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Advance in Tribology Study of Polyelectrolyte Multilayers

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Abstract

This review introduced the preparation and structural characterization of polyelectrolyte multilayers in recent years and also summarized the tribology research progress of the polyelectrolyte multilayers, including tribological properties, surface adhesion characteristics, and wear resistance properties. Statistics analysis indicated that nanoparticles-doped polyelectrolyte multilayers present better friction and wear performance than pristine polyelectrolyte multilayers. Furthermore, the in situ growth method resulted in improved structural order of nanoparticles composite molecular deposition film. In situ nanoparticles not only reduced the molecular deposition film surface adhesion force and friction force but also significantly improved the life of wear resistance. That was due to the nanoparticles that possessed a good load-carrying capacity and reduced the mobility of the polymer-chain segments, which can undergo reversible shear deformation. Based on this, further research direction of in situ nanoparticles molecular deposition film was proposed.

Keywords: tribology, polyelectrolyte multilayers, nanoparticles, friction, antiwear

1. Introduction

With the development of micro-/nanotechnology, the integration of miniaturized mechanical components with microelectronic components has spawned a new technology; it is well known as microelectromechanical systems (MEMS)/nanoelectromechanical systems (NEMS) [1]. Due to the large surface-area-to-volume ratios of surface and bulk micromachine, micromechanism brings the role of surface and interfacial forces into the

foreground [2]. Thus, the surface adhesion and friction greatly affect the safety and service life of MEMS or micromechanisms. So the need of developing nanolubricating technique is becoming increasingly urgent. Thin organic films as a more effective modification for antifriction treatments involve the application of a molecular film to the micromachine surface [3]. In the recent two decades, with the development of MEMS, magnetic storage, and recording systems, Langmuir-Blodgett (LB) films and self-assembled (SA) films were applied to reduce the frictional force between the contacted surfaces of different materials. However, both LB films and SA films were limited in use because of their own shortages: instability and the cost of the apparatus for the LB film, and the difficulty of multilayers assembling for the SA film [4].

Decher et al. [5–8] introduced a method for preparing multilayers by the consecutive deposition of oppositely charged polyelectrolytes from dilute aqueous solution by way of intermolecular electrostatic forces onto charged substrates. Polyelectrolyte multilayers (PEMs) through this molecular deposition process have been intensively investigated in recent years. The popularity of this molecular deposition procedure is due to its simplicity, versatility, and systematical control over the structure and the thickness of the resulting films. Moreover, the materials used in molecular deposition studies can be macromolecules [6], small organic molecules [7] or inorganic compounds [8], biomacromolecules such as proteins [9], DNA [10], or even colloids [11]. Previous work has reported that polyelectrolyte multilayers can decrease the adhesive force on a surface [12], so as to modify the friction surface and reduce the friction force [13, 14]. This shows that the polyelectrolyte multilayers are ideally suited to combat the tribological challenges in MEMS. Up to now, the friction and wear behaviors of polyelectrolyte multilayers were studied popularly. Pavoor et al. has reported that the preparation of a poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) polyelectrolyte multilayers using layer-by-layer method, and the capacity for these multilayers induced wear reduction at large scales under dry condition [15]. The mechanical property of polyelectrolyte multilayers was characterized by using a nanoindentation tester. The results indicated that the elastic modulus and hardness of the films were independent of the contact depth over a range of penetration where artifacts arising from the free surface and the underlying glass substrate were insignificant [16]. Furthermore, nanoparticles can reduce friction and enhance the lubrication performance of the lubricant [17]. Nanoparticles were also applied to prepared composite polyelectrolyte multilayers, such as TiO_2 [18], graphite oxide (GO) [18], graphene oxide [19], SiO_2 [20], Ag [21], and so on. The tribological investigation of nanoparticles composite polyelectrolyte multilayers shows that the nanoparticles in the polymer films could enhance the antiwear life of polyelectrolyte multilayers. Then, it indicated that these composite films can improve the tribological performance greatly.

In this review, the correlation between the parameters and the performance was calculated. We defined chemical composition parameter as the molecular structure and ionization behavior of polyelectrolyte. As a result, it substantially facilitates our fundamental understanding in the mechanism of lubrication and antiwear performance that enables us to design molecular film lubricants with well tribological properties.
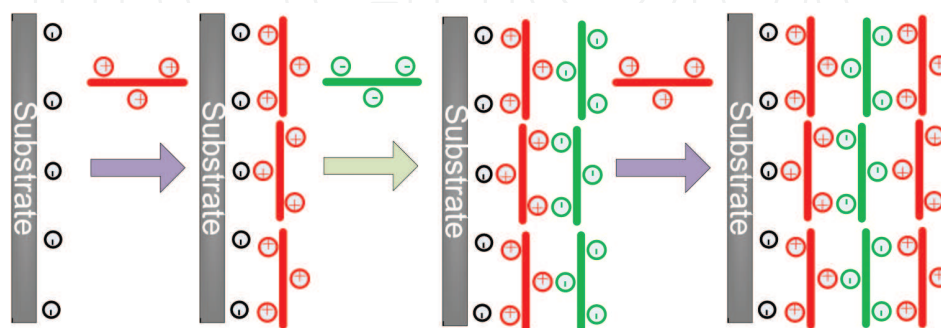
2. Effects of chemical composition of polyelectrolyte

Since the invention of layer-by-layer method, many polyelectrolytes are used for preparing multilayers. It mainly includes polycations and polyanions. These groups dissociate in aqueous solutions. Polyelectrolyte thus has properties of both electrolytes as salts and polymer as high-molecular-weight compounds. Like salts, their solutions are electrically conductive. Like polymers, their solutions are often viscous. Charged molecular chains are commonly present in soft-matter systems. Due to its ionization properties, different polyelectrolytes have been utilized in the formation of ultrathin materials known as polyelectrolyte multilayers. During layer-by-layer deposition, a suitable growth-charged substrate is dipped back and forth between dilute baths of positively and negatively charged polyelectrolyte solutions. As shown in the schematic diagram (**Figure 1**), during each dip process an amount of polyelectrolyte molecular is adsorbed on the substrate and the surface charge is reversed.

The statistic analysis was conducted based on the experimental results collected from 42 papers that were related to tribological study of polyelectrolyte multilayers, as listed in **Table 1**. Based on **Table 1**, we can divide reported polyelectrolytes into different types based on their characteristic (strong or weak polyelectrolyte, terminal group). It can be found that the main polyelectrolytes used in references were PAA, PAH, poly(diallyl dimethylammonium chloride) (PDDA), and poly(4-styrenesulfonic acid) sodium salt (PSS). Then, we principally review these polyelectrolyte multilayers including the nanoparticles composite films.

The factors affecting the micro- or nanofrictional behavior of polyelectrolyte multilayers include the characteristics of molecule assembled, surface morphology, and mechanical properties of the films.
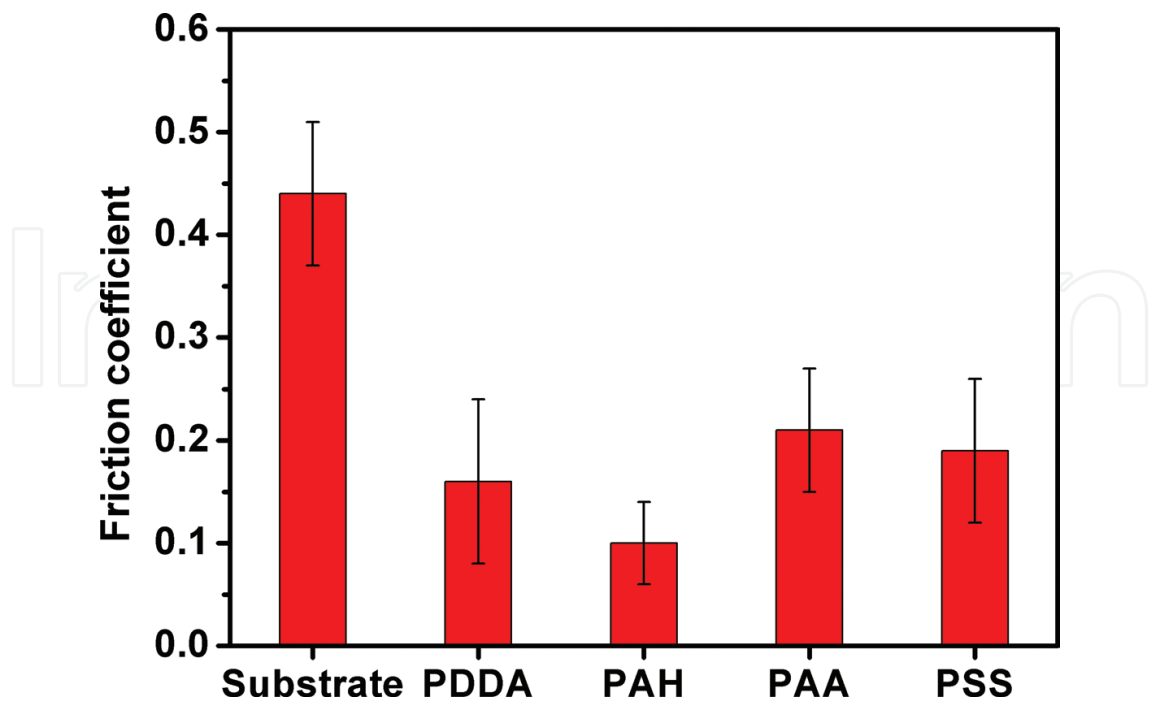
The characteristics of the outermost layer molecules forming the films have essential effects on the frictional properties of the polyelectrolyte multilayers. **Table 1** lists the different structures adsorbed on the substrate according to the last adsorbed layer polyelectrolyte. **Figure 2** shows the friction coefficient comparison based on different outermost layer polyelectrolyte. According to the results, the polyelectrolyte multilayer-modified substrate shows a lower friction coefficient than that for the bare substrate (glass or silicon). It demonstrated the lubricating

Figure 1. The schematic diagram of deposition process of polyelectrolyte multilayers (redrawn from Refs. [5–8]).

Materials	Abbreviation of molecular	Cationic or anionic (C or A)	References
Poly(acrylic acid)	PAA	A	[15, 16, 18, 20–22, 24–26, 34, 35, 38, 39, 41–43, 45, 47, 49, 51, 55, 57]
Poly(allylamine hydrochloride)	PAH	C	[15, 16, 18, 20, 21, 24, 25, 33, 36, 38–40, 44, 45, 52, 54–57]
Poly(diallyl dimethylammonium chloride)	PDDA	C	[22, 23, 26–28, 30–32, 34, 35, 43, 46–51, 53]
Polyethylenimine	PEI	C	[25, 26, 33, 39, 40, 42, 44, 52]
Poly(4-styrenesulfonic acid) sodium salt	PSS	A	[23, 25, 27, 28, 31–33, 36, 40, 44, 46, 48, 50, 52–54]
Poly(L-lysine)	PLL	C	[29]
Hyaluronic acid	HA	A	[29, 37, 44]
Natural biopolymers chitosan	CHI	C	[37]
Deoxyribonucleic acid	DNA	A	[33]
Diazoresin	DR	C	[41]

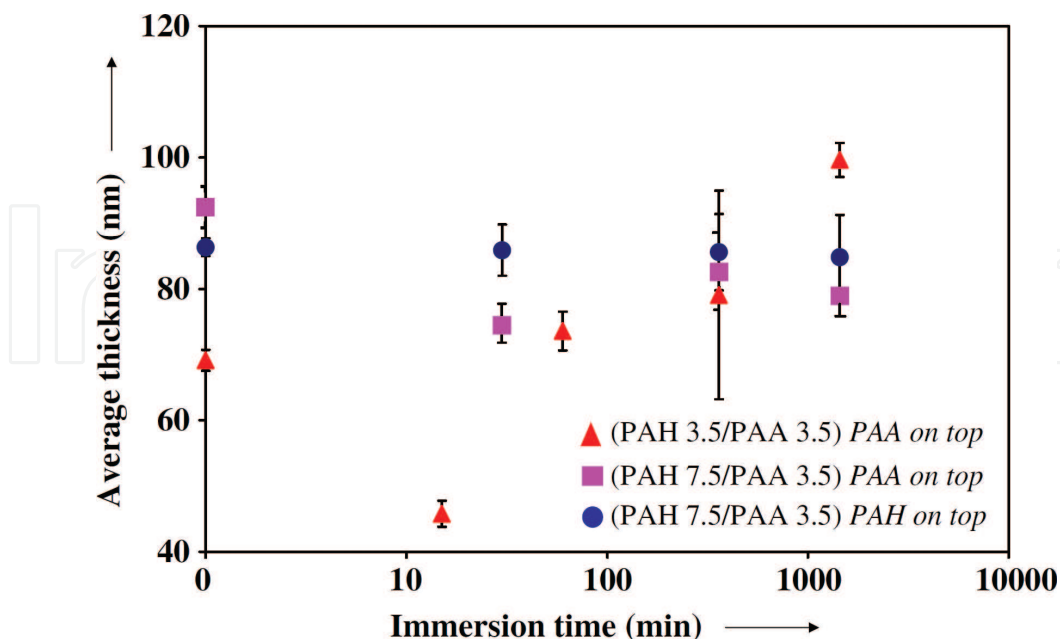**Table 1.** Summary of polyelectrolytes used for tribology.

Figure 2. Friction coefficient comparison based on the outermost layer polyelectrolyte.

and antifriction properties of polyelectrolyte multilayers. The polyelectrolyte deposited on the substrate can reduce the friction force, which is mainly influenced by the surface layer. In this case, PAH layer was believed to be the lowest friction coefficient. From the macrofriction tests, the polycationic layer is a better element for improving tribological performance.

Pavoor et al. [15, 57] investigated the tribological behavior of PAH/PAA film on UHMWPE. To examine the behavior of PEM structure in the presence of biological lubricant solution, PAH/PAA film with PAA as the last adsorbed polyelectrolyte is used. The lubricant solution was prepared by diluting the bovine calf serum to a protein concentration of 23 g/L, containing 20 mMol of the sodium salt of ethylenediaminetetraacetic acid (EDTA) and 0.2% by weight of sodium azide. Moreover, a film with PAH as the last adsorbed layer was also investigated. For film with different periods of time immersing in the lubricant solution, the average thickness after immersion was observed by using a profilometer (as shown in **Figure 3**). It shows that a slight decrease in thickness was observed initially for the PAA-topped layer films, but without an obvious effect on the thickness for the PAH adsorbed last. The corresponding friction tests show that the average friction coefficient slightly increased after PEMs deposited on UHMWPE surface. But the use of the PAH/PAA film reduced ultra-high molecular weight polyethylene (UHMWPE) wear by up to 33% compared with the uncoated sample. Furthermore, the capacity for PEM-induced wear reduction was confirmed at larger scales of tests in the dry state a pin on disk tester [57].

It is well known that the mechanical properties influence the tribological behavior of lubricant. Pavoor et al. [16] investigated the mechanical characteristics of PAH/PAA PEMs using nanoindentation tester. The elastic modulus and hardness of the films were demonstrably

Figure 3. Average PEM thickness (on glass substrates) after immersion in bovine calf serum–containing lubricant for different times (adapted from Ref. [15]).

free of the influence by the underlying supporting material. The mechanical properties of these PEMs can be altered significantly by varying the pH values of the PAH and PAA assembly solutions. Furthermore, in the dry state, the PEM behaviors are virtually unaffected by whether the linkages among the functional groups of the parent polyelectrolytes are ionic or covalent in nature. The essence of mechanical strength of PEMs lies in the linkage density in the film. The modulus values of these interpenetrated polyelectrolyte structures in the swollen state (in water) are about two orders of magnitude lower than the corresponding values in dry conditions. Then, in the swollen state, chemical cross-links do augment the modulus values due to the smaller amount of water uptake in cross-linked PEMs. Gao et al. [58] composed capsules of PSS/PDDA using layer-by-layer deposition on melamine formaldehyde colloidal templates. The results indicated that the elasticity modulus of the PSS/PDDA multilayer as obtained by the osmotic pressure method is 136 MPa, which is considerably smaller than that of the PSS/PAH PEMs. The apparent difference between the PSS/PAH capsules and PSS/PDDA capsules with regard to their stability and elasticity is explained as the result of the different chemical nature of PAH and PDDA. It is due to an overall weaker interaction between PDDA and PSS compared with the PAH and PSS interaction.

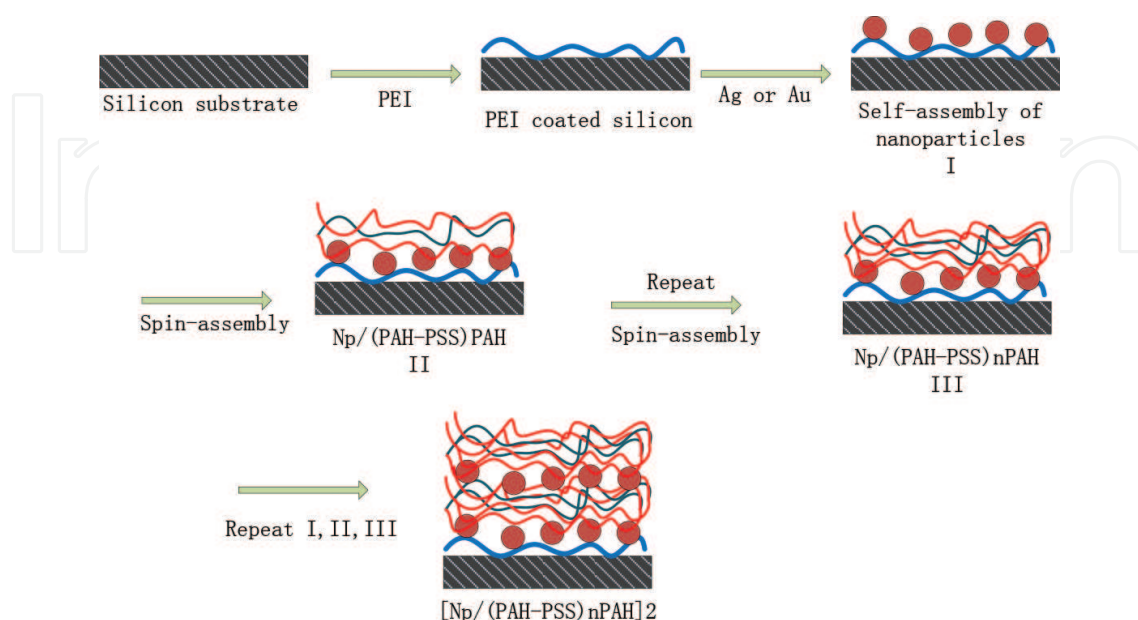## 3. Effect of nanoparticle doped into PEMs

In recent years, nanoparticles composite ultrathin films have increasingly attracted a wide attention. Due to the assemble characteristic of PEMs, many nanoparticles as formation materials were introduced for preparing composite PEMs. **Table 2** lists the different nanoparticles used to prepare nanoparticles-doped PEMs. For example, Cassagneau et al. synthesized nanoparticles or nanoplates and used these nanoparticles to prepare composite multilayers [59, 60]. Feng et al. [56] prepared surface-charged graphite oxide (GO) solution and formed PAH/GO multilayers by layer-by-layer method. Furthermore, they synthesized PAA-coated

Nanoparticles/nanoplates	Abbreviation	References
Titanium dioxide	TiO_2	[18, 56, 59]
Graphite oxide	GO	[18, 60]
Silicon dioxide	SiO_2	[20]
Copper	Cu	[23, 32, 48, 53]
Copper sulfide	CuS	[22, 35, 43, 49, 51]
Zinc sulfide	ZnS	[47, 49, 66]
Copper hydroxide	$Cu(OH)_2$	[50, 69]
Rare earth	RE	[36]
Silver	Ag	[21, 30, 34, 46, 54, 61, 65, 68]
Gold	Au (or complex)	[34, 46, 52, 55, 64, 67]

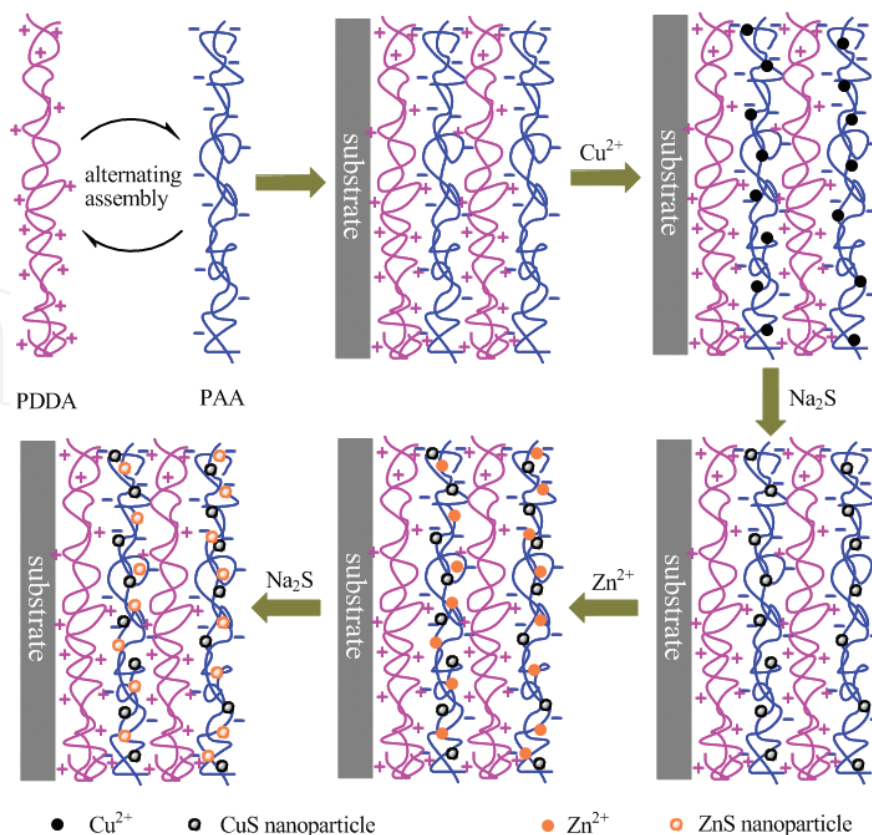**Table 2.** Summary of different nanoparticles used to prepare nanoparticle-doped PEMs.

TiO_2 nanoparticles and prepared PAH/PAA(TiO_2) multilayers by using the same method [18]. Nanocomposite (PAH-PSS) containing Au or Ag film was fabricated on a silicon substrate using spin-assisted layer-by-layer self-assembly technique [52, 54] where the fabrication process is shown in **Figure 4**. Xiao et al. [30] synthesized sodium citrate-protected silver nanoparticles and prepared PDDA/Ag composite films. AFM images indicated that the additional nanoparticles were formed on the substrate. With the number of deposited cycles and increasing deposition time, the particles show an obvious tendency to aggregate, and large particle clusters are observed in the sample.

The above-mentioned method as commonly used step is that the prepared nanoparticles or nanoplatelets (surface modified) were processed using surface modification firstly, and then the substrates were coated by nanoparticles or nanoplatelets and polymers layer by layer using molecular deposition method. However, it is difficult to prepare nanoparticles composite MD films using the above-mentioned steps, since it is difficult to control the size of nanoparticles, preventing the reunion of nanoparticles and making the nanoparticles dispersed in the film uniformity. Recently, polyelectrolyte multilayers have emerged as a useful vessel for novel nanomaterial synthesis [61–64]. The studies show that various nanomaterials with desirable shape and composition can be synthesized by loading the reactants into the PEMs interior and then performing appropriate reactions such as reduction, sulfuration, and so on. This reaction can be called as in situ synthesis. Logar et al. [65, 66] has synthesized the Ag and ZnS nanoparticles in situ in PAH/PAA PEMs. Gold nanoparticles could be synthesized in the PEMs [67]. This indicated that the in situ nucleation and growth of nanoparticles appeared in PEM films. This technique can be used for synthesizing nanoparticles in the polymer structure domain as nanoreactor that can bind metal cations from an aqueous solution. Then, the postbinding chemistries include reduction, hydroxide, sulfidation, and growth nanoparticles from the cationic precursors [49, 50, 68]. For instance, the schematic diagram of the preparation process of in situ CuS/ZnS nanoparticles hybrid PEMs is shown in **Figure 5**.

Figure 4. Schematic of fabrication of silver nanoparticle-polyelectrolyte multilayers (redrawn from Refs. [52] and [54]).
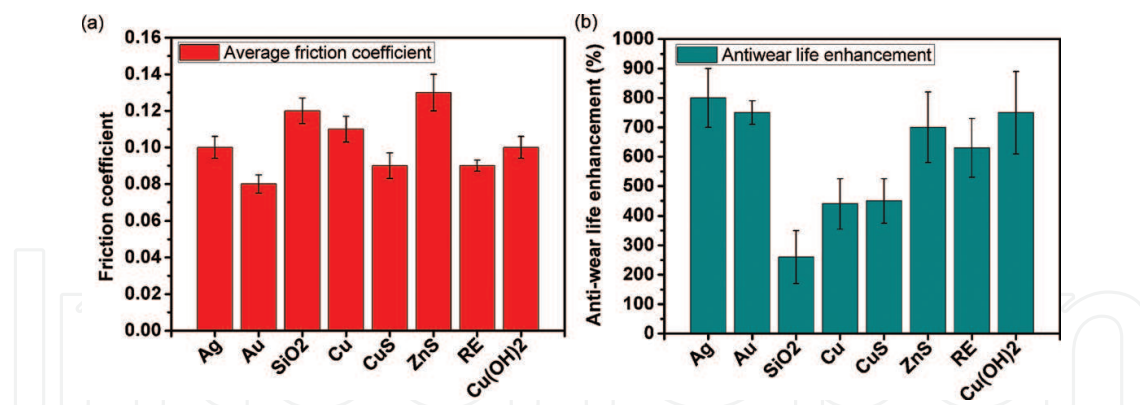
Figure 5. The schematic diagram of preparation of in situ CuS/ZnS nanoparticles hybrid polyelectrolyte multilayer thin film (adapted from Ref. [49]).

Moreover, some polyelectrolyte solution mixed with metal ions can form polymer complexes. The study shows that the in situ gold and silver nanoparticles in polyelectrolyte multilayer film can be prepared by alternate immersion of a substrate in PDDA-AuCl^{4-} complexes solution and PAA-Ag^{+} complexes solution followed by the reduction of the metal cations (Au^{3+}, Ag^{+}) through immersion of NaBH$_4$ solution [34]. The AFM, SEM, TEM, XPS, and UV-vis spectrum measurements demonstrated the Au and Ag nanoparticles distributed in the polyelectrolyte multilayers uniformly.

The tribological properties of nanoparticles-doped composite PEMs were investigated by microtribometer [21–23, 52–56]. The statistic results of friction and wear behaviors are shown in **Figure 6**. It can be seen that the friction coefficient of nanoparticles-doped composite PEMs has a slight decrease compared with pure PEMs (contrast **Figure 2**). However, the antiwear life has an obvious improvement with nanoparticles hybrid into PEM films. The antiwear life (sliding time or reciprocation cycles) was determined by the time or cycles when the friction coefficient increased sharply. The results indicated that the PEMs filled with nanoparticles showed better tribological performance than the pristine PEMs. This is quite evident that nanoparticles within the PEMs can enhance antiwear life of PEMs. From the tribometer tests, this is due to the nanoparticles possessing good load-carrying capacity and decreasing the mobility of the polymer-chain segments which can undergo reversible shear deformation, and the higher shear force must be overcome during relative motion, which results in the increased friction coefficient and shorter antiwear life.

Figure 6. Tribological performance comparison based on different nanoparticle-doped PEMs: (a) average friction coefficient and (b) antiwear enhancement.

More recently, Yang and Guo researched the tribological properties of PEMs filled with in situ nanoparticles. Some conclusions were presented. The in situ nanoparticles exhibited higher durability because of the inorganic nanoparticles enhancing the load-carrying capacity. The main wear mechanism was adhesive wear, and the in situ nanoparticles mitigated plastic deformation and slowed down adhesive wear [69]. AFM has been used extensively to measure adhesive force between surfaces at nanoscale. The surface adhesive force is between the AFM tip and the film surface by force-curves mode under ambient condition. AFM tests showed that the adhesive forces between the probe and the sample surface decreased, indicating that the surface interactions between the probe and the sample are reduced by compositing in situ nanoparticles [22, 49]. The adhesive force is mainly dependent on the surface interaction between the probe and the sample surfaces. It is well known that, when the surface is hydrophilic, they would easily form meniscus by adsorbed water molecules in air, thus they had higher adhesive force. From the ultrapure water-contact angle measurement, the nanoparticles-filled PEMs film was more hydrophobic than the pristine PEM film and show a lower surface adhesion.
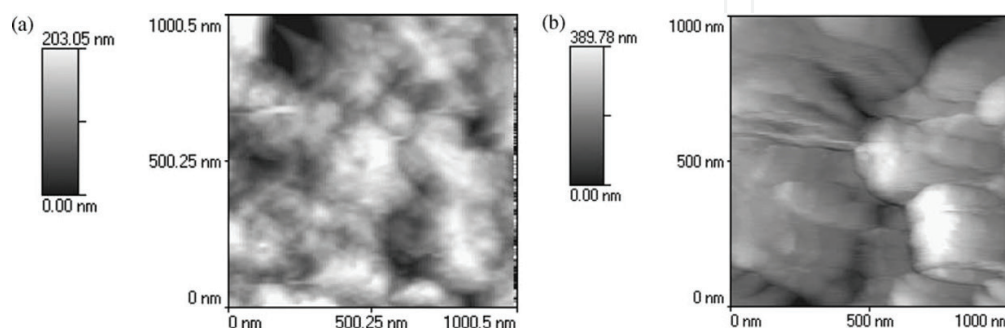
Surface wettability of a solid surface can be controlled by two factors: one is the change and design of geometrical structure (such as surface roughness) in micro- or nanosurface structure [70–72]; the other is surface modification with chemical component (surface-free energy) [73, 74]. Therefore, hydrophobic surfaces can be obtained by using low surface energy materials such as fluoroalkylsilane [75, 76] and wax [77, 78]. In the meantime, the hydrophobicity of the surface can also be increased by enhancing surface roughness [79]. The previous study shows that the surface wetting and adhesion can be changed by using layer-by-layer method [80]. These surface properties have an effect on the tribological behavior of PEMs. A 4.5-bilayer PDDA/PSS PEM on quartz or silicon plate was prepared by spin-assisted layer-by-layer assembly technique. Then, PDDA/PSS doped with Cu nanoparticles was built by immersing PDDA/PSS PEMs in Cu^{2+} and $NaBH_4$ solutions to allow nucleation of Cu nanoparticles [23]. The relationship between water wettability and tribological properties of PDDA/PSS doped with Cu nanoparticles films showed that the adhesion and tribological behavior were closely related to their wettability. That is, the PEMs with stronger hydrophobicity have a lower surface energy, which show a lower friction and longer antiwear life. Guo et al. [36] fabricated lanthanum hybrid PEMs using the layer-by-layer and self-assembly methods. The (PAH/PSS)/ RE film has a larger water-contact angle and lower surface energy than PAH/PSS PEMs. The

microtribology study showed that the (PAH/PSS)/RE film with a very low friction coefficient of about 0.09 and a longer antiwear life was obtained than that for the pure PAH/PSS film.

4. Nanotribology of PEMs

The PEMs are desired for the application of MEMS to reduce the adhesion and friction. AFM is a mighty instrument for investigating the nanotribological behavior of PEMs. Wang et al. [4] have investigated the nanotribological of different molecular deposition films by AFM. The test results showed that the process of the anionning and the depositing of a monolayer molecular film on an Au substrate and the process of decorating an alkyl-terminal to molecular deposition film surfaces were all capable of lowering the frictional force and improving the nanolubrication property. Moreover, the film decorated with alkyl chains had lower frictional forces than the undecorated films. Accordingly, it provided a significant thought to seek for a new nanolubrication film. Zhang et al. [18] investigated the surface roughness, hardness, and nanofriction force of PAH/GO and PAH/PAA(TiO_2) PEMs. Both of them were heated to change the film forming dynamic force from electrostatic force to covalent bond so as to increase the bonding strength of the films. The surface roughness increased, and the friction force was significantly decreased after heating for PAH/GO PEMs. However, the surface roughness and nanofriction force of PAH/PAA(TiO_2) PEMs both decreased slightly after heating. The AFM images of the five-layer PAH/PAA(TiO_2) before and after heating are shown in **Figure 7**. It was found that these films had a much smaller friction force than their substrates and the friction force was dependent on the morphology and/or hardness of the films.
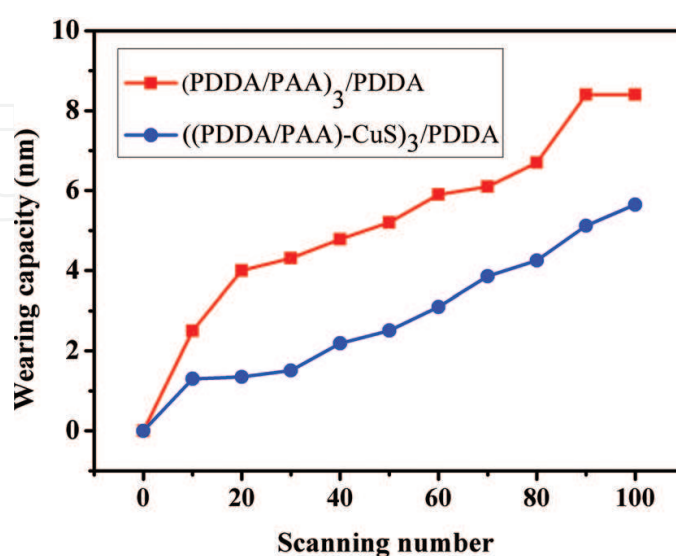
The nanofriction coefficient of the PDDA/GO was found to decrease with increasing load. However, the decrease in nanofriction coefficient reduced noticeably and maintained if the load was beyond a specific value [81]. The effect of load on nanofrictional properties of different Ag nanoparticles-doped PEMs, whose number of bilayers was one to five, respectively, was investigated by Guo et al. [21]. The nanofriction increased linearly for different bilayer composite PEMs with the increasing load. With the bilayer number (thickness) increasing, the fitting friction coefficient decreased slightly from 0.06 (one and two bilayers) to 0.05 (three to five bilayers).

Figure 7. AFM images of five-layer PAH/PAA(TiO_2) before (a) and after (b) heating (adapted from Ref. [18]).

The effects of scanning speed of AFM tip on the nanotribological behavior of PEMs were investigated [30]. All the substrates deposited with PDDA/Ag film were found with a lower nanofriction force than the clean substrate at different scanning speeds with a normal load of 5 nA. And with the increase of the scan rate, the increasing amplitude of the friction force of all the films was apparently less than that of the clean substrate. It might be concluded that the films decrease the adhesion force of the substrates. Also, the friction force of the trilayer film was the smallest. This was corresponding with the surface roughness. In these experiments, the surface roughness of trilayer film was the smallest among the films.

Guo et al. [43] prepared PDDA/PAA and containing CuS PEMs on quartz and glass substrates. It was found that the CuS nanoparticles were homogeneously distributed throughout the whole film. And these films had a much smaller friction force than their substrates and higher antiwear life than pristine PDDA/PAA PEMs. **Figure 8** shows the surface wearing capacity of the pristine and CuS nanoparticles-doped PEMs. From the wear tests, it can be found that the wearing capacity increases with the times of reciprocating scan with AFM tip. The pristine PEM's antiwear capacity is lower than that of the CuS nanoparticles-doped PEMs. From the curves, the wearing capacity of pristine PEMs was about 90 scanning times. But the CuS nanoparticles-doped PEMs have not been destroyed after 100 scanning times. Moreover, they also prepared the in situ Au nanoparticles hybrid PEMs [55]. The nanotribological investigation showed that the PAH/PAA PEMs with in situ Au nanoparticles have a lower surface adhesion and friction force than the pure PAH/PAA PEMs. It is due to the nanoparticles in situ synthesized in polyelectrolyte multilayers making the surface morphology change and load-carrying capacity to increase. Under a normal load, the pure PAH/PAA multilayer deformation against a probe tip was larger than the PAH-Au/PAA film. From the friction force tests, it can be found that the PEMs with in situ nanoparticles exert good load capacity. Therefore, a slight and gradual increase of friction forces could be observed. Furthermore, with the increasing of normal load, the deformation of pure PAH/PAA PEMs enhanced, which caused the friction force to increase.

Figure 8. The surface-wearing capacity of pristine and CuS nanoparticle-doped PEMs (adapted from Ref. [43]).

5. Conclusions

Very promising prospects for the tribological application of PEM films have been put forward by recent research. The investigation of PEMs has been extended due to their modification of substrate and reduction of surface friction performance. However, some challenges still exist in applying PEM films into practical application. Thus, for preparing more varieties of PEM films that have better tribological performance and promote the use of PEMs in MEMS or NEMS, some key problems in the research of PEMs should be addressed, such as optimizing conditions of preparation, improvement of the antiwear performance, friction and antiwear mechanism, as well as clarifying the parameters influencing the tribological properties of PEM films. Some new nanolubricant materials could be introduced into PEMs to improve the tribological behavior of PEMs, thereby enhancing the bonding strength between layers and substrates to further improve the antiwear life. Furthermore, more attention needs to be paid to research the antifriction, antiwear, and repair mechanism of in situ nanoparticles-doped PEMs, as well as the tribological investigation in different conditions, such as atmosphere, liquid medium, and so on in order to assess the application prospect of these PEM films.

Acknowledgements

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