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Macrotribological Studies of Poly(*L*-lysine)-*graft*-Poly(ethylene glycol) in Aqueous Glycerol Mixtures

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Abstract We have investigated the tribological properties of surfaces with adsorbed poly(*L*-lysine)-*graft*-poly(ethylene glycol) (PLL-*g*-PEG) sliding in aqueous glycerol solutions under different lubrication regimes. Glycerol is a polar, biocompatible liquid with a significantly higher viscosity than that of water. Macrotribological performance was investigated by means of pin-on-disk and mini-traction-machine measurements in glycerol-PLL-*g*-PEG-aqueous buffer mixtures of varying compositions. Adsorption studies of PLL-*g*-PEG from these mixtures were conducted with the quartz-crystal-microbalance technique. The enhanced viscosity of the glycerol-containing lubricant reduces the coefficient of friction due to increased hydrodynamic forces, leading to a more effective separation of the sliding partners, while the presence of hydrated polymer brushes at the interface leads to an entropically driven repulsion, which also helps mitigate direct asperity–asperity contact between the solid surfaces under boundary-lubrication conditions. The combination of polymer layers on surfaces with aqueous phases of enhanced viscosity thus enables the friction to be reduced by several orders of magnitude, compared to the behavior of pure water, over a large range of sliding speeds. The individual contributions of the polymer and the aqueous glycerol solutions in reducing the friction have been studied across different lubrication regimes.

Keywords Boundary lubrication · Aqueous lubrication · Glycerol · Polymer brushes · Viscosity

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1 Introduction

The study of macromolecules at the solid–liquid interface has led to improved understanding and new technologies in many fields including colloid science, biomedicine, and tribology [1]. Klein et al. have studied the shear forces between polymer-bearing surfaces with the surface-forces apparatus, to understand the frictional forces at the interface. These studies show that when two surfaces covered with a high density of terminally attached polymers are immersed in a good solvent and brought into contact, the swollen polymer brushes reduce interfacial frictional forces [2]. As they approach each other, opposing polymer brushes exhibit repulsive forces due to osmotic effects on the one hand and the free-energy penalty (due to reduced configurational entropy) resulting from the overlap of the brush layers on the other. There have been several studies, both theoretical [3] and experimental [4, 5] that have investigated the origin of frictional forces between contacting brushes at different shear rates. For water-soluble polymer brushes in aqueous environments, the presence of bound (or 'hydration') water surrounding the polymer chains can result in structural forces between the hydrated brushes [6]. Strongly hydrated polymers, together with a continuous rapid exchange of bound water with other free water molecules, keep the surfaces separated while maintaining a high fluidity at the brush–brush interface at high compressions, thus leading to a very low coefficient of friction [7, 8].

Aqueous lubrication is of interest in a number of technological applications where lubrication with oil presents contamination problems. This is the case, for example, in the food, textile, and pharmaceutical industries. The adsorption of synthetic, hydrated polymer brushes at the interface overcomes the drawback of the low viscosity of

water and, to some extent, mimics the situation encountered in nature [9]. Adsorption of the poly(L-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG) copolymer has been extensively used [10, 11] as a facile approach for the attachment of water-compatible polymer brushes to surfaces. Studies have been conducted to understand the lubrication properties of these polymer brushes both at macroscopic [11, 12] and at nanoscopic scales [13, 14] in aqueous environments. PLL-g-PEG contains a positively charged polypeptide backbone that adsorbs spontaneously via electrostatic interactions onto several metal oxide surfaces, such as TiO_2, Nb_2O_5, and SiO_2 at neutral pH. In aqueous media, PEG chains become hydrated to form "brush-like" structures at the interface, which reduce the frictional forces when surfaces are rubbed against each other. If sheared off under tribological stress, the electrostatically attached polymers can immediately be replaced by molecules readsorbing from solution and thus can act as better lubricants when compared to covalently attached polymers [15], since the latter generally require specific, non-aqueous reaction conditions for reattachment.

Along with polymer architecture [11], the quality of the solvent surrounding the polymer brush is an important parameter for determining both adsorption kinetics and lubrication properties [16–18]. For end-grafted polymers in poor solvents, the cohesive forces between polymer molecules (both inter- and intrachain) or polymers and surface dominate, resulting in a dense collapsed structure of the polymer when adsorbed on the surface (pancake structure). In contrast, good solvents can induce, at low surface coverages, a structure resembling that of the free polymer chains in solution (mushroom structure), or, at high coverages, a significant stretching of the polymers leading to a polymer brush. Several studies have been conducted to understand the effect of solvent quality on the structure and stability of brushes [18, 19]. The structural changes and preferential solvation of polymer brushes have been studied in detail [20–22] by varying the solvent quality using binary solutions, which contain varying volume fractions of good and bad solvents in the solution. Müller et al. [22] studied the frictional properties of adsorbed PLL-g-PEG polymers on silica surfaces using colloidal-probe AFM for binary mixtures of water and 2-propanol. They observed little or no variation in the frictional properties of the brushes until the critical volume fraction of $\phi = 0.85$ (2-propanol) is reached, beyond which the friction increases remarkably with even a slight increase in the volume fraction of the solvent.

In this study, we have investigated the tribological properties of PLL-g-PEG copolymer brushes in binary mixtures of buffer solution and glycerol. Studies of the fluidity of water, when it is confined as a molecularly thin film between two solid surfaces, show that there is only a nominal increase in the viscosity of the confined water at the interface [23]. In contrast to the behavior of oils, the low pressure-viscosity coefficient of water can impose a major constraint for aqueous tribology at high loads, since the boundary regime is extended to higher speeds. Increasing viscosity by the addition of water-compatible viscous fluids is an alternative approach to rectifying this situation. Glycerol is a polar, biocompatible, and highly viscous liquid, which readily dissolves in water. As PEG does not dissolve in glycerol, glycerol behaves as a poor solvent in the buffer-solution–glycerol binary mixture. We have conducted tribological tests at various speeds and loads with buffer-solution–glycerol solutions of different compositions and viscosities and explored the effect of polymer brushes across different lubrication regimes. It was found that a combination of polymer brushes and the enhanced viscosity obtained by glycerol addition provided effective lubrication over a wide range of speeds, and therefore lubrication regimes. While the enhanced viscosity fluids were highly effective in extending the hydrodynamic regime to lower speeds, it was clear that the polymer brushes enhanced lubrication within the boundary and mixed regimes. The adsorption kinetics of polymers from viscous binary solutions has also been investigated. Lastly, a calculation of the lubricating film thickness at the interface determines the importance of polymer brushes at the interface under different lubrication regimes.

2 Materials and Methods

All tribological experiments were conducted with a steel ball loaded against a glass disk. HEPES [10 mM of 4-(2-hydroxyethyl)-1-piperazine-1-ethanesulfonic acid (Sigma, St. Louis, MO, USA), with 6.0 M NaOH solution] was used as the aqueous buffer to maintain the pH at 7.4. Due to the low isoelectric point of silicon dioxide (~ 2), negative charges reside on the surface at neutral pH. These negatively charged surfaces adsorb the positively charged backbones of PLL-g-PEG copolymers to form brush-like structures spontaneously upon immersion in the aqueous-polymer-containing solution.

2.1 Materials Used

PLL-g-PEG copolymer was purchased from SuSoS AG (Dübendorf, Switzerland). The specific copolymer used, PLL(20)-g(3.6)-PEG(5), with a PLL molecular weight of 20 kDa, PEG side chains of molecular weight 5 kDa, and a grafting ratio (number of lysine units/number of PEG chains) of 3.6 shows maximum adsorption on the surface and optimum brush density to maintain a hydrated and stretched brush structure [11]. For all tribological

experiments, a polymer concentration of 0.25 mg/ml in HEPES was used, which is a sufficient concentration for the rapid re-healing of the polymers following tribocontact [15]. Different volume percentages of either glycerol or ethylene glycol in HEPES (0, 25, 50, and 75% v/v) were used as binary mixtures to vary the viscosity of the solution at the tribological contact. Glycerol (ABCR GmbH, Karlsruhe, Germany) and ethylene glycol (Aldrich-Sigma, Steinheim, Germany) were used without further processing. PLL-*g*-PEG does not dissolve either in pure glycerol or pure ethylene glycol, and thus experiments with the undiluted liquids were not conducted. Viscosities of the mixtures according to their volume fractions are given in Table 1. All polymer solutions were freshly prepared just before the experiment and were homogenized in a sonicator for 15–20 min before use.

2.2 Tribological Experiments

Disks and balls used for the tribological tests were sonicated in ethanol absolute (Scharlau, Analytical grade, ACS, Sentmenat, Spain) in Teflon boxes for 30 min. N_2-dried samples were then plasma-treated in an oxygen environment (for pin-on-disk) and in air (for MTM) for 90 s to remove adventitious organic matter. Treated disks and balls were transferred to the polymer solution and the experiments conducted after soaking for a minimum of 30 min.

2.3 Pin-on-disk Measurements

Pin-on-disk tribometers (CSEM, Neuchâtel, Switzerland) were used to measure macroscopic frictional forces under pure sliding conditions. Two tribometers operating in different speed ranges were employed to enable the sliding speed to be varied over a wide range. The slower tribometer measures frictional forces in the speed range of 0.1–20 mm/s and the faster tribometer from 25 to 400 mm/s. A fixed pin that holds the steel ball (diameter = 6 mm, DIN 5401-20 G20, Hydrel AG, Romanshorn, Switzerland) was

Table 1 Dynamic viscosities (mPa s) for different percentages of glycerol and ethylene glycol in water at 25 °C [33, 34]

Concentration of glycerol/ethylene glycol in water (vol.%)	Dynamic viscosity of glycerol–water mixture at 25 °C (mPa s)	Dynamic viscosity of ethylene-glycol–water mixture at 25°C (mPa s)
0	0.893	0.893
25	1.81	1.5
50	5.04	2.8
75	27.7	7.75
100	945	14

brought into contact with the flat, rotating glass slide (2.5×2.5 cm^2, 1-mm thick; Super Frost microscope slides, Menzel Gläser, Braunschweig, Germany with a composition as specified by the manufacturer: 72.2% SiO_2, 14.3% Na_2O, 1.2% K_2O, 6.4% CaO, 4.3% MgO, 1.2% Al_2O_3, 0.03% Fe_2O_3, and 0.3% SO_3). RMS roughness values of the steel ball and the glass disk were measured by AFM as 32 and 5 nm, respectively. A stainless steel cup held the polymer solution (capacity ∼20 ml) such that the pin and disk were completely immersed in the solution. The coefficient of friction (μ) is plotted as a function of number of laps under a normal load of 2 N for all experiments (Hertzian contact pressure = 0.34 GPa). Experiments were conducted at ambient temperature and a fresh track and new pin were used for every measurement. Data acquisition and operating speeds were controlled by means of *Tribo X* software (InstrumX version 2.5A, CSM Instruments, Switzerland). Friction coefficients were averaged over 200 laps for speeds above 20 mm/s and over 50 laps for speeds below 20 mm/s.

2.4 Mini-Traction-Machine Measurements

The mini-traction-machine (MTM, PCS instruments, London, UK) was used to measure frictional forces in rolling contact between PEG-coated surfaces immersed in the copolymer solutions. In the experimental setup, a 9.5-mm radius steel ball (AISI 52100, RMS roughness = 11 nm, PCS Instruments, London, UK) was brought into contact with a 46-mm diameter glass disk (RMS roughness = 2 nm, PCS Instruments, London, UK). Only one track with a radius of 20.7 mm per disk was used. The rotation of the ball and the disk can be independently controlled and thus a mixture of sliding and rolling can be achieved. The slide/roll ratio (SRR) is defined as the percentage ratio of the difference between the ball and the disk speed to the mean of ball (u_{ball}) and disk speed (u_{disk}); SRR = $(u_{ball} - u_{disk})/[(u_{ball} + u_{disk})/2]$. The SRR varies from 0 to 200% with SRR = 0% ($u_{ball} = u_{disk}$) representing pure rolling and SRR = 200% for complete sliding conditions. A SRR of 10% was used for all experiments to maintain the conditions of near-pure rolling. Using the manufacturer's software (PCS Instruments, MTM version 1.0, London, UK) the speed can be varied from 0 to 2500 mm/s. A load of 10 N was applied (Hertzian contact pressure = 0.42 GPa) and the coefficient of friction measured as a function of the mean speed of the disk and the ball. A temperature of 25 °C was maintained by means of a water bath. New disks and balls were used for every measurement.

2.5 Quartz Crystal Microbalance

The quartz crystal microbalance (QCM) is a mass-sensing device. In contrast to many other mass-sensing techniques

that work under liquids, QCM is sensitive to the mass of both the adsorbed polymer layer and the mass of the solvent associated with it. The measurements were performed with a commercially available QCM with dissipation monitoring (Q-sense, Gothenburg, Sweden).

AT-cut quartz crystals (diameter = 25 mm) coated with SiO_2 (QSX 303, LOT Oriel Group, Germany) with a fundamental frequency of 5 MHz were used to study the mass of the polymer adsorbed from different HEPES–glycerol mixtures. QCM oscillators can be used to monitor the change in mass (Δm) by measuring the change in resonance frequency (Δf) of the crystal resonator during polymer adsorption. Frequencies can be measured over different overtones ($n = 1$ to $n = 13$), which have different surface-sensitivities associated with them. According to the Sauerbrey equation, the mass of the adsorbed polymer along with its associated water molecules can be calculated by:

$$m_{Sauerbrey} = -C\frac{\Delta f}{n}$$

where $m_{Sauerbrey}$ is the wet mass of the polymer adsorbed, Δf is the change in frequency of the quartz crystal upon adsorption, C is the characteristic constant of the instrument and n is the shear wave number.

Quartz crystals were cleaned in ethanol for 30 min and then ozone-treated for 30 min before placing them in the QCM chamber. Inlet and outlet tubing and the QCM chambers were rinsed with ultra pure water (GenPure UV, TKA GmbH, Niederelbert, Germany) before use. The fundamental frequencies were characterized in pure water. The chamber is designed to provide a non-perturbing exchange of liquids over the quartz crystal by means of a pump. A flow rate of 20 μl/min was used and the chamber temperature was maintained at 25 °C during all of the measurements.

3 Results and Discussion

3.1 Tribological Studies of PLL-*g*-PEG in Aqueous Glycerol Solutions

The coefficient of friction (μ) under sliding, measured with the pin-on-disk tribometer, has been plotted as a function of speed (0.1–400 mm/s) for different HEPES–glycerol mixtures in Fig. 1. μ was observed to decrease with increasing sliding velocity, implying the onset of the mixed lubrication regime. Since hydrodynamic forces are viscosity-dependent, increasing the volume fraction of glycerol in the mixture leads to an additional decrease in μ (within the mixed lubrication regime), for a given speed range. A polymer-free HEPES–glycerol solution with a glycerol 75% v/v showed a 55% (from 0.45 to 0.2)
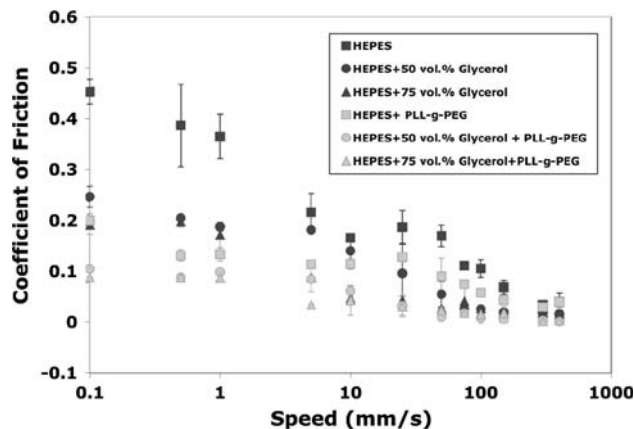

Fig. 1 Speed dependence of coefficient of friction (μ) from pin-on-disk measurements for different compositions of HEPES–glycerol mixtures with (▢) and without (■) polymer

reduction in friction at a sliding velocity of 0.1 mm/s in comparison to pure HEPES solution at the same speed. The coefficient of friction values in the absence of polymer appear to converge at 150 mm/s irrespective of the viscosity of the operating fluid, suggesting that asperity contacts between surfaces are no longer occurring; the frictional forces originate only from viscous dissipation within the fluid film, and thus the coefficient of friction at the interface diminishes to a very low value.

PLL-*g*-PEG, when adsorbed from HEPES onto glass and steel surfaces, has been observed to reduce the coefficient of friction at the sliding interface [12]. The adsorption of PLL-*g*-PEG polymers from viscous HEPES–glycerol solutions has been observed by means of the QCM technique (Fig. 2). The change in the fundamental frequency of the crystal measured in real time provides an indication of the adsorption kinetics of the polymer along with the total adsorbed polymer mass (including that of the associated solvent). Since the adsorbed polymer will undergo a mushroom-brush transition during the adsorption process, the mass fraction of solvent associated with the polymer changes. Figure 2 shows the changes in frequency of the crystals in the 7th overtone while adsorbing PLL-*g*-PEG from different binary mixtures of HEPES and glycerol (0, 25, and 50% v/v of glycerol in HEPES). The percentage of glycerol in HEPES never exceeded 50%, as the free flow of higher concentration solutions through the thin inlet tubing was restricted due to the high viscous drag present.

In the polymer-adsorption studies carried out with different HEPES–glycerol solutions, the baseline was first obtained in HEPES buffer and the solution subsequently exchanged with the HEPES–glycerol mixture (arrow marked 'A' in Fig. 2). A decrease in the resonant frequency of the crystal was observed due to the drag forces
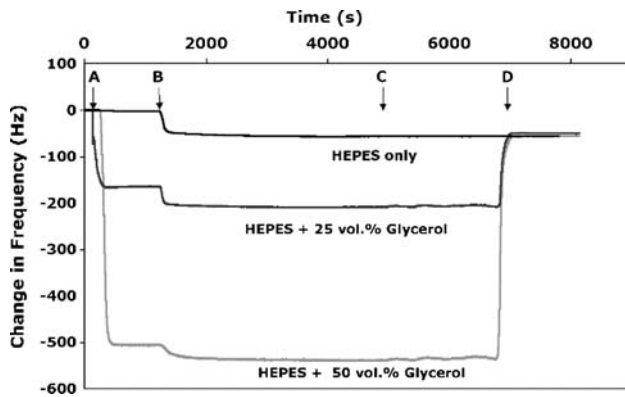
Fig. 2 Change in oscillating frequency of QCM crystal coated with SiO₂ with time during the adsorption of PLL-*g*-PEG from different compositions of HEPES–glycerol mixtures. The baseline was obtained in HEPES for all experiments. *A* Injection of HEPES–glycerol mixtures without polymer, *B* injection of PLL-*g*-PEG dissolved in corresponding HEPES–glycerol mixture, *C* rinsing of the physisorbed polymer with HEPES–glycerol solutions, *D* exchanging the solution back to HEPES

on the crystal originating from the viscosity of the solution. PLL-*g*-PEG dissolved in a HEPES–glycerol solution of the same mixing ratio, at a polymer concentration of 0.25 mg/ml, was injected into the cell (B). The kinetics of adsorption of the copolymers onto the bare SiO₂ surface are observed. The adsorption was carried out in flow mode until no further decrease in the frequency was seen. The crystal was then rinsed with the HEPES–glycerol mixture to remove any physisorbed or loosely bound copolymers from the crystal (C). The solution was finally exchanged back to HEPES solution (D) and the change in the frequency with respect to the baseline noted.

The total mass of copolymer adsorbed on the SiO₂ surfaces from HEPES–glycerol mixtures is comparable to that adsorbed from pure HEPES solution. The changes in frequency and the corresponding mass of the polymer for different HEPES–glycerol ratios have been tabulated (Table 2). In calculating the adsorbed polymer mass on the crystal, the effect of dissipative forces arising from the viscosity of the HEPES–glycerol solutions is eliminated by taking the difference in frequencies measured in pure HEPES solution before and after adsorption for all HEPES–glycerol mixtures. We also note that the viscoelastic nature of the polymer is not considered in the mass calculations from the Sauerbrey equation. The polymer on the surface is considered to be stiff and rigid to calculate the wet mass of the polymer. This is a gross approximation, and thus the calculated mass can only be considered for comparing the amount of mass adsorbed from different solutions. The calculated masses show a comparable adsorption of the polymer onto the SiO₂-coated quartz surface from different HEPES–glycerol solution compositions.

Table 2 The change in frequency and the corresponding mass of PLL-*g*-PEG adsorbed on the SiO₂-coated QCM crystal from HEPES–glycerol mixtures

Concentration of glycerol in water (vol.%)	Change in frequency upon polymer adsorption relative to baseline (Hz)	Mass of the adsorbed polymer, including solvent (from Sauerbrey equation) (ng/cm²)
0	−55	135
25	−54	133
50	−55	135

The wet mass of the polymer is calculated from the Sauerbrey equation. The visco-elastic properties of the polymer in the solution are neglected ($C = 17.7$ ng cm^{-2} Hz^{-1} for a 5 MHz crystal and $n = 7$th overtone)

The polymer, when adsorbed from viscous solutions assists in the reduction in the coefficient of friction (Fig. 1) under the boundary- and mixed-lubrication conditions of pin-on-disk tribometry. The reduction in the friction was observed to be about 60% (from 0.25 to 0.1) at 0.1 mm/s when the polymer was adsorbed at the interface from 50% v/v HEPES–glycerol solution in comparison to a similar system with no polymer at the interface. The coefficient of friction also appears to converge at high speed (150 mm/s) in the presence of polymer for all HEPES–glycerol mixtures, indicating no effect of the polymer on friction as the surfaces become completely separated by a fluid film.

A MTM, in nearly pure rolling contact, can be operated at higher speeds in comparison to pin-on-disk experiments. Thus, MTM can be used to characterize the lubrication behavior of PLL-*g*-PEG copolymer in HEPES–glycerol mixtures in lubrication regimes beyond boundary lubrication. Milder shear stresses are applied to the adsorbed copolymer in rolling contact as compared to the sliding pin-on-disk experiments. Thus, the values of coefficient of friction for MTM measurements are observed to be much lower than for pin-on-disk experiments for the same speeds and solvent conditions, since the removal of polymer from the surface by shear (itself a dissipative process) is a less frequent occurrence. Coefficients of friction for different percentages of glycerol in HEPES (0, 50, and 75% v/v) are plotted against mean speed, the average speed of the ball and the disk at a constant SRR of 10%, in Fig. 3. In MTM measurements, the coefficient of friction was obtained for contact speeds ranging from 10 to 2500 mm/s. At lower operating speeds, MTM results show behavior similar to those observed under sliding conditions with pin-on-disk (Fig. 1). Again there is an initial decrease in the friction coefficient with increasing speed in the presence of viscous lubricant. In pure HEPES solution, the coefficient of friction between bare surfaces decreases by three orders of magnitude as the contact speed is increased from the lowest
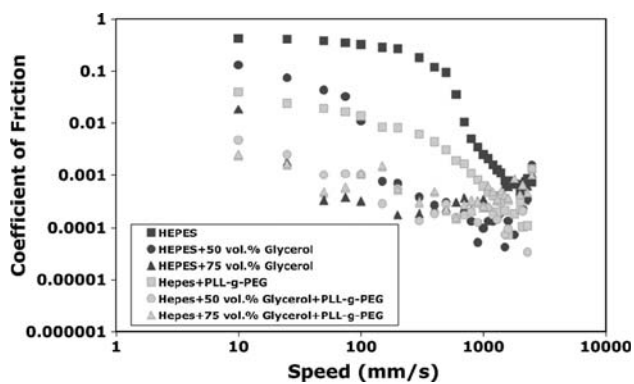
Fig. 3 Speed dependence of coefficient of friction (μ) from mini-traction-machine measurements for different compositions of HEPES–glycerol mixtures with (▨) and without (■) polymer. A rotating steel ball is brought into contact with a rotating glass disk under an applied load of 10 N and with a track radius of 20.7 mm. The mean speed of the ball and disk varied from 0 to 2500 mm/s with a SRR of 10%

(10 mm/s) to the highest value (2500 mm/s). At 10 mm/s with MTM, the addition of 50% v/v glycerol to the pure HEPES solution reduces the coefficient of friction from 0.5 to 0.2 and addition of polymer to the 50% HEPES–glycerol solution further reduces the friction by more than an order of magnitude (from 0.2 to 0.006). As the viscosity of the lubricants is increased, the onset of hydrodynamic lubrication is shifted to lower speeds (Fig. 3). In addition to viscosity-related effects, the adsorption of polymer at the interface assists in the further reduction of the friction in the boundary and the mixed regime, by reducing asperity contact, as also observed in sliding contact (pin-on-disk).

At higher operating speeds, the viscous solutions form a complete lubricating film. For 50% v/v glycerol in HEPES solution, the coefficient of friction increases with increasing speed above 1000 mm/s, indicating the onset of full-fluid-film lubrication. Upon complete film formation between the contacts, the presence of polymer at the interface no longer has any effect on the frictional properties and thus the frictional curves (Fig. 3) show similar behavior with and without polymer. At high lubricant viscosity (i.e., 75% v/v glycerol in HEPES) the increase in friction forces occurs at speeds as low as 100 mm/s due to the onset of the hydrodynamic regime at much lower contact speeds.

The effect of polymer brushes in different lubrication regimes is seen in Fig. 4a and b, in which the Stribeck curves obtained from pin-on-disk and MTM measurements are plotted, respectively. The coefficient of friction is plotted against speed multiplied by viscosity for all HEPES–glycerol mixtures both in the presence and the absence of the polymer. As expected, the effect of polymer in reducing the friction is predominantly seen in the boundary-lubrication regime. The effect of polymer on the friction is also extended to the mixed-lubrication regime
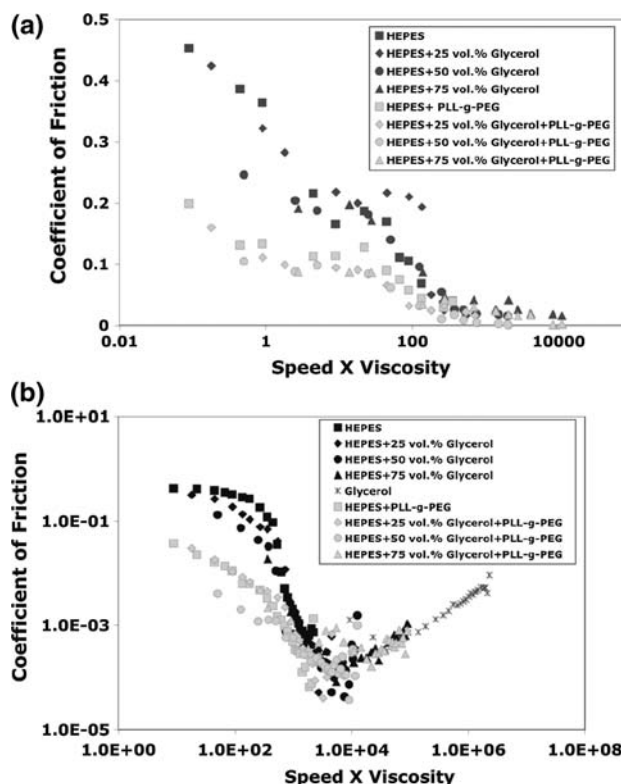

Fig. 4 a (Speed × viscosity) dependence of coefficient of friction (μ) from pin-on-disk measurements for different HEPES–glycerol mixtures with (▨) and without (■) polymer, **b** (Speed × viscosity) dependence of coefficient of friction (μ) from mini-traction-machine measurements for different HEPES–glycerol mixtures with (▨) and without (■) polymer

where there still exists a partial contact between the surfaces. In the hydrodynamic regime, the presence of polymer did not affect the frictional properties.

Similar studies have been conducted with different ratios of ethylene glycol in HEPES solution. Figure 5
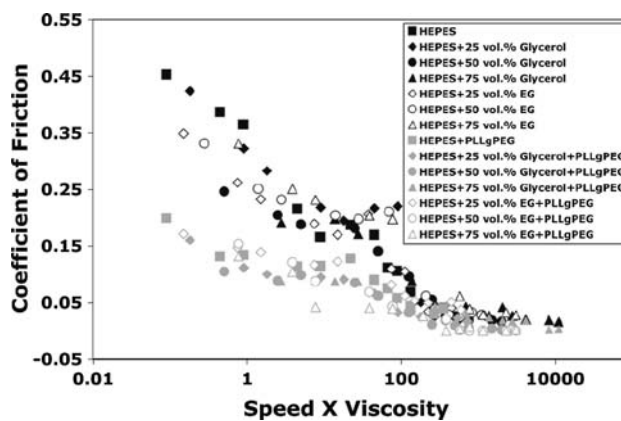

Fig. 5 (Speed × viscosity) dependence of coefficient of friction (μ) from pin-on-disk measurements for different compositions of HEPES–glycerol and HEPES–ethylene glycol (EG) mixtures with (▨, ▢) and without (■, □) polymer

shows the results of pin-on-disk studies for both HEPES–glycerol and HEPES–EG solutions and the similarity of the curves indicates that it is purely the effect of viscosity of the lubricant that is being observed.

3.2 "Rehealing" Studies of PLL-*g*-PEG in Aqueous Glycerol Mixtures

There is a continuous shear of the polymer at the interface when the two contacting surfaces slide against each other. Under the conditions used in the pin-on-disk tribological experiments, the shear forces exerted on the polymer chains in the vicinity of underlying asperities were comparable to the binding strength of the polymer to the substrate and thus the polymer was partially removed from the interface after each cycle. In order to maintain a low coefficient of friction over a large number of rotations there is a need for either a strong polymer attachment with the surface or replacement of the sheared polymer by fresh polymer from the bulk solution. PLL-*g*-PEG interacts with the surface via a weak electrostatic attraction and thus the polymer is partially sheared from the interface under tribological stress. Lee et al. [15] have studied the rehealing of the tribo-stressed contact by diffusion of the polymer to the surface by means of tribometry and fluorescence microscopy. It was shown that a high concentration of polymer in the bulk lubricant (0.25 mg/ml) will provide sufficient polymer in the vicinity of the stressed area and thus rehealing of the sheared area can occur before the onset of the next rotation. The diffusivity of PLL-*g*-PEG and the concentration of the polymer in the vicinity of the contact are important parameters that influence the rehealing process. By maintaining the same concentration as used by Lee et al., we have explored the effect of solution viscosity (and thus the diffusion rate of the PLL-*g*-PEG) on the rehealing mechanism. Viscosity was varied by adding different volume fractions of either glycerol or ethylene glycol to HEPES solution.

Figure 6 shows the rehealing properties of adsorbed PLL-*g*-PEG in the presence of PLL-*g*-PEG-containing viscous solutions, as measured with the pin-on-disk tribometer. Figure 6a (0% v/v glycerol) and b (50% v/v glycerol) are representative graphs for the different viscosities tested. Four sets of experiments were conducted for each mixture of HEPES with glycerol or ethylene glycol. All experiments were conducted at a sliding velocity of 0.5 mm/s on a track of radius 3 mm under a 2-N load in the presence of 20 ml of the lubricant solution. The number of rotations used for the experiment was increased with increasing lubricant viscosity, i.e., 50 revolutions for 0% glycerol and 200 for 50% v/v glycerol in HEPES. For *Case I*, the bare steel/glass pair was brought into contact in the presence of solutions of different viscosity (data not
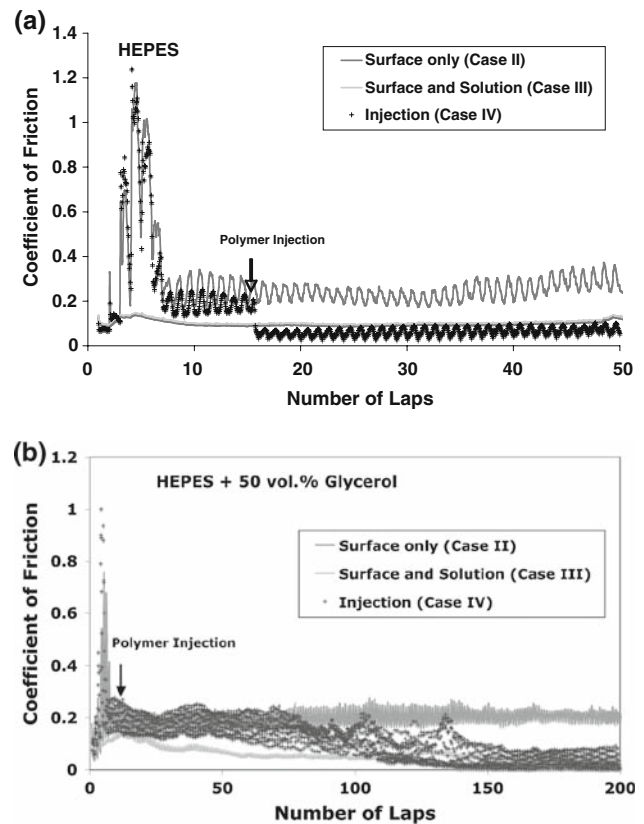

Fig. 6 Coefficient of friction (μ) versus number of laps for sliding contact between a steel pin and a glass disk in a pin-on-disk tribometer. **a** For HEPES solution as lubricant fluid **b** For 50 vol.% glycerol in HEPES as lubricant fluid. Case II concerns the tribopair pre-incubated in an aqueous-polymer-containing glycerol solution, while the solution in the cup does not contain any dissolved polymer. In Case III, the surface was also pre-coated with polymer in a similar way, and also the solution in the cup contains the polymer at a concentration of 0.25 mg/ml. Case IV represents surfaces that are similarly pre-coated with polymer but the polymer concentration of the solution in the cup is changed from 0 to 0.25 mg/ml following the injection of the polymer solution into the cup at the 13th lap (load = 2 N, sliding speed = 5 mm/s and track radius = 3 mm)

shown). A running-in effect was observed within the first few laps and the coefficient of friction achieved a steady value. The friction at a bare steel/glass contact decreased with increasing viscosity of the solution, as previously described (Fig. 1). For *Case II*, both the pin and the disk were pre-incubated in an aqueous glycerol or ethylene glycol solution containing polymer at a concentration of 0.25 mg/ml for 30 min. The solution in the cup during tribological measurements had the same percentage of glycerol or ethylene glycol in HEPES as used for the adsorption, but with no dissolved polymer. Due to the prior adsorption of the polymer at the interface, the first 3–5 laps show a low coefficient of friction. However, due to high tribological stresses the polymer was sheared away from the contact—with no polymer in the solution to heal the

track, the coefficient of friction reached the friction coefficient of bare contact as observed for Case I. In *Case III*, the pin and the disk were pre-incubated in the polymer solution for 30 min and the cup contained a HEPES–glycerol solution with PLL-*g*-PEG polymer at a concentration of 0.25 mg/ml. The graph shows a low value of μ for all laps due to continuous replacement of polymer, implying rapid rehealing of the sheared contact area during the tribological test. Rapid rehealing of the contact by the polymer from the bulk solution to the surface was observed for all cases, irrespective of the viscosity of the solution. Finally, for *Case IV*, samples incubated in HEPES–glycerol–PLL-*g*-PEG for 30 min were first run in polymer-free HEPES–glycerol or HEPES–ethylene glycol mixtures (15 ml). The system displayed a low coefficient of friction in the initial laps but soon the value of μ reached that of the bare contact, as seen for Case II. The contact was run for several laps under these conditions to ensure complete removal of polymer from the track. After lap 13, a 5-ml mixture of aqueous glycerol or ethylene glycol with a polymer concentration of 1 mg/ml was injected into the cup, so that the overall concentration of the solution in the cup was brought to 0.25 mg/ml. The μ value decreased from that seen in the later stages of Case II to that obtained for the polymer-lubricated contact (Case III). At low viscosities, the decrease in friction was observed immediately—within one rotation of the tribo pair. With higher viscosities, however, the number of rotations required to observe the onset of rapid rehealing was increased.

Figure 7 shows the time required to establish rapid rehealing of the contact for different percentages of glycerol or ethylene glycol in HEPES buffer. The rate of diffusion of PLL-*g*-PEG to the surface to establish the rapid rehealing process is seen to be highly viscosity-dependent,
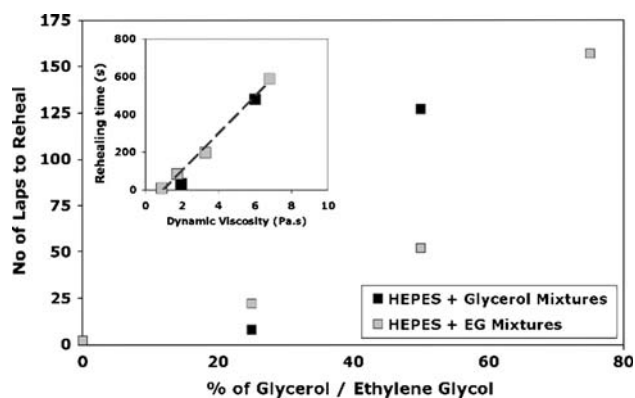

Fig. 7 Number of laps or time required for the onset of rapid rehealing of the PLL-*g*-PEG layer in the contact for different compositions of HEPES–glycerol (■) and HEPES–ethylene glycol (EG) (▢) solutions are shown. *Inset* rehealing time has a linear relationship with the bulk dynamic viscosity of aqueous glycerol and EG solutions, irrespective of the volume fractions

taking less than one lap for pure HEPES solution but more than 125 laps (500 s) for 50% glycerol in HEPES. The effect of viscosity of the solution on the diffusion of the polymer to the interface is shown in Fig. 7 (inset) which plots the time required to establish the rapid rehealing process against the dynamic viscosity of the glycerol or ethylene glycol solution. The rate of diffusion of the polymer through the solution is a function of the size of the polymer and the viscosity of the solution. With the help of the Einstein–Stokes equation the diffusion rate of the polymer through a solution can be expressed as [24]:

$$D = \frac{kT}{6\pi\eta R}$$

where D is the Fickian diffusion constant of the polymer, η is the dynamic viscosity, and R is the effective radius of the molecule. Making the simplifying assumption that the extended volume of a PLL-*g*-PEG copolymer molecule is similar in all the HEPES–glycerol mixtures, the rate of diffusion should be inversely proportional to the viscosity of the solution. A straight line through all the data points (Fig. 7 inset) shows the linear dependence of the time to onset of rapid rehealing on the viscosity of the solution and hence its dependence on the (rate of diffusion)$^{-1}$ of PLL-*g*-PEG in the viscous solution.

According to Lee et al. [15], the rapid rehealing properties observed for PLL-*g*-PEG can be attributed to the fast adsorption kinetics of the polymer through a low-viscosity bulk solution to the surface. The present rehealing studies of PLL-*g*-PEG in viscous solutions also show a rapid replacement of the polymer when the surfaces are significantly covered with polymer, i.e., after a fraction has been removed by shear (Case III). However, similar kinetics were not observed for surfaces from which polymer had been completely tribologically removed (Case IV). This suggests that the time required to reestablish a monolayer of polymer on these essentially bare contact regions is noticeably increased with increasing viscosity. In the case of the largely covered surface (Case III), the need for polymer adsorption to reestablish the monolayer is much less pronounced, and therefore the effects of viscosity less noticeable on the timescales probed in these experiments. The experiments of Case IV show that adsorption is slowed down by diffusion of molecules from the bulk solution, which, in turn, is slowed down at higher viscosities.

The adsorption kinetics of the PLL-*g*-PEG from HEPES–glycerol mixtures, as monitored by QCM measurements, also show that the rate of adsorption of the polymer onto the surface has a clear dependence on the concentration of the glycerol in the solution (Fig. 2). The time required to form a fully covered polymer film on the surface increases with increasing glycerol content in the HEPES–glycerol solution.

3.3 Film-thickness Calculations for Lubricants Consisting of PLL-g-PEG in Aqueous Glycerol Mixtures

While solutions of PLL-g-PEG in water or buffer solution have previously been shown to lubricate a variety of contacting materials in the boundary-lubrication regime [11, 25–27], hydrodynamic lubrication was not observed with these solutions, except at very high speeds. The use of aqueous glycerol solutions of PLL-g-PEG means that while PLL-g-PEG can still function as a boundary lubrication additive, the intrinsically higher viscosity of the base fluid leads to hydrodynamic lubrication at lower speeds than observed with water or HEPES. Calculations of lubrication regimes and film-thickness values for hard contacts in aqueous glycerol mixtures are presented in this section. In addition to their intrinsically higher viscosities at ambient pressures, the pressure-viscosity coefficients, α, of aqueous glycerol mixtures, which are higher than that of water, can further improve the load-bearing capacity of hard contacts and can thus modify the operative lubrication regime. Theoretical models suggest that the elasticity of the contact material and the viscosity of the lubricant are the two main parameters determining the nature of the fluid film formed between the contacting surfaces [28]. Depending on the relative magnitudes of these quantities, fluid-film lubrication can be divided into four regimes, namely iso-viscous rigid (IR), piezo-viscous rigid (VR), iso-viscous elastic (IE), and piezo-viscous elastic (VE). The equations for calculating the dimensionless viscosity and elasticity parameters for the contact are given by Hamrock and Dowson [28, 29].

Dimensionless viscosity parameter, $g_v = \dfrac{GW^3}{U^2}$

Dimensionless elasticity parameter, $g_E = \dfrac{W^{8/3}}{U^2}$

where G, W, and U represent the dimensionless material parameter, dimensionless load parameter, and dimensionless speed parameter, respectively. These parameters are generalized for different contact geometries (for example, elliptical or line contact) and contacting materials (such as elastomers to steel) and are defined as given below:

Dimensionless material parameter, $G = \alpha E'$

Dimensionless load parameter, $W = \dfrac{w}{E'R_x^2}$

Dimensionless speed parameter, $U = \dfrac{\eta_0 u}{E'R_x}$

where α is the pressure-viscosity coefficient of the lubricant, E' the effective elastic modulus, w the applied load, η_0 the viscosity of the lubricant, u the mean speed of the contact, and R_x the effective radius of the contact in the sliding direction.

The calculated values are plotted on the lubrication maps in Fig. 8. The pressure-viscosity coefficients for pure water and pure glycerol have been taken from the literature [30, 31] and linear interpolation of these values approximates the values for intermediate aqueous glycerol mixtures (Table 3). Operating conditions of POD and MTM experiments are used as input parameters to calculate the non-dimensional elastic (g_E) and viscosity (g_v) parameters. The contact area is considered to be circular and thus an ellipticity parameter (k) equal to 1 is used for the steel ball in contact with the glass (silica) disk ($E' = 112$ GPa, $R_x = 9.53 \times 10^{-3}$ m). Values of g_V plotted against g_E lie in the isoviscous-elastic regime (Fig. 8). The thickness of the lubricating film is calculated from the dimensionless film thickness parameter derived for the isoviscous-elastic regime [29]:

Dimensionless film thickness parameter,

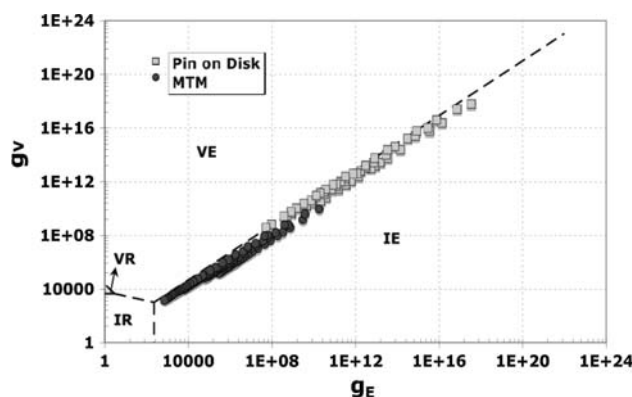$$\left(\hat{H}_{\min}\right) = 8.70 g_E^{0.67}\left(1 - 0.85 e^{-0.31k}\right)$$

Fig. 8 All MTM (●) and pin-on-disk (▢) data at different concentrations of aqueous glycerol mixtures, plotted on a lubrication-regime map, obtained from the Esfahanian–Hamrock–Dowson equations [28] for a circular contact (ellipticity parameter $k = 1$). The four different regimes in the dimensionless viscosity (g_V) versus elastic (g_E) parameter plot are iso-viscous rigid (IR), iso-viscous elastic (IE), piezo-viscous rigid (VR), and piezo-viscous elastic (VE). All the values reported in this study lie in the iso-viscous elastic regime. It should be noted that while the equations in [28] apply to rolling contact, the model can also be used for sliding geometries at the low speeds used in our pin-on-disk experiments [35]

Table 3 Pressure-viscosity coefficient values (α) for different concentrations of glycerol in water (vol.%)

Concentration of glycerol in water (vol.%)	0	25	50	75	100
Pressure-viscosity coefficient (α) ($\times 10^{-9}$ m^2 N^{-1})	0.75	1.5	2.25	3	3.74

The intermediate pressure viscosity values are approximated by linear interpolation of the pure water and glycerol α values [30, 31]

also, $\left(\hat{H}_{\min}\right) = H\left(\frac{W}{U}\right)^2$ where H is the dimensionless film thickness, $H = \frac{h}{R_x}$ and h is the film thickness of the lubricating film between the contacts. The values of h are plotted against speed for different HEPES–glycerol mixtures (Fig. 9a).

In actual tribological contacts, the surfaces coming into contact will have a non-negligible roughness in comparison to the lubricating film thickness formed at the interface. The relative magnitude of the film thickness in comparison to the surface roughness is given by the λ ratio [32].

$$\lambda = \frac{h_{\min}}{\sqrt{\left(\sigma_{\mathrm{pin}}^2 + \sigma_{\mathrm{disk}}^2\right)}}$$

where σ_{pin} is the RMS surface roughness of the pin, σ_{disk} is the RMS surface roughness of the disk, $h_{\min}$ is the minimum film thickness, and the λ ratio estimates the lubrication regime for rough surfaces.

The RMS roughness values for steel ball and silica disk used for MTM are 11 and 2 nm, respectively (obtained from PCS instruments) and those for the steel ball and glass

wafer used for POD experiments are 32 and 5 nm, respectively (measured by AFM). Figure 9b plots the λ values against speed for all of the POD and MTM experiments. The curves show that all the contacts during POD measurements were in the boundary-lubrication regime. Though there was an increase in the λ value with addition of glycerol, the values still lie below 1, indicating a high probability for asperity contact. For MTM measurements, on the other hand, although contacts tested at high speeds and in viscous lubricant (0.5 or 0.75 volume fraction of glycerol in HEPES) showed λ values above 3, for other operating conditions the λ values indicated either the boundary- or mixed-lubrication regime. Thus, there is a need for adsorbed copolymers of PLL-g-PEG on the sliding surfaces to reduce the interfacial friction generated at the asperity contacts, even in the presence of aqueous viscous lubricants.

4 Conclusions

It is has been shown that when poly(L-lysine)-g-poly(ethylene glycol) is dissolved in aqueous glycerol solutions, the tribological properties can be improved both in the boundary- and the mixed-lubrication regimes. Different percentages of glycerol in HEPES have been used to vary the viscosity of the solvent, which enables hydrodynamic lubrication to take place over a wider speed range than for the pure HEPES case. The effect of the polymer (in glycerol-containing solution) in different lubrication regimes was demonstrated by means of a Stribeck plot, which shows that the presence of polymer at the interface can reduce the friction as long as there exists asperity–asperity contact between the tribo pair; the viscous solvents separate the contacting surfaces due to hydrodynamic forces and the presence of hydrated polymer brushes reduces the interfacial friction between contacting surface asperities. Also, Esfahanian–Hamrock–Dowson film-thickness calculations show that the lubricating HEPES–glycerol films formed in our pin-on-disk experiments are very thin, so that numerous asperity–asperity contacts are expected, and thus the presence of copolymer at the surface is necessary to further reduce the friction. In mini-traction-machine measurements in rolling contact, on the other hand, the full-fluid-film-lubricated region could be examined, in which the presence of the polymer was found to have negligible effect.

Quartz-crystal microbalance measurements showed that the total amount of adsorbed polymer appeared unaffected by the presence of glycerol. The kinetics of adsorption of PLL-g-PEG from the HEPES–glycerol solution to the interface was investigated to help understand the effect of the increased viscosity on the rehealing of the tribo-stressed
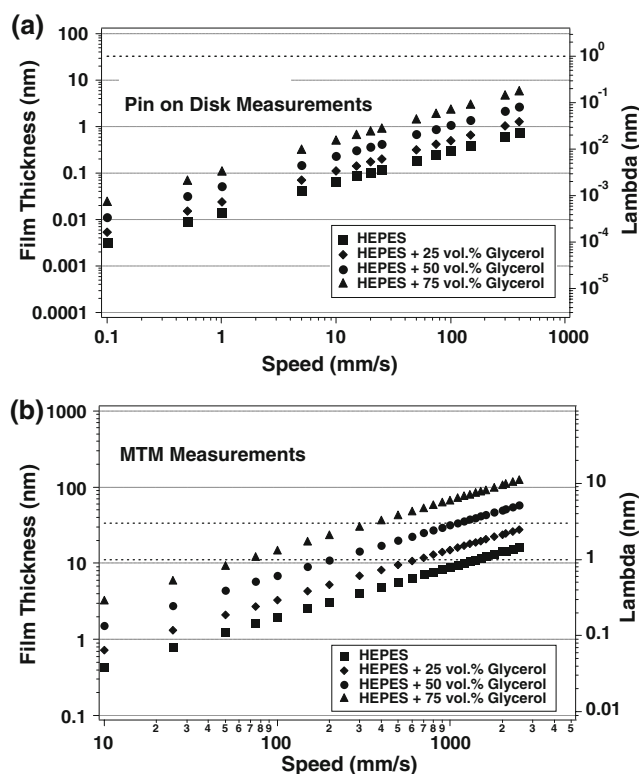

Fig. 9 Fluid-film-thickness (left axis) and λ values (right axis) as a function of speed, calculated from the Esfahanian–Hamrock–Dowson equations [28, 29] (steel-on-glass contact) for **a** pin-on-disk and **b** MTM measurements from this study for different HEPES–glycerol mixtures. λ values are indicated to enable estimation of film formation on the rough surfaces. $\lambda < 1$ represents boundary lubrication, $\lambda > 3$ represents full-fluid-film lubrication and $1 \leq \lambda \leq 3$ represents the mixed regime

contact. Although there is an inverse relation between the viscosity, the solvent, and the rate of diffusion of the polymer to the interface, the time required for the polymer to reheal wear-damaged polymer layers appears to be less than that between contacts in successive laps, and thus re-healing of the contact remains independent of the viscosity of the solvent under the conditions investigated. These results show that the use of HEPES–glycerol solutions as a viscosity-enhanced solvent for PLL-g-PEG can expand the applicability of aqueous lubrication to a significantly larger range of operating conditions.

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