Tribological properties of micro/nano-textured surfaces under physiological conditions

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DOI:
10.33612/diss.253871011

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SUMMARY

In the last decade, surface texturing in micro/nano scale has been extensively used in biomedical engineering to modulate mammalian cell adhesion and proliferation, implant integration with human body and infection prevention. However, the tribological implications of texturing under wet physiological conditions have not been well quantified. This thesis is designed to investigate and understand the fundamentals and general phenomena of the tribological effects of surface texturing with the typical ordered patterns (i.e., micro/nanopore and microline) on different materials, from the most commonly textured hard material and soft material (i.e., materials for fundamental study, such as hard silicon (Si), in Chapter 2, and soft polydimethylsiloxane (PDMS) in Chapter 4) to the trendiest type of material for cell study today (i.e., hydrogels, such as poly(2-hydroxyethyl methacrylate) (pHEMA) hydrogels in Chapter 3 and Chapter 5) in tissue engineering and tribology, under physiologically relevant conditions. Throughout this thesis, ordered pattern for surface texturing is selected to be studied over random pattern; it is for a clear scope of the relationships between the pattern and surface tribological properties while limiting the random unpredictable behaviors during the tribological tests.

Chapter 2 investigates the tribological effects of micro- and nanopore patterns on hard hydrophilic silicon sliding against soft hydrophobic polydimethylsiloxane (PDMS) immersed in aqueous liquid with various viscosities, simulating the sliding of textured implant surface against soft tissue. The experimental results show that the silicon surfaces with pore textures at both micro- and nanoscale feature sizes confer a higher coefficient of friction (COF) than an untextured one. It is attributed to the texture's edge effect caused by the periodic pore patterns between the two sliding objects with a large difference in material stiffness. For the same solid area fraction, a nanopored surface shows higher COF than a micropored surface because of a significantly higher texture edge length per unit area. For micropored surfaces with a similar texture edge length per unit area, the increase in COF is more pronounced with an increase in the pore size because of the greater stress at the rims of the larger pores. The COFs of both micro- and nanoscale pores generally decrease from ~10 to 0.1 with an increase in surrounding aqueous viscosity transitioning from a boundary lubrication to mixed lubrication regime, whereas that of an untextured surface decreases from ~1 to 0.01 transitioning from a mixed lubrication to hydrodynamic lubrication regime. Compared to hydrophilic hard probe sliding against textured hydrophobic soft substrate, the hydrophobic soft probe sliding against textured hydrophilic hard substrate produces a significantly higher COF under similar physiological conditions due to the larger edge effect.

The applications of hydrogels in tissue engineering as implants have rapidly grown in the last decade. However, the tribological properties of hydrogels in physiologically relevant conditions, especially those of textured hydrogels, have remained largely unknown due to the complexity of their mechanical and chemical properties. In Chapter 3, we experimentally investigated the tribological properties of micropored poly (2-hydroxyethyl methacrylate) (pHEMA) with the lateral pore dimensions varied compared to untextured pHEMA, the most commonly used hydrogel in ophthalmology, under physiologically relevant conditions. The pHEMA specimens were slid against a smooth glass curve under varying loads (6 - 60 mN, leading to an average contact pressure of 10 - 21 kPa) and sliding speeds (1 - 10 mm/s) in phosphate-buffered saline (PBS, pH 7.4) at 33°C to mimic the physiological conditions in human eyes. At relatively low loads and sliding speeds (e.g., 6 mN and 1 mm/s), the micropored pHEMA did not reduce the dissipated frictional energy significantly. However, at relatively high loads and sliding speeds (e.g., 60 mN and 10 mm/s), the micropored pHEMA resulted in significantly lower frictional energy (reduced by up to 68%) dissipation than the untextured pHEMA. The effect was more pronounced with the micropores with smaller dimensions. Those are attributed to the greater amount and retentivity of the interfacial fluid supported by the free water squeezed out of the micropores with the smaller dimensions under the higher load and sliding speed. These results suggest that the use of micropore texturing on hydrogels in practice, such as for ocular applications, can be leveraged to reduce friction and wear in physiological conditions and hence lower the chance of inflammation near eye implants or keratoprosthesis.

In Chapter 4 we characterize the tribological properties of micropored PDMS under physiological conditions and investigate the effect of adsorbed lubricious molecules on friction. In this study, untextured and micropored PDMS surfaces were slid against curved smooth glass surfaces under the contact pressures of 10 to 400 kPa, sliding speeds of 0.1 to 5 mm/s in aqueous solutions with viscosity of 1 to 1000 mPa·s. Reconstituted human whole saliva (RHWS) at pH 7 and porcine gastric mucin (PGM) at both pH 2 and 7 were used as lubricious coatings on PDMS. While the micropore-texturing delayed the transition of lubrication regimes, it increased the COF. Although RHWS and PGM coatings decreased the COF significantly, the protein coatings could not help the COF of micropored surfaces getting lower than that of untextured surfaces. The results suggest textured polymeric surfaces could generate larger friction under physiological conditions and lead to a higher chance of inflammation nearby the implants.

During the last few decades, researchers in biomedical fields have had growing interest in applying hydrogels as soft implants and for tissue engineering applications due to their high biocompatibility and mechanical similarity with human tissue. Furthermore, microtextured hydrogel surfaces, e.g., microlined hydrogels have been tested and used on implant surfaces specifically to achieve a desired cell alignment. But some recent studies have shown that texturing could cause an increase in friction, which in the long run could induce wear of the surrounding soft tissue, leading to tissue inflammation and reducing the implant's lifetime. In Chapter 5, microlined pHEMA hydrogel (solid area fraction = 0.2 to 1) reveals that due to the open groove channels on the surface, microlined pHEMA textures can store the liquid inside the grooves, potentially lubricating the interface. The tribological properties of the microlined pHEMA got significantly affected by the applied load and its texture parameters. In this study, microline texturing resulted in reduced friction in most cases under the relatively high load. It was because most of the line textures underneath the contact interface were being fully compressed by the relatively high load, which forced more of the liquid stored inside the grooves up directly into the contact interface when comparing to the relatively low load, while the rest of the liquid could still escape sideways along the grooves. Our study also reveals that texture width or scale (for ridges and grooves) plays a more important role than the textured depth or solid area fraction at the interface. These results suggest that the hydrogel surface with fine microlines, i.e., a relatively small width for both ridges and grooves could further provide a relatively steady contact and slow down sideway escape of the liquid underneath the contact interface through the groove channels, further helping to lower the friction.

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SAMENVATTING

De micro/nano oppervlaktetextuur van een materiaal is een veel onderzochte materiaaleigenschap en heeft toepassingen in bijvoorbeeld het moduleren van hechting en proliferatie van lichaamscellen, de integratie van implantaten in het menselijk lichaam en infectiepreventie. De tribologische implicaties zijn hierin onderbelicht geweest en dan specifiek de effecten van gebruik van getextureerde oppervlakten in fysiologische omstandigheden. Dit proefschrift is het resultaat van onderzoek naar de effecten van materiaalinteractie tussen materialen met verschillende (micro/nano) texturen, onder fysiologisch relevante condities voor toepassingen in tissue engineering. Hiervoor zijn typische gestructureerde texturen (bijvoorbeeld micro- en nanoporiën of 'mircolines') gemaakt op verscheidene materialen. Denk aan silicium (Si), een hard materiaal gebruikt in **Hoofdstuk 2**, of polydimethylsiloxaan (PDMS), een zacht materiaal gebruikt in **Hoofdstuk 4**, of hydrogelen zoals het poly(2-hydroxyethyl methacrylaat) (pHEMA) hydrogel, gebruikt in **Hoofdstuk 3** en **5.** In deze thesis is ervoor gekozen om met gestructureerde texturen te werken ten opzichte van willekeurige structuren om onvoorspelbaarheden tijdens wrijvingsmetingen te limiteren.

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In **Hoofdstuk 2** zijn de tribologische effecten (wrijving, lubricatie en slijtage) onderzocht van hydrofiel silicium met microporie- en nanoporietexturen tegen een oppervlakte van PDMS in een vochtige omgeving met variërende viscositeit. In de experimenten werd het glijden van een implantaat tegen zacht weefsel nagebootst. De resultaten laten zien dat er meer wrijving plaats vindt bij de texturen met micro- en nanoporiën dan bij de texturen zonder deze poriën in de oppervlakte. De resultaten worden toegeschreven aan het randeffect. Bij het toepassen van kleine gaten (de micro- of nanoporiën) in het materiaal, ontstaan ook randen. Bij het glijden zorgen deze randen voor hogere wrijving. Als de wrijvingscoëfficiënten vergeleken worden tussen nanoporie- en microporietexturen, dan geldt voor dezelfde solide-oppervlaktefractie, een veel hogere wrijvingscoëfficiënt voor de nanoporietextuur. Het randeffect wordt verondersteld hiervoor verantwoordelijk te zijn omdat blijkt dat er significant meer randlengte is bij de nanoporietexturen dan bij de microporietexturen. Als een oppervlaktetextuur wordt gekozen in de micro-range, maar met dezelfde randlengte als bij de nanoporietextuur, geldt dat de wrijving hoger wordt. Dit is toe te wijzen aan de toegenomen poriegrootte. Dit geeft een hogere mate van stress op de randen doordat het materiaal dieper de porie ingeduwd wordt. Bij het verhogen van de viscositeit van de omgevingsvloeistof neemt de wrijvingscoëfficiënt af voor beide oppervlaktetexturen. Wanneer dezelfde textuur is aangebracht op het zachte PDMS en wanneer er gegleden wordt tegen een vlak silicium oppervlakte, dus omgedraaid in vergelijking met hierboven, geeft dat een lagere wrijvingscoëfficiënt. Het randeffect is hier minder aanwezig omdat de randen minder hard zijn.

Omdat er een snel stijgende toepassing van hydrogelen in de biomedische industrie is, zoals bijvoorbeeld voor implantaattechnologie in de oogheelkunde, hebben we in **Hoofdstuk 3** onderzocht wat de tribologische eigenschappen zijn van de (in de oogheelkunde veelgebruikte) pHEMA hydrogel, zowel ongetextureerd als met microporietexturen. pHEMA-monsters met gevarieerde porieafmetingen werden tegen een gladde, afgeronde glazen (silicium) oppervlakte bewogen. De drukkrachten en glijsnelheden varieerden van 6 – 60 mN (resulterende in oppervlaktedruk van 10 – 21 kPa) en 1 - 10 mm/s en de experimenten werden gedaan in voor het oog fysiologisch relevante omstandigheden (in een fosfaat gebufferde zoutoplossing met pH 7,4 op 33°C). Onder lage druk en glijsnelheden (zoals 6 mN en 1 mm/s) verschilde de energiedissipatie nagenoeg niet tussen ongetextureerd pHEMA vergeleken met pHEMA met microporietexturen. Dit was anders onder hoge druk en glijsnelheden (zoals 60 mN en 10 mm/s), waar de pHEMA met microporietextuur het energieverlies door wrijving met 68% verminderde. Hoe kleiner de afmetingen van de microporiën waren, hoe hoger de reductie was. Verondersteld wordt dat in de kleinere poriën de in het glijvlak aanwezige vloeistof beter vastgehouden wordt en het aanwezige water dat zich in de poriën bevindt, er uitgeperst wordt. Dit zorgt voor de lagere energiedissipatie en dat betekent dat er minder wrijving en slijtage optreedt. Als deze bevindingen worden toegepast in de oogheelkunde, dan kunnen implantaten gemaakt worden die de kans op implantaat gerelateerde ontstekingen verkleinen.

In **Hoofdstuk 4** wordt de vraag gesteld wat het effect op de wrijving is van aangehechte lubricerende moleculen op PDMS. Hiervoor zijn van nature beschikbare lubricerende moleculen uit speeksel en maagslijmvlies gebruikt en in oplossing gebracht (pH 7 voor speeksel en pH 2 en pH 7 voor mucine uit de varkensmaag). De oplossingen werden gebruikt om lubricerende coatings aan te brengen op de PDMS met en zonder microporietextuur. Tijdens experimenten werd het PDMS tegen een gladde afgeronde glazen (silicium) oppervlakte gegleden onder invloed van 10 tot 400 kPa en glijsnelheden van 0.1 tot 5 mm/s in waterige oplossingen met viscositeit variërend tussen 1 en 1000 mPa·s. De lubricerende moleculen verlaagden de wrijvingscoëfficiënt significant, maar zonder verschil tussen het PDMS met of het PDMS zonder microporietextuur. Zonder lubricerende coating blijft de PDMS met microporie textuur 'langer' in het grenslubricatieregime dan de ongetextureerde, resulterende in hogere wrijvingscoëfficiënten. Dit zou betekenen dat microporie-getextureerde PDMS door de hogere wrijving tot een hogere kans op ontstekingen bij implantaten kan lijden.

De interesse in het gebruik van hydrogelen in de biomedische industrie is de laatste jaren flink toegenomen. De biocompatibiliteit en de op weefsel gelijkende mechanische eigenschappen zijn daar de reden van. Specifieke 'microlined hydrogels' (hydrogelen met ribbeltexturen in de micrometer range) zijn al gebruikt om cellen in een gewenste oriëntatie te laten groeien. Hierboven en in andere studies werd al aangetoond dat het aanbrengen van textuur, meer wrijving, en dus mogelijk ontstekingen aan het zachte weefsel teweegbrengen. Dit kan de duurzaamheid van de implantaten aantasten. In **Hoofdstuk 5** zijn pHEMA hydrogelen met een microline-textuur (solide-oppervlaktefracties van 0.2 tot 1) gebruikt. Dit hoofdstuk toont aan dat de microline-textuur kan fungeren als opslag van vloeistof en zo mogelijk de oppervlakte kan lubriceren. De tribologische waarden van de pHEMA veranderden significant onder de toenemende druk, maar ook naar mate de dimensies van de microlines aangepast werden. Doordat er relatief hoge druk op de microlines toegepast werd, werden ze dermate dichtgedrukt dat de opgeslagen vloeistof in de contactoppervlakte geperst werd. Dit leidt ertoe dat in nagenoeg alle geteste pHEMA microline-texturen een lage wrijvingscoëfficiënt gemeten werd. Uit de studie blijkt ook dat de wijdte van de microlines, of de schaal waarin ze toegepast zijn, een belangrijkere rol spelen dan de diepte van de tussenliggende ruimte of de solide-oppervlaktefractie. De resultaten suggereren dat een fijne mircoline-textuur een stabiel contactoppervlakte bewerkstelligt en dat deze textuur de mogelijkheid biedt dat de vloeistof door de kanalen kan wegvloeien en daarmee kan helpen om wrijving te reduceren.

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ACKNOWLEDGEMENTS

My dissertation would not be possible without the help of many people, especially my very supportive advisors. I am here, taking this opportunity to express my sincere appreciation to all of them.

First and foremost, I want to thank **Prashant**, as my advisor in UMCG. I appreciate all his contributions of time, effort, and ideas to my research throughout these years. He always encouraged me when I doubt my own ability and guided me being creative when solving a tough problem. His curiosity and passion in research had opened my mind to the amazing world of biomedical field. I also want to thank Prashant for his help with the communication between other UMCG staffs and me while I'm physically not in the Netherlands.

Inge, as one of my promoters in UMCG, thank you for helping and advising me on completing my thesis, especially at the final stage. I appreciate your valuable suggestions very much.

I also want to express my sincere gratitude to **Prof. Chang-Hwan Choi**, my lead advisor in Stevens Institute of Technology (Hoboken, NJ, USA), for his constant support and help during these years. I apricate the space you gave me in research most of the time, allowing me to learn how to think independently; but you also kept your eyes on my research progress and advised me with some key suggestions when I needed help. Your carefulness and patience in research had inspired me as a model. Thank you for teaching and guiding me how to plan my research strategically.

Meanwhile, without the support and encouragement from my co-advisor in Stevens, **Prof. Xiaojun Yu**, and my former advisor, **Prof. Robert Chang**, I would not have been able to start, continue and complete my thesis. Thank you for trusting me, I could not ask for more from you.

My sincere gratitude also goes to the members of the reading committee, **Prof. A.I. Vakis, Dr. P. van Rijn, Prof. dr. M. Masen**, and **Prof. Xiaojun Yu**, for taking the time to critically read my thesis and approving it for the final defense.

As part of our research group in UMCG, I want to thank **Hans** first. Hans, thank you for being so patient with my research plan. You were always there when I had problem with experiment, from the beginning till the end of my Ph.D. study. I enjoyed working with you and chatting with you during all the small breaks.

Jeroen, thank you for disusing research with me all the time, and patiently listening to my annoying complaints about life. I also gratefully thank for your precious time for translating the summary of my thesis and showing me various farm animals in the Netherlands.

Sara, thank you for helping with my research and talking through my struggles. **Rebecca**, thank you for teaching me experiment patiently. **Hongping**, although I did not work with you closely on research, I still want to thank you for your support and encouragement. **Ke Ren** and **Fenghua**, thank you for being my paranymph and helping me so much in the last few months.

Besides my advisors and lab mates in UMCG, I would like to thank the whole UMCG BME department. Whenever I got "lost" in the lab or even in the middle of hallway that

I was not familiar with, there was always somebody stood up to help me. I loved such a caring and cooperative working environment and will miss everybody for a very long time. BME staffs: **Joop**, **Betsy**, **Ed**, **Ina**, **Way** and **Willy**, thank you for helping me whenever I needed. **Brandon**, **Philipp**, **Damla**, **Gwenda**, thank you for sharing your experience and valuable opinions in research with me. **Dr. P. van Rijn**, thank you again, for always being helpful to my research and introducing me to your students when I had difficulties with handling polymers and hydrogels.

There had been so many amazing people I met in UMCG: **Niar**, I feel so grateful to meet you. You had brought so much sunshine into my life. I always amazed by your enthusiasm towards life. You made me understand your culture in such a positive way. Thanks for always keeping your door open for me. **Vera**, thank you for listening to me and teaching me our DIY projects; I will miss our lunch breaks. **Victor**, thank you for traveling with me and being there when I needed a bike-ride after work.

Lei Song, **Chongxia**, I remember when I first visited UMCG and did not know any methods in data analysis and basic experimental protocols, you were the first two people who offered me help with those, even though we did not work in the same group. Thank you for being so patient to me at work and introducing the real Sichuan hotpot to me.

Speaking of hotpot, my hotpot and game-night crews in the Netherlands: **Bingran**, **Feifei** (Qiutong), **JP**, **Fangjie**, **Qihui**, **Yingruo**, **Lu Yuan**, **Can Wang**, thank you for making me feel so included as a family. And thank you for bringing me so much laughter and so many delicious foods to my life.

Another person who introduced me to delicious food was my first landlord in the Netherlands, **Dr. Junping Hou**. Thank you for trusting me and letting me stay with your family. Thank you for saving nice and warm home-made dumplings and noodles for me when I got back from work. Also, thank you for encouraging me all the time! You are such a wonderful and kind teacher to me.

To the two former UMCG-Stevens dual doctoral program graduates, **Ferdi** and **Eva** (Yi Wang), thank you so much for the support and help you gave to me. I had been always taking you two as great examples in academia.

To research crews back in Stevens in the USA, **Amin**, **Wei Xu**. **Youhua**, **Xiaotian** and **Jian**, thank you for sharing your experimental methods to me and being so patient when helping me.

Jennifer, as one of the few female Ph.D. students in the mechanical department in Stevens, you could always understand my feelings. Thank you for being so supportive to my work and life. I hope we can get bubble tea together again very soon!

Hoa, you are the best roommate I've ever had. Being a doctor in a hospital already made you so busy every day, but you could still take time to listen to my happiness and frustrations after your work. I miss our times of sharing food, going to the same gym, and practicing martial arts together.

Xueyang Liu, you are such a talented musician and I am so happy that we became friends. Thank you for teaching me cello so patiently when I had zero experience. Also thank you for always encouraging me and believe in me. You are the one who showed me how tough and powerful a woman could be.

Jin Kuang (Lei Qian), **Xiao Xiang Zhu** (Xiyu Zhu), **Huihui** (Minhui Gu), **Sha La** (Xiaowen Xia), **Er Hao Ji** (Mengyi Gong), you guys were the first group of friends I had when I moved to the USA. Thank you for being on my side all the time when I felt desperate and needed help.

Here, I also want to thank my parents for always loving and supporting me unconditionally. **爸爸，妈妈，**感谢这么多年来的养育，你们辛苦了。无论我们相距多远相隔多久，请务必记得，我永远爱你们。愿我们早日重逢，珍重！

Finally, I want to thank two more important persons in my life:

Paula, thank you for always believing in me. You were the one who taught me how to love myself and be myself truly, which has completely changed my life.

Ben, my dear husband, you are the best thing to have ever happened in my life. Since we met and for the last entire 8 years, you have always been standing by my side encouraging me to be the person who I want to be. Thank you for helping me through all those tough times.

One last special thanks to my dog, my little angel, **Daisy**, for her endless love and cuddles during the last couple of years throughout the pandemic.