Durability Improvement of Concentrated Polymer Brushes by Multiscale Texturing

Seiya Watanabe (✉ s-watanabe@rs.tus.ac.jp)

Tokyo University of Science: Tokyo Rika Daigaku <https://orcid.org/0000-0001-7422-8452>

Eri Kodama

Tokyo University of Science: Tokyo Rika Daigaku

Chiharu Tadokoro

Saitama University

Keita Sakakibara

Kyoto University: Kyoto Daigaku

Ken Nakano

Yokohama National University: Yokohama Kokuritsu Daigaku

Shinya Sasaki

Tokyo University of Science: Tokyo Rika Daigaku

Yoshinobu Tsujii

Kyoto University: Kyoto Daigaku

Research Article

Keywords: Polymer brush, Nano-periodic structure, Surface texture, AFM

Posted Date: April 1st, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-363726/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Concentrated polymer brushes (CPBs) are promising soft-material coatings for improving tribological properties under severe sliding conditions, even in the macroscopic scale. Therefore, they are expected to be applied to mechanical sliding components. However, the durability of CPBs has remained challenging for industrial applications. Previous studies revealed that applying a groove texture to the CPB substrate is effective in improving the durability of CPBs. In order to achieve further improvement of durability of CPBs, we attempted to apply the periodical structure, which is a microfabricated structure corresponding to a surface roughness $0.02\text{ }\mu\text{m}$, whereas the groove texture applied in previous studies has widths and depths in micrometres. In this study, the effect of the nano-periodic structure in addition to the groove texture applied to the CPB substrate on the durability of CPB is investigated. The results demonstrate a significant improvement in the durability of CPBs by up to 90% compared with non-textured CPB when an appropriate nano-periodic structure is applied (i.e. a nano-periodic structure oriented parallel to the groove texture).

Introduction

Polymer brushes are a kind of polymer thin films in which polymers are grafted onto a substrate with high density and form a brush shape structure; they have been extensively studied as tribo-materials [1-8]. In particular, polymer brushes with a normalised graft density higher than 10% is known as a 'concentrated polymer brush (CPB)' [9]. CPBs in good solvents have been reported to exhibit ultralow friction in both micro [10] and macro [11-14] scale sliding; therefore, their application to mechanical components such as bearings and oil seals is expected. The challenge of applying CPBs for actual industrial applications is their durability against friction. Applying a surface texture to the substrate is one of the key methods to improve the durability of CPBs. Surface texturing is a surface modification technique to improve anti-wear and frictional properties by the geometrical modification of surfaces to be slid [15-19]. A previous study demonstrated that applying surface textures onto the substrate of CPBs effectively improved their durability; furthermore, when a groove texture was applied, the durability of CPBs increased by 36% [20]. In this study, in order to achieve further improvement of the durability of CPBs, we applied nano-periodic structures to the substrate of CPBs in addition to groove surface textures, similar to the previous study [20]. Nano-periodic structures were fabricated based on the following processes: when a metal surface was irradiated by a femtosecond laser with its laser fluence compatible with the energy required for the laser abrasion of the metal used, a striped groove structure with a period shorter than the wavelength of the incident laser light was formed on the metal surface [21,22]. This period can be controlled by the laser fluence [21], wavelength [23], and number of pulses [23] of the femtosecond laser. The striped groove was formed orthogonal to the polarisation of the incident light such that the direction of the striped groove can be controlled via laser polarisation. For example, when a femtosecond laser with parallel polarisation in the scanning direction was scanned on an AISI 52100 surface, as shown in Fig. 1 (a), a nano-periodic structure (shown in Fig. 1 (b)) was formed. By changing the polarisation of the femtosecond laser, nano-

periodic structures with different orientations against the direction of laser scanning were formed, as shown in Fig. 2.

In this study, we investigated the combined effect of nano-periodic structures that correspond to a surface roughness (R_a) of 0.02 μm and a groove texture on the friction durability of CPBs swollen by an ionic liquid. The phenomena at sliding surfaces are discussed herein.

Methods

2. Experimental details

2.1. Specimens and lubricants

A disc ($\varphi 24 \text{ mm} \times t 7.9 \text{ mm}$) and cylinder ($\varphi 6 \text{ mm} \times l 8 \text{ mm}$) made of AISI 52100 were used as test specimens. Nano-periodic structures and surface textures were applied to the disc specimens by femto- and picosecond lasers (PiCooLs, L.P.S. Works, JP). The detailed texture patterns are summarised in Section 2.2. CPBs based on poly(methyl methacrylate) (PMMA) were grafted onto the discs with and without surface textures via surface-initiated atom transfer radical polymerisation (SI-ATRP) [24]. The thickness of the CPBs under dry conditions was approximately 1000 nm, as measured via ellipsometry. The CPBs were swollen using an ionic liquid, i.e. *N*-(2-Methoxyethyl)-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (MEMP-TFSI), which is a good solvent for PMMA. The thickness of the CPBs increased up to 2000–2500 nm via swelling by MEMP-TFSI. The molecular structures of PMMA and MEMP-TFSI are shown in Table 1. The thickness of the CPBs was controlled by the polymerisation time. In this study, the CPBs grafted on the textured discs were prepared in the same lot. MEMP-TFSI of volume 300 μL was applied onto a dried CPB disc and stored for 96 h under low vacuum conditions. The swollen CPB discs used in the friction test were unmodified.

2.2. Surface texture

In this study, we applied nano-periodic structures and a groove texture to AISI 52100 discs. A groove texture with a depth of 300 nm, width of 10 μm , and pitch of 110 μm was applied to the AISI 52100 disc substrate. The femtosecond laser for the nano-periodic structure was scanned with a pitch of 10 μm along the groove texture. This laser scanning induced undulation on the surface, corresponding to $R_a = 0.11 \mu\text{m}$. Three types of orientations of the nano-periodic structures, namely 0°, 45°, and 90°, against the scanning direction of the femtosecond laser, were prepared; these test samples are referred to hereinafter as Nano 0, Nano 45, and Nano 90, respectively. The pitch and corresponding roughness of the nano-periodic structures were 400 nm and 20 nm, respectively. The number-average molecular weight and polydispersity index of PMMA (free polymer simultaneously produced during the SI-ATRP) are 1.70×10^6 and 1.26, respectively. The dry thickness of the CPBs on these textured steel discs was 1102 nm, and the graft density and normalised (dimensionless) graft density were 0.46 chains/ nm^2 and 0.26, respectively. The topographic images captured via Atomic Force microscopy (AFM) measurements are shown in Fig. 3.

2.3. Friction durability test

To analyse the durability of CPBs on surface-modified discs against friction, we performed friction tests with increasing applied loads. A reciprocating friction tester (SRV4, optimal, DE) with a cylinder-on-disc geometry was used, and the applied load was increased from 5 to 70 N by 1 N every 1 min. The detailed conditions of the friction test are summarised in Table 2. In this study, the load when the friction coefficient exceeded 0.03 was defined as the 'limit load' of the CPBs and used as the durability index. We tested the CPBs on each textured disc three times.

The reciprocating friction tests were conducted in both the perpendicular and parallel directions against a groove texture. The nano-periodic structures comprised three orientation types; therefore, the tests were classified into six categories (3 different orientation samples $\times$ 2 sliding directions). Herein, we denote the result of the sliding test as 'sample name – sliding direction'. For example, when Nano 0 is slid to perpendicular to the groove texture, it is denoted as 'Nano 0-Per (instead of PII in the case of sliding to the parallel direction)'. The test combinations are shown in Table 3.

2.4. Surface analyses

The macro image of the wear track was captured using a laser microscope (VK-X 150, KEYENCE®JP). Nano- and microscale observations were conducted using AFM (S-image®SII®JP), and the resultant residual polymers on the wear tracks were evaluated from force-distant curve measurements. A pyramidal Si cantilever with a spring constant of 20 N/m was used. The relationship between the force-distant curve and the amount of polymers at the wear track is shown in Fig. 4. The force-distant curve shows the behaviour where (i) the CPB was worn out; (ii) less polymers exist, allowing the sharp cantilever to penetrate into the CPB [25]; and (iii) polymers exist sufficiently. The details of the analysis are published elsewhere [20].

Results

3.1. Friction durability of textured CPB surfaces

The limit load where the friction coefficient exceeded 0.03 in each test is summarised in Fig. 5. The detailed friction behaviour is shown in Supporting Information (S-1). The limit loads were 26.0 N for non-textured, 44.3 N for Nano 0-Per, 43.3 N for Nano 45-Per, 31.3 N for Nano 90-Per, 49.3 N for Nano 0-PII, 40.6 N for Nano 45-PII, and 33.6 N for Nano 90-PII. The surface-modified samples exhibited increased durability as follows: 70% for Nano 0-Per, 67% for Nano 45-Per, 20% for Nano 90-Per, 90% for Nano 0-PII, 56% for Nano 45-PII, and 29% for Nano 90-PII compared with non-textured samples. For the case where the nano-periodic structure was oriented 0° and 45° against the groove texture, the durability improved significantly; meanwhile, that oriented at 90° indicated a moderate increase in durability.

3.2. Mechanism of durability improvement by multi-scaled surface texturing

To clarify the mechanism of wear and exfoliation of CPBs, it is important to analyse the surface being worn rather than after it has worn out. Therefore, in addition to the duration friction tests, we performed a test that halted when the friction coefficient exceeded 0.06 and observed the surface. For the 0° and 45° orientations of the nano-periodic structures shown in Fig. 6 (a) and (b), respectively, the exfoliation of the polymers starting from the edge of the groove texture was not observed; however, the exfoliation from the edge of the texture was observed in the 90° orientation of the nano-periodic structure. This result indicates that the appropriate nano-periodic structure is effective in suppressing the exfoliation starting from the edge of the groove texture. Notably, the wear of the CPB occurred from the centre of the reciprocating surface, whereas the sliding condition of the edge of the reciprocating was more severe owing to the sliding speed.

To discuss the detailed mechanism of the wear of CPBs on textured substrates, we performed force-distant curve measurements on the wear track of the surface halfway during the friction test (at the same point as shown in Fig. 6). The topographic images and force-distant curves of Nano 0-Per, Nano 45-Per, and Nano 90-Per are shown in Figs. 7 (a), (b), and (c), respectively. In the cases of Nano 0-Per and Nano 45-Per shown in Figs. 7 (a) and (b), respectively, the force curves at both inside (blue and black circles) and outside (red and green circles) the groove texture suggest the wear of polymers. (The 3D topographic images are shown in Supporting Information (S-2).) In the case of Nano 90-Per shown in Fig. 7 (c), the exfoliation of polymers starting from the edge of the groove texture was observed.

The topographic images and force-distant curves of Nano 0-P11, Nano 45-P11, and Nano 90-P11 are shown in Figs. 8 (a), (b), and (c), respectively. Groove structures were not indicated from these results. In the cases of Nano 0-P11 and Nano 45-P11 shown in Figs. 8 (a) and (b), respectively, the force-distant curves suggest the wear of polymers. Note that the inside and outside the wear track could not be distinguished from the topographic images. In the case of Nano 90-P11 shown in Fig. 8 (c), the exfoliation of polymers occurred at many points.

Discussion

First, we consider the effect of the nano-periodic structure on the CPB substrate. Ramakrishna et al. reported the effect of the nanoscale surface roughness on the lubrication properties of semi-diluted polymer brushes [26]. They reported that the polymer brushes on spherical surfaces with a radius of 6 nm resulted in a higher friction owing to the less-stretched polymer chains, resulting in a smaller repulsion force between the polymer brush and the counter surface. In our study, we did not observe an increase in the friction coefficient when a nano-periodic structure was applied. The radius of the nano-periodic surface in this study is estimated to be 202 nm (the details of the calculation are described in the Supporting Information (S-3)). The thickness of the CPB after swelling is estimated to be above 2000 nm, which is much larger than the radius of the nano-periodic structure. Furthermore, the curved surface of the nano-periodic structure continuously appeared in contrast to the sparse appearance of the embedded particles in a previous study [26]. The surface radius of the nano-periodic structure continuously appeared in a plane. Therefore, it can be hypothesised that polymer chains grafted on a certain asperity are affected by the steric hindrance with other polymer chains on the neighbouring asperity. This causes the

polymer brushes to stretch vertically. Based on this hypothesis, the nano-periodic structure induces an increase in the grafted area and leads to a denser polymer brush layer than that on a flat surface. Further, the graft density at the nano-periodic structure surface (0.46 chains/nm²) is larger than that at the flat surface (0.35 chains/nm² [20]). This increase in the graft density contributed to better durability of the CPB.

Subsequently, we consider the effect of the orientation of the groove texture and nano-periodic structures. A previous study reported that the exfoliation of polymers starts from the edge of the groove texture [20]. The results of the limit loads shown in Fig. 5 indicate that sliding parallel to the groove texture tends to yield better durability than sliding perpendicular to the same orientation of the nano-periodic structures. In addition, the exfoliation of the CPB was observed for Nano 90-Per by AFM measurements, as shown in Fig. 7(c). Therefore, we consider that the edge of groove texture worked as the origin of exfoliation when the groove slid vertically, as mentioned in a previous study.[20] Focusing on the effect of the orientation of the nano-periodic structures and the groove textures, the parallel orientation of the nano-periodic structure along the groove texture tends to yield better durability than the perpendicular orientation analogue. A previous study verified that the supply of an ionic liquid, which is a good solvent, to the contact region plays an important role in maintaining the CPB [12]. From the laser microscope image shown in Fig. 6, it is found that the wear of the CPB started from the centre of the reciprocating direction. This indicates that the CPB wear was caused by the starvation of MEMP-TFSI. Based on this mechanism of wear of the CPB, we consider that the orientation of the nano-periodic structure along with the groove texture acts as a lubricant path at the nanoscale and contributes to providing the MEMP-TFSI to the sliding area, which prevents the starvation of the MEMP-TFSI and improves the friction durability.

The comparison of the progress ratio of durability of the surface-modified sample with that of the non-textured CPB sample is summarised in Fig. 9. The data for the samples having a groove texture are based on previous research [20]. The result demonstrates that the application of nano-periodic structures together with a groove texture to the CPB substrate significantly improved the durability of the CPB.

Conclusion

Applying nano-periodic structures and a groove texture to the CPB substrate effectively improved the durability of the CPB through nano-periodic structures, which increased the graft density and induced the formation of a semi-diluted polymer layer at the outermost surface. The results demonstrated an improvement in the durability of the CPB by up to 90% compared with that of the non-textured sample. To achieve such improvements, the nano-periodic structure must be oriented along the groove texture and the laser track, which is formed during the fabrication of nano-periodic structures.

Declarations

6. Acknowledgments

This work was financed by the Accelerated Innovation Research Initiative Turning Top Science and Ideas into High-Impact Values (ACCEL) of the Japan Science and Technology Agency (JST).

7. Funding

This work was supported by the Accelerated Innovation Research Initiative Turning Top Science and Ideas into High-Impact Values (ACCEL) of the Japan Science and Technology Agency (JST).

8. Ethics declarations

The authors have no conflicts of interest to declare.

References

- [1] Parnas, R.S., Cohen, Y.: A terminally anchored polymer chain in shear flow: Self-consistent velocity and segment density profiles. *Rheologica Acta* 33, 485-505 (1994)
- [2] Klein, J., Kumacheva, E., Mahalu, D., Perahia, D., Fetters, L.J.: Reduction of frictional forces between solids surfaces bearing polymer brushes. *Nature* 370, 634-636 (1994)
- [3] Klein, J.: Shear of polymer brushes. *Colloid and Surfaces A: Physicochemical and Engineering Aspects* 86, 63-76 (1994)
- [4] Müller, M., Lee, S., Spikes, H.A., Spencer, N.D.: The influence of molecular architecture on the macroscopic lubrication properties of the brush-like co-polyelectrolyte poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG) adsorbed on oxide surfaces. *Tribol. Lett.* 15, 395–405 (2003)
- [5] Kobayashi, M., Terayama, Y., Hosaka, N., Kaido, M., Suzuki, A., Yamada, N., Torikai, N., Ishihara, K., Takahara, A.: Friction behavior of high-density poly(2-methacryloyloxyethyl phosphorylcholine) brush in aqueous media. *Soft Matter* 3, 740–746 (2007)
- [6] Heeb, R., Bielecki, R.M., Lee, S., Spencer, N.D.: Room-temperature aqueous-phase fabrication of poly(methacrylic acid) brushes by UV-LED-induced, controlled radical polymerization with high selectivity for surface-bound species. *Macromolecules* 42, 9124-9132 (2009)
- [7] Irfachsyad, D., Tildesley, D., Malfreyt, P.: Dissipative particle dynamics simulation of grafted polymer brushes under shear. *Phys. Chem. Chem. Phys.* 4, 3008-3015 (2002)
- [8] Bielecki, R.M., Benetti, E.M., Kumar, D., Spencer, N.D.: Lubrication with Oil-Compatible Polymer Brushes. *Tribol. Lett.* 45, 447-487 (2012)
- [9] Tsujii, Y., Ohno, K., Yamamoto, S., Goto, A., Fukuda, T.: Structure and Properties of High-Density Polymer Brushes Prepared by Surface-Initiated Living Radical Polymerization. *Adv. Polym. Sci.* 197, 1-45 (2006)

- [10] Tsujii, Y., Nomura, A., Okayasu, K., Gao, W., Ohno, K., Fukuda, T.: AFM studies on microtribology of concentrated polymer brushes in solvents. *J. Phys.: Conf. Ser.* 184, 012031 (2009)
- [11] Sakata, H., Kobayashi, M., Otsuka, H., Takahara, A.: Tribological Properties of Poly(methyl methacrylate) Brushes Prepared by Surface-Initiated Atom Transfer Radical Polymerization. *Polymer Journal* 37, 767-775 (2005)
- [12] Sato, K., Okubo, H., Hirata, Y., Tadokoro, C., Nakano, K., Tsujii, Y., Sasaki, S.: Macroscopic tribological properties of thick concentrated polymer brush on rough steel under lubrication with ionic liquid. *Jurnal Tribologi* 20, 97-113 (2019).
- [13] Okubo, H., Tadokoro, C., Sakakibara, K., Nakano, K., Sasaki, S., Tsujii, Y.: Super-Low Friction of Thermal-Treatment-Concentrated Polymer Brushes (TT-CPBs) under Boundary Lubrication: A Practical Method to Shorten the Swelling Time of CPBs in Solvents. *Tribology Online* 14, 226-236 (2019)
- [14] Tadokoro, C., Sato, K., Nagamine, T., Nakano, K., Sasaki, S., Sato, T., Sakakibara, K., Tsujii, Y.: Concentrated Polymer Brush as Reciprocating Seal Material for Low Leakage and Low Friction. *Tribology Transactions* 63, 20-27 (2020)
- [15] Etsion, I., Burstein, L.: A Model for Mechanical Seals with Regular Microsurface Structure. *Tribology Transactions* 39, 677-683 (2008)
- [16] Fesanghary, M., Khonsari, M.M.: On the optimum groove shapes for load-carrying capacity enhancement in parallel flat surface bearings: Theory and experiment. *Tribol. Int.* 67, 254-262 (2013)
- [17] Nakano, M., Miyake, K., Korenaga, A., Sasaki, S., Ando, Y.: Tribological properties of patterned NiFe-covered Si surfaces. *Tribol. Lett.* 35, 133-139 (2009)
- [18] Yamakiri, H., Sasaki, S., Kurita, T., Kasashima, N.: Laser surface texturing of silicon nitride under lubrication with water. *Tribol. Int.* 44, 579-584 (2011)
- [19] Zhong, Y., Zheng, L., Gao, Y., Liu, Z.: Numerical simulation and experimental investigation of tribological performance on bionic hexagonal textured surface. *Tribol. Int.* 129, 151-161 (2019)
- [20] Watanabe, S., Kodama, E., Sakakibara, K., Sasaki, S., Tsujii, Y.: Effect of Surface Texturing on the Durability of Concentrated Polymer Brushes. *Tribol. Int.* 155, 106668 (2020)
- [21] Sakabe, S., Hashida, M., Tokita, S., Namba, S., Okamuro, K.: Mechanism for self-formation of periodic grating structures on a metal surface by a femtosecond laser pulse. *Phys. Rev. B* 79, 033409 (2009)
- [22] Okamuro, K., Hashida, M., Miyasaka, Y., Ikuta, Y., Tokita, S., Sakabe, S.: Laser fluence dependence of periodic grating structures formed on metal surfaces under femtosecond laser pulse irradiation. *Phys. Rev. B* 82, 165417 (2010)

[23] Vorobyev, A.Y., Guo, C.: Femtosecond laser-induced periodic surface structure formation on tungsten. J. Appl. Phys. 104, 063523 (2008)

[24] Hsu, S-Y, Kayama, Y, Ohno, K, Sakakibara, K, Fukuda, T, Tsujii, Y.: Controlled Synthesis of Concentrated Polymer Brushes with Ultralarge Thickness by Surface-Initiated Atom Transfer Radical Polymerization under High Pressure. Macromolecules 53, 132-137 (2020)

[25] Dunér, G., Thormann, E., Dédinaité, A., Claesson, P.M., Matyjaszewski, K., Tilton, R.D.: Nanomechanical mapping of a high curvature polymer brush grafted from a rigid nanoparticle. Soft Matter 8, 8312-8320 (2012)

[26] Ramakrishna, S.N., Espinosa-Marzal, R.M., Naik, V.V., Nalam, P.C., Spencer, N.D.: Adhesion and Friction Properties of Polymer Brushes on Rough Surfaces: A Gradient Approach. Langmuir 29, 15251-15259 (2013)

Tables

Due to technical limitations, table 1 is only available as a download in the Supplemental Files section.

Table 2 Details of friction test

Normal load	[N]	5–70
Time interval	[min]	1
Frequency	[Hz]	10
Stroke	[mm]	1
Lubricant	[μL]	300
Temperature	[°C]	28

Due to technical limitations, table 3 is only available as a download in the Supplemental Files section.

Figures

Figure 1

Laser-induced nano-periodic structure: (a) topographic image (AFM); and (b) laser-induced periodic surface structure (SEM)

Figure 2

Various directions of laser-induced periodic surface structure

Figure 3

Topographic image of surface before sliding test

Figure 4

Assessment of amount of polymer remaining on disc specimens

Figure 5

Summary of limit loads when friction coefficient increased significantly

Figure 6

Laser microscope image of wear track when friction coefficient exceeded 0.06

Figure 7

Topographic images and force curves of (a) Nano 0-Per, (b) Nano 45-Per, and (c) Nano 90-Per. Colours of force curve correspond to colours of circles in topographic images. The dashed line shows the area of groove texture.

Figure 8

Topographic images and force curves of (a) Nano 0-PII, (b) Nano 45-PII, and (c) Nano 90-PII. Colours of force curve correspond to colours of circles in topographic images.

Figure 9

Progress ratio of durability of surface-modified sample compared with that of non-textured CPB sample

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Table3Specificationsofcombinationofnano.docx](#)
- [Table1MolecularstructureofPMMAandMEMP.docx](#)
- [Supportinginformation.docx](#)