of 0.4 m/s. The layer on this EPDM disk has a thickness of almost 9 µm, compared to the layer thickness in Figure 2 of 4 µm, that was obtained at a sliding velocity of 0.2 m/s; both sliding experiments were performed at an applied load of 2 N. This indicates that the development of the layer is affected by the conditions in the contact, therefore it could be hypothesized that the development of the tribo-modified surface layer is energy driven, similar to the development of surface layers in metallic materials.

Concluding, the tribologically modified surface shows a considerable decrease in mechanical properties that strongly affect the frictional behaviour of the tribo-system in which the elastomer operates.

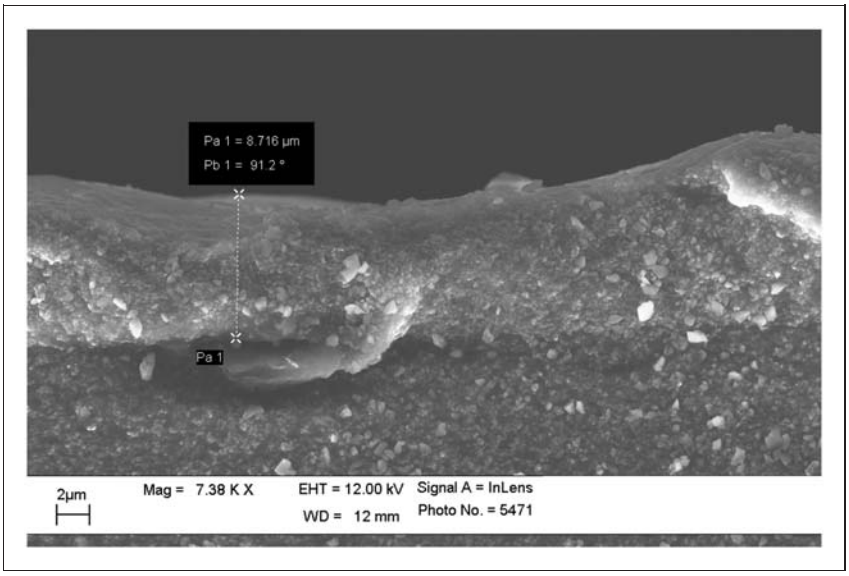

Figure 6. Cross-section of the surface of the EPDM track, generated at an sliding velocity of 0.4 m/s.

Therefore, the existence of interfacial layers should be taken into account when analysing friction with elastomers.

Funding

This research received grant from the Dutch Polymer Institute (DPI).

Acknowledgements

This work is part of the Research Programme of the Dutch Polymer Institute DPI, the Netherlands, Project nr. #664. The authors are grateful to Mr C. Hintze from the Leibniz Institut für Polymerforschung for providing EPDM disks and tensile test data and to Mr M. Smithers from the MESA + Institute for Nanotechnology, for the SEM analysis and fruitful discussions.

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