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Tracey T.M. Ho, Nichola Selway, Marta Krasowska, Gleb E. Yakubov, Jason R. Stokes, David A. Beattie

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FORMATION AND TRIBOLOGY OF FUCOIDAN/CHITOSAN POLYELECTROLYTE MULTILAYERS ON PDMS SUBSTRATES

TRACEY T. M. HO^A, NICHOLA SELWAY^C, MARTA KRASOWSKA^{A,B}, GLEB E. YAKUBOV^{C,D}, JASON R. STOKES^{C,D}, DAVID A. BEATTIE^{A,B}*

^A FUTURE INDUSTRIES INSTITUTE, UNIVERSITY OF SOUTH AUSTRALIA, MAWSON LAKES
CAMPUS, MAWSON LAKES, SA 5095

^B SCHOOL OF INFORMATION TECHNOLOGY AND MATHEMATICAL SCIENCES,
UNIVERSITY OF SOUTH AUSTRALIA, MAWSON LAKES CAMPUS, MAWSON LAKES, SA
5095

^C SCHOOL OF CHEMICAL ENGINEERING, THE UNIVERSITY OF QUEENSLAND, BRISBANE,
QLD 4072, AUSTRALIA

^D AUSTRALIAN RESEARCH COUNCIL CENTRE OF EXCELLENCE IN PLANT CELL WALLS,
THE UNIVERSITY OF QUEENSLAND, BRISBANE, QLD 4072, AUSTRALIA

* CORRESPONDING AUTHOR: DAVID.BEATTIE@UNISA.EDU.AU

ABSTRACT

POLYSACCHARIDE POLYELECTROLYTE MULTILAYERS (PEMs) BASED ON FUCOIDAN AND CHITOSAN WERE FORMED BY LAYER-BY-LAYER (LBL) ASSEMBLY ON POLYDIMETHYLSILOXANE (PDMS) SUBSTRATES. THE SURFACE AND AQUEOUS LUBRICATION PROPERTIES OF THE PEM FILMS ARE EVALUATED FOR TWO TYPES OF FUCOIDAN EXTRACTED FROM SEPARATE SEAWEED SPECIES (*FUCUS VESICULOSUS* – FV AND *UNDARIA PINNATIFIDA* – UP). ZETA POTENTIAL AND ATOMIC FORCE MICROSCOPY (AFM) IMAGING REVEAL THAT THE PEM LAYERS ARE FORMED WITH CONSISTENT CHARGE REVERSAL AS EACH POLYSACCHARIDE LAYER IS ADSORBED TO THE PDMS SUBSTRATE, AND THAT THERE IS AN ASSOCIATED INCREASE IN THICKNESS OF THE MULTILAYER. THE MULTILAYERS CONTAINING FV FUCOIDAN ARE FOUND TO BE THICKER THAN THOSE CONTAINING UP FUCOIDAN. SOFT TRIBOLOGY MEASUREMENTS USING MATCHING PDMS TRIBO-PAIRS ARE USED TO SHOW THAT THE FILMS ARE ROBUST UNDER ROLLING/SLIDING CONTACTS AND EFFECTIVE UNDER AQUEOUS LUBRICATING CONDITIONS. THE FRICTION IN THE BOUNDARY LUBRICATION REGIME IS SUBSTANTIALLY DECREASED (RELATIVE TO NATIVE HYDROPHOBIC PDMS) BY THE PRESENCE OF THE MULTILAYERS, WITH SOME DEPENDENCE ON WHETHER FUCOIDAN OR CHITOSAN IS IN THE OUTER LAYER (5 OR 5.5 BILAYERS) FOR FV FUCOIDAN. THE LOWEST FRICTION COEFFICIENT IS OBTAINED FOR THE MULTILAYER WITH THE THICKEST (AND LIKELY MOST HYDRATED) COATING – THE (FV/CHITOSAN) 5.5 BILAYER SYSTEM. THE RESULTS SUGGEST THAT PEMs INVOLVING NATURALLY DERIVED POLYSACCHARIDES SUCH AS FUCOIDAN, WHICH HAS NOTABLE ANTIMICROBIAL PROPERTIES AND IS RESISTANT TO ENZYMATIC DEGRADATION, MAY PROVIDE OPPORTUNITIES IN SURFACE COATING DESIGN IN BIOMATERIALS APPLICATIONS FOR FRICTION REDUCTION.

KEYWORDS: POLYELECTROLYTE MULTILAYER; FUCOIDAN; CHITOSAN; PDMS;
LUBRICATION

ACCEPTED MANUSCRIPT

Introduction

AQUEOUS LUBRICATION IS UBIQUITOUS IN NATURAL BIOLOGICAL SYSTEMS, WITH MACROMOLECULES AND STRUCTURED SURFACES PRODUCING EXCEPTIONALLY LOW FRICTION [1-3]. THE STUDY OF BIOMIMETIC LUBRICATION, A FIELD OF RESEARCH THAT AIMS TO EXPLOIT THE LUBRICATION MECHANISMS SEEN IN BIOLOGICAL SYSTEMS FOR BIOMATERIALS AND OTHER APPLICATIONS [4, 5], HAS IN THE MOST PART FOCUSED ON THE LUBRICATING PROPERTIES OF SINGLE ADSORBED LAYERS OF MACROMOLECULES OR SURFACTANTS, WITH A HEAVY EMPHASIS ON SURFACE GRAFTED LAYERS (E.G. YU ET AL. [6]). CHEN *ET AL.* DEMONSTRATED FRICTION COEFFICIENTS COMPARABLE TO THAT IN HUMAN JOINTS THROUGH THEIR STUDY OF A BIOCOMPATIBLE POLYZWITTERION BRUSH [1]. RAVIV AND CO-WORKERS DEMONSTRATED THE REMARKABLE LUBRICATING ABILITY OF CHARGED POLYELECTROLYTE BRUSHES ATTACHED TO SURFACES AT SLOW SLIDING VELOCITIES AND PRESSURES UP TO SEVERAL ATMOSPHERES [7]. THE LUBRICATING PROPERTIES OF SINGLE LAYERS OF ADSORBED POLYELECTROLYTES HAVE ALSO BEEN STUDIED [8]. IT MAY BE EXPECTED THAT SUCH LAYERS WOULD NOT ACT AS EFFECTIVE LUBRICANTS, BUT THE EVIDENCE PROVES OTHERWISE; SINGLE-LAYER COATINGS, INCLUDING SINGLE LAYERS OF POLYSACCHARIDES AND BRUSH CO-POLYMERS, HAVE BEEN SHOWN TO HAVE EXCEPTIONAL LUBRICATING PROPERTIES [9-12].

A METHOD TO EXPAND THE THICKNESS OF HYDRATED COATINGS OF ADSORBED POLYMER FILM IS TO USE MULTIPLE LAYERS OF ALTERNATIVELY CHARGED POLYELECTROLYTES. RELATIVE TO SINGLE ADSORBED LAYERS, ONE WOULD THUS EXPECT THAT POLYELECTROLYTE MULTILAYER (PEM) FILMS TO HAVE SUPERIOR TRIBOLOGICAL PROPERTIES. WHILST THIS IS EMERGING TO BE THE CASE, THERE ARE

ONLY A HANDFUL OF STUDIES IN THE LITERATURE ON THIS TOPIC. ONE OF THE FIRST OF SUCH PAPERS WAS PUBLISHED BY BURKE *ET AL.*, IN 2003 [13], IN WHICH THEY USED POLY(L-LYSINE) AND HYALURONIC ACID TO MAKE MULTILAYERS OF VARYING PROPERTIES (CONTACT ANGLE, THICKNESS, COEFFICIENT OF FRICTION) BY CONTROLLING THE PH AT WHICH THE POLYMER LAYERS WERE FORMED. IN THAT WORK, LATERAL FORCE MICROSCOPY (PERFORMED WITH THE ATOMIC FORCE MICROSCOPE (AFM)) WAS USED TO DETERMINE FRICTION COEFFICIENTS. PAVOOR *ET AL.* PUBLISHED TWO PAPERS IN 2003 AND 2006 ON THE LUBRICATION OF STEEL AND GLASS [13] AND STEEL AND ULTRA-HIGH-MOLECULAR-WEIGHT POLYETHYLENE (UHMWPE) [14] USING MULTILAYERS OF POLY(ALLYL AMINE HYDROCHLORIDE) (PAH) AND POLY(ACRYLIC ACID) (PAA). THE STUDIES EMPLOYED TRIBOLOGICAL TESTING, AND DETERMINED THAT FOR THEIR SYSTEM, MULTILAYER DEBRIDEMENT AND RETENTION OF COATING FLAKES IN THE CONTACT RESULTED IN REDUCED WEAR BUT INCREASED FRICTION RELATIVE TO UNCOATED SURFACES. THE MAJORITY OF THESE EXPERIMENTS INVOLVED COATING OF THE MULTILAYER ON ONLY ONE SURFACE. ANOTHER PAA/PAH MULTILAYER FRICTION STUDY WAS PUBLISHED BY DAI *ET AL.* IN 2005, IN WHICH THEY USED AFM IMAGING AND LATERAL FORCE MICROSCOPY TO STUDY THE INFLUENCE OF AMINATED C₆₀ NANOPARTICLE ADDITIVES WITHIN THE MULTILAYER STRUCTURE ON LAYER PROPERTIES AND FRICTION [15].

BONGAERTS *ET AL.* [16] STUDIED THE MACROSCALE FRICTIONAL BEHAVIOUR OF CROSS-LINKED CHITOSAN (CH)/HYALURONIC ACID (HYALURONIC ACID TERMINATING) POLYSACCHARIDE-BASED PEMS ON POLYDIMETHYLSILOXANE (PDMS) SURFACES. PDMS IS A VERY RELEVANT MATERIAL FOR STUDIES OF BIOLUBRICATION, AS IT IS COMMONLY USED IN BIOMATERIAL APPLICATIONS. FURTHERMORE, IT IS

REPRESENTATIVE OF COMPLIANT TISSUE SURFACES (E.G. SOFT ORAL SURFACES, SKIN ETC.), AND LUBRICATION STUDIES ARE THEREFORE OF RELEVANCE FOR UNDERSTANDING NATURAL LUBRICATION MECHANISMS AND DEVELOPING BIOMIMETIC ADVANCED MATERIALS. BONGAERTS ET AL [16] USED CHEMICAL CROSS-LINKING TO ACHIEVE BETTER ANTI-WEAR RESISTANCE TO THE FILMS, AND SOLUTION/FORMATION CONDITIONS WERE OPTIMISED TO PRODUCE HIGHLY HYDRATED OUTER LAYERS (HYALURONIC ACID). FURTHERMORE, THE EXPERIMENTS WERE PERFORMED WITH SYMMETRIC OPPOSING LUBRICANT LAYERS, COATING THE BALL AND DISC TRIBOPAIR OF PDMS (BALL AND DISC), MAKING THIS WORK OF GREATER RELEVANCE FOR UNDERSTANDING RUBBING CONTACT IN PRACTICAL SCENARIOS (FOR WHICH BOTH SURFACES WOULD BE COATED), AND ALSO ENSURING THAT ASPECTS SUCH AS BRIDGING ADHESION CAN BE ASSESSED.

THE WORK PRESENTED IN THIS MANUSCRIPT PROGRESSES OUR UNDERSTANDING OF POLYELECTROLYTE MULTILAYER LUBRICATION, BY STUDYING A NEWLY FORMULATED POLYSACCHARIDE-BASED POLYELECTROLYTE MULTILAYER LUBRICANT. FUCOIDAN IS A SULFATED POLYELECTROLYTE EXTRACTED FROM SEAWEED, WITH NOTED ANTIMICROBIAL PROPERTIES AND RESISTANCE TO DEGRADATION BY MAMMALIAN ENZYMES [17, 18]. THESE PROPERTIES, IN ADDITION TO ITS PLANT-BASED SOURCE, MAKE IT AN ATTRACTIVE OPTION FOR BIOMATERIALS APPLICATIONS, INCLUDING BIOLUBRICATION. IN EARLIER WORK FROM OUR GROUP, WE COMPARED THE BUILD-UP CHARACTERISTICS OF FUCOIDAN/CHITOSAN MULTILAYERS CONSTRUCTED FROM TWO DIFFERENT TYPES OF FUCOIDAN, *FUCUS VESICULOSUS* (FV) AND *UNDARIA PINNATIFIDA* (UP). OUR DATA INDICATED THAT THERE IS A CLEAR ALTERATION IN THE MULTILAYER PROPERTIES DEPENDING ON THE EXACT TYPE OF FUCOIDAN USED: UP FUCOIDAN

PRODUCED A THINNER, DENSER, AND SMOOTHER MULTILAYER THAN FV FUCOIDAN [19]. IN THIS PAPER, WE INVESTIGATE THE BUILD-UP CHARACTERISTICS OF FV AND UP MULTILAYERS (WITH CHITOSAN) ON PDMS USING ZETA POTENTIAL MEASUREMENTS AND AFM IMAGING (OUR PREVIOUS STUDIES WERE ON RIGID SOLID SURFACES: E.G. SILICON WAFERS [19] AND ZnSe [20]). THIS CHARACTERISATION INFORMATION IS COUPLED WITH A STUDY OF THE LUBRICATION OF PDMS SURFACES COATED WITH THE TWO MULTILAYER TYPES. IN ADDITION TO INVESTIGATING THE TWO DIFFERENT MULTILAYERS, THE EFFECTS OF THE OUTER LAYER IDENTITY (FUCOIDAN OR CHITOSAN) ON LUBRICATION WERE ALSO STUDIED. IN ADDITION TO ALTERING THE CHARGE ON THE SURFACE OF THE MULTILAYER (POSITIVE FOR CHITOSAN; NEGATIVE FOR FUCOIDAN), THE IDENTITY OF THE OUTER LAYER OF POLYELECTROLYTE MULTILAYERS IS KNOWN TO AFFECT THE HYDRATION OF THESE SYSTEMS [20, 21], AND ADHESION BETWEEN SURFACES COATED WITH MULTILAYERS [22].

Materials and Methods

SOLUTIONS AND SUBSTRATES

TECHNICAL GRADE (FROM THE MARITECH ® RANGE OF FUCOIDANS) *FUCUS VESICULOSUS* FUCOIDAN (FV) AND *UNDARIA PINNATIFIDA* FUCOIDAN (UP) WERE SUPPLIED BY MARINOVA PTY LTD (AUSTRALIA) WITH PURITIES OF 93 % AND 96 %, RESPECTIVELY. SCHEMATIC DIAGRAMS OF THE TWO POLYMERS ARE GIVEN IN FIGURE 1. CHITOSAN (CH; HIGH MOLECULAR WEIGHT, ≥ 75% DE-ACETYLATION, >800 cP FOR 1 WT% SOLUTION IN 1 % ACETIC ACID) AND POLYETHYLENEIMINE (PEI, 25 kDa) WERE PURCHASED FROM SIGMA-ALDRICH (AUSTRALIA). GLACIAL ACETIC ACID, POTASSIUM CHLORIDE (KCl, 99% AR), ETHANOL (100% UN-DENATURED, 99.5% v/v, AR), ISOPROPNOL (AR), SULFURIC ACID (H₂SO₄, 98% w/w, AR), AND 30% HYDROGEN PEROXIDE (H₂O₂, AR) WERE PURCHASED FROM CHEM-SUPPLY (AUSTRALIA). KCl USED FOR ALL SOLUTION PREPARATION WAS CALCINED AT 550 °C FOR OVER 8 HOURS TO REMOVE ANY ORGANIC IMPURITIES, RECRYSTALISED, AND THEN CALCINED AT 550 °C FOR OVER 8 HOURS AGAIN. POTASSIUM HYDROXIDE (KOH, VOLUMETRIC GRADE) AND HYDROCHLORIC ACID (HCl, VOLUMETRIC GRADE) WERE PURCHASED FROM SHARLAU, SPAIN.

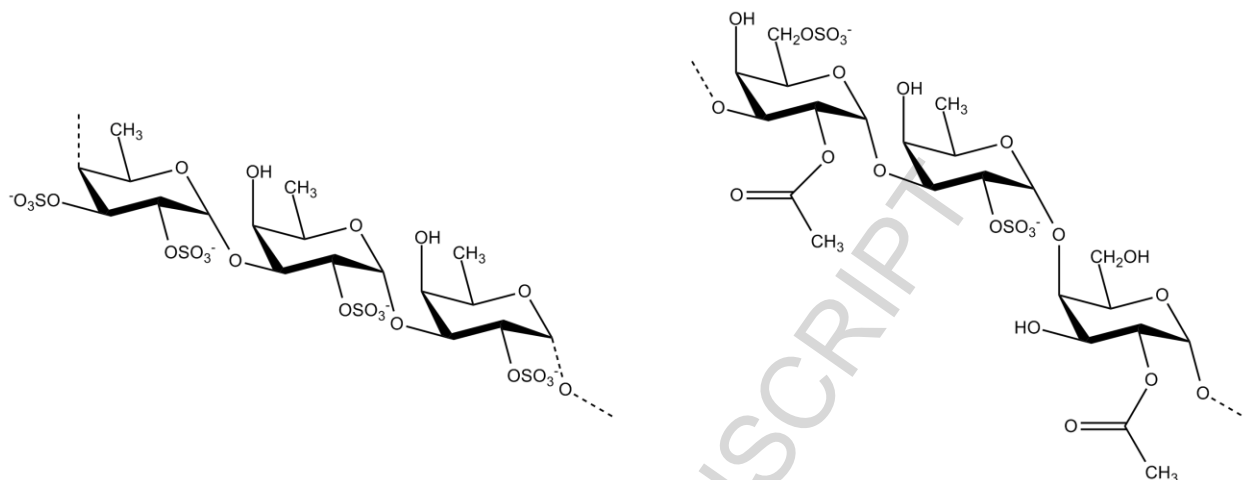


Figure 1: Schematic chemical structures of *Fucus vesiculosus* fucoidan (left – abbreviated to FV) and *Undaria pinnatifida* fucoidan (right – abbreviated to UP). Major structural differences include a small but significant amount of acetylation of sugar monomers in UP, and the presence of galactose monomers in UP, in addition to fucose (dominant in FV).

ALL SOLUTIONS WERE MADE WITH MILLI-Q WATER OF RESISTIVITY OF 18.2 MΩCM, AN INTERFACIAL TENSION OF 72.4 mN·m⁻¹ AT 22 °C, AND A TOTAL ORGANIC CARBON COMPONENT OF LESS THAN 4 mg L⁻¹. BACKGROUND ELECTROLYTE USED IN ALL EXPERIMENTS WAS 0.1 M KCL AT pH 6. FV AND UP FUCOIDAN SOLUTIONS (500 PPM) WERE PREPARED IN 0.1 M KCL, STIRRED OVERNIGHT TO ALLOW FULL DISSOLUTION, AND THEN pH ADJUSTED (pH = 6). A CHITOSAN STOCK SOLUTION (10,000 PPM) WAS PREPARED IN 0.1 M ACETIC ACID AND STIRRED OVERNIGHT. THE SOLUTION WAS THEN DILUTED TO 500 PPM IN 0.1 M KCL, AND pH ADJUSTED TO 6 PRIOR TO ALL EXPERIMENTS. NO PRECIPITATION OF CHITOSAN WAS OBSERVED AFTER pH ADJUSTMENT. PEI (500 PPM) WAS PREPARED IN 0.1 M KCL AND USED AT ITS NATIVE pH. ALL POLYSACCHARIDE SOLUTIONS WERE USED WITHIN 24 HOURS FROM PREPARATION. ALL FUCOIDAN SOLUTIONS WERE FILTERED USING A 0.45 μm PTFE FILTER (GRACE DAVISON DISCOVERY SCIENCE, AUSTRALIA).

MINI TRACTION MACHINE (MTM) DRILLED PDMS (POLYDIMETHYLSILOXANE) BALL WITH A RADIUS OF 9.5 mm AND 4 mm THICK POLYDIMETHYLSILOXANE (PDMS) DISC

WITH A RADIUS OF 23 MM (MADE FROM SYLGARD 184, DOW, MI) WERE PURCHASED FROM PCS INSTRUMENTS LTD (U.K.), AND WERE USED FOR TRIBOLOGY (MTM) EXPERIMENTS. BOTH BALL AND DISC SURFACES WERE SONICATED FOR 5 MIN IN ISOPROPNOL, FOLLOWED BY 15 MIN SONICATION IN MILLI-Q WATER, FOLLOWED BY DRYING WITH A STREAMING OF NITROGEN GAS. BOTH SURFACES WERE THEN PLASMA CLEANED FOR 99S TO RENDER THE SURFACE HYDROPHILIC PRIOR TO ALL EXPERIMENTS.

POLYDIMETHYLSILOXANE, PDMS, (SYLGARD 184, DOW CORNING, MI) COATED SILICA SURFACES USED FOR PEM ASSEMBLY FOR ZETA POTENTIAL DETERMINATION AND AFM IMAGING WERE PREPARED USING A SPIN COATER (SPINCOATER, P6700, SPECIALTY COATING SYSTEMS INC., USA). SILICON WAFERS (P-TYPE, <100>, SI-MAT SILICON MATERIALS, GERMANY) WERE USED FOR AFM IMAGING AND GLASS DISCS (KNITTEL GLASBEARBEITUNGS GMBH, GERMANY) FOR ZETA POTENTIAL MEASUREMENTS. PDMS COATED SILICON WAFERS WERE PREPARED BY PIPETTING ENOUGH VOLUME OF 0.1 % PDMS IN HEXANE ONTO A PIRANHA CLEANED 12 × 12 MM SILICON WAFER/GLASS DISC TO COMPLETELY COVER THE EDGES. THE SPIN SETTINGS INCLUDED AN INITIAL RAMP OF 2 SEC TO 1500 RPM FOR 1 SEC FOLLOWED BY 2000 RPM FOR 60 SEC. AFTER THE SPIN COATING, THE PDMS COATED WAFERS WERE PLACED INTO AN OVEN AT 120 °C FOR 8 HOURS TO CURE. ONCE CURED, THE PDMS COATED WAFERS WERE SONICATED FOR 5 MIN IN ISOPROPNOL TO REMOVE ANY RESIDUAL SOLVENTS, THEN SONICATED FOR 15 MIN IN MILLI-Q WATER, FOLLOWED BY DRYING IN A STREAM OF NITROGEN GAS. THE SURFACES WERE PLASMA CLEANED FOR 99S TO RENDER THE SURFACE HYDROPHILIC PRIOR TO ALL EXPERIMENTS.

ZETA POTENTIAL DETERMINATION

THE ZETA POTENTIAL VALUES FOR SUBSTRATES AND POLYELECTROLYTE MULTILAYER COVERED SUBSTRATES FOR EACH STAGE OF FORMATION WERE DETERMINED USING THE ZETASPIN APPARATUS (ZETAMETRIX, USA). A GLASS DISC SAMPLE IS ATTACHED TO A SAMPLE HOLDER. THE SAMPLE HOLDER IS MOUNTED ON A ROTATING ARM, AND IS IMMERSSED INTO A LIQUID CELL, PLACED A CERTAIN DISTANCE ABOVE THE REFERENCE ELECTRODE WITHIN THE LIQUID CELL. THE ROTATION OF THE SAMPLE IS SET AT A ROTATION RATE OF 3000 RPM, WHERE THE SAME ROTATION RATE WAS MODULATED BY A SQUARE WAVE TO AVOID UNSTEADY DRIFT DURING SAMPLE ROTATION. THE STREAMING POTENTIAL IS MEASURED AS THE JUMP IN THE RECORDED VOLTAGE AS THE MOTOR SWITCHES THE SAMPLE ROTATIONS FROM OFF TO ON AND BACK OFF AGAIN. THE ZETA POTENTIAL, ζ WAS DETERMINED FROM STREAMING POTENTIAL MEASUREMENTS USING THE FOLLOWING FORMULA [23]:

$$\zeta \cong \frac{1.96\kappa_l v_k^{1/2}}{\varepsilon a \Omega^{3/2}} \frac{1}{2 \left(1 - \frac{z}{a} - \frac{1}{2 \left(\frac{z^2}{a^2} + 1 \right)^{1/2}} \right)} \phi_s \quad (1)$$

WHERE: κ_l IS THE LIQUID CONDUCTIVITY, v_k IS THE KINEMATIC VISCOSITY, ε IS THE LIQUID PERMITTIVITY, a IS THE DISC (SAMPLE) DIAMETER, Ω IS THE SAMPLE ROTATION RATE (IN RADIANS PER SECOND), AND z IS THE DISTANCE BETWEEN THE SAMPLE AND THE REFERENCE ELECTRODE AND ϕ_s IS THE STREAMING POTENTIAL.

THE ZETA POTENTIAL FOR EACH LAYER WAS DETERMINED BY DIPPING A GLASS SLIDE ATTACHED TO THE END OF THE SAMPLE HOLDER INTO THE POLYELECTROLYTE SOLUTION FOR 15 MINUTES FOLLOWED BY AN IMMERSION IN 0.1 M KCL AT PH 6 FOR 5

MINUTES, FOLLOWED BY RINSING IN 0.1 M KCL, AND ANOTHER RINSING IN 1×10^{-3} M KCL. THE RINSING IN 1×10^{-3} M KCL WAS PERFORMED TO AVOID ANY CHANGES IN IONIC STRENGTH OF THE MEASUREMENT CELL AS THE MEASUREMENTS WERE PERFORMED AT 1×10^{-3} M KCL. THE MEASUREMENTS WERE PERFORMED AT THE LOWER SALT CONCENTRATION DUE TO THE SCREENING EFFECTS PRESENT AT THE HIGHER SALT CONCENTRATION USED FOR POLYELECTROLYTE MULTILAYER DEPOSITION, WHICH PREVENT ACCURATE/MEANINGFUL MEASUREMENT OF THE ZETA POTENTIAL.

ATOMIC FORCE MICROSCOPY (AFM) IMAGING

AFM IMAGES OF THE PEM FILMS WERE ACQUIRED *IN SITU* USING THE MULTIMODE 8 WITH NANOSCOPE V CONTROLLER (BRUKER, USA) PLACED ON AN ACTIVE ANTI-VIBRATION TABLE (VISION ISO STATION, NEWPORT, USA), AND EQUIPPED WITH A VERTICAL ENGAGEMENT SCANNER “J” (MAXIMUM SCAN RANGE 125 μM IN THE X- AND Y-DIRECTION, AND 5 μM IN THE Z-DIRECTION) IN THE SCANASYST MODES IN 0.1 M KCL AT PH 6. SCANASYST MODE SILICON NITRIDE CANTILEVERS WITH A RESONANCE FREQUENCY BETWEEN 40 AND 75 KHZ, A SPRING CONSTANT BETWEEN 0.12 AND 0.48 N m^{-1} , AND A SHARP SILICON (NOMINAL TIP RADIUS 2 NM) TIP (SCANASYST-FLUID+, BRUKER, USA) WERE USED FOR IMAGING. ALL IMAGES WERE TAKEN AT HIGH (512×512 OR HIGHER) RESOLUTION WITH A SCAN SIZE OF $5 \times 5 \mu\text{m}^2$. SCAN RATES EMPLOYED IN IMAGING WERE 0.99 Hz OR LOWER. FILM THICKNESS DETERMINATION WAS PERFORMED BY INITIALLY CREATING A SCRATCH (USING A SCALPEL BLADE) ACROSS THE FILM TO EXPOSE THE SUBSTRATE PROVIDING AN IMAGING ‘STEP’ IN THE HEIGHT IMAGE. THE CROSS SECTION OF THE ‘STEPS’ WERE ANALYSED AT MULTIPLE LOCATIONS TO DETERMINE THE DIFFERENCES IN HEIGHT BETWEEN THE SURFACE OF THE FILM AND THE BARE SUBSTRATE. ALL AFM IMAGES WERE ANALYSED USING NANOSCOPE

ANALYSIS v 1.5 (BRUKER, USA) AND WSxM 4.0 SPMAGE 09 EDITION (NANOTEC, SPAIN) [45] SOFTWARE PACKAGES.

MACROSCALE TRIBOLOGY

THE MINI TRACTION MACHINE (MTM, PCS INSTRUMENTS LTD., U.K.) WAS USED TO CHARACTERISE THE TRIBOLOGICAL PROPERTIES OF PDMS SURFACES COATED WITH PEMs. USING THE MTM IT IS POSSIBLE TO DETERMINE THE MACROSCALE FRICTION COEFFICIENT OVER A WIDE RANGE OF ENTRAINMENT SPEEDS AND LOADS.

IN THE MTM EXPERIMENTAL SET UP, A PDMS BALL IS PRESSED AGAINST A PDMS DISC AT AN APPLIED NORMAL LOAD THAT IS CONTINUOUSLY MONITORED BY A FORCE SENSOR, ILLUSTRATED IN FIGURE 1. BOTH THE BALL AND DISC ARE ROTATED AT DIFFERENT SPEEDS RESULTING IN A RELATIVE MOTION BETWEEN THE SURFACE OF THE BALL AND THE DISC. THIS RELATIVE MOTION LEADS TO A SLIDE-TO-ROLL RATIO (SRR) WHICH IS DEFINE AS:

$$\text{SRR} = \frac{V_{\text{ball}} - V_{\text{disc}}}{U} \quad (2)$$

WHERE V_{BALL} AND V_{DISC} ARE THE SURFACE VELOCITIES OF THE BALL AND DISC, RESPECTIVELY, AND U IS THE ENTRAINMENT SPEED DEFINED AS:

$$U = \frac{V_{\text{ball}} + V_{\text{disc}}}{2} \quad (3)$$

THE APPARENT FRICTION COEFFICIENT μ IS DEFINED AS:

$$\mu = \frac{F_f}{L} \quad (4)$$

WHERE L IS THE LOAD APPLIED AND F_F IS THE LATERAL FRICTION FORCE EXERTED ON THE BALL AS MEASURED THROUGH A FORCE TRANSDUCER. THE FRICTION COEFFICIENT CAN BE DETERMINED AT CONSTANT LOAD FOR VARYING ENTRAINMENT SPEED, TO YIELD THE CLASSIC STRIBECK CURVE FOR LUBRICATED CONTACTS. IN THIS WORK WE WILL DENOTE THE COEFFICIENT THUS DETERMINED FROM EQUATION 4 AS μ_{xN} , WHERE x IS THE LOAD VALUE IN NEWTONS (AS IT IS A MEASUREMENT AT CONSTANT LOAD). ANOTHER COEFFICIENT CAN BE DETERMINED BY LINEAR REGRESSION ANALYSIS OF A PLOT OF LOAD VERSUS F_F , WHEN EXPERIMENTS ARE PERFORMED AT CONSTANT ENTRAINMENT SPEED. THIS LATTER VALUE IS DENOTED AS μ IN THE REMAINDER OF THE MANUSCRIPT. THE DISTINCTION BETWEEN THE TWO FRICTION COEFFICIENTS IS OFTEN AMPLIFIED BY TERMING THE FORMER THE ‘TRACTION COEFFICIENT’.[24]

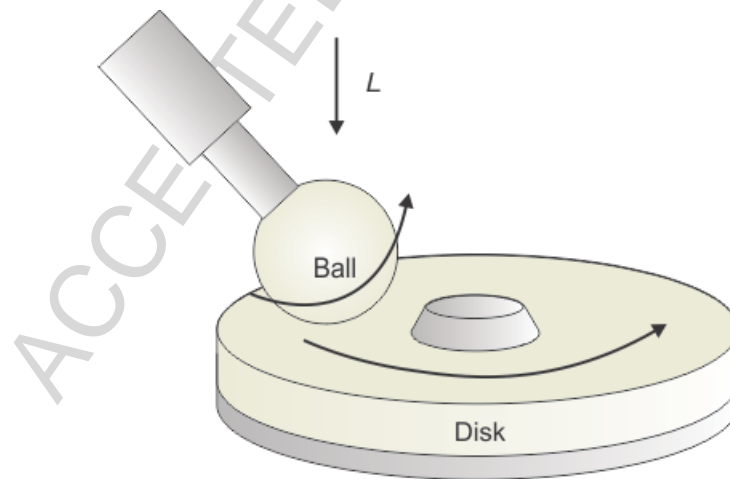


Figure 2: Schematic representation of the mini traction machine (MTM).

MTM MEASUREMENTS WERE PERFORMED ON 5 AND 5.5 LAYER PEM COATED PDMS BALL AND DISK AT THE TEMPERATURE OF $24\pm 2^\circ\text{C}$ IN 0.1 M KCL SOLUTION AT PH 6. A

SRR OF 50% WAS USED IN ALL EXPERIMENTS. THIS PARTICULAR BALANCE OF SLIDING AND ROLLING COMPONENTS IS RELEVANT FOR SPECIFIC BIOLUBRICATION EXAMPLES, SUCH AS ORAL LUBRICATION AND JOINT LUBRICATION. SOFT COMPLIANT SURFACES ARE KNOWN TO PRODUCE BOTH ROLLING AND SLIDING MOTION IN LUBRICATED CONTACTS, LEADING TO THE DEVELOPMENT OF TRIBOLOGY METHODOLOGIES THAT CAN ACCOUNT FOR THE DUAL NATURE OF THE RELATIVE MOTION OF SURFACES IN CONTACT [25, 26]. THE MULTILAYER LUBRICANTS CHOSEN FOR THIS STUDY HAVE POTENTIAL APPLICATION AS SURFACE COATINGS FOR JOINT IMPLANTS, AND THEREFORE A COMBINATION OF ROLLING AND SLIDING IS APPROPRIATE FOR THE TESTWORK. FOR THE SPEED DEPENDENT EXPERIMENTS, A LOAD OF $L = 2$ N IN THE ENTRAINMENT SPEED RANGE OF $U = 1$ -1000 MM/S WAS USED. FOR THIS LOAD, THE CONTACT AREA BETWEEN THE TWO SURFACES IS 12.7 MM^2 , PRODUCING AN AVERAGE PRESSURE IN THE CONTACT OF 160 KPA. THE ENTRAINMENT SPEED $U = 4$ MM/S IN THE LOAD RANGE OF $L = 2$ -7 N WAS USED FOR THE LOAD DEPENDENT EXPERIMENTS.

RESULTS

ZETA POTENTIAL MEASUREMENTS

THE ZETA POTENTIAL MEASUREMENTS FOR THE BUILD-UP OF (FV/CH) AND (UP/CH) MULTILAYERS (UP TO BILAYER 5.5) ARE GIVEN IN FIGURE 3. THE DATA FOLLOW THE CLASSIC SAW-TOOTH PROFILE, WITH CHARGE REVERSAL UPON ADDITION OF EACH POLYMER LAYER. FOR BOTH SYSTEMS, THE INITIAL MEASUREMENT POINT FOR OXYGEN-PLASMA TREATED PDMS WAS APPROX. -50 mV. UPON THE ADSORPTION OF PEI (USED AS THE ANCHORING LAYER FOR SUBSEQUENT ADSORPTION), A CHARGE REVERSAL OCCURS WITH A VALUE OF APPROX. 90 mV. THE BUILD-UP OF THE TWO

MULTILAYERS (UP AND FV WITH CHITOSAN) GIVES VALUES OF ZETA POTENTIAL: FUCOIDAN LAYERS HAVE NEGATIVE VALUES BETWEEN -40 AND -45 mV; CHITOSAN LAYERS HAVE POSITIVE VALUES OF APPROX. 30 mV. THERE IS VERY LITTLE VARIATION BETWEEN THE TWO FUCOIDAN MULTILAYER SYSTEMS IN TERMS OF THE MEASURED ZETA POTENTIAL WHEN ADSORBED ON PDMS. SLIGHTLY GREATER VARIATION WAS SEEN WHEN THE MULTILAYERS ADSORBED ON SILICON WAFER SUBSTRATES [19], WITH FV MULTILAYERS HAVING SLIGHTLY MORE NEGATIVELY CHARGED LAYERS WHEN FUCOIDAN WAS THE OUTER LAYER, AND SLIGHTLY LESS POSITIVE VALUES WHEN CHITOSAN WAS THE OUTER LAYER. NEVERTHELESS, THE MULTILAYERS APPEAR TO FORM IN A SIMILAR MANNER REGARDLESS OF THE SUBSTRATE TYPE.

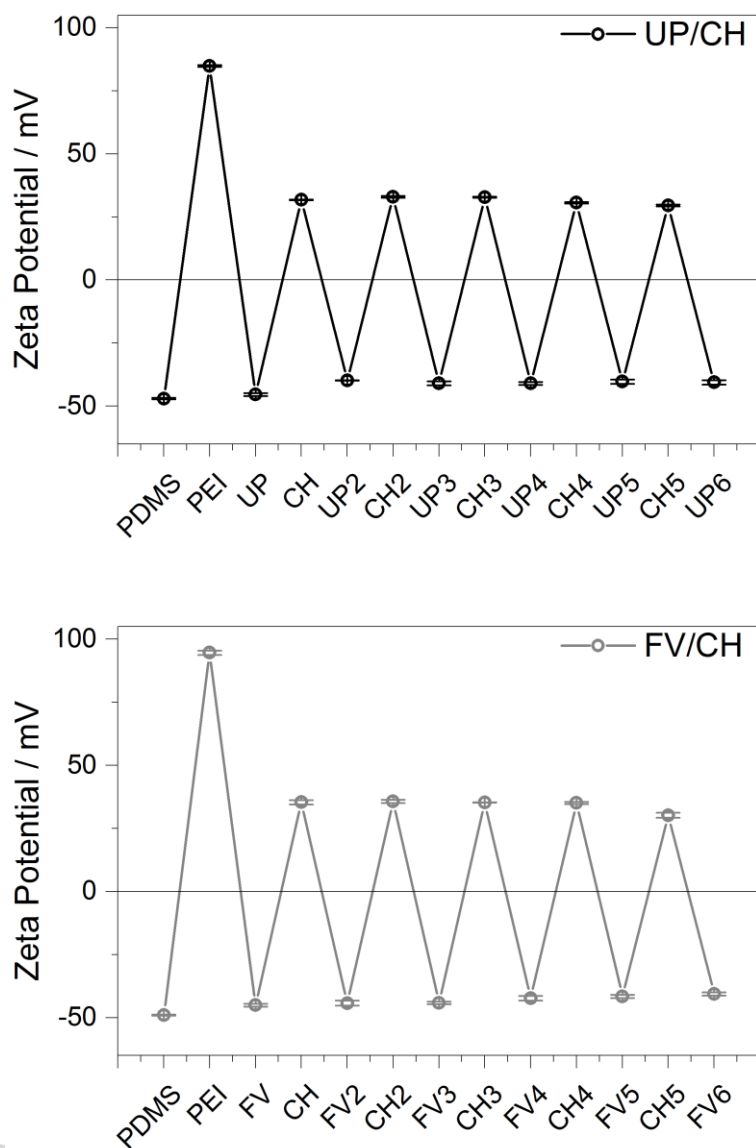


FIGURE 3: ZETA POTENTIAL MEASUREMENTS OF MULTILAYERS OF FUCOIDAN AND CHITOSAN FORMED ON PDMS SUBSTRATES: UP/CH (TOP) AND FV/CH (BOTTOM). MEASUREMENTS WERE PERFORMED IN 1×10^{-3} M KCL AT PH 6. FORMATION OF MULTILAYER WAS FROM 500 PPM POLYMER SOLUTIONS, 0.1 M KCL, PH 6.

AFM Imaging

PRIOR TO ADSORBING THE POLYMER MULTILAYERS, THE OXYGEN-PLASMA TREATED PDMS SUBSTRATES WERE CHARACTERISED USING *IN SITU* AFM IMAGING. NOT ONLY DID THIS ALLOW FOR THE DETERMINATION OF THE PDMS SURFACE ROUGHNESS, THE THICKNESS OF PDMS FILMS COATED ON SILICON SURFACES WAS ALSO OBTAINED. THICKNESS WAS DETERMINED BY GENTLY SCORING AND REMOVING THE PDMS COATING FROM PART OF THE SILICON WAFER PIECE, USING A SCALPEL BLADE. THIS METHODOLOGY WAS EMPLOYED FOR THE AFM IMAGING OF MULTILAYERS ON BARE SILICON WAFER, AND WAS SHOWN TO NOT DAMAGE THE WAFER SURFACE, THUS ALLOWING FOR UNAMBIGUOUS DETERMINATION OF LAYER THICKNESSES [19]. FIGURE S.1 IN THE SUPPORTING INFORMATION CONTAINS A REPRESENTATIVE AFM IMAGE OF THE PDMS-COATED WAFER PIECES. THE AVERAGE HEIGHT (H_A) OF THE PDMS MEASURED FROM THE STEP FROM THE AFM IMAGE IS 10.1 NM WITH AN R_{RMS} ROUGHNESS OF 0.9 NM.

SUBSTRATES SUCH AS THE ONE CHARACTERISED IN FIGURE S.1 WERE USED FOR MULTILAYER DEPOSITION. FOR BOTH THE FV AND UP FUCOIDANS, MULTILAYERS WITH CHITOSAN WERE BUILT UP TO CONSIST OF 5 AND 5.5 BILAYERS, I.E. WITH CHITOSAN (5) AND FUCOIDAN (5.5) AS THE OUTER LAYER. AS WITH THE BARE PDMS SUBSTRATE, THE MULTILAYER FILMS WERE CHARACTERISED USING AFM. THE IMAGES WERE RECORDED IN THE PEM FORMATION SOLVENT (0.1 M KCL, PH 6), ENSURING THAT THE MULTILAYER HAS THE SAME THICKNESS AND MORPHOLOGY AS WHEN FORMED. AFM IMAGES RECORDED FOR THE 5- AND 5.5-BILAYERS OF (FV/CH) AND (UP/CH) ARE GIVEN IN FIGURE 4 AND FIGURE 5, RESPECTIVELY.

UPON INSPECTION OF FIGURE 4, IT CAN BE SEEN THAT THE MULTILAYERS OF FV/CH ARE COVERING THE SURFACE WITH A MORPHOLOGY THAT INDICATES THAT THE MULTILAYER IS FORMING BOTH VERTICALLY FROM THE SUBSTRATE, BUT ALSO WITH EVIDENCE OF ISLAND FORMATION. THIS IS SEEN FROM THE DISTINCT INCREASE IN THE AVERAGE HEIGHT ALONG THE EXAMINED 2D CROSS SECTIONS (RELATIVE TO THAT FOR PDMS), AND FROM THE ARRAY OF DISTRIBUTED LARGER FEATURES. THE MULTILAYER THICKNESS WAS DETERMINED AS FOR THE MULTILAYERS ON SILICON AND FOR THE PDMS UNDERLAYER ITSELF, BY REMOVAL OF PART OF THE LAYER WITH A SCALPEL BLADE. NOTE: THE AVERAGE HEIGHT VALUES IN THE HISTOGRAM REQUIRE SUBTRACTION OF THE AVERAGE HEIGHT OF THE PDMS FILM TO GET THE TRUE HEIGHT OF THE MULTILAYER: 43.2 NM FOR (FV/CH)₅; 65.8 NM FOR (FV/CH)_{5.5}. THESE THICKNESS VALUES ARE SIGNIFICANTLY LOWER THAN THAT DETERMINED FOR (FV/CH)₆ MULTILAYERS ADSORBED ON BARE SILICON WAFER PIECES (APPROX. 134 NM). FURTHERMORE, THE (FV/CH)₅ LAYER THICKNESS IS LOWER THAN THAT DETERMINED FOR A (FV/CH)₄ MULTILAYER ON A BARE SILICON WAFER (APPROX. 56 NM). IT IS CLEAR THAT THERE IS BUILD-UP, BUT THE SUBSTRATE CHANGE HAS RESULTED IN A CHANGE IN BUILD-UP CHARACTERISTICS. THAT BEING SAID, THERE IS A SIGNIFICANT INCREASE IN HEIGHT BETWEEN MULTILAYERS 5 AND 5.5. THIS IS CONSISTENT WITH THE EXPECTED INCREASE IN ADSORBED AMOUNT WHEN FUCOIDAN ADSORBS, WHICH ALSO RESULTS IN AN INCREASE IN LAYER HYDRATION AND AN INCREASE IN SOFTNESS (AS DETERMINED VIA QCM EXPERIMENTS ON SILICA [19]).

THE AFM IMAGES OF THE MULTILAYERS COMPOSED OF FUCOIDAN FROM *UNDARIA PINNATIFIDA* AND CHITOSAN ARE GIVEN IN FIGURE 5. AS WITH THE *FUCUS VESICULOSUS* MULTILAYERS, THE MORPHOLOGY IS ONE OF COMPLETE LAYER WITH

ISLAND FEATURES ON TOP, AND WITH A DISTINCT INCREASE IN LAYER THICKNESS AFTER THE ADSORPTION OF THE FUCOIDAN TO MAKE THE (UP/CH)_{5.5} MULTILAYER (26.9 NM TO 33.4 NM). THIS HEIGHT INCREASE IS SMALLER THAN THAT OBSERVED FOR THE FV/CH MULTILAYERS, INCREASING IN THICKNESS BY ONLY 20% RELATIVE TO THE 5-BILAYER SYSTEM (THE INCREASE FOR THE FV/CH SYSTEM IS ALMOST 50%). BASED ON THE COMPARISONS OF THE TWO MULTILAYER SYSTEMS FROM OUR EARLIER WORK [19], THIS DECREASE IN THICKNESS FOR THE ACETYLATED FUCOIDAN (UP) IS EXPECTED, DUE TO GREATER INTER-POLYMER HYDROGEN BONDING INTERACTIONS. NOTE: THE HEIGHTS OF THE UP/CH MULTILAYERS ON PDMS ARE SIGNIFICANTLY LOWER THAN THOSE OBSERVED FOR (UP/CH)₄ AND (UP/CH)₆ MULTILAYERS ON SILICON WAFER PIECES (APPROX. 48 AND 105 NM, RESPECTIVELY).

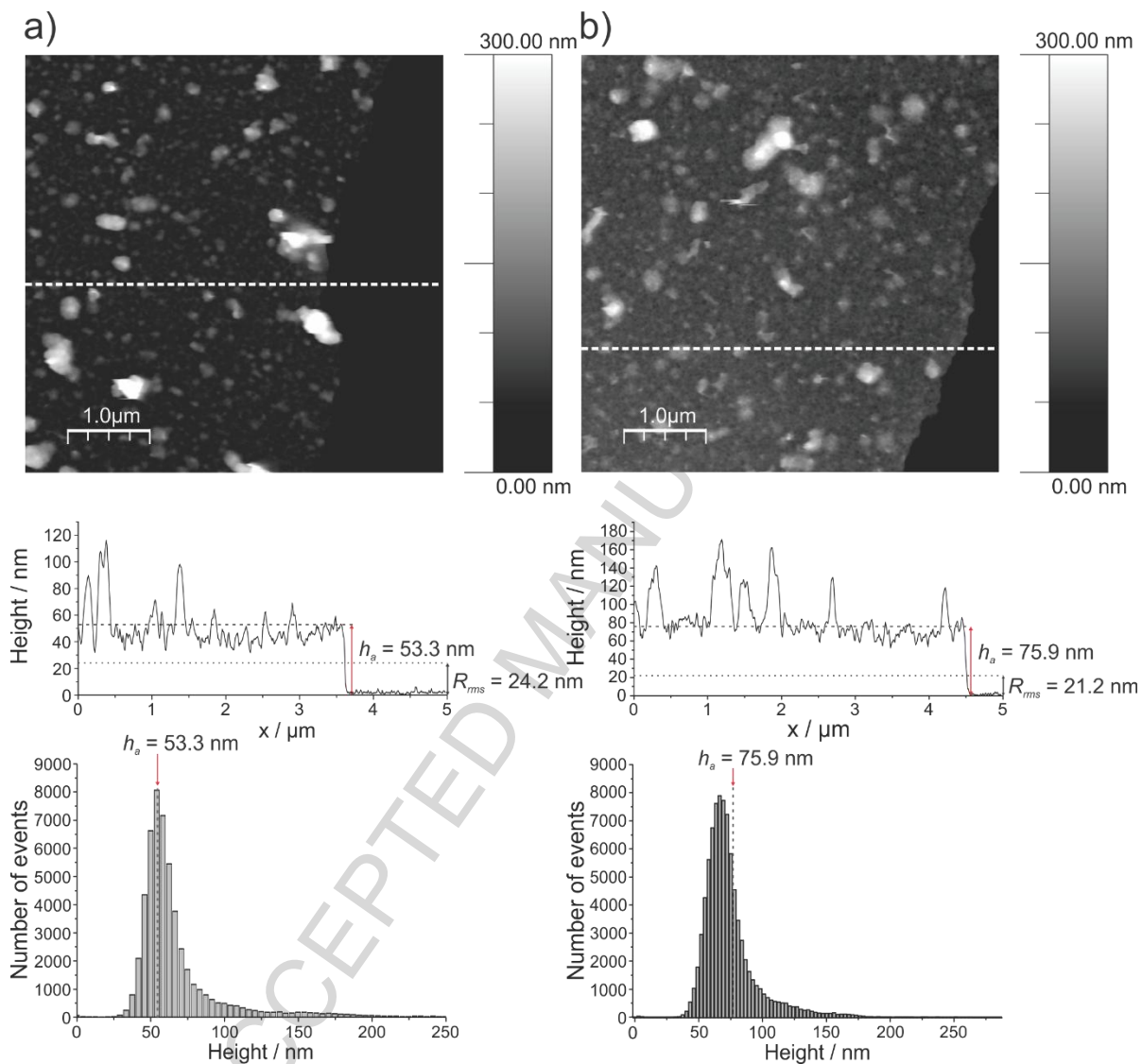


FIGURE 4: TOP - AFM 5 × 5 μm² TOPOGRAPHIC HEIGHT IMAGE OF A) (FV/CH)₅ AND B) (FV/CH)_{5.5} ON PDMS-SILICA, RECORDED IN 0.1 M KCL, PH 6 ELECTROLYTE. MIDDLE – CROSS SECTION OF THE TOPOGRAPHIC IMAGE (INDICATED BY DASHED WHITE LINE). BOTTOM – RELATIVE HEIGHT HISTOGRAM FOR THE TOPOGRAPHIC HEIGHT IMAGE.

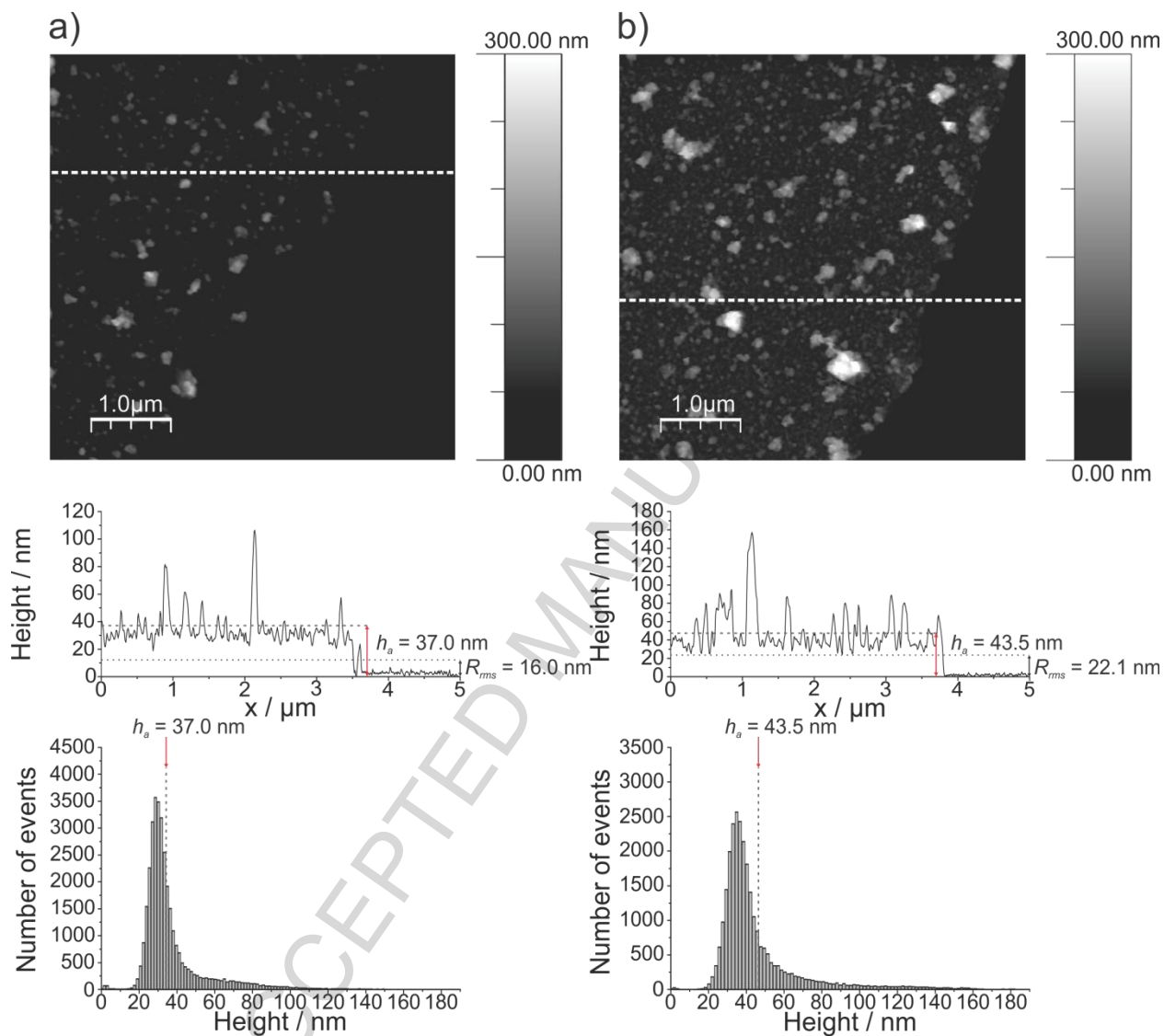


FIGURE 5: TOP - AFM $5 \times 5 \mu\text{m}^2$ TOPOGRAPHIC HEIGHT IMAGE OF A) $(\text{UP/CH})_5$ AND B) $(\text{UP/CH})_{5.5}$ ON PDMS-SILICA, RECORDED IN 0.1 M KCL, PH 6 ELECTROLYTE. MIDDLE – CROSS SECTION OF THE TOPOGRAPHIC IMAGE (INDICATED BY DASHED WHITE LINE). BOTTOM – RELATIVE HEIGHT HISTOGRAM FOR THE TOPOGRAPHIC HEIGHT IMAGE.

Table 1: Multilayer film thickness and roughness for (UP/CH) and (FV/CH) polyelectrolyte multilayers coated on PDMS.

	h_a (nm)	R_{rms} (nm)	Area Ratio Actual/Projected
(UP/CH) ₅	26.9 ± 1.5	16.0 ± 1.3	1.27 ± 0.04
(UP/CH) _{5.5}	33.4 ± 2.9	22.1 ± 2.8	1.28 ± 0.03
(FV/CH) ₅	43.2 ± 1.6	24.2 ± 2.4	1.23 ± 0.05
(FV/CH) _{5.5}	65.8 ± 3.6	21.2 ± 2.8	1.25 ± 0.04

THE COMPLETE COMPARISON BETWEEN THE MULTILAYERS ON PDMS CAN BE SEEN WITH THE EXTRACTED DATA FROM THE IMAGE PROCESSING (AVERAGE HEIGHT, RMS ROUGHNESS, AND RATIO OF ACTUAL SURFACE AREA TO PROJECTED SURFACE AREA) – GIVEN IN TABLE 1. THE DATA REVEAL ONE ADDITIONAL POINT OF DIFFERENCE BETWEEN THE TWO FUCOIDAN SYSTEMS: THE VALUE OF R_{RMS} INCREASES FOR UP/CH UPON GOING FROM 5 TO 5.5 BILAYERS. THERE IS NO SUCH INCREASE IN GOING FROM 5 TO 5.5 BILAYERS FOR FV/CH. THAT BEING SAID, THE INCREASE IN ROUGHNESS FOR UP/CH IS SMALL, AND MUCH SMALLER THAN THE INCREASE IN ROUGHNESS SEEN WHEN MULTILAYERS ARE COMPARED AT 2, 4, 6, 8, AND 10 BILAYERS CHARACTERISED IN OUR EARLIER WORK [19]. THE RATIO OF ACTUAL TO PROJECTED SURFACE AREAS PROVIDES EVIDENCE (BEYOND VISUAL INSPECTION OF THE IMAGES) THAT THE MORPHOLOGY OF THE MULTILAYERS REMAINS THE SAME UPON THE ADSORPTION OF THE LAST FUCOIDAN LAYER.

Friction Characteristics

THE LUBRICATING PROPERTIES OF PEMs FORMED ON PDMS BALLS AND DISCS WERE STUDIED USING THE MINI TRACTION MACHINE (MTM) IN 0.1 M KCL pH 6 AS THE BACKGROUND LIQUID. MEASUREMENTS WERE MADE AS A FUNCTION OF FLUID ENTRAINMENT SPEED (TO DETERMINE THE LUBRICANT STRIBECK CURVE), AND AS A FUNCTION OF APPLIED LOAD. IN THE CASE OF THE ENTRAINMENT SPEED VARIATION, MEASUREMENTS WERE MADE AS A FUNCTION OF DECREASING AND INCREASING SPEED. IN ADDITION, MULTIPLE SWEEPS IN SPEED WERE PERFORMED FOR EACH MULTILAYER SAMPLE (AND FOR MULTIPLE SAMPLES) TO VERIFY THE ROBUSTNESS AND REPRODUCIBILITY OF THE LUBRICATION PERFORMANCE (SEE FIGURE S.2 IN THE SUPPORTING INFORMATION).

BEFORE CONSIDERING THE PERFORMANCE OF THE MULTILAYERS AS LUBRICANTS, IT IS INSTRUCTIVE TO CONSIDER THE PERFORMANCE OF THE UNDERLYING MATERIAL (PDMS). PDMS, BOTH NATIVE/HYDROPHOBIC AND PLASMA-TREATED/HYDROPHILIC, WAS CHARACTERISED IN DETAIL USING THE SAME INSTRUMENT TYPE USED IN THIS STUDY, IN THE PAPER BY BONGAERTS *ET AL.* [16]. PDMS REQUIRES SURFACE MODIFICATION BEFORE USE IN BIOMATERIALS APPLICATIONS, AS THE NATIVE HYDROPHOBIC MATERIAL UNDERGOES SIGNIFICANT NON-SPECIFIC PROTEIN ADSORPTION [27]. MAKING PDMS HYDROPHILIC THROUGH CHEMICAL TREATMENT OF THE BASE MATERIAL CAN REDUCE THIS FOULING, BUT THE PDMS SURFACE WILL EVENTUALLY REVERT TO ITS NON-POLAR STATE, AND THEREFORE MORE DURABLE SURFACE TREATMENTS (SUCH AS GRAFTED PEG CHAINS OR MULTILAYER FILMS) [27] ARE REQUIRED TO MAKE SURE THAT PDMS IS FIT FOR PURPOSE. FURTHERMORE, HYDROPHOBIC/NATIVE PDMS HAS VERY POOR AQUEOUS LUBRICATION PROPERTIES

(COEFFICIENT OF FRICTION REACHING 1 AT QUITE HIGH SPEEDS – I.E. BELOW 100 MM/S) [16]. IN THIS EARLIER WORK, THE HYDROPHILIC PDMS (I.E. OXYGEN PLASMA TREATED) HAS MUCH BETTER AQUEOUS LUBRICATING PROPERTIES: NO HIGHER THAN 0.1 FRICTION COEFFICIENT OVER THE FULL RANGE OF ENTRAINMENT SPEEDS.[16] THE MECHANISM BEHIND THE ENHANCED LUBRICATION HAS THE SAME ORIGIN AS THE LOW-FOULING NATURE, I.E. THE HYDRATION OF THE SURFACE. ONCE PDMS REVERTS BACK TO NON-POLAR/HYDROPHOBIC, THIS BETTER FRICTION PERFORMANCE WILL ALSO DISAPPEAR.

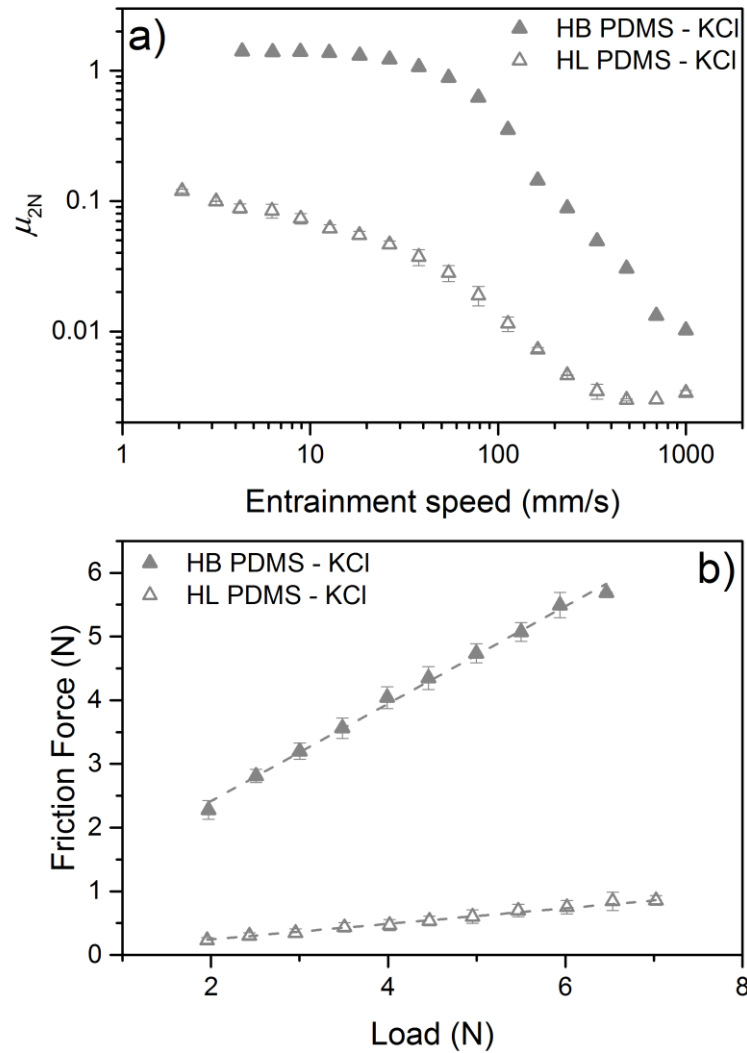


Figure 6: (a) Plot of μ_{2N} (friction coefficient, determined at $L = 2\text{N}$) versus entrainment speed; and (b) the load-dependent friction forces measured at an entrainment speed of $U = 4\text{ mm/s}$ for: (full triangles) bare hydrophobic (HB) PDMS and (empty triangles) bare hydrophillic (HL) PDMS.

ALTHOUGH MUCH IS ALREADY REPORTED IN THE LITERATURE ON THE PERFORMANCE OF PDMS IN AQUEOUS LUBRICATION (E.G. THE PAPER BY BONGAERTS *ET AL.* [16]), TO ENSURE THAT THE COMPARISON BETWEEN THE MULTILAYERS STUDIED IN THIS WORK AND THE UNDERLYING SUBSTRATE WAS AS ACCURATE AS POSSIBLE, FRESH MEASUREMENTS HAVE BEEN MADE USING EXACTLY THE SAME SOURCE OF PDMS

MATERIALS, AND AT THE SAME AQUEOUS SOLUTION CONDITIONS. PLOTS OF μ_{2N} (FRICTION COEFFICIENT, DETERMINED AT $L = 2N$) VERSUS ENTRAINMENT SPEED FOR BOTH NATIVE/HYDROPHOBIC AND PLASMA-TREATED HYDROPHILIC PDMS ARE GIVEN IN FIGURE 6. ALSO GIVEN IS THE DATA FOR THE LOAD-DEPENDENT FRICTION FORCES MEASURED AT AN ENTRAINMENT SPEED OF $U = 4$ MM/S AND $SRR = 50\%$ FOR BOTH PDMS SAMPLES (AVERAGE AND STANDARD DEVIATION FROM THREE EXPERIMENTS EACH COMPRISED OF FOUR REPLICATES). AS EXPECTED, WITH KCL SOLUTION AS THE LUBRICATING LIQUID, HYDROPHILIC PDMS GIVES DRAMATICALLY LOWER FRICTION THAN NATIVE/HYDROPHOBIC PDMS. AGAIN, AS STATED ABOVE, DUE TO REASONS OF HIGH FRICTION (NATIVE/HYDROPHOBIC PDMS) AND IMPERMANENCE OF LOW FRICTION (HYDROPHILIC PDMS WHICH WILL REVERT TO HYDROPHOBIC OVER TIME), NEITHER MATERIAL COULD BE USED IN A PRACTICAL APPLICATION OF AQUEOUS LUBRICATION, REQUIRING THE PDMS TO BE TREATED WITH A LONGER LASTING LUBRICIOUS SURFACE COATING.

PLOTS OF μ_{2N} (FRICTION COEFFICIENT, DETERMINED AT $L = 2N$) VERSUS ENTRAINMENT SPEED FOR BOTH THE (UP/CH) AND (FV/CH) MULTILAYER SYSTEMS ARE SHOWN IN FIGURE 7 (ALONG WITH DATA FOR HYDROPHILIC PDMS IN THE PRESENCE OF KCL SOLUTION AT PH 6, FOR EASE OF COMPARISON). MEASUREMENTS WERE MADE WITH BOTH INCREASING AND DECREASING SPEED, AND SWEEPS WERE MADE 5 TIMES, IN ORDER TO MONITOR ANY HYSTERETIC OR TRANSIENT EFFECTS. AN AVERAGE VALUE FROM TWO DIFFERENT SWEEPS IS GIVEN FOR EACH DATA POINT IN THE PLOT. BEFORE GOING INTO SPECIFIC COMPARISONS OF THE TWO DIFFERENT FUCOIDANS AND THE TWO DIFFERENT OUTER LAYERS, IT IS WORTH MENTIONING THAT THE VALUES OF μ_{2N} FOR THE (UP/CH) MULTILAYERS AND ONE OF THE (FV/CH) MULTILAYERS ARE SLIGHTLY

HIGHER THAN HYDROPHILIC PDMS IN THE MIXED/BOUNDARY LUBRICATION REGIME (ENTRAINMENT SPEEDS BELOW 100 MM/S), BUT MUCH LOWER THAN HYDROPHOBIC/NATIVE PDMS (SEE FIGURE 6). ALL FOUR LUBRICANT SYSTEMS ARE CHARACTERISED BY AN INCREASE IN THE VALUE OF μ_{2N} WITH DECREASING ENTRAINMENT SPEED, ATTRIBUTED TO AN INCREASE IN SURFACE CONTACT AND/OR INTERACTION BETWEEN OPPOSING PEMs. IN TERMS OF THE (UP/CH) MULTILAYERS, NO DIFFERENCE IS SEEN BETWEEN THE TWO DIFFERENT OUTER LAYERS, INDICATING THAT THERE MAY NOT BE AS STARK A DIFFERENCE IN SURFACE MECHANICAL PROPERTIES AT THIS RELATIVELY EARLY STAGE OF UP/CH FILM BUILD-UP, PERHAPS DUE TO LATERAL INHOMOGENEITY AND INTER-LAYER DIFFUSION.

THE SITUATION IS VERY DIFFERENT FOR THE TWO (FV/CH) MULTILAYERS. THE (FV/CH)₅ MULTILAYER HAS PERFORMANCE VERY SIMILAR TO BOTH (UP/CH) MULTILAYERS IN TERMS OF LUBRICATION (ALL REACHING A VALUE OF AROUND $\mu_{2N} = 0.25$ AT THE LOWEST SPEED). HOWEVER, THE ADDITION OF THE 5.5 OUTER FUCOIDAN LAYER RESULTS IN A MARKED DECREASE IN THE VALUE OF μ_{2N} , WITH A 40-50% DECREASE ONCE LUBRICATION ENTERS THE MIXED/BOUNDARY REGIME (BELOW 10 MM/S). INTERESTINGLY, THIS IS THE ONLY MULTILAYER OUT OF THE FOUR INVESTIGATED IN THIS COMPARISON THAT HAS A LAYER THICKNESS OF OVER 50 NM. IT IS VERY LIKELY THAT THE THICKER (AND HIGHLY HYDRATED) OUTER FV FUCOIDAN LAYER HAS AFFECTED IN A POSITIVE MANNER THE ABILITY OF THE MULTILAYER TO LUBRICATE THE PDMS-PDMS ROLLING/SLIDING CONTACT, AND HAS ALSO RESULTED IN A LOWER VALUE OF μ_{2N} AT ENTRAINMENT SPEEDS BELOW 100 MM/S THAN THOSE OBSERVED FOR THE PLASMA-TREATED HYDROPHILIC PDMS (IN THE PRESENCE OF THE SAME AQUEOUS SOLUTION OF KCl). FURTHERMORE, IT SHOULD BE NOTED THAT

LUBRICATING ABILITY OF THE (FV/CH)_{5.5} MULTILAYER IMPROVES OVER THE COURSE OF MULTIPLE SPEED SWEEPS (SHOWN IN FIGURE S.2), INDICATIVE OF A SHEAR-INDUCED SHIFT IN MECHANICAL PROPERTIES OR TRANSIENT WEAR EFFECT.

THE LOAD-DEPENDENT FRICTION FORCES MEASURED AT AN ENTRAINMENT SPEED OF $U = 4$ MM/S AND SRR = 50% FOR 5 AND 5.5-BILAYER OF (FV/CH) AND (UP/CH) (AND FOR BARE HYDROPHILIC PDMS IN KCL SOLUTION) ARE GIVEN IN FIGURE 8 (AVERAGE AND STANDARD DEVIATION FROM THREE EXPERIMENTS EACH COMPRISED OF FOUR REPLICATES). THE LINEAR DEPENDENCE IN THE LOAD-DEPENDENT FRICTION FORCES IS OBSERVED IN THE RANGE OF THE APPLIED LOAD, THEREBY OBEYING THE CLASSICAL AMONTON'S RELATIONSHIP FOR THE FRICTION COEFFICIENT $\mu = F_f/L$, WHERE F_f IS THE FRICTION FORCE AND L IS THE LOAD. THE LINEAR REGRESSION OF EACH SYSTEM RESULTED IN THE FRICTION COEFFICIENT (μ) AND ASSOCIATED STANDARD ERROR, WHICH IS GIVEN IN TABLE 2. THESE RESULTS SHOW THAT (FV/CH)_{5.5} IS THE MOST LUBRICATING MULTILAYER OUT OF THE SYSTEMS STUDIED, WITH A FRICTION COEFFICIENT OF $\mu = 0.073 \pm 0.002$. THIS ALSO SHOWS THAT (FV/CH)₅ IS THE LEAST LUBRICATING, AND THAT BOTH 5 AND 5.5-BILAYERS OF (UP/CH) HAVE THE SAME FRICTION COEFFICIENT VALUES, WITHIN EXPERIMENTAL ERROR. HOWEVER, AS WITH THE STRIBECK CURVE DATA, IT IS CLEAR THAT (FV/CH)₅ IS CLOSE IN BEHAVIOUR TO BOTH (UP/CH) MULTILAYERS. THE LINEAR REGRESSION ANALYSIS TO EXTRACT THE FRICTION COEFFICIENT HAS ALSO BEEN PERFORMED FOR HYDROPHILIC PDMS, YIELDING A VALUE HIGHER THAN ALL FOUR MULTILAYER SYSTEMS ($\mu = 0.124 \pm 0.001$). ALTHOUGH THE DATA IN FIGURE 6 INDICATE THAT HYDROPHILIC PDMS MATCHES OR BETTERS THE PERFORMANCE OF THE MULTILAYERS AT LOW LOAD, A MORE

DEMANDING SCENARIO (HIGHER LOADS AND LOW SPEED – SEE FIGURE 8) GIVES THE PERFORMANCE EDGE TO THE MULTILAYER COATINGS.

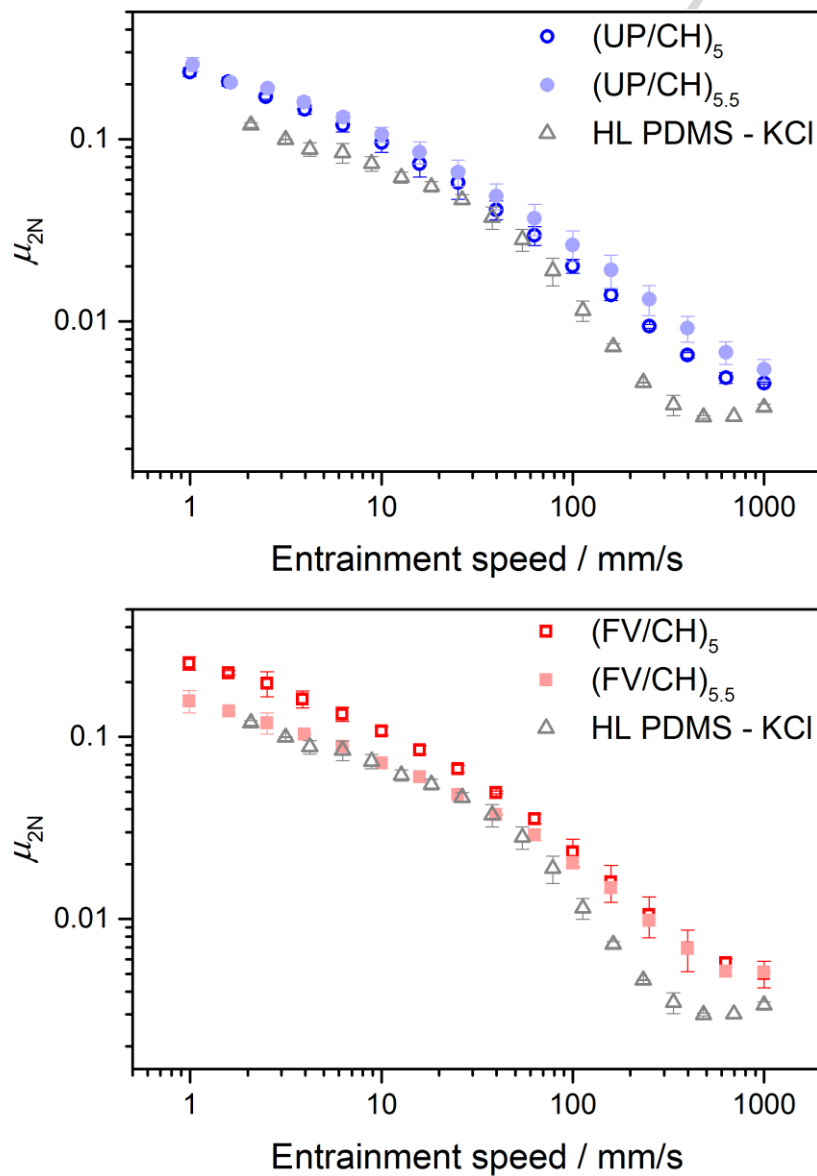


FIGURE 7: PLOTS OF μ_{2N} (FRICTION COEFFICIENT, DETERMINED AT $L = 2N$) VERSUS ENTRAINMENT SPEED FOR: TOP - (UP/CH)₅ (○) AND (UP/CH)_{5.5} (●), BOTTOM - (FV/CH)₅ (□) AND (FV/CH)_{5.5} (■) IN 0.1 M KCL pH 6. ALSO INCLUDED ARE THE DETERMINED VALUES FOR BARE HYDROPHILIC PDMS IN THE SAME ELECTROLYTE.

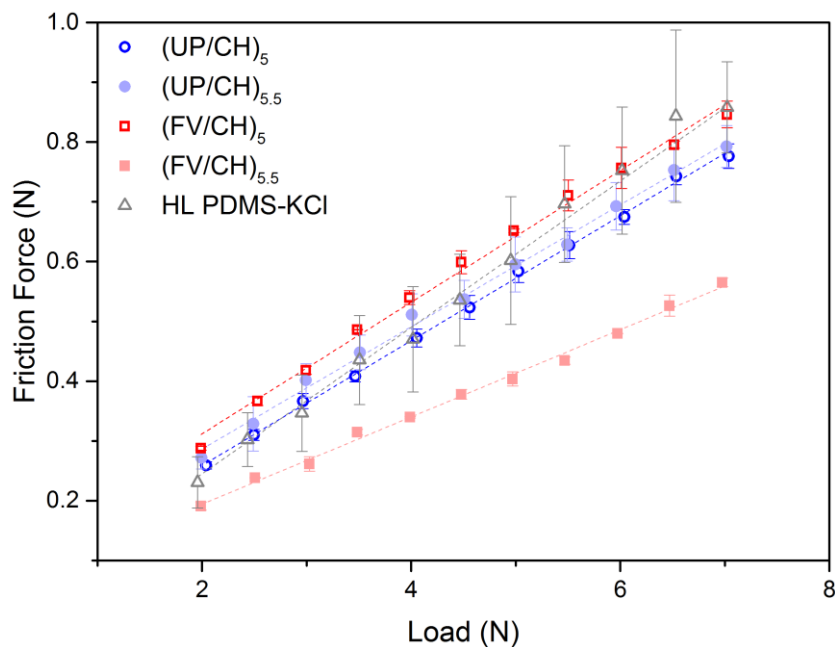


FIGURE 8 THE LOAD-DEPENDENT FRICTION FORCES MEASURED AT AN ENTRAINMENT SPEED OF $U=4$ MM/S OF (○) (UP/CH)₅, (●) (UP/CH)_{5.5}, (□) (FV/CH)₅, AND (■) (FV/CH)_{5.5}, IN 0.1 M KCL PH 6. ALSO INCLUDED ARE THE MEASURED VALUES FOR BARE HYDROPHILIC PDMS IN THE SAME ELECTROLYTE SOLUTION.

TABLE 2: DETERMINED FRICTION COEFFICIENT, μ , (LINEAR REGRESSION FROM DATA IN FIGURES 6 AND 8) FOR (UP/CH) AND (FV/CH) POLYELECTROLYTE MULTILAYER SYSTEMS AT ENTRAINMENT SPEED $U = 4$ MM/S (ALSO GIVEN IS THE VALUE FOR HYDROPHILIC PDMS)

	FRICTION COEFFICIENT, μ
(UP/CH) ₅	0.104 ± 0.001
(UP/CH) _{5.5}	0.102 ± 0.002
(FV/CH) ₅	0.113 ± 0.003
(FV/CH) _{5.5}	0.073 ± 0.002
HYDROPHILIC	0.124 ± 0.001

PDMS

DISCUSSION

THERE ARE TWO ISSUES THAT REQUIRE DISCUSSION WITH REGARD TO THE CHARACTERISATION AND LUBRICATING PROPERTIES OF THE MULTILAYERS. FIRST, IN TERMS OF THE CHARACTERISATION OF THE FILMS, IT IS CLEAR THAT, ALTHOUGH THE GENERAL MORPHOLOGY OF THE FILMS IS SIMILAR TO THOSE FORMED ON SILICA/SILICON WAFER PIECES, THE THICKNESS IS LOWER. THE MOST OBVIOUS EXPLANATION IS THAT THE SUBSTRATE HAS HAD SOME INFLUENCE ON THE BUILD-UP, WHICH IS PERHAPS EXPECTED AS THE STUDIES PERFORMED HERE ARE FOR MULTILAYERS WITH RELATIVELY FEW BILAYERS, AND THUS ANY SUBSTRATE EFFECTS WILL BE AT THEIR HIGHEST. ALTHOUGH THE THICKNESS HAS BEEN AFFECTED, THE ZETA POTENTIAL MEASUREMENTS WOULD INDICATE THAT THE BUILD-UP ON THE TWO SUBSTRATES IS SIMILAR, ALBEIT WITH SOME VARIATION IN THE MAGNITUDE OF THE ZETA POTENTIAL OBTAINED WHEN EACH LAYER ADSORBS. IN THIS WORK, THE ZETA POTENTIAL UPON ADSORPTION OF FUCOIDAN WAS APPROX. -40 TO -45 mV, AND THAT UPON ADSORPTION OF CHITOSAN WAS APPROX. +30 mV. THESE VALUES WERE OBTAINED FOR BOTH FV AND UP FUCOIDAN. FOR BUILD-UP ON SILICON WAFERS, THE VALUES ARE DIFFERENT FOR THE TWO FUCOIDANS: APPROX. -35 mV AND + 35 mV FOR FV/CH; APPROX. -30 mV AND +40 mV FOR UP/CH [19]. REGARDLESS OF THE DIFFERENCES BETWEEN MULTILAYERS PRODUCED ON PDMS RELATIVE TO SILICA, THE AFM CHARACTERISATION GIVES US AN ANCHORING POINT TO INTERPRET THE LUBRICATING PROPERTIES OF THE LAYERS.

IT IS DIFFICULT TO COMPARE THE COEFFICIENT OF FRICTION OF THE FUCOIDAN MULTILAYERS WITH THOSE OF OTHER MULTILAYER SYSTEMS IN THE WIDER LITERATURE, AS THEY HAVE BEEN DETERMINED USING VARYING SUBSTRATES (STEEL, GLASS, UHMWPE) [13-15, 28], AND WITH VARYING MEASUREMENT TECHNIQUES: LATERAL FORCE AFM [13, 15], PIN-ON-DISC TRIBOMETERS AND FLEXURE DEVICES [14, 28]. FURTHERMORE, AS MENTIONED IN THE INTRODUCTION IN MANY OF THESE STUDIES, THE LUBRICANT LAYER WAS ONLY APPLIED TO ONE SURFACE, WHICH WOULD BE EXPECTED TO RESULT IN HIGHER FRICTION BETWEEN THE TWO SURFACES AND GREATER WEAR OF THE LUBRICANT LAYER.

THE ONE SYSTEM FOR WHICH COMPARISON IS MOST VALID IS WORK PUBLISHED ON CROSS-LINKED (HA/CH) MULTILAYERS [16]. BOTH STUDIES ARE ON POLYSACCHARIDE-BASED POLYELECTROLYTE MULTILAYERS, AND BOTH REPORT DATA ON LUBRICATION OF SOFT SUBSTRATES, WITH BOTH CONTACTING SURFACES COATED WITH POLYMER LUBRICANT. THE RESULTS OF THE TWO STUDIES ALLOW US TO COMPARE AND CONTRAST THE BUILD-UP AND LUBRICATION PERFORMANCE OF TWO SEEMINGLY VERY SIMILAR SYSTEMS. IN THE WORK REPORTED HERE, THE COEFFICIENT OF FRICTION OF ALL FUCOIDAN MULTILAYERS WAS FOUND TO BE AN ORDER OF MAGNITUDE HIGHER THAN THOSE OBTAINED FOR CHEMICALLY CROSS-LINKED (HA/CH) MULTILAYERS [16]. THAT BEING SAID, THE FUCOIDAN MULTILAYERS DO HAVE MUCH LOWER COEFFICIENTS OF FRICTION THAN THAT OF HYDROPHOBIC PDMS (SEE FIGURE 6), WHICH INDICATES THAT THEY ARE EFFECTIVE LUBRICANTS. FURTHERMORE, THEY ALSO PRODUCE FRICTION COEFFICIENTS AT LOW LOAD (μ_{2N}) THAT ARE EQUAL TO OR BETTER THAN HYDROPHILIC PDMS (SEE FIGURES 6 AND 7). ALL MULTILAYERS GIVE SIGNIFICANTLY

LOWER DETERMINED FRICTION COEFFICIENTS (μ , FROM LINEAR REGRESSION OF LOAD-DEPENDENT MEASUREMENTS OF FRICTION FORCE) THAN HYDROPHILIC PDMS.

ALTHOUGH WE DO NOT HAVE QCM-D CHARACTERISATION FOR THE FUCOIDAN MULTILAYERS ON PDMS, THE DATA WE HAVE FOR THE SAME MULTILAYERS ON SILICA-COATED QCM SENSORS [19] ALLOWS US TO MORE CLOSELY COMPARE THE TWO DIFFERENT MULTILAYER SYSTEMS (CROSS-LINKED (HA/CH) AND (FUCOIDAN/CH)). THE FREQUENCY AND DISSIPATION DATA FOR THE TWO SYSTEMS [16, 19] INDICATE THAT AT THE SAME POINT IN THE FORMATION CYCLE (5 BILAYERS), THE FREQUENCY CHANGE IS LOWER AND THE DISSIPATION CHANGE IS HIGHER FOR THE (HA/CH) CROSS LINKED SYSTEM, IMPLYING A LOWER ADSORBED MASS AND A HIGHER HYDRATION CONTENT RELATIVE TO THE FUCOIDAN MULTILAYERS STUDIED IN THIS WORK.

CROSS-LINKING MAY HAVE BEEN EXPECTED TO RESULT IN LOWER HYDRATION FOR THE (HA/CH) SYSTEM (RELATIVE TO THE (FUCOIDAN/CH) SYSTEMS), BUT IT WOULD APPEAR THAT THE DOMINANT EFFECT FOR HYDRATION WAS THE FORMATION CONDITIONS OF THE TWO SYSTEMS. THE (HA/CH) SYSTEM WAS FORMED AT pH 4.3, WITH ONLY PARTIAL CHARGING OF THE CARBOXYL GROUPS OF THE HA COMPONENT, LEADING TO LOWER ION PAIRING BETWEEN POLYANION AND POLYCATION, AND A LESS DENSE/MORE HYDRATED MULTILAYER. FUCOIDAN POLYMERS ARE STRONG POLYELECTROLYTES (FULLY CHARGED UNDER MOST pH CONDITIONS) AND IN THIS WORK MULTILAYERS WERE FORMED AT A pH FOR WHICH THE CHITOSAN IS ALSO HIGHLY CHARGED. THIS HAS LED TO MORE ION PAIRING BETWEEN POLYANION AND POLYCATION, AND A MORE DENSE/LESS HYDRATED MULTILAYER. EVIDENTLY, THIS LOWER HYDRATION HAS RESULTED IN POORER LUBRICATION PERFORMANCE RELATIVE TO THE (HA/CH) SYSTEM. IT IS POSSIBLE ALSO THAT THE CROSS-LINKED NATURE OF THE (HA/CH)

WOULD ENHANCE THE WEAR RESISTANCE OF MULTILAYER LUBRICANT RELATIVE TO NON-CROSS LINKED SYSTEMS. THE (HA/CH) SYSTEM WAS SEEN TO BE RESILIENT TO DRYING/REHYDRATION CYCLING DURING FRICTION MEASUREMENTS [16]. HOWEVER, THE (FUCOIDAN/CH) SYSTEMS STUDIED HERE ALSO SHOW REASONABLE WEAR RESISTANCE, WITH SIMILAR FRICTION PERFORMANCE OVER MULTIPLE SWEEPS OF ENTRAINMENT SPEED AND MULTIPLE RUNS OF MEASUREMENT (SEE FIGURE S.2).

ONE OTHER LITERATURE COMPARISON THAT MAY YIELD SOME INSIGHT INTO OUR OBSERVATIONS COMES BY LOOKING AT THE WORK OF DAI *ET AL.* ON PAH/PAA MULTILAYERS THAT HAD BEEN HEAT TREATED TO INDUCE CROSS LINKING [15]. THE CROSS LINKING WAS OBSERVED TO REDUCE THE DEGREE OF AFM TIP-INDUCED DAMAGE DURING LATERAL FORCE MEASUREMENT (IN WHICH THEY OBSERVED THE REMOVAL OF THE TOP 1/4 OF THEIR MULTILAYER – FOR BOTH CROSS-LINKED AND NON CROSS-LINKED – BUT WITH LONGER RESISTANCE TO REMOVAL FOR THE CROSS LINKED SYSTEM). INTERESTINGLY, IN THE WORK OF DAI *ET AL.*, THE MORPHOLOGY OF THE MULTILAYERS HAD ISLAND FEATURES THAT WERE REMOVED DURING THE SCANNING ACTION OF THE AFM TIP, LEAVING BEHIND A SMOOTH RESIDUAL POLYMER FILM, WHICH WAS RESPONSIBLE FOR THE MAJORITY OF THE LUBRICATION. IT IS POSSIBLE THAT IN THE FUCOIDAN SYSTEM THE ROUGH FEATURES OF THE MULTILAYER ARE REMOVED DURING THE INITIAL SLIDING PERIOD IN THE MTM, WHICH COULD EXPLAIN THE TRANSIENT CHANGES IN FRICTION OBSERVED IN FIGURE S.2 FOR FV (ALTHOUGH IT IS NOT OBSERVED FOR THE UP MULTILAYERS). IF TRUE, THEN THE THICKNESS DEPENDENCE OF THE FRICTION COEFFICIENT MIGHT BEST BE CORRELATED WITH THE THICKNESS OF THE SUB-LAYER ON WHICH THE ISLAND FEATURES ARE LOCATED, AS IT IS THIS MATERIAL THAT WILL BE RETAINED IN THE SLIDING CONTACT. THE

DETERMINED SUB-LAYER THICKNESSES FOR 5 AND 5.5-BILAYERS OF (UP/CH) WERE 22.9 NM AND 25.2 NM, RESPECTIVELY, SHOWING A THICKNESS INCREASE OF ONLY 10%, AS OPPOSED TO NEARLY DOUBLE FOR (FV/CH), WITH A THICKNESSES FOR 5 AND 5-5 BILAYERS OF 31.8 NM AND 61.5 NM, RESPECTIVELY. THIS INCREASED RELATIVE THICKNESS INCREASE WITH LAYER NUMBER FOR THE (FV/CH) SYSTEM ON PDMS IS IN AGREEMENT WITH OUR OBSERVATIONS FOR THE TWO MULTILAYERS FORMING ON SILICON WAFER, WITH (FV/CH) SHOWING A MARKED NON-LINEAR INCREASE IN THICKNESS WITH LAYER NUMBER (DETERMINED FROM SPECTROSCOPIC ELLIPSOMETRY AND AFM [19]), WHEREAS (UP/CH) MULTILAYERS INCREASED IN THICKNESS ALMOST LINEARLY [19, 20]. THE INCREASED THICKNESS (AND MOST LIKELY THE INCREASED HYDRATION) OF FV FUCOIDAN/CHITOSAN MULTILAYERS WOULD APPEAR TO BE MORE ADVANTAGEOUS FOR LUBRICATION THAN THE INTER-POLYMER HYDROGEN BONDING BETWEEN UP FUCOIDAN AND CHITOSAN [19], SINCE IT LIKELY FACILITATES BETTER DYNAMIC DE-WETTING/RE-WETTING OF THE AQUEOUS LUBRICANT ON THE TRIBO-SURFACES.

CONCLUSIONS

THE MACROSCALE FRICTIONAL PROPERTIES OF FUCOIDAN/CHITOSAN PEMs MADE FROM TWO DIFFERENT EXTRACTS OF FUCOIDAN (UP AND FV) WERE STUDIED. THE LOWEST COEFFICIENT OF FRICTION WAS OBSERVED FOR THE FV/CH SYSTEM, WHEN FV WAS THE OUTER LAYER. THE LOWEST FRICTION FOR THE (FV/CH)_{5.5} SAMPLE CORRELATED WITH THE INCREASED THICKNESS OF THE LAYER, AS DETERMINED FROM AFM IMAGING. THE LUBRICATION OF PDMS SURFACES COATED WITH THE MULTILAYERS MATCH OR

IMPROVES UPON THAT OF BARE HYDROPHILIC PDMS (AND IS MUCH BETTER THAN BARE HYDROPHOBIC PDMS) AT LOW LOAD, AND ALL SURPASS HYDROPHILIC PDMS AT INCREASED LOAD. GIVEN THAT THESE MULTILAYERS WOULD BE EXPECTED TO HAVE MORE STABLE HYDRATION/HYDROPHILICITY (AND THUS LUBRICATION) OVER A LONGER TIME PERIOD THAN HYDROPHILIC PDMS, THEY REPRESENT A VIABLE OPTION FOR LUBRICATING SOFT BIOMATERIALS. THE LOWER HYDRATION WITHIN THE MULTILAYER IS MOST LIKELY RESPONSIBLE FOR THE POORER PERFORMANCE OF THESE MULTILAYERS RELATIVE TO PREVIOUSLY STUDIED HYALURONIC ACID/CHITOSAN MULTILAYERS. HOWEVER, FUCOIDAN-BASED MULTILAYERS HAVE POTENTIAL SECONDARY BENEFITS (ENHANCED ANTIMICROBIAL EFFECT; RESISTANCE TO ENZYMATIC DEGRADATION) THAT COULD MAKE THEM MORE DESIRABLE WHEN DEPLOYED AS A BIOMATERIALS SURFACE COATING.

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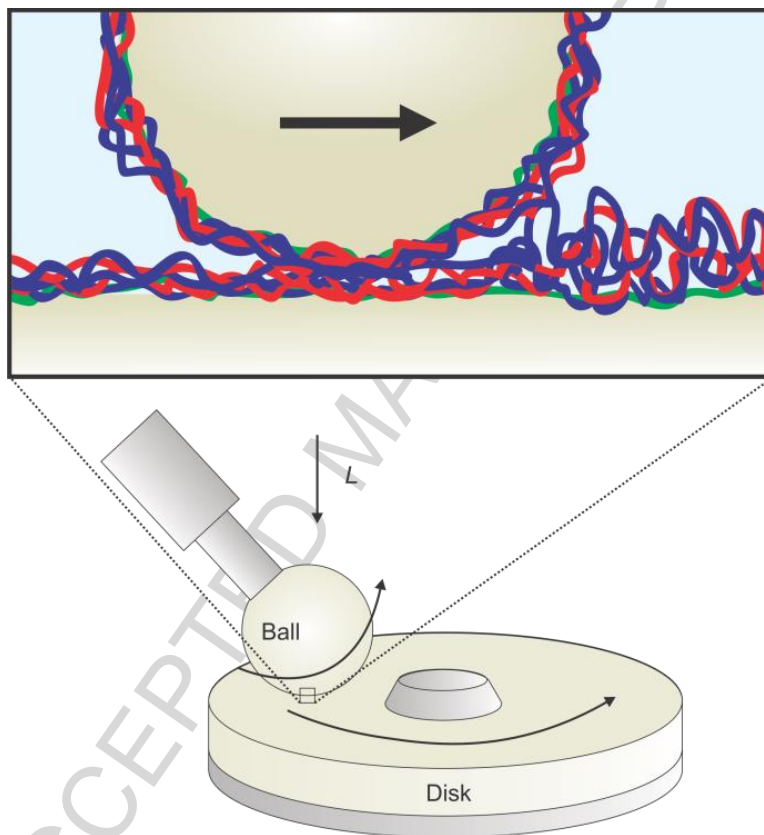
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Graphical Abstract



HIGHLIGHTS:

- NATURAL POLYSACCHARIDE POLYELECTROLYTE MULTILAYER LUBRICANT FORMED ON SOFT PDMS SUBSTRATES USING FUCOIDAN AND CHITOSAN
- ZETA POTENTIAL DETERMINATION AND AFM CONFIRM THE SEQUENTIAL BUILD-UP OF THE LUBRICANT (LAYER-BY-LAYER)
- FRICTION-REDUCING PROPERTIES STUDIED USING SOFT TRIBOLOGY MEASUREMENTS, REVEALING EFFECTIVE AQUEOUS LUBRICATION
- THICKNESS (AND ASSUMED HIGHER HYDRATION) SEEN TO BE MORE IMPORTANT FOR REDUCTION OF FRICTION