Design of dual hydrophobic–hydrophilic polymer networks for highly lubricious polyether-urethane coatings

Citation for published version (APA):

Albers, P. T. M., Govers, S. P. W., Laven, J., van der Ven, L. G. J., van Benthem, R. A. T. M., de With, G., & Esteves, A. C. C. (2019). Design of dual hydrophobic–hydrophilic polymer networks for highly lubricious polyether-urethane coatings. *European Polymer Journal*, 111, 82-94.
<https://doi.org/10.1016/j.eurpolymj.2018.12.004>

Document license:
TAVERNE

DOI:
[10.1016/j.eurpolymj.2018.12.004](https://doi.org/10.1016/j.eurpolymj.2018.12.004)

Document status and date:
Published: 01/02/2019

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Design of dual hydrophobic–hydrophilic polymer networks for highly lubricious polyether-urethane coatings

Peter T.M. Albers^{a,d}, Stefan P.W. Govers^a, Jozua Laven^{a,b}, Leendert G.J. van der Ven^a,
Rolf A.T.M. van Benthem^{a,c}, Gijsbertus de With^{a,b,*}, A. Catarina C. Esteves^{a,*}

^a Laboratory of Physical Chemistry, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, the Netherlands

^b Laboratory of Materials and Interface Chemistry, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, the Netherlands

^c DSM Materials Science Center, Netherlands, P.O. Box 18, 6160 MD Geleen, the Netherlands

^d Dutch Polymer Institute (DPI), P. O. Box 902, 5600AX Eindhoven, the Netherlands

ARTICLE INFO

Keywords:

Lubricious polymer coating
Aqueous lubrication
Hydrophilic coating
Polymer friction
Dual hydrophobic/hydrophilic

ABSTRACT

Bio-lubricated surfaces found in nature have inspired the design of low friction polymer coatings for biomedical applications. This work presents a systematic study of the relation between the network structure parameters and the macroscopic friction properties of highly lubricious dual hydrophobic/hydrophilic polyurethane (PU) coatings in an aqueous environment. Chemically cross-linked PU coatings were prepared by adding poly(ethylene glycol) mono-methyl ether (mPEG) as hydrophilic dangling chains, or poly(ethylene glycol) (PEG)-diol as hydrophilic elastically active network chains, to poly(propylene glycol) (PPG)-PU coating formulations. The friction behaviour of the water swollen coatings was measured using a custom-made water immersed tribology setup. Addition of the PEG segments or mPEG dangling chains to hydrophobic PPG coatings greatly enhances the lubricious properties of the coatings. These dual hydrophobic/hydrophilic diol PU network exhibit a surface with a lower coefficient of friction compared to reference coatings from either individual precursors, demonstrating a large synergistic effect between the hydrophobic PPG and the hydrophilic PEG in the coatings. Based on network structure and surface chain considerations it is hypothesized that the existence of a thin and softer hydrated surface layer on top of a less hydrated, more rigid, coating bulk layer gives rise to the observed enhanced lubricious properties, hereby mimicking to some extent bio-lubricated systems, such as cartilage.

1. Introduction

Hydrophilic low friction non-fouling surfaces are of great importance for bio-medical devices in dynamic contact with the human body, to reduce tissue damage and bacterial infections [1–3]. When the material of the device does not meet the required low friction specifications in an aqueous environment, a lubricious polymer coating layer can be applied to achieve the desired surface properties [1,4,5].

A common approach for designing lubricious polymer top-layers is to make use of polymer brushes [6–10]. The inspiration for using surface brushes for lubrication in an aqueous environment originates from bio-lubricated systems found in nature [6,10–12]. It is known that polymer chains on the surface of articular cartilage play an important role on its mechanical and lubrication properties [13–16]. The friction and lubrication mechanisms of cartilage do not solely depend on polymer chains on the surface but on a complex combination of

different lubrication processes, which is not yet completely understood [10,11,14]. Greene et al. revealed that the hyaluronic acid/lubricin (HA-LUB) top layer on porcine cartilage have a highly complex physically cross-linked network structure which ensures the lubrication of the cartilage by the continuous presence of a fluid layer, maintained via different lubrication mechanisms which relate to the total load and shear velocity applied [14]. At high pressures, the HA chains become physically “anchored” to the surface resembling a tethered surface brush which maintains a thin interfacial fluid layer. Therefore it is believed that the capacity of polymer chains to retain a highly hydrated layer on top of a more rigid, less hydrated bulk structure seems to be a crucial part of biological lubrication mechanisms [6,10,17].

The tribological properties of polymer brushes densely grafted on solid surfaces have been extensively investigated, namely by Benetti et al. [18–22], and it has been demonstrated that the topological features of the chains play a major role on their lubricating properties, e.g.

* Corresponding authors at: Laboratory of Physical Chemistry, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, the Netherlands (A.C.C. Esteves).

E-mail addresses: g.dewith@tue.nl (G. de With), a.c.c.esteves@tue.nl (A.C.C. Esteves).

<https://doi.org/10.1016/j.eurpolymj.2018.12.004>

Received 21 September 2018; Received in revised form 28 November 2018; Accepted 2 December 2018

Available online 03 December 2018

0014-3057/ © 2018 Elsevier Ltd. All rights reserved.

loops and cyclic polymer brushes show enhanced lubricious properties in comparison to linear polymer chains [23–26]. One of the concerns with the use of surface polymer brushes for lubricating properties has been their low mechanical stability, in particular weak resistance to wear. For polymer brushes grafted from surfaces, significant efforts have been made to improve their stability against degrafting by hydrolysis, in water and salt solutions [27–30]. Furthermore, the clever design of “brush-gel” grafted layers, by introducing covalent cross-linking in between the polymer brushes is another way of improving their mechanical resistance. Such crosslinked brush-gel systems show tunable (higher) moduli but also generally higher coefficient of friction due to the additional constraints given by the surface tethering of the chain ends and intermolecular crosslinking [31,32].

One other alternative is to use fully crosslinked hydrogel-like polymer networks which have proven to effectively reduce the friction forces between the top layer and counter surface in an aqueous environment [5,33–38]. A reduction of the frictional forces at the surface of hydrogels scales with an increase in mesh size of the network, giving rise to a higher water content and lower network moduli [39–41]. Hence, the increase of the lubricating properties of hydrogel-like coatings typically goes at the expense of the mechanical integrity of these polymeric systems.

Looking at the general engineering features of the biological lubricious surfaces described above, a highly simplified interpretation of the system is the picture of a dual-layer structure comprising a rigid bulk material with a moderate level of hydration combined with a highly hydrated soft surface layer. Such a dual-structure combination can be used to design a new type of lubricious polymer coatings consisting of a hydrophobic polymer network containing hydrophilic polymer segments (chains or loops) at the surface. The dual hydrophilic/hydrophobic polymer network segments provide for the required high lubricity and improved mechanical (bulk) properties, respectively.

In this work the effect of the presence of hydrophilic poly(ethylene glycol) (PEG) segments in chemically cross-linked hydrophobic poly(propylene glycol) (PPG) polyurethane (PU) coatings on the resulting lubricious properties of the coatings in an aqueous environment is investigated. For this purpose, hydroxyl-terminated polyethers and a triisocyanate cross-linker were selected as network precursors. The hydrophilic PEG precursors were added to the coating formulations as hydrophilic dangling chains (PEG mono-methyl ether (mPEG)) as well as elastically active network chains (PEG-diol precursors) (see Fig. 1). The molar mass and concentration of the hydrophilic precursors in the PPG coatings were varied and two different PPG network precursor molar masses (1000 and 2000 g·mol⁻¹) were used. The dual hydrophobic/hydrophilic PU coatings were characterized in terms of water uptake, surface hydrophilicity, effective indentation modulus and macroscopic aqueous friction behaviour against a glass counter surface. The influence of variations in the network structure parameters on these coating properties is presented. Moreover the difference between the incorporation of hydrophilic network segments as a dangling chain or as an elastically active network chain is evaluated.

2. Materials and methods

Poly(ethylene glycol) (PEG) with different molar masses ($M_n = 1000, 2000, 4000$ and 6000 g·mol⁻¹) and poly(ethylene glycol) mono-methyl ether (mPEG) ($M_n = 1000$ and 2000 g·mol⁻¹) (Sigma Aldrich) (all PDI < 1.06 (SEC)) were dried before use, at room temperature in a desiccator with P₂O₅ as desiccant for at least 72 h. Poly(propylene glycol) (PPG) ($M_n = 1000$ and 2000 g·mol⁻¹), PEG ($M_n = 400$ g·mol⁻¹) and mPEG ($M_n = 750$ g·mol⁻¹) (Sigma Aldrich) (all PDI < 1.04 (SEC)) were stored in a moisture free desiccator before use. Trimerized hexamethylenediisocyanate (tHDI) (equivalent functional weight of 183 g·mol⁻¹ NCO (manufacturer value)) was kindly provided by Perstorp as tolonate HDT-LV2, stored under an inert atmosphere and used as received. Cyclohexanone (99.8%) (Sigma

Fig. 1. Overview of selected network precursors for the preparation of the dual hydrophobic PPG – hydrophilic PEG PU coatings and schematic of the coating network structures.

Aldrich) was dried with molecular sieves before use. Dibutyltin dilaurate (95%) (DBTDL) and (3-aminopropyl)triethoxysilane (> 98%) (APTES) were purchased from Sigma Aldrich and used as received.

2.1. Coatings preparation: Substrate and primer

The coating preparation procedure was optimized to yield PPG coatings with sufficient adhesion to a glass substrate when immersed in water. Contact of oxygen with the network precursors was minimized as much as possible to prevent possible degradation of the polymers during network preparation. The vials were thoroughly flushed with argon every time they were opened and before closure. Moreover, the lid was wrapped with parafilm tape after closure. All glassware was dried in an oven at 100 °C for at least 14 h prior to use. The coatings were applied on substrates (soda-lime glass, extra low iron content), (49 × 49 × 1 mm³) containing a primer layer. Primer precursor stock solutions (typically 10 ml) of PEG 6000 g·mol⁻¹ (10 wt%) and of tHDI (50 wt%) were made by dissolving PEG and tHDI in cyclohexanone at 55 °C and room temperature, respectively. This was done in closed glass vials under an argon blanket and continuous stirring. The primer formulation solutions (typically 10 ml) were prepared in a glass vial by mixing the primer precursor stock solutions at 55 °C under an argon blanket after which APTES was added in a NCO:OH:NH₂ molar ratio of 1.3:1:0.3 and stirred for 1 h before application. The glass substrates were pre-cleaned by several steps: rubbed with a tissue soaked with ethanol, dried in an oven at 100 °C for at least 14 h, and were given a UV-ozone treatment (Novascan PSD-UVT) for 10 min and heated afterwards at 65 °C.

The primer solution (0.4 ml) was then spin coated (Laurell WS-650SX-6NPP/LITE) for 15 s at 1000 rpm. The coated substrates were positioned on top of a preheated (65 °C) heating element placed in a chamber (with a volume of approximately 1.5 dm³), which after closure was continuously flushed with dry N₂ (± 150 l·h⁻¹ at 1 bar). The primers were formed by a solvent evaporation step of 90 min at 65 °C, to remove both the solvent as well as the oxygen present, followed by a final cure step of 14 h at 150 °C under a dry N₂ flow (± 150 l·h⁻¹ at 1 bar). The cured primers were immersed in demineralized water for at least 14 h to remove any extractable components. The extracted primers

were allowed to dry at ambient conditions and were further dried at 20 mbar at 40 °C for at least 2 h before the top-coats were applied.

Before the top-coat coating application, the extracted and dried primed substrates received a UV-ozone treatment (Novascan PSD-UVT) for 12 s and were positioned on top of a preheated (65 °C) heating element placed in chamber (with a volume of approximately 1.5 dm³) continuously flushed with dry N₂ (± 150 l h⁻¹ at 1 bar).

2.2. Coatings preparations: Dual top-coats

For the top coats, stock solutions (typically 10 ml) of PPG or (PPG/(m)PEG) (10 wt%) and of tHDI (25 wt%) in cyclohexanone were made at room temperature. This was done in closed glass vials under an argon blanket and continuous stirring. The weight ratios of the selected PPG and mPEG precursors in each stock solution were chosen in such a way to that prescribed molar OH_{mPEG}:NCO ratios, i.e. 1:9 or 1:30 for all PPG/mPEG PU coatings, were obtained in order to be comparable. Stock solutions of PPG and PEG precursors were made based on the mass ratio between the hydrophobic PPG and the hydrophilic PEG diol-precursors. Coating formulation solutions (typically 5 ml) were prepared in a glass vial by mixing the network precursor stock solutions at room temperature under an argon blanket. The NCO:OH molar ratio of each formulation was kept at 1.1 to ensure full conversion of the OH-groups. Just before application the coating solutions were heated to 65 °C and were mixed with a 10 mg·ml⁻¹ DBTDL solution in cyclohexanone (approximately 0.2 wt% DBTDL, with respect to the weight of the coating precursors). The mixtures were then applied over the pre-treated primer, as described above.

Per coating, approximately 0.5 ml of the coating formulation was drop casted with a pipet on the primed substrate in one continuous motion. After closure of the chamber, the coating was formed by a solvent evaporation step of 90 min at 65 °C, to remove both the solvent and the oxygen present, followed by a final cure step of 12 h at 125 °C under a dry N₂ flow (± 150 l h⁻¹ at 1 bar). The cured coating was immersed in demineralized water for at least 14 h to remove any extractable components. The extracted coating was allowed to dry under ambient conditions and further dried at 20 mbar at 40 °C for at least 2 h and stored in a moisture free desiccator. From here onwards, reference PPG-diol based PU coatings will be named PPG (X), PPG coatings containing mPEG dangling chains are named PPG(X)-mPEG(Y) (OH_{mPEG}:NCO), whereas the dual PPG-PEG-diol PU coatings are named PPG(X)-PEG(Z), where X = M_n of used PPG, Y = M_n of used mPEG and Z = M_n of used PEG (*hydrophilic fraction of the diol precursors*).

2.3. Coatings characterization

Fourier transform infrared spectroscopy (FTIR) spectra of cured networks were recorded in attenuated total reflection (ATR) mode using a Varian 670-IR equipped with a diamond Specac Golden Gate ATR stage. Given the large overlap of the C=O urethane stretch vibration (1720 cm⁻¹) and the isocyanurate C=O stretch vibration (1675 cm⁻¹) present in the networks, and moreover the C–N urethane stretch vibration band (1550 cm⁻¹) being located at the fingerprint region, a reliable quantitative analysis of NCO to urethane conversion from the IR absorbance spectra is impracticable. Therefore, only the disappearance of the N=C=O asymmetric stretch vibration at 2270 cm⁻¹ was used to analyze the NCO conversion of the cured networks at the surface. A Bruker Veeco Dektak 150 profilometer was used to measure the dry thickness of the coatings. A scratch was made to completely remove a small part of the coating, after which the height profile across the interface of the exposed substrate and the coating was measured at four random locations per coating. All the PPG coatings had an average dry film thickness of ≈ 20 μm, unless stated otherwise.

The hydrophilicity of the coatings was evaluated by static captive air bubble contact angle CA_{air} measurements in water using a Data Physics OCA 30 goniometer. A coating, swollen to equilibrium for at

least 14 h, was placed upside-down in a glass container filled with demineralized water. An air bubble with a volume of approximately 4 μl was placed on the coating surface after which the static air contact angle was measured. The static CA_{air} was measured at five different locations per sample.

The weights of the substrates, the primers and the coating were measured gravimetrically before and after each application, curing and extraction step. The amount of extractable material *L* is calculated via $L = ((m_i - m_0)/m_i) \cdot 100\%$, where *m_i* and *m₀* are the initial weights of a network after curing and of an extracted dry coating, respectively. Every extracted coating was immersed in demineralized water again to swell to equilibrium for at least 14 h. The swollen weight of the coating *m_{eq}* was measured gravimetrically directly after the coating was taken out of the water and after gentle removal of all excess water with absorbing lint free paper. The absolute water uptake is given by the ratio of the equilibrium swollen weight of the coating and the dry coating as $\text{water uptake} = (m_{eq}/m_0) \cdot 100\%$. The coating properties of the dual PPG-(m)PEG PU coatings are analyzed with respect to the fraction (*φ_{PEG}*) of hydrophilic diol precursor in the coating. This fraction is given by $\varphi_{PEG} = (m_{PEG})/(m_{PEG} + m_{PPG})$, where *m_{PEG}* is the mass of the (m)PEG-precursor and *m_{PPG}* the mass of the PPG-diol in the coating formulation solution.

Nano-indentation measurements on completely immersed swollen coatings were performed using an optical interferometer-based Piuma Nanoindenter (Optics11 B.V. (NL)). Two different probes (Optics11 B.V.) were used throughout the measurements of the whole dataset. The probes were equipped with a spherical glass tip (with a radius of 19.0 and 19.5 μm, respectively) connected to a cantilever (with a stiffness of 17.3 and 18.9 N·m⁻¹, respectively). Every coating, swollen to equilibrium for at least 14 h, was immersed in a petri dish filled with demineralized water after which the indentation modulus was measured at five random locations. Generally, each indentation was done by a piezoelectrically controlled downward movement of the indenter head of 18.6 μm at a velocity of 1.86 μm·s⁻¹. The probe was held at the maximum depth for 5 s after which it was withdrawn within 1 to 2 s. The load–displacement curve of each indentation was recorded and the effective indentation modulus *E** was calculated using standard Hertzian contact mechanics for a rigid indenter and an elastic half space [42,43] as given by

$$a^3 = \frac{3}{4} \frac{PR}{E^*} \text{ and } \delta = \frac{a^2}{R}, \quad (1)$$

where *a* is the radius of the circle of contact, *P* is the applied load, *R* is the radius of the indenter and *δ* is the indentation depth. The value of *E** is calculated at 5% of the total load to ensure an indentation depth to film thickness ratio *δ/h* < 0.1, preferably < 0.05, in order to minimize the effect of the modulus of the substrate on the measured coating response [44].

An AR-1000N Rheometer (TA Instruments) was adapted to use as a tribology setup for the measurement of the macroscopic friction response of the coatings immersed in water. See [Supporting Information \(SI-1\)](#) for an overview of the used equipment. The custom-made indenter head contains three spherical optical grade N-BK7 glass lenses (Borosilicate Crown glass), with a large radius of curvature (*R* = 0.25 m) and a diameter of 0.025 m, mounted with the centers of the lenses located in a triangular arrangement, at 0.0145 m out of the center of the indenter head. This shallow curvature is chosen to ensure a large contact area between the indenters and the coating (in the order of mm² per lens), thereby minimizing the contact pressure (in the order of 50–150 kPa) and ensuring a close-to-homogeneous stress distribution in the deformed coatings. The indenter head is mounted to the rotating shaft of the rheometer via a single, specially designed leaf spring for making each of the lenses carefully follow the surface of the coating with equal contact forces, while assuring that the center of the triangular lens arrangement is kept at the shaft axis. A cup which can contain the measurement medium (demineralized water) and the immersed

coating was mounted on the bottom plate of the rheometer. The tribometer can be operated in a velocity window between 10^{-3} to $70 \text{ rad}\cdot\text{s}^{-1}$ and up to a normal load of 20 N, with a bandwidth of 0.1 N around the set-point at a constant longitudinal position of the rotating shaft. Forces are recorded with a normal force resolution of 0.0057 N and a torque resolution of 0.01 $\mu\text{N}\cdot\text{m}$. All series of measurements were performed in demineralized water at approximately 20°C . Coatings, swollen to equilibrium for at least 14 h, were immersed and equilibrated in the setup at a normal load of 0.5 N for 30 min prior to the measurements. Each measurement was divided stepwise into different constant velocity segments (ranging from 10^{-3} to $30 \text{ rad}\cdot\text{s}^{-1}$). Depending on the rotation speed in a velocity segment test, a full circular path at the sample surface was probed either once (at very low speeds) or more often (at high speeds) (see also [Supporting Information SI-2](#)). A stationary equilibration time of 1 min was allowed between each velocity step. The absolute applied normal load and measured torque were averaged over the total segment time, with the first 30 s excluded. From the resulting average torque T_ω and normal load F_N , the Coefficient of Friction (CoF) was calculated via

$$\text{CoF} = \frac{T_\omega/r}{F_N}, \quad (2)$$

where r is the distance between the center of the indenter head and the center of a lens ($r = 0.0145 \text{ m}$ in this study). A raw data example of a typical measured friction response is given in [SI-3](#).

3. Results and discussion

3.1. PPG films with hydrophilic mPEG dangling chains

3.1.1. Network properties of PPG-mPEG

To be able to compare the lubricious properties of the different coatings prepare, it is crucial to ensure a reproducible and reliable network formation. Several of the cross-linked coatings prepared were analyzed with IR spectroscopy which showed a complete absence of the vibrational NCO band at 2270 cm^{-1} of the tHDI crosslinker, indicating the complete consumption of the NCO groups initially added (see [Supporting Information \(SI\) SI-4](#) for typical spectra).

An overview of the amount of extractable material L , the water uptake, the effective indentation modulus E^* and the captive air bubble contact angle in water (CA_{air}) of all prepared coatings containing mPEG dangling chains is given in [Table 1](#). The values of L are all in a similar range and therefore all coatings are considered to be comparable. A few randomly selected coatings, after extraction in water, were also submitted to extraction in acetone, but no additional material leached out. The amounts of extractable material, both in water and in acetone, are

small enough to conclude that representative and reliable network structures are formed for the further studies.

The measured water uptake and CA_{air} of the coatings are plotted against the molar mass (M_n) of the added mPEG dangling chains in [Fig. 2a](#) and [b](#), respectively. The water uptake of the PPG reference coatings is approximately 8 wt%, which is as expected for coatings prepared with these hydrophobic precursors. Although for most of the prepared coatings the water uptake did not exceed 20 wt%, it increased up to 56 wt% for the coatings containing the highest concentration ($\text{OH}_{\text{mPEG}}:\text{NCO} = 1:9$) of the longest mPEG chains ($2000 \text{ g}\cdot\text{mol}^{-1}$). A clear, almost linear, relation is seen in [Fig. 2a](#) for the water uptake of the coatings with respect to the mPEG chain length for both the PPG1000 and the PPG2000 systems. Moreover, a higher concentration of mPEG in both PPG coatings gives rise to a higher water uptake. Overall, the addition of mPEG has a larger effect on the absolute water uptake of the PPG1000 coatings compared to the addition to the PPG2000. This is counter-intuitively attributed to the higher cross-link density of the former, as it results in a higher density of hydrophilic dangling chains in the network and eventually on the surface of the coating as well. [Fig. 2a](#) shows clear trend of rising water uptake with both increasing number and increasing length of the mPEG precursors.

The former trend is also reflected in a rising trend of the CA_{air} in [Fig. 2b](#). The effect of the mPEG chain length on the CA_{air} is, however, less pronounced, when compared with the effect on the water uptake. This may be attributed to the fact that PEG chains tend to adsorb at the air-water interfaces at the contact location, leading to only minimal variations of the contact angle around 140° (CA_{air}), as previously reported by Leermakers et al. [45]. Note that a higher air bubble contact angle (measured in water) corresponds to a lower water contact angle, $\text{CA}_{\text{water}} \approx 180^\circ - \text{CA}_{\text{air}}$.

The measured effective indentation moduli E^* of the top surface of the PPG1000 and the PPG2000 coatings are plotted against the M_n of the mPEG dangling chains in [Fig. 3](#). Generally, the addition of the mPEG to the PPG2000 coatings does not significantly influence the measured effective modulus, as seen in [Fig. 3b](#). This shows that the effective response of these coatings during the indentation experiments is similar, regardless of the presence, or length, of the mPEG chains in the coating.

The mPEG dangling chains do however influence the material response of the PPG1000 coatings ([Fig. 3a](#)). The effective moduli of all PPG1000-mPEG coatings with the lowest concentration of mPEG ($\text{OH}_{\text{mPEG}}:\text{NCO} = 1:30$) (open circles) are similar, and moreover approximately 30% lower compared to the reference PPG1000 coatings. The moduli of the PPG1000 with the higher concentration of mPEG ($\text{OH}_{\text{mPEG}}:\text{NCO} = 1:9$) (solid circles) are somewhat scattered. Since a small addition of mPEG ($\text{OH}_{\text{mPEG}}:\text{NCO} = 1:30$ ratio) apparently lowers

Table 1

Overview of amount of extractable material L , water uptake, effective indentation modulus E^* and captive air bubble contact angle in water CA_{air} of PPG coatings with and without mPEG. The number of samples per coating type is typically 4 (10 for PPG coatings without mPEG). Dry thickness of the coatings is typically $20 \mu\text{m}$. The error shows the mean absolute deviation from the mean value.

PPG [$\text{g}\cdot\text{mol}^{-1}$]	mPEG [$\text{g}\cdot\text{mol}^{-1}$]	$\text{OH}_{\text{mPEG}}:\text{NCO}$ [–]	L [%]	Water uptake [wt%]	E^* [MPa]	CA_{air} [°]
1000	no	–	1.2 ± 0.3	7.9 ± 0.8	10.4 ± 1.0	136 ± 2
1000	750	1:30	1.4 ± 0.1	10.2 ± 0.9	7.0 ± 0.2	$136 \pm < 0.5$
		1:9	1.7 ± 0.3	19.8 ± 1.4	4.8 ± 0.3	$143 \pm < 0.5$
1000	1000	1:30	1.1 ± 0.6	12.8 ± 1.4	7.0 ± 0.1	138 ± 1
		1:9	2.1 ± 0.3	27.5 ± 0.4	8.2 ± 0.4	$144 \pm < 0.5$
1000	2000	1:30	0.8 ± 0.3	20.3 ± 0.5	7.3 ± 0.1	$139 \pm < 0.5$
		1:9	4.3 ± 0.3	56.3 ± 0.4	4.3 ± 0.1	$144 \pm < 0.5$
2000	no	–	1.1 ± 0.4	7.6 ± 0.7	5.4 ± 0.5	$133 \pm < 0.5$
2000	750	1:30	0.8 ± 0.3	6.2 ± 0.4	4.9 ± 0.2	$139 \pm < 0.5$
		1:9	1.5 ± 0.1	14.7 ± 2.3	4.3 ± 0.1	$144 \pm < 0.5$
2000	1000	1:30	1.3 ± 0.1	9.9 ± 0.7	5.4 ± 0.2	$136 \pm < 0.5$
		1:9	1.7 ± 0.5	25.0 ± 0.8	5.1 ± 0.3	$141 \pm < 0.5$
2000	2000	1:30	0.6 ± 0.1	14.8 ± 0.5	4.9 ± 0.2	$140 \pm < 0.5$
		1:9	1.8 ± 0.2	51.0 ± 1.7	5.2 ± 0.3	144 ± 1

Fig. 2. (a) Mean water uptake and (b) mean captive air bubble contact angle in water CA_{air} of PPG coatings (PPG1000 (circles) and PPG2000 (squares)) containing mPEG dangling chains ($OH_{mPEG}:NCO = 1:9$ (solid symbols) and $OH_{mPEG}:NCO = 1:30$ (open symbols)) plotted against the molar mass M_n of the mPEG. The error bars show the mean absolute deviation. Smooth curves are drawn to guide the eye.

the effective moduli of the PPG1000 independently of the mPEG precursor mass, it can be expected that the addition of a higher concentration of mPEG chains possibly decreases the modulus of PPG1000 even further. Following this line of thought, only for the PPG1000-mPEG1000 (1:9) coatings (8.2 ± 0.4 MPa) the measured effective modulus is unexpectedly high (note that without this data point the remaining data show a clear trend), which is attributed to an experimental fault (see note at SI). This is supported by the fact that no deviations in other properties such as the amount of extractable material, water uptake or contact angle are seen for the PPG1000-mPEG1000 (1:9) coatings, while no network structure arguments can be found for the apparent deviating E^* of these coatings.

3.1.2. Friction behaviour of PPG-mPEG coatings

The friction response of the water immersed coatings was measured with the custom-made tribology set-up as described in the *experimental part*. The variation of the mean Coefficient of Friction (CoF) with the radial sliding velocity (v) applied on the water swollen reference PPG

coatings is given in Fig. 4. The friction response of the coatings becomes similar at velocities above approximately 3 rad·s^{-1} . This shows the transition to the hydrodynamic lubrication regime where the friction response is governed by the viscous shear of the liquid medium in the gap being thereby independent of the network architecture [46]. At lower velocities, the indenters make physical contact with the coating surface and differences in network (surface) architecture give rise to a different friction response [35,47].

While the CoF of the reference PPG1000 coatings (solid symbols), on increasing the speed, gradually reduces to a value below 0.2 at a sliding velocity of 0.03 rad·s^{-1} , the CoF of PPG2000 only reaches a similar value at a much higher sliding velocity (between 0.3 and 1 rad·s^{-1}). Since both coatings have a similar water uptake ($\approx 8 \text{ wt\%}$), an explanation for this different behaviour is most likely related to the rigidity of the coatings. The coatings prepared with PPG of 1000 g·mol^{-1} have almost a two-fold higher effective modulus compared to the ones of PPG of 2000 g·mol^{-1} (10.4 ± 1.0 and 5.4 ± 0.5 MPa respectively, see Table 1) due to a higher cross-link

Fig. 3. Mean effective indentation modulus E^* of swollen PEG-PU coatings containing mPEG dangling chains ($OH_{mPEG}:NCO = 1:9$ (solid symbols) and $OH_{mPEG}:NCO = 1:30$ (open symbols)) plotted against the molar mass M_n of the mPEG chains of (a) PPG1000 coatings and (b) PPG2000 coatings. The indentation measurements are performed with the coatings completely immersed in water. The error bars show the mean absolute deviation.

Fig. 4. Mean Coefficient of Friction (CoF) versus radial velocity v of water swollen PPG1000 coatings (solid symbols) and PPG2000 coatings (open symbols). The CoF is measured in demineralized water against a glass counter surface with a total normal load F_N of 0.5 N. $1 \text{ rad}\cdot\text{s}^{-1} = 0.0145 \text{ m}\cdot\text{s}^{-1}$. The error bars show the mean absolute deviation. Smooth curves are drawn to guide the eye.

density, and a higher fraction of tHDI moieties in the PUPPG1000 coatings as compared to the PUPPG2000 coatings. Therefore these coatings are more rigid and thus will likely deform to a smaller extent during the friction measurements. It is specifically shown for rubber on ice contact that an increase in rubber stiffness decreases the coefficient of friction between the surfaces by reducing surface ploughing [48]. Therefore, less deformation of the surface will reduce the surface plowing effects and will hereby decrease the absolute frictional forces on the polymer surface [46,48,49].

The CoFs for PPG coatings containing hydrophilic mPEG chains are given in Fig. 5. Note that Fig. 5b, c and d contain a broken vertical axis for highlighting the differences in the low CoF regime. The most striking general feature is that the addition of mPEG dramatically reduces the high CoF values found for the reference PPG systems, both by increasing the mPEG molar mass and molar concentration, especially at the lowest velocities and regardless of the length of PPG-diol precursor used. In spite of fact that their CoF is significantly lower, it is interesting to note that the PPG-mPEG coatings show similar features in their friction response to the reference PPG coatings (references data also shown in Fig. 5), which is particularly true for the coatings which contain the lowest amount of chains ($\text{OH}_{\text{mPEG}}:\text{NCO} = 1:30$, i.e. Fig. 5a and c). This shows that, although the friction response of the matrix network prevails for the dual coatings, its contribution diminishes upon addition of longer mPEG chains, especially at higher concentration of mPEG.

For the PPG2000 coatings with a low dangling chain content (Fig. 5a) it can be seen that the CoF for velocities below $0.1 \text{ rad}\cdot\text{s}^{-1}$ is reduced upon increasing the length of the added dangling chains. When a higher concentration of the same mPEG is added to a PPG2000 coating (1:9; compare Fig. 5a and b), a further decrease of the CoF is observed (note the different y axis scale). This absolute decrease in CoF (compared with the reference level) is the smallest for the coatings which contain the shortest mPEG ($750 \text{ g}\cdot\text{mol}^{-1}$, solid triangles), whereas the absolute CoF of the other two PPG2000-mPEG coatings is comparable.

For the PPG1000 coatings, it is striking to see that the addition of the shortest mPEG chains ($M_n = 750 \text{ g}\cdot\text{mol}^{-1}$) at the lowest concentration ($\text{OH}_{\text{mPEG}}:\text{NCO} = 1:30$) (Fig. 5c, solid circles) reduces the CoF by three-fold already in the very low velocity regime (below

$0.1 \text{ rad}\cdot\text{s}^{-1}$). Note that the water uptake of these coatings is only slightly increased (about 2 wt%) as compared to the reference PPG1000 (Table 1).

Concurrently, a further increase in chain concentration is significantly decreasing the CoF of the coatings for all chain lengths (1:30 vs 1:9 in Fig. 5c and d, respectively). The PPG coatings with the lowest friction response are clearly the PPG1000-mPEG1000 (1:9) systems (Fig. 5d, open circles) with a CoF below 0.012 for the whole velocity range between $3\cdot 10^{-3}$ and $1 \text{ rad}\cdot\text{s}^{-1}$, while the water uptake of these coatings is still $< 30 \text{ wt}\%$.

Another interesting result is the friction response of the coatings which contain the longest mPEG chains ($2000 \text{ g}\cdot\text{mol}^{-1}$, semi-filled circles) compared to the PPG1000 coatings which contain the other mPEG chain lengths. It can be seen that the CoF of these coatings is higher than the CoF of the PPG1000-mPEG1000 coatings (open circles) at most velocities and is even higher than the CoF of the PPG1000-mPEG750 coatings for the $\text{OH}_{\text{mPEG}}:\text{NCO}$ ratio of 1:30 at low velocities (solid circles Fig. 5c). This observation suggests an additional contribution to the friction force for the PPG coatings with relatively long mPEG chains.

In Fig. 6 a closer look is taken at the effect of the mPEG dangling chains in PPG coatings at a sliding velocity of $0.1 \text{ rad}\cdot\text{s}^{-1} = 1.45 \text{ mm}\cdot\text{s}^{-1}$, a velocity relevant for the insertion of bio-medical devices [50–52]. As mentioned, the overall addition of mPEG dangling chains results in a large decrease of the CoF of the coatings. The relative reduction of the CoF is the largest for the PPG2000 coatings since the reference level (PPG systems without mPEG) at this velocity is much higher compared to the PPG1000 coatings. Nevertheless, the lowest absolute CoF values are observed for the PPG1000-mPEG systems. Moreover, it can be seen that in general the CoF decreases further upon adding more mPEG chains to the coatings, from a 1:30 to a 1:9 M ratio, regardless of the mPEG chain length. The only coating system which clearly does not follow this trend is PPG1000mPEG2000 (1:9) (light gray bars, Fig. 6a), which is, at the same time, the only coating system with a high amount of mPEG chains for which the dangling chain mass is larger than the mass of PPG-diol precursor. This observation again points towards an additional contribution to friction by adhesion between the surface (dangling) polymers and the tribo-counter surface, for the PPG coatings with relatively long mPEG chains.

3.2. PPG coatings with diol-PEG network segments

3.2.1. Network properties and friction behaviour of the PPG-PEG coatings

In the previous section it was shown that the addition of hydrophilic coating precursors as dangling network chains reduces the coefficient of friction of the PPG coatings tremendously, while a relatively low overall water uptake is maintained. In order to see if this friction reduction is a result of the presence of dangling chains on the surface of the coatings, or is mainly due to the addition of hydrophilic network precursors to the network of the coatings, the properties of dual hydrophobic/hydrophilic PPG-PEG coatings were studied.

The PPG-PEG coatings were prepared with a similar dry film thickness and the fraction of extractable material was found to be similar to the PPG-mPEG coatings. The only exception were the reference PEG coatings, which were prepared with a dry film thickness of approximately $10 \mu\text{m}$ to prevent delamination. Two molar masses of PEG (M_n of 1000 and $2000 \text{ g}\cdot\text{mol}^{-1}$) were selected for the coatings and the volume fraction of PEG ϕ_{PEG} was varied (see Table 2). Coatings with ϕ_{PEG} between 0.4 and 0.8 were also prepared but showed macroscopic phase separation, hence they were not characterized further.

The amount of extractable material L , water uptake, effective indentation modulus E^* and static captive air bubble contact angle CA_{air} are given in (Table 2). (See SI-4 for a graphical representation of data of the last three parameters.) The properties of the reference PPG and PEG PU coatings are also shown for comparison purposes.

The water uptake of the PPG-PEG networks seems to scale almost

Fig. 5. Mean Coefficient of Friction (CoF) versus radial velocity v of water swollen PPG coatings containing different concentrations of mPEG dangling chains ($M_n = 750, 1000$ or $2000 \text{ g}\cdot\text{mol}^{-1}$) (a) PPG2000-mPEG $\text{OH}_{\text{mPEG}}:\text{NCO} = 1:30$, (b) PPG2000-mPEG $\text{OH}_{\text{mPEG}}:\text{NCO} = 1:9$, (c) PPG1000-mPEG $\text{OH}_{\text{mPEG}}:\text{NCO} = 1:30$ and (d) PPG1000-mPEG $\text{OH}_{\text{mPEG}}:\text{NCO} = 1:9$. The values of the PPG1000 coatings (solid squares) and PPG2000 coatings (solid diamonds) are given as reference coating without mPEG dangling chains. The CoF is measured in demineralized water against a glass counter surface with a total normal load F_N of 0.5 N . $1 \text{ rad}\cdot\text{s}^{-1} = 0.0145 \text{ m}\cdot\text{s}^{-1}$. The error bars show the mean absolute deviation. Smooth curves are drawn to guide the eye.

linearly with the fraction of hydrophilic PEG in the coating, for both PPG precursor masses. Furthermore, the addition of a small fraction of hydrophilic diol ϕ_{PEG} (6.5 wt%) to the network is already sufficient to give rise to a significant increase in the hydrophilicity (higher CA_{air}) of the coatings' surface, especially for the most hydrophobic reference PPG2000 coatings. On further increasing the hydrophilic fraction, the surface hydrophilicity increases only slightly, and possibly approaches the values for the reference PEG coatings. It can be seen that the coatings containing PPG and PEG, both with a mass of $2000 \text{ g}\cdot\text{mol}^{-1}$, are slightly more hydrophilic than those containing PPG and PEG, both with a mass of $1000 \text{ g}\cdot\text{mol}^{-1}$. This is attributed to the presence of a lower volume fraction of fairly hydrophobic cross-linker moieties in the latter coatings, since tHDI is less hydrophilic compared to PEG.

Turning now to the effective modulus E^* , the addition of PEG to the hydrophobic PPG1000 networks results in a significant drop in effective modulus compared to both the reference PPG1000 coating and the reference PEG1000 coating, whereas the effective modulus of the dual networks with different PEG is rather comparable. At the same time, the addition of PEG results in a slight increase of the effective modulus for PPG2000 networks compared to the individual reference PPG and PEG coatings. Furthermore, the absolute values of the effective moduli are

comparable for the three different hydrophilic PEG fractions for both coating types.

The friction behaviour of the PPG1000-PEG1000 and PPG2000-PEG2000 coatings is given in Fig. 7a and b, respectively. The addition of PEG to PPG coatings results for both PPG molar masses in a large decrease of the friction response of the coatings in the velocity range from 10^{-3} up to $3 \text{ rad}\cdot\text{s}^{-1}$. The CoF also seems to decrease upon increasing PEG content up to the PEG fraction of 0.33. This effect is most pronounced with the PPG2000-PEG2000 coatings, for which the CoF is even extremely low (down to values below 0.025!) in the whole velocity range from 10^{-3} up to $1 \text{ rad}\cdot\text{s}^{-1}$, for a hydrophilic fraction of diol precursors of 0.33 (which is a 25-fold decrease at some velocities).

Although missing data points for ϕ_{PEG} in the region between above 0.333 and 0.865 make it impossible to determine the exact ϕ_{PEG} value for a minimum friction in this velocity range, it becomes evident that the low-friction properties of dual coatings are a result of a synergistic effect of the intrinsic properties of both the hydrophobic PPG and the hydrophilic PEG. A possible explanation of this phenomenon will be discussed later.

The previous section showed a strong influence of the hydrophobic/hydrophilic balance of the diol-precursors on the friction behaviour of

Fig. 6. Mean Coefficient of Friction (CoF) (at $v = 0.1$ rad·s⁻¹ = 1.45 mm·s⁻¹) of water swollen PPG coatings containing different mPEG dangling chains (750 g·mol⁻¹ (dark gray bars), 1000 g·mol⁻¹ (white bars) and 2000 g·mol⁻¹ (light gray bars) in different concentrations for (a) PPG1000 coatings and (b) PEG2000 coatings. The measured CoF of PEG1000 and PEG2000 coatings are given as reference coating without mPEG dangling chains (patterned bars). The CoF is measured in demineralized water against a glass counter surface with a total normal load F_N of 0.5 N. The error bars show the mean absolute deviation.

the PU coatings. In order to determine if there is an additional chain length dependency on the network- and friction properties of the PPG-PEG coatings, the M_n of the PEG was varied in a PPG1000-PEG coating with a constant overall hydrophilic fraction, of the total diol components, of 0.2. The measured values for L , the water uptake, E^* and the CA_{air} of these coatings are shown in Table 3. (See SI-5 for a graphical representation of data of the last three parameters).

Although the overall fraction of PEG is constant at a fraction of 0.2, it can be seen that an increase in the M_n of PEG up to 2000 g·mol⁻¹ results in an increase in water uptake and surface hydrophilicity, while the effective modulus decreases. No significant differences between the addition of PEG of 2000 g·mol⁻¹ and 4000 g·mol⁻¹ (at a constant ϕ_{PEG} of 0.2) are seen between all measured properties. This shows that the distribution of the hydrophilic fraction in the coating (i.e. more, but short PEG chains versus less, but longer PEG chains) is influencing these network properties up to the molar mass of 2000 g·mol⁻¹. It should be noted that a change in the amount of diol precursors in the network also slightly changes the amount of cross-linker moieties, which is inevitable when maintaining the same stoichiometry for all coatings as the total amount of functional OH-groups differs in each formulation.

Fig. 8 shows the friction response of the PPG-PEG coatings with varying PEG molar mass. Although the fraction of PEG is constant for each coating, large differences in friction response can be seen. The

addition of the hydrophilic fraction by means of a high concentration of short chains (i.e. PEG with a M_n of 400 g·mol⁻¹) does not change the friction behaviour notably compared to the reference PPG1000. However, the CoF decreases upon increasing the PEG-diol length in the low and medium velocity regime up to the PEG mass of 2000 g·mol⁻¹. No significant differences in friction can be observed between the coatings prepared with PEG2000 and PEG4000 for which also all the other investigated network properties are similar. Next to the results on the dependency of the overall hydrophilic fraction of the networks shown in the previous section, these results show a clear hydrophilic diol chain length dependency of the friction properties of the PPG-PEG coatings.

3.3. Qualitative comparison of the network structure–friction relations between PPG-mPEG and PPG-PEG coatings

In order to assess the differences between the addition of the hydrophilic network precursors as dangling chains or as elastic active network chains, the friction response of the coatings presented in previous sections with a similar ϕ_{PEG} fraction of 0.2, is compared in Fig. 9. The friction behaviour of the corresponding reference PEG and PPG coatings is also given for comparison. Fig. 9 shows a clear difference in friction behaviour between coatings with the two types of added hydrophilic network precursors. For both PPG coatings, the addition of

Table 2

Overview of amount of extractable material L , water uptake, effective indentation modulus E^* and captive air bubble contact angle in water CA_{air} of dual PPG-PEG PU coatings. The number of samples per coating type is typically 4 (10 for PPG coatings without PEG). The error shows the mean absolute deviation from the mean value.

PPG [g·mol ⁻¹]	PEG [g·mol ⁻¹]	ϕ_{PEG} [-]	L [%]	Water uptake [wt%]	E^* [MPa]	CA_{air} [°]
1000	no	0	1.2 ± 0.3	7.9 ± 0.8	10.4 ± 1.0	136 ± 2
1000	1000	0.065	0.5 ± 0.1	11.0 ± 0.8		139 ± < 0.5
	1000	0.143	0.6 ± 0.2	14.5 ± 0.5	7.0 ± 0.3	139 ± < 0.5
	1000	0.200	0.1 ± 0.1 [#]	17.9 ± 0.6	6.8 ± 0.1	139 ± < 0.5
	1000	0.333	0.2 ± 0.2 [#]	29.5 ± 1.1	6.6 ± 0.4	140 ± < 0.5
	1000	1	2.5 ± 1.3	99.5 ± 9.0	8.3 ± 1.1	142 ± 1
2000	no	0	1.1 ± 0.4	7.6 ± 0.7	5.4 ± 0.5	133 ± < 0.5
2000	2000	0.065	1.3 ± 0.8	13.5 ± 1.0		139 ± < 0.5
	2000	0.143	1.0 ± 0.1	19.6 ± 1.1	6.1 ± 0.1	140 ± < 0.5
	2000	0.200	1.7 ± 0.4	28.3 ± 0.5	6.4 ± 0.2	142 ± < 0.5
	2000	0.333	1.0 ± 0.4	48.9 ± 0.7	5.8 ± 0.3	141 ± < 0.5
	2000	1	0.8 ± 0.4	156.5 ± 18.2	5.1 ± 0.2	146 ± 1

[#] Amount of extractable material of two samples was undetectable.

Fig. 7. Mean Coefficient of Friction (CoF) versus radial velocity v of the water swollen dual PPG1000–PEG1000 coatings (a) and dual PPG2000–PEG2000 coatings (b) with various hydrophilic diol fractions φ_{PEG} . The CoF is measured in demineralized water against a glass counter surface with a total normal load F_N of 0.5 N. $1 \text{ rad}\cdot\text{s}^{-1} = 0.0145 \text{ m}\cdot\text{s}^{-1}$. The error bars show the mean absolute deviation. Smooth curves are drawn to guide the eye.

Table 3

Overview of the amount of extractable material L , water uptake, effective indentation modulus E^* and captive air bubble contact angle in water CA_{air} of dual PPG-PEG coatings with different PEG masses at a constant PEG fraction of 0.2. The number of samples per coating type is typically 4 (10 for PPG1000 without PEG). The error shows the mean absolute deviation from the mean value.

PPG [$\text{g}\cdot\text{mol}^{-1}$]	PEG [$\text{g}\cdot\text{mol}^{-1}$]	φ_{PEG} [–]	L [%]	Water uptake [wt%]	E^* [MPa]	CA_{air} [°]
1000	no	0	1.2 ± 0.3	7.9 ± 0.8	10.4 ± 1.0	136 ± 2
1000	400	0.2	0.7 ± 0.3	12.3 ± 0.3	7.9 ± 0.5	$138 \pm > 0.05$
	1000	0.2	$0.1 \pm 0.1^{\#}$	17.9 ± 0.6	6.8 ± 0.3	$139 \pm > 0.05$
	2000	0.2	0.6 ± 0.1	22.9 ± 0.1	6.8 ± 0.2	$142 \pm > 0.05$
	4000	0.2	0.4 ± 0.3	24.5 ± 0.7	7.0 ± 0.1	$141 \pm > 0.05$

[#] Amount of extractable material of two samples undetectable.

Fig. 8. Mean Coefficient of Friction (CoF) versus radial velocity v of the water swollen dual PPG1000–PEG coatings for different PEG–diol molar masses M_n at a constant hydrophilic diol fraction ($\varphi_{\text{PEG}} = 0.2$). The CoF is measured in demineralized water against a glass counter surface with a total normal load F_N of 0.5 N. $1 \text{ rad}\cdot\text{s}^{-1} = 0.0145 \text{ m}\cdot\text{s}^{-1}$. The error bars show the mean absolute deviation. Smooth curves are drawn to guide the eye.

the hydrophilic fraction as a dangling chain (mPEG, open circles) is superior for obtaining low friction when compared to the addition as a hydrophilic diol network precursor (PEG, closed circles). This

difference between the presence of mPEG or PEG is smaller for the 2000 $\text{g}\cdot\text{mol}^{-1}$ coatings (i.e. networks with the lower cross-link density). Furthermore, while the addition of the PEG, at velocities below $0.1 \text{ rad}\cdot\text{s}^{-1}$, leads to a reduction of the CoF which is less for PPG1000 than for M_n PPG2000 (difference of solid circles versus squares between Fig. 9a and b), an opposite trend is found for the addition of the hydrophilic mPEG. Now the friction reduction is more pronounced for PPG1000 case than for the PPG2000 systems (difference of open circles and squares between Fig. 9a and b).

This result can be qualitatively explained by taking into account the conformation of the hydrophilic chains at the surface and in the network structure when a counter surface is pressed against the polymer surface. This is depicted in Fig. 10 for both type of coatings.

Similar to the dangling chains, the diol-loops at the surface of the coating will be fully hydrated when immersed in water. Although they may have less configurational freedom due to the fact that both ends are connected to the network, they are most likely still be able to deform upon compression because there is sufficient surface span at the swollen network surface and low restriction from the far-neighboring chains. Hence, the presence of the loops also results in a hydrated top surface (hydration layer) which gives rise to the reduced friction response when a counter surface slides over the coating surface.

It should be noted that the systems compared here, contain a relatively small fraction of PEG ($\varphi_{\text{PEG}} = 0.2$) hence, it is unlikely that they are in the dense polymer brush regime. This may also explain why these results differ significantly from previous works in the literature, namely from Benetti et al. [23,24] Israelachvili et al. [25,26] and Klein [53] who showed that surfaces with dense polymer loops exhibit improved lubricity as compared to linear grafts, due to the reduced deformation

Fig. 9. Overview of mean Coefficient of Friction (CoF) versus radial velocity ν of the water swollen reference PPG coatings and reference PEG PU coatings as well as the PPG-mPEG and PPG-PEG at a constant PEG fraction ($\phi_{\text{PEG}} = 0.2$) for the coatings with precursors of $1000 \text{ g}\cdot\text{mol}^{-1}$ (a) and with precursors of $2000 \text{ g}\cdot\text{mol}^{-1}$ (b). The CoF is measured in demineralized water against a glass counter surface with a total normal load F_N of 0.5 N . $1 \text{ rad}\cdot\text{s}^{-1} = 0.0145 \text{ m}\cdot\text{s}^{-1}$. The error bars show the mean absolute deviation. Smooth curves are drawn to guide the eye.

of the loops which are sterically restricted by the close-neighboring polymer loops. Unfortunately, it was not possible to prepare polymer networks with a higher fraction of mPEG chains ($\phi_{\text{mPEGmax}} = 0.2$) as they were very unstable, i.e. high amount of leachables and in some cases delamination occurred due to extensive swelling in water. Hence we cannot discuss on how the lubrication properties would be on polymer networks with higher fraction of PEG dangling chains versus loops, which would approach the dense polymer brush regime.

The results we obtained for water uptake and surface hydrophilicity support our explanation. In order to form a loop which sufficiently “sticks out” of the surface as a coiled segment and create a (fully) hydrated surface layer, the hydrophilic diol precursors need to have a sufficient length. This can explain the results on the PEG-diol chain length dependency seen above, where the very short chains are not able to reduce the friction response, while the longer chains are. Moreover this explains why the PPG2000-PEG2000 coatings outperform the PPG1000-PEG1000 in terms of friction behaviour, as shown in Fig. 9. The hydrated layer resulting from the shorter PEG $1000 \text{ g}\cdot\text{mol}^{-1}$ is less capable to prevent adhesion with the counter surface and maintaining the lubricating hydration layer during sliding.

From our results it is clear that in our networks the presence of a small fraction of mPEG dangling chains provides a lower friction response, which indicates that the hydration layer created by the dangling chains on the surface is more efficient in reducing the adhesion with the counter-surface. A factor which possibly contributes to this observation is that upon compression the surface dangling chains will deform and adopt a conformation comparable to the compressed coiled loops (see Fig. 10). However, the dangling chains still have more freedom to deform over the span of the swollen network during the sliding of the counter surface, as compared to the dangling loops, resulting also in a more efficient hydration layer which enhances the lubricious properties, as reported by Klein and co-authors [54–56].

As shown before, the addition of hydrophilic dangling chains to the PPG1000 coatings generally results in a lower friction response compared to adding them to PPG2000 systems. Since the latter coatings have a lower cross-link density, the density of the dangling chains on the surface (at fixed $\text{OH}_{\text{MPEG}}/\text{NCO}$ ratios) is also lower. Most likely this difference in surface coverage, in combination with a higher indentation modulus, results in superior lubricious properties of the PPG1000 coatings. Recalling that for PPG coatings containing a high amount of mPEG dangling chains (1:9) it was found that relatively long mPEG

chains (PPG1000-mPEG2000) cause an increased friction response compared to shorter chains (PPG1000-mPEG1000), it can be concluded that an optimum surface coverage and chain length ratio exists. When the combination of the dangling chain length and surface coverage exceeds the optimal ratio, the scenario of an oversaturation of dangling chain segments can possibly result in additional adhesive contacts with the counter surface during shear (sliding), thereby giving rise to an additional contribution to the friction force.

Finally, it is known that surface ploughing results in an increase in the coefficient of friction due to plastic deformation of the surface [46], which can be reduced by the application of a hard thin surface layer [49,57,58]. Therefore the observed differences between reference PPG coatings can be explained by this ploughing effect. Finite element modeling has also shown that a thin soft layer on top of a stiffer substrate can reduce the overall frictional forces due to an improved redistribution of the stresses, although the penetration depth is slightly increased [59]. This latter scenario is similar to the representation of the dual hydrophobic/hydrophilic PU coatings prepared in this work when considering the thin hydrated top surface of the coatings as a thin soft layer on top of a more rigid substrate. Following this line of thought, the extreme synergistic effect of the PPG-diol and PEG-diol precursors within the dual hydrophobic/hydrophilic coatings, giving rise to a tremendous increase in lubricating performance compared to the coatings prepared from the individual networks, can be explained.

Whereas a hydration layer (and the possibility to maintain this layer at applied contact pressures and during sliding) is necessary for a low friction response, this layer is absent for the reference hydrophobic PPG coatings, given the unfavorable interaction of water with the hydrophobic network components. Although this hydration layer is also present for the reference hydrophilic PEG coatings, the homogeneously hydrated coatings are mechanically weaker which leads to increased surface ploughing. When combining both the hydrophobic PPG and the hydrophilic PEG into a single network, a dual structure is created when immersed in water. This dual structure consists of a thin hydrated soft layer on top of a stiffer bulk coating layer, which combines the required surface hydration layer of the hydrophilic segments with an improved resistance against deformation of the hydrophobic segments. Furthermore, the hydrophilic chains will feel a repulsion from the hydrophobic matrix when immersed in water, which will act as an additional enthalpic contribution in favor of “pushing” the hydrophilic segments outwards to the interface, where their presence aids the

Fig. 10. Simplified schematic representation of the surface of dual hydrophobic/hydrophilic cross-linked polymer coatings containing (a) hydrophilic dangling network chains and (b) hydrophilic diol precursors giving rise to hydrophilic dangling “loops” (black dots: chemical cross-links, grey chains: hydrophobic precursors, blue chains: hydrophilic chains, red crosses: free chain ends). From left to right: possible surface chain conformations under unloaded, statically loaded and sliding under load conditions, respectively. The coatings and counter surfaces are supposed to be completely immersed in water where only the surface hydrated layers are shown in the representation. The dimensions are out of proportion compared to the real testing conditions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lubrication between the surfaces. Moreover the system exhibits the required dual layer design to enhance stress redistributions and the surface chain mobility for maintaining the required hydration layer during sliding.

3.4. Qualitative evaluation of the dual hydrophobic/hydrophilic PU coatings with respect to commercial benchmarks

In view of the intended application of the dual coating on biomedical devices, their lubricious performance is compared with (commercial) benchmarks for lubricious polymer coatings. Fig. 11 shows the friction behaviour of the PPG2000-PEG2000 ($\phi_{\text{PEG}} = 0.333$) coatings (solid circles), the PPG1000-mPEG1000 (1:9) coatings (open circles) and benchmarks for a urinary tract catheter coating (black squares) and a cardiovascular coating (black stars). The commercial coatings (DSM

Biomedical BV, Geleen, NL) were also measured against a glass counter surface with the custom-made tribometer used in this work. These were prepared via a dipcoating process with a subsequent UV-curing step to obtain coatings comprised of a crosslinked hydrogel based on PVP (polyvinylpyrrolidone) as hydrophilic polymer/component. The commercial coatings had a swollen thickness of approximately 5–20 μm ¹ and showed good wet adhesion to the primed substrates when immersed in water. Seven samples of each coating type were prepared on similar substrates as used for the coatings in this work (including PEG6000 primer layer). A comparison of the gravimetrically measured water uptake and effective immersed indentation modulus of all coatings shown in Fig. 11 is given in Table 4. The friction response of the

¹ Personal communication with DSM Biomedical BV (Geleen, NL) (March 2017 and April 2018).

Fig. 11. Mean Coefficient of Friction (CoF) versus radial velocity v of water swollen PPG2000-PEG2000 ($\phi_{\text{PEG}} = 0.333$) coatings (closed circles) and PPG1000-mPEG1000 (1:9) coatings (open circles) and commercial benchmark coatings (urinary tract formulation: squares, cardiovascular formulation: stars). The CoF is measured in demineralized water against a glass counter surface with a total normal load F_N of 0.5 N. $1 \text{ rad s}^{-1} = 0.0145 \text{ m s}^{-1}$. The error bars show the mean absolute deviation. Smooth curves are drawn to guide the eye.

Table 4

Gravimetrically measured water uptake [wt%] and effective indentation modulus E^* [kPa] of the commercial benchmark coatings (averages of 7 samples, see the main text for an elaboration on these coatings). Data for the PPG2000-PEG2000 ($\phi_{\text{PEG}} = 0.333$) and PPG1000-mPEG1000 (1:9) coatings are given for comparison. The error shows the mean absolute deviation.

Coating	Water uptake [wt%]	E^* [kPa]
benchmark urinary tract catheter formulation	> 500	175 (± 15)
benchmark cardiovascular catheter formulation	> 700	170 (± 18)
this work PPG2000-PEG2000 ($\phi_{\text{PEG}} = 0.333$)	49 (± 7)	5800 (± 300)
this work PPG1000-mPEG1000 (1:9)	28 (± 4)	8200 (± 400)

cardiovascular catheter coating (black stars) is significantly lower compared to the friction response of the urinary tract catheter coating (black squares) for all sliding velocities up to 3 rad s^{-1} . Moreover, the commercial coatings show a gradual decrease in CoF from low to higher velocities before eventually entering the hydrodynamic lubrication regime, for which the minimum is located at a lower velocity for the cardiovascular catheter coatings compared to the urinary tract catheter coatings.

First of all, the dual coatings prepared in this work exhibit a friction response which is significantly less dependent on the sliding velocity compared to the commercial coatings. Therefore this behaviour suggests that the presence of hydrophilic dangling chains on a network with a high cross-link density (at least in the range of the systems studied in this work) gives rise to a surface which is able to maintain a constant friction response over a broad velocity range, while the highly (homogeneously) swollen commercial coatings are not able to do so. Furthermore, both dual coating types clearly outperform the urinary tract catheter coatings in terms of absolute lubricious properties. Compared to the cardiovascular catheter coatings, the dual diol PU coatings (solid circles) show a comparable CoF at velocities between 0.03 and 3 rad s^{-1} and even a significantly lower CoF at lower sliding

speeds. Next to a coating with a comparable performance, the PPG1000-mPEG1000 (1:9) coatings (open circles) significantly outperform the benchmarks in the whole velocity range, exhibiting a CoF below 0.012 in the whole velocity range between $3 \cdot 10^{-3}$ and 1 rad s^{-1} . Moreover, the outstanding lubricious properties are accompanied with a 15-fold lower water uptake and a 45-fold higher effective indentation modulus as can be seen from Table 4. This increased rigidity of the PU coatings can be expected to provide them with a higher wear resistance. This subject will be discussed in a follow up publication.

4. Conclusions

This work shows for the first time a systematic study on the relation between the network structure parameters and friction properties of dual hydrophobic/hydrophilic network PU coatings in an aqueous environment. Chemically cross-linked PU coatings were prepared by adding hydrophilic dangling chains (mPEG) as well as hydrophilic elastically active network chains (PEG) to PPG coating formulations. The dangling mPEG and network PEG-diol chain mass and concentration was systematically varied in coatings with two different PPG-diol precursor masses. The water uptake, indentation moduli, surface hydrophilicity and the macroscopic wet friction response of water swollen coatings against a glass counter surface immersed in water were measured.

The addition of either hydrophilic dangling network chains or fully connected network segments has shown to tremendously enhance the lubricating properties of the PPG coatings, while maintaining a low water uptake of approximately 20–40 wt%. Generally, the coefficient of friction of the coatings containing hydrophilic mPEG chains decreased more for longer chains as well as for higher concentrations of chains, except for one case in which the mPEG chains were longer than the PPG-diol network precursor used (for both concentrations studied). These coatings showed an increase in friction response compared to the coatings with shorter dangling chains at similar PPG mass. This phenomenon was attributed to additional adhesive contacts between the coating and the counter surface.

The presence of the hydrophilic precursors as elastically active network components (PEG segments) also greatly enhanced the lubricating properties, but generally to a lesser extent. The fact that the friction coefficient of the dual hydrophobic/hydrophilic coatings is significantly less compared to the CoF of both individual reference PPG and PEG coatings, demonstrates a large synergistic effect between the intrinsic properties of both the hydrophobic PPG and the hydrophilic PEG in the coatings.

All results can qualitatively be understood based on network and surface chain structure considerations. All hypotheses for this interpretation are related to the assumption that the lowest friction response is expected when the coating structure is able to maintain the most efficient hydration layer, hereby minimizing the amount of adhesive contacts between both surfaces while easily dissipating induced stresses in the top-layer. The results suggest that such a type of coating is able to maintain a stable and constant hydration layer over a broad velocity range.

In addition, the friction behaviour of the dual hydrophobic/hydrophilic PU coatings with the highest lubricious properties were compared to commercial benchmarks for urinary tract and cardiovascular catheter coatings. The coatings with the lowest friction response studied (PPG1000-mPEG1000 (1:9)) showed a CoF below 0.012 in the whole velocity range between $3 \cdot 10^{-3}$ and 1 rad s^{-1} , while the water uptake of these coatings is $< 30 \text{ wt\%}$. These coatings significantly outperform the benchmarks over the whole velocity range. Furthermore, their outstanding lubricious properties are accompanied by a 15-fold lower water uptake and a 45-fold higher effective indentation modulus. This clearly shows that a highly (homogeneously) swollen bulk is not a crucial requirement for a lubricious coating and

that, by a clever coating design, highly lubricious polymer surfaces can be created with a rigid and low swelling coating bulk.

Acknowledgements

This research forms part of the research program of the Dutch Polymer Institute (DPI), project #780. We thank Jérôme Lebouille and Patty van Alphen (DSM Biomedical BV, Geleen, The Netherlands) for preparation of the benchmark coatings and the information thereof.

Funding

This work was financially supported by the Dutch Polymer Institute [DPI#780].

Appendix A. Supplementary material

Custom made tribometer, friction measurement segments, example raw friction data, FTIR spectra of cured coatings and graphical representation of coating properties of PPG-PEG coatings. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2018.12.004>.

References

- [1] P. Wyman, *Coatings for Biomedical Applications – Chapter 1 Hydrophilic Coatings for Biomedical Applications in and ex vivo*, Woodhead Publishing Limited, Cambridge, 2012.
- [2] R.J. LaPorte, *Hydrophilic Polymer Coatings for Medical Devices – Structure/Properties, Development, Manufacture and Applications*, CRC Press LLC, Boca Raton, 1997.
- [3] K.H. Dellimore, A.R. Helyer, S.E. Franklin, *J. Mater. Sci. Mater. Med.* 24 (8) (2013) 1825–1835.
- [4] S. Nagaoka, R. Akashi, *Biomaterials* 11 (6) (1990) 419–424.
- [5] A. Niemczyk, M. El Fray, S.E. Franklin, *Tribol. Int.* 89 (2015) 54–61.
- [6] S. Lee, N.D. Spencer, *Science* 319 (5863) (2008) 575–576.
- [7] R. Tadmor, J. Janik, J. Klein, L.J. Fetters, *Phys. Rev. Lett.* 91 (2003) 11.
- [8] Y. Ohseido, R. Takashina, J.P. Gong, Y. Osada, *Langmuir* 20 (16) (2004) 6549–6555.
- [9] S.S. Perry, X.P. Yan, F.T. Limpoco, S. Lee, M. Muller, N.D. Spencer, *ACS Appl. Mater. Interfaces* 1 (6) (2009) 1224–1230.
- [10] N.D. Spencer, *Aqueous Lubrication – Natural and Biomimetic Approaches*, World Scientific Publishing Co., Pte. Ltd., Singapore, 2014.
- [11] H. Zeng, *Polymer Adhesion, Friction and Lubrication*, John Wiley & Sons Inc, Hoboken, New Jersey, 2013.
- [12] A. Dedinaite, *Soft Matter* 8 (2) (2012) 273–284.
- [13] L. Han, D. Dean, P. Mao, C. Ortiz, A.J. Grodzinsky, *Biophys. J.* 93 (5) (2007) L23–L25.
- [14] G.W. Greene, X. Banquy, D.W. Lee, D.D. Lowrey, J. Yu, J.N. Israelachvili, *Proc. Natl. Acad. Sci. USA* 108 (13) (2011) 5255–5259.
- [15] A. Singh, M. Corvelli, S.A. Unterman, K.A. Wepasnick, P. McDonnell, J.H. Elisseeff, *Nat. Mater.* 13 (10) (2014) 988–995.
- [16] J. Seror, L.Y. Zhu, R. Goldberg, A.J. Day, J. Klein, *Nature Comm.* (2015;6.).
- [17] M. Muller, S. Lee, H.A. Spikes, N.D. Spencer, *Tribol. Lett.* 15 (4) (2003) 395–405.
- [18] J. Klein, E. Kumacheva, D. Mahalu, D. Perahia, L.J. Fetters, *Nature* 370 (6491) (1994) 634–636.
- [19] U. Raviv, R. Tadmor, J. Klein, *J. Phys. Chem. B* 105 (34) (2001) 8125–8134.
- [20] U. Raviv, J. Frey, R. Sak, P. Laurat, R. Tadmor, J. Klein, *Langmuir* 18 (20) (2002) 7482–7495.
- [21] L. Chai, J. Klein, *Macromolecules* 41 (5) (2008) 1831–1838.
- [22] J. Klein, Y. Kamiyama, H. Yoshizawa, J.N. Israelachvili, G.H. Fredrickson, P. Pincus, L.J. Fetters, *Macromolecules* 26 (21) (1993) 5552–5560.
- [23] G. Morgese, L. Trachsel, M. Romio, M. Divandari, S.N. Ramakrishna, E.M. Benetti, *Angew. Chem.-Int. Ed.* 55 (50) (2016) 15583–15588.
- [24] E.M. Benetti, M. Divandari, S.N. Ramakrishna, G. Morgese, W.Q. Yan, L. Trachsel, *Chem.-A Eur. J.* 23 (51) (2017) 12433–12442.
- [25] T. Kang, X. Banquy, J.H. Heo, C.N. Lim, N.A. Lynd, P. Lundberg, D.X. Oh, H.K. Lee, Y.K. Hong, D.S. Hwang, J.H. Waite, J.N. Israelachvili, C.J. Hawker, *ACS Nano* 10 (1) (2016) 930–937.
- [26] X. Banquy, J. Burdyska, D.W. Lee, K. Matyjaszewski, J. Israelachvili, *J. Am. Chem. Soc.* 136 (17) (2014) 6199–6202.
- [27] Y.L. Yu, G.J. Vancso, S. de Beer, *Eur. Polym. J.* 89 (2017) 221–229.
- [28] S. de Beer, E. Kutnyanszky, P.M. Schon, G.J. Vancso, M.H. Muser, *Nature Commun.* (2014;5.).
- [29] M. Chen, W.H. Briscoe, S.P. Armes, H. Cohen, J. Klein, *Eur. Polym. J.* 47 (4) (2011) 511–523.
- [30] D. Paripovic, H.A. Klok, *Macromol. Chem. Phys.* 212 (9) (2011) 950–958.
- [31] A. Li, S.N. Ramakrishna, P.C. Nalam, E.M. Benetti, N.D. Spencer, *Adv. Mater. Interfaces* 1 (2014) 1.
- [32] A. Li, E.M. Benetti, D. Tranchida, J.N. Clasohm, H. Schonherr, N.D. Spencer, *Macromolecules* 44 (13) (2011) 5344–5351.
- [33] J.H.H. Bongaerts, J.J. Cooper-White, J.R. Stokes, *Biomacromolecules* 10 (5) (2009) 1287–1294.
- [34] B.S. Kim, J.S. Hrkach, R. Langer, *Biomaterials* 21 (3) (2000) 259–265.
- [35] J.P. Gong, *Soft Matter* 2 (7) (2006) 544–552.
- [36] A.A. Pitenis, J.M. Uruena, R.M. Nixon, T. Bhattacharjee, B.A. Krick, A.C. Dunn, T.E. Angelini, W.G. Sawyer, *J. Tribol.-Trans. ASME* 138 (2016) 4.
- [37] A.A. Pitenis, J.M. Uruena, K.D. Schulze, R.M. Nixon, A.C. Dunn, B.A. Krick, W.G. Sawyer, T.E. Angelini, *Soft Matter* 10 (44) (2014) 8955–8962.
- [38] B. van Bochove, J.J. Rongen, G. Hannink, T.G. van Tienen, P. Buma, D.W. Grijpma, *Polym. Adv. Technol.* 26 (12) (2015) 1428–1432.
- [39] A.A. Pitenis, J.M. Uruena, A.C. Cooper, T.E. Angelini, W.G. Sawyer, *J. Tribol.-Trans. ASME* 138 (2016) 4.
- [40] M. Du, Y. Zhang, Y.H. Song, Q. Zheng, *J. Polym. Sci. Part B-Polym. Phys.* 52 (11) (2014) 765–772.
- [41] S. Oogaki, G. Kagata, T. Kurokawa, S. Kuroda, Y. Osada, J.P. Gong, *Soft Matter* 5 (9) (2009) 1879–1887.
- [42] H. Hertz, *J. reine und angewandte Mathematik* 92 (1882) 156–171.
- [43] K.L. Johnson, *Contact Mechanics*, first ed., Cambridge University Press, Cambridge, 1985.
- [44] A.C. Fischer-Cripps, *Nanoindentation*, second ed., Springer Science + Business Media, New York, 2004.
- [45] M.A.C. Stuart, W.M. de Vos, F.A.M. Leermakers, *Langmuir* 22 (4) (2006) 1722–1728.
- [46] S. Hsu, C. Ying, F. Zhao, *Friction* 2 (1) (2013) 1–26.
- [47] J. Gong, Y. Osada, *J. Chem. Phys.* 109 (18) (1998) 8062–8068.
- [48] N.A. Isitman, A. Kriston, T. Fülöp, *Tribol. Trans.* (2017) 1–9.
- [49] K. Komvopoulos, N. Saka, N.P. Suh, *J. Tribol.-Trans. ASME* 109 (2) (1987) 223–231.
- [50] F. Arai, R. Fujimura, T. Fukuda, M. Negoro, *IEEE International Conference on Robotics and Automation*, vols. I-IV, Proceedings, 2002, pp. 2944–2949.
- [51] C. Tercero, S. Ikeda, T. Uchiyama, T. Fukuda, F. Arai, Y. Okada, Y. Ono, R. Hattori, T. Yamamoto, M. Negoro, I. Takahashi, *Int. J. Med. Robotics Comput. Assisted Surgery* 3 (1) (2007) 52–58.
- [52] J.C. Nickel, M.E. Olson, J.W. Costerton, *Urology* 29 (5) (1987) 501–503.
- [53] J. Klein, *J. Phys.-Condensed Matter* 12 (8A) (2000) A19–A27.
- [54] J. Klein, *Friction* 1 (1) (2013) 1–23.
- [55] A. Gaisinskaya, L.R. Ma, G. Silbert, R. Sorkin, O. Tairy, R. Goldberg, N. Kampf, J. Klein, *Faraday Discussions* 156 (2012) 217–233.
- [56] U. Raviv, S. Giasson, N. Kampf, J.F. Gohy, R. Jerome, J. Klein, *Nature* 425 (6954) (2003) 163–165.
- [57] K. Holmberg, A. Laukkanen, H. Ronkainen, K. Wallin, S. Varjus, J. Koskinen, *Surf. Coatings Technol.* 200 (12–13) (2006) 3810–3823.
- [58] H. Ronkainen, A. Laukkanen, K. Holmberg, *Wear* 263 (2007) 1315–1323.
- [59] S. Krop, *Contact Mechanics of Filled Thermoplastic and Thermoset Polymer Systems*, vol. PhD thesis: Eindhoven University of Technology, 2016.