Nanofriction of Graphene/Ionic Liquid-Infused Block Copolymer Homoporous Membranes

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ABSTRACT: We have infused graphene/ionic liquid into block copolymer homoporous membranes (HOMEs), which have highly ordered uniform cylindrical nanopores, to form compact, dense, and continuous graphene/ionic liquid (Gr/IL) lubricating layers at interfaces, enabling a reduction in the friction coefficient. Raman and XPS analyses confirmed the parallel alignment of the cation of ILs on graphene by the π–π stacking interaction of the imidazolium ring with the graphene layer. This alignment loosens the lattice spacing of Gr in Gr/ILs, leading to a larger lattice spacing of 0.36 nm in Gr of Gr/ILs hybrids than the pristine Gr (0.33 nm). The loose graphene layers, which are caused by the coexistence of graphene and ILs, would make the sliding easier, and favor the lubrication. An increase in the friction coefficient was observed on ILs-infused block copolymer HOMEs, as compared to Gr/ILs-infused ones, due to the absence of Gr and the unstably formed ILs film. Gr/ILs-infused block copolymer HOMEs also exhibit much smaller residual indentation depth and peak indentation depth in comparison with ILs-infused ones. This indicates that the existence of stably supported Gr/ILs hybrid liquid films aids the reduction of the friction coefficient by preventing the thinning of the lubricant layer and exposure of the underlying block copolymer HOMEs.

1. INTRODUCTION

Friction is one of the major causes that result in losses of energy and material in mechanical processes.1 Lubrication is a principal focus to reduce the losses and thereby improve energy efficiency and mechanical durability. To meet low friction requirements, ionic liquids (ILs) were studied.2,3 ILs are considered to be potential candidates for lubricant applications, owing to low vapor pressure, high chemical and thermal stabilities, nonflammability, high conductivity, and excellent solubility for a wide range of organic and inorganic compounds.4–6 However, as a liquid lubricant, ILs suffer from rheological thinning under high loads7 and are thus easily squeezed out and depleted.

Slippery liquid-infused porous surface (SLIPS)8–10 which is inspired by Nepenthes pitcher plants,11 consists of an ultrasmooth (defect-free) lubricating liquid layer locked in place by a functionalized porous or textured solid. This surface can repel almost any immiscible liquids, and thus enables the liquids to slide easily off the surface.12 SLIPS makes it possible to stabilize ILs13 to minimize the “rheological thinning” weakness, thus forming a slippery interface better suitable for higher load applications. Previously, we employed mesoporous TiO2 films to provide porous surface matrix to further immobilize ILs,14 but no significant frictional difference was observed from the nonimmobilized ones. The hydration layers (water molecules surrounded) bound to polymer surfaces turn out to be able to support large pressures without being squeezed out and have remarkable properties in the context of lubrication.15–17 Hence, it is highly desirable to find one kind of substrates with homogeneous and uniform pore structures to stabilize and hold the lubricating ILs film.

Anodized aluminum oxide (AAO) membranes with monodispersed pores seem to be a candidate for this task. However, the AAO membranes are too fragile to survive repeated experimental tests. Alternatively, block copolymer homoporous membranes (HOMEs) with highly ordered uniform pores prepared by selective swelling18,19 are expected to serve as the desired porous substrate because of their good mechanical robustness and high pore regularity. Moreover, their pore sizes can be tuned as desired by adjusting the swelling condition in experimental tests. Additionally, the friction behavior of polymer films is of both fundamental and applied interest, including lubrication, M/NEMS (micro/nano electromechanical devices), biomedical

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implants, contact lenses, and so on, where low friction is at a premium.\textsuperscript{6,20−22} It was previously reported that both friction and adhesion forces of polymer surfaces could be controlled and switched by the use of binary polystyrene/poly(2-vinylpyridine) copolymers.\textsuperscript{23,24} Encouraged by the success of SLIPS and hydration lubrication mechanism, we introduce the block copolymer homoporous membranes (HOMEs) to trap the lubricating ILs and hold them in the surrounding network. It is noteworthy that, in a comparison with the properties of pure ILs lubricants, the addition of nanomaterials as additives in ILs could enhance friction reduction performance,\textsuperscript{25−27} and impart greater chemical/structural stability through the formation of better wear resistant molecular arrangements as hybrids.\textsuperscript{28} Graphene layers, which serve as additives in ILs lubricant and viscosity modifiers, markedly reduce frictional forces, most probably due to the ability of graphene to separate two contact surfaces.\textsuperscript{22,28}

We therefore, in this work, have utilized graphene as additives in ILs to form a hybrid that is incorporated in block copolymer HOMEs. In the present case, 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF$_6$], not an excellent lubricant, but being studied extensively, serve as well-defined model ILs to study the frictional behavior in graphene/ILs-infused block copolymer HOMEs.

2. EXPERIMENTAL SECTION

Preparation of Graphene/ILs Hybrid. A graphene/ILs suspension of 0.125 mg/mL was prepared by mixing 2.5 mg commercially available graphene platelets (from Ji Cang Nano Technology Co. Ltd., Nanjing, China) with 20 mL 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF$_6$] ILs (from J&K Scientific Ltd., Beijing, China). The graphene/ILs hybrid was sonicated for 2 h followed by continuous mixing using a magnetic stirrer for 48 h. A stable-uniform dispersion composed of graphene/ILs was seen to develop in the vial. Then this suspension was diluted to the concentration of 0.075 mg/mL as suggested by a previous study.\textsuperscript{7}

Preparation of Graphene/IL-Infused Block Copolymer HOMEs. Block copolymer HOMEs used in this work were prepared from polystyrene-b-poly(2-vinylpyridine) (PS-b-P2VP) block copolymers according to our previous method. In brief, thin films with a thickness of ∼120 nm of the block copolymer with a molecular weight of 290 kDa and 72 kDa for the PS and P2VP blocks, respectively, purchased from Polymer Source, were first annealed in chloroform to perpendicularly align the P2VP cylinders, and then swelling-treated in ethanol at different temperatures to cavitate P2VP cylinders.\textsuperscript{19} The graphene/ILs hybrid with concentration of 0.075 mg/mL (100 μL) was infused into the HOMEs by spin coating at 5000 rpm for 60 s.

Friction and Adhesion Forces Measurements. Friction force measurements were performed on a Dimension Icon atomic force microscopy (AFM, Bruker, USA) in contact mode at ambient conditions. Si$_3$N$_4$ cantilever tips (DNP-10, A tip, tip radius = 20 nm) with a nominal spring constant of 0.35 N/m were employed throughout the experiments, and the scan rate was 2 Hz. The measurements were performed under varied applied loads, using lateral force images derived from trace and retrace tracks of 2 μm X 2 μm under the tip at a 90° scan angle to the cantilever long axis. The normal spring constant of each AFM tip was calibrated using undeformed deflection sensitivity of the supported cantilever to transform the normal load signals (in V) into true normal load (in N). The calibration procedure was performed whenever a different cantilever was used. The average lateral force, given in terms of an output voltage signal (half-difference of the average lateral deflection signal on the photodetector of the forward and reverse traces, in V) was then transformed into a true friction force (in N) from the torsion of the cantilever.\textsuperscript{22,29} Here, the friction coefficient, μ, defined as the constant of proportionality between the measured friction and applied load, is the conventional means of quantifying friction. Friction force data presented in this work are the average of three measurements at multiple sample positions. The adhesion force derived in terms of tip deflection versus the distance of separation can be acquired from the force jump during retraction, which represents the pull-off force required to separate the tip after contact. At least 100 separate force curves were recorded for each specimen surface.

Phased Imaging. Tapping mode phase images, using AFM, are used to detect and quantify changes in composition across the ILs- and graphene/ILs-infused ones.

Helium Ion Microscopy (HIM). The surface morphology of block copolymer HOMEs was also characterized by helium ion microscope (Orion NanoFab, Zeiss, Germany).

Transmission Electron Microscopy (TEM). The detailed structural characterization of the graphene/ILs hybrid and pure graphene sheets was performed by TEM using a Model JEM-2100 transmission electron microscope (JEOL, Japan), operated at 200 kV.

Ellipsometry. The M-2000 Ellipsometer (J.A. Woollam Co., Inc., USA) was used to measure the film thickness of block copolymer HOMEs.

X-ray Photoelectron Spectroscopy (XPS). XPS analysis was conducted on an Escalab 250Xi Imaging X-ray photoelectron spectrometer with a monochromatic Al Kα X-ray small spot source (1486.6 eV).

Raman Spectroscopy. A Horiba Labram HR 800 Raman spectroscope was utilized to acquire the spectra in the range from 600 to 2800 cm$^{-1}$. A 514 nm He-Cd laser was used to excite the Raman scattering. The laser power on the sample surface was 20 mW. The scattered light was detected using a thermoelectrically cooled charge-coupled device (CCD).

Contact Angle Measurements. Contact angles were measured by JC2000D2 (Shanghai Zhongchen Digital Technology Apparatus Co., Ltd. Shanghai, China) at room temperature and ambient humidity. Three drops of ILs, and graphene/IL hybrids were respectively placed on each polymer sample using a manual syringe fixture.

Nanoindentation Tests. G200 (Agilent Technologies, USA) nanoindenter was used to perform nanoindentation tests. The nanoindenter monitors and records the load and displacement of the three-sided pyramidal diamond (Berkovich) indenter during indentation, in the following way: loading to 10 mN, holding for 5 s, and complete unloading. The same rates (3 mN/s) were used for loading and unloading. A total of 6 indentations were made at random-selected, different positions on the specimen surface, correspondingly.

3. RESULTS AND DISCUSSION

We examined the morphology of the annealed block copolymer HOMEs supported by Si under different swelling temperatures. As observed from AFM height images in Figure 1a, the annealed film which was immersed in ethanol at 50 °C for 1 h, followed by air drying at room temperature, exhibiting highly ordered pores on the surface. These pores are near-perfectly hexagonally arranged, with a pore diameter of ∼35 nm (P35, left panel). As the swelling temperature increases to 70 °C, the pore diameters increase to be ∼60 nm (P60, middle panel). The surface undulation with ridges and valleys were observed on P60, due to the higher swelling temperature, which leads to a stronger degree of both the deformation of the PS matrix and the overall P2VP chains\textsuperscript{19} in PS-b-P2VP (polystyrene-b-poly(2-vinylpyridine)) block copolymer HOMEs, and thus, larger pore diameter. A conflation between the enlarged inner pores and the limited space determined by the supporting membrane, results in the waved surface.\textsuperscript{30} The surface undulation shows no significant influences, as we expected, on the lubricant (Gr/ILs hybrid, or neat ILs) distribution on membrane surfaces, from the images taken by the optical microscopy (see Figure S1). In detail, Gr/ILs hybrids spread well and homogeneously on both P35 and P60, while neat ILs
scattered locally on both P35 and P60. The hexagonally patterned pores with uniform diameters on block copolymer HOMEs were examined further by helium ion microscope (HIM, insets) and cross-section profiles in Figure 1c. Surface root-mean-square (rms) roughness values of P35 and P60, independent of the image size for a uniformly distributed surface morphology, determined from the height images are 8.42 and 15 nm, respectively, quantifying the surface roughness.

A typical HIM (helium ion microscope) image of a collection of pristine graphene is shown in the left panel of Figure 2a, and it is found that graphene sheets have a large size, and some are stacked together. TEM observation of the graphene/ILs (Gr/ILs) is possible, as the negligible volatility of ILs prevents the evaporation. The typical electron micrograph of the Gr/ILs hybrid is represented in the right panel of Figure 2a. The Gr/ILs hybrid formed individual spherical shaped (∼20–80 nm) graphene colloidal nanoparticles probably derived from the supernatant phase,38 and embedded in ILs are clearly visible in the TEM image. IL molecules could prevent graphene sheets from agglomeration,31 and the well-dispersed graphene nanophases would act as viscosity modifiers,34 to further improve the mechanical resistance of the surface. However, large-sized sheets accompanied by nanoflakes are also visible with the nanoparticles embedded in them.

Figures 2b,c show the AFM surface height and phase images of various systems. As clearly seen in typical AFM topographic and phase images (Figure 2b), block copolymer HOMEs serve as effective supports for Gr/ILs, and the infused Gr/ILs hybrid formed stably uniform films over HOMEs (P35, P60). Pure ILs show relatively poor wetting behavior on P35 and P60 (Figure 2c). As confirmed in contact angle measurements (insets), neat ILs formed liquid films with a contact angle of 43.2° and 41.6° over P35 and P60 surfaces. With the addition of graphene nanoplatelets, block copolymer HOMEs exhibit better wettabilities, confirmed by the smaller values of contact angle toward Gr/ILs hybrid (40.4° and 35.6°, respectively for P35 and P60). There were no marked differences in contact angle values toward P35 and P60, for both Gr/ILs and pure ILs, but just a small decrease in contact angles for Gr/ILs or ILs on P60 surfaces.

Graphene nanoplatelets are not observable in AFM images because of the small amount of graphene in ILs. The cross-section profiles shown in Figure 2d suggest that Gr/ILs-coated polymer surfaces are more homogeneous than ILs-coated ones, which would be confirmed further by the values of rms roughness. In the case of ILs wetted block copolymer HOMEs, the rms roughness values are 0.233 and 0.66 nm, respectively, for ILs-P35 and ILs-P60. When ILs were mixed with graphene nanoplatelets, rms roughness values of the graphene-ILs hybrid wetted polymer surfaces increased slightly to 0.255 nm for Gr/ILs-P35, but decreased to 0.247 nm for Gr/ILs-P60. The difference in roughness values among the different ILs- and Gr/ILs-infused HOMEs systems is not very significant, but much smaller than bare block copolymer HOMEs surfaces (8.42 and 15 nm, respectively, for P35, P60).

As shown in Figure 3a, Raman spectrum with peaks typical for pristine graphene, including two intense features: G peak located at 1580 cm⁻¹ corresponding to the in-plane vibration of the sp²-bonded carbon in a hexagonal lattice, and G’ band at around 2700 cm⁻¹ originating from a two phonon double resonance process.32,33 The bulk neat ILs, [BMIM][PF₆], revealed C–C and C–N stretching vibrations of the imidazolium ring at around 1567 cm⁻¹, symmetrical deformation vibrations of alkyl chain at around 1421 cm⁻¹, and in-plane wagging vibrations of alkyl chain at around 1026 cm⁻¹. The vibrational bands of anions are assigned at 741 cm⁻¹ due to the expansion and contraction of the respective anions.35 The weak Si Raman peaks observed in both ILs and Gr/ILs samples as shown in Figure 3a are caused by the Si substrate employed in Raman measurements. The normal Raman spectrum of block copolymer HOMEs (P35, P60) are shown in the right panel of Figure 3a. Since the thicknesses of block copolymer HOMEs are relatively small, i.e., 126 ± 0.51, 181 ± 1.7, 120 ± 1.14 nm, respectively, for P35, P60, obtained from ellipsometry, only bands characteristic of the Si substrate were observed.

As shown in the Raman spectra of Gr/ILs- and ILs-infused block copolymer HOMEs (Figure 3b), the presence of ILs is discernible by the occurrence of characteristic bands appeared at approximately 741, 1026, 1421, and 1567 cm⁻¹ (right panel, Figure 3b). However, the characteristic bands of imidazolium rings and anions at around 1567 and 741 cm⁻¹ were shifted to higher wavenumbers (1568 and 743 cm⁻¹, respectively) in Gr/ILs-infused block copolymer HOMEs surfaces (Gr/ILs-P35 and Gr/ILs-P60, left panel, Figure 3b). These blue shifts in graphene-ILs hybrid-infused HOMEs indicate the presence of strain due to the strong interaction between graphene and ILs, and ILs are probably “confined” in graphene layers through π–π stacking interactions with the conjugated structures of graphene layers and different hydrogen bonding interactions of respective anions.34,36 The characteristic bands of graphene (1580 cm⁻¹) in Gr/ILs-P35 and Gr/ILs-P60 (left panel, Figure 3b) well matched with that observed in pristine graphene (left panel, Figure 3a), but weaker in the intensity, due to the small volume fraction of graphene relative to ILs. As discussed in Figure 2, the well-spread Gr/ILs hybrid wicked into thin porous block copolymer HOMEs, so that the ILs signals were relatively weak on Gr/ILs-infused block copolymer HOMEs, while the
characteristic band of Si substrate is stronger which is in a similar manner to that observed in P35 and P60. The intensities of all the peaks related to ILs in the right panel of Figure 2b were greatly enhanced, because of the thicker ILs droplets locally scattered on HOMEs (see the photograph in Figure 5b), which can be confirmed by AFM force curves using a borosilicate glass sphere (radius = 5 μm, Novascan Technologies, Inc. USA) as shown in Figure 3c. When (1) the sphere surface can be wetted by the liquid for a strong capillary attraction (contact angle <90°), and (2) the sphere...
radius is larger than the film thickness, so that the sphere but not the whole cantilever is immersed in the liquid, the film thickness can be directly inferred from the jump-in position. The film thickness is the difference between the jump-in position of the piezo and the zero-force point on the contact line (horizontal double headed arrow in Figure 3c). The differences for Gr/ILs-P35, Gr/ILs-P60, ILs-P35 and ILs-P60 were 117, 194, 409, 725 nm, respectively, and we identify this with the film thickness. Liquid film thicknesses in ILs-P35 and ILs-P60 used in the analyses were obtained in the small droplet, to avoid the whole cantilever immersed in the big liquid droplet as shown in the photograph in Figure 5b.

The stacked XPS survey spectra of the Gr, neat ILs, block copolymer HOMEs, Gr/ILs hybrid-infused, and ILs-infused block copolymer HOMEs are exhibited in Figure 4a. The neat ILs were spin-coated on Si substrate to prepare a specimen for XPS characterization, and clearly revealed the presence of C 1s, N 1s, F 1s, P 2p, and O 1s, with Si 2p coming from the underlying Si substrate. The survey XPS analysis of Gr shows a presence of C 1s and O 1s peaks. The appearance of C 1s and N 1s peaks in P35, P60 arises from polystyrene and poly(2-vinylpyridine) block copolymers HOMEs. Similar peaks, C 1s, O 1s (weak intensity), N 1s, F 1s, and P 2p were found to be present in ILs-P35, ILs-P60, Gr/ILs-P35, and Gr/ILs-P60, as well as a weak signal of Si 2p in Gr/ILs-P60.

In Figure 4b, there were only two peaks arising from the high-resolution C 1s XPS spectra for P35 and P60, where the peak at 285.9 eV was assigned to the C atoms bonded to the N atoms of poly(2-vinylpyridine) in block copolymers HOMEs, while the second peak at 284.8 eV originates from the C–C bond. The patterns of the fitting peak treatment for the XPS spectra of C 1s in pristine graphene (Gr) can be divided into three types of carbon bonds: C–C (284.6 eV), C–O (285.1 eV), and C–O–C (286.1 eV). High-resolution C 1s XPS spectra of Gr/ILs- and ILs-infused HOMEs material as well as ILs on Si (Gr/ILs-P35, Gr/ILs-P60, ILs-P35, ILs-P60, ILs-Si) show three major components. The peak at ~287.2 eV is attributable to C=O bonds probably from the oxidation in ILs caused by adsorbed water, the peak at ~286.3 eV assigned to C=OH, and the peak at ~284.8 eV due to C–C bonds. The high-resolution O 1s peak at 532.2 eV in ILs-Si, P35, and P60 in Figure 4c is from O=Si in the native SiO2 of the substrate, while another peak at 534.7 eV (O=C=O) in P35 and P60, is caused by the annealing and swelling process in preparing block copolymer HOMEs, which may break C–H bonds, to form O=C=O bonds. The O 1s peaks in Gr at ~532.2 and 533.6 eV binding energy were assigned to O in C=O, and C–O=C.
Figure 4. (a) XPS overview spectra, high-resolution (b) C 1s, (c) O 1s, (d) N 1s, and (e) F 1s scans for Gr, neat ILs, block copolymer HOMEs, Gr/ILs hybrid-infused, and ILs-infused block copolymer HOMEs.
The O 1s signal of ILs-P35 and ILs-P60 can be deconvoluted to 531.5 eV (C=O) and 533 eV (OH), while 531.5 eV (C=O) and 532.6 eV (O–Si) for Gr/ILs-P35, Gr/ILs-P60. The observed O–Si bond in Gr/ILs-P35, Gr/ILs-P60 is attributed to the well-spread Gr/ILs hybrid wicked into porous block copolymer HOMEs to form thin-uniform liquid films, and thus O–Si from the native oxide layers of the underlying Si substrate appeared. These results demonstrate that the graphene were noncovalently functionalized with [BMIM]-[PF_6] ILs, and the noncovalent functionalization of graphene was effective for increasing dispersibility in the polymer matrices without damaging the graphene surface structure.

C 1s regions show the presence of C–C, C–OH, and C=O functional groups in both ILs- and Gr/ILs- infused block copolymers HOMEs. However, the severe overlap of peaks restricted a detailed analysis of these regions. Therefore, we focused on the N 1s and F 1s regions, which can provide information about the [BMIM] cations and [PF_6] anions.
respectively. The N 1s spectrum of P35 and P60 shows a single nitrogen peak at 399.0 eV (Figure 4d), coming from the pyridyl group\(^{54}\) of poly(2-vinylpyridine) in block copolymers HOMEs. The ILs-Si spectrum features one signal at binding energies of 401.7 eV, corresponding to the imidazole ring nitrogen of ILs.\(^{38}\) The N 1s peak of the Gr/ILs- infused HOMEs material (Gr/ILs-P35 and Gr/ILs-P60) shows no significant change in binding energy (401.7 eV), compared to neat ILs- infused spectrum (ILs-P35, ILs-P60). However, a reasonable broadening was observed in N 1s peak of Gr/ILs-P35, Gr/ILs-P60 compared with ILs-P35, ILs-P60, suggesting that the delocalized \(\pi\) electrons in the imidazolium ring are affected due to its interaction with the graphene layers. This is because the adsorption of the [BMIM] cation on graphene is mainly driven by the \(\pi-\pi\) stacking interaction of the imidazolium ring with graphene layers,\(^{46}\) in a good agreement with the Raman results we discussed earlier. This result validates the parallel alignment of the [BMIM] cation due to the \(\pi-\pi\) stacking effect.\(^{36,46}\) By contrast, the F 1s peaks in Gr/ILs-P35 and Gr/ILs-P60 are similar to ILs-P35 and ILs-P60 spectra in terms of binding energy (\(\sim686\) eV, assigned to the \(\mathrm{P-F}\) linkage of the \([\text{PF}_6]\) anion\(^{47}\)), but the line broadening still occurs in the former (Figure 4e). This indicates that the \([\text{PF}_6]\) anions in ILs are also affected by the delocalized \(\pi\) electrons from the graphene layers.

The friction coefficient is determined from the gradient of the friction force-normal load data in the linear regime. The observed friction coefficients from Figure 5a, which are summarized in Figure 5b exhibit higher values (0.323 and 0.23) on bare cylindrical P35 and P60 surfaces, respectively. The friction reduction found in P60, is attributed to the structural variations of block copolymer HOMEs. The infusion of Gr/ILs hybrid enables a reduction in the friction coefficient (0.262 and 0.179, respectively, for Gr/ILs-P35 and Gr/ILs-P60), due to the robust adsorbed Gr/ILs hybrid lubricating layer at interfaces, lubricating copolymer surfaces more effectively. Few layer thickness (>20 layers) of graphene is clearly discernible in the pristine Gr, and the interplanar distance was measured to be 0.33 nm, as shown in the left panel of Figure 5c. High-resolution TEM analysis of the Gr/ILs reveals a lattice spacing of 0.36 nm (see the right panel of Figure 5c), which is larger than pure Gr. According to the
findings in XPS results, the parallel alignment of the [BMIM] cation by the $\pi-\pi$ stacking interaction of the imidazolium ring with graphene layer,\textsuperscript{36} loosens the lattice spacing of Gr in Gr/ILs. The loose graphene layers, which is caused by the coexistence of graphene and ILs, would make the sliding easier, and favor the lubrication. The enlarged spacing of graphene colloidal nanoparticles is shown in the schematic of non-covalent functionalization of Gr with ILs in Figure 5c. The compact, dense and continuous tribofilm was therefore formed on the surface of the counterpart due to interaction of ILs with the laminated-structured graphene.

The cylindrical features of block copolymer HOMEs can provide a large capillary force to hold the Gr/ILs hybrid, which would be observed later in AFM force-distance curves (Figure 7), and form a homogeneous and stable lubricating layer (the photograph and schematics in the left panel of Figure 5b) to lower friction coefficient. The lubrication of ILs to bare cylindrical P60 surface is slight, which could be observed from the nonsignificant change in the friction coefficient (0.22) on ILs-P60. In comparison with Gr/ILs-infused block copolymer HOMEs, an increase in the friction coefficient was observed on ILs-infused ones. Friction measurements were performed on the homogeneous Gr/ILs hybrid film in Gr/ILs-P35, Gr/ILs-P60, while on the nonuniformly distributed ILs droplet in ILs-P35 and ILs-P60 (schematics in Figure 5b), to evaluate the different friction characteristics between Gr/ILs and ILs films. The thicker ILs droplets on ILs-P35 and ILs-P60 (409 and 725 nm in film thickness, respectively) represent higher amounts of solution remained on the film surface; however, the unexpected higher friction was observed on the two surfaces. Therefore, the lower friction coefficient observed on thinner Gr/ILs hybrid film (117, 194 nm in film thickness respectively), exhibits a hint that the addition of graphene platelets in the ILs plays a significant role on friction characteristics that were observed in AFM results. It should be noted that the nanotribological performance was found in our preliminary exploration, to be improved with the increase in graphene addition. However, excess graphene added into ILs would tend to form irreversible
agglomerates, not able to disperse stably and homogeneously in ILs, leading to a reduction of the effective graphene dose. We are still optimizing the graphene concentration dissolved into ILs.

It is noticeable that nonzero intercepts with the vertical axis were observed in the friction-load relationship in Figure 5a. This occurrence of friction at zero load is contributed by the adhesion force. Adhesion, between an AFM tip and a sample, arises, mainly, from van der Waals, electrostatic, and attractive capillary meniscus forces. The capillary force dominates on bare block copolymer HOMEs at atmosphere environment due to the formation of a water meniscus between the AFM tip and the copolymer surface, demonstrating an adhesion contribution resulting from the coupling of both the tip-copolymer surface adhesion and meniscus force. However, the adhesion in the other cases in this work, is considered solely a property of copolymer-liquid layers-tip interfaces, because the capillary force is effectively eliminated when the tip is immersed in a liquid environment, i.e., graphene/ILs hybrid or pure ILs. Nonmeniscus adhesive forces arising from the van der Waals and electrostatic interactions between the tip and sample will be significantly influenced by changes in liquid media and the support. As exhibited in Figure 5a, the friction force extrapolated at zero load differs as the liquid varies, indicating that the adhesion contribution to friction is different.

To obtain further insight into the molecular reorganization taking place during friction, we recorded high-resolution traces of friction force as a function of lateral displacement at a constant normal load of ~40 nN. Typical friction force “loops” obtained during AFM imaging, as shown in Figure 6, show that the friction does not remain constant as a function of distance. The sliding dynamics with irregular distribution are clearly visible in the friction loop when the AFM tip encounters the surfaces we studied, including block copolymer HOMEs, graphene/ILs hybrid-, and ILs- infused block copolymer HOMEs. The magnitude and irregularity of the sliding friction in the line traces of Gr/ILs-P60, and bare block copolymer HOMEs, i.e., P35 and P60 are reduced. The respective friction trace of Gr/ILs-P60 exhibit uniform friction distribution regardless of the scan distance (Figure 6b, right panel). In contrast to the friction behavior of Gr/ILs-P60, the well-known stick–slip effects were detected in the friction signal of bare block copolymer HOMEs, P35 and P60 (Figure 6a), and the periodicity of stick–slip directly reflects the surface pattern: 35 and 60 nm cylindrical pore size. ILs-P35 and ILs-P60 show oscillations in friction signals, which do not remain constant as a function of distance (Figure 6c). The frictional strength, can be expressed by the difference between forward and backward friction lines (the width of the friction loop), falling in the order: ILs-P60 > ILs-P35 > Gr/ILs-P35 > Gr/ILs-P60 > P35 ≈ P60, in good agreement with the friction forces shown in Figure 5.

Multiple measurements (at least 100) of force curves were performed in all cases. As force curves were consistent, only one representative curve of each specimen is shown here. As shown in Figure 7a, the AFM tip jumped toward the P35 surface with an attractive force of 1.72 nN at a distance of 6 nm in the approach (red) and 2.5 nN at ~6.3 nm toward the P60 surface. The magnitude of the force decreased until the tip made contact with the surface. When retracting, the tip lost contact with the surface at an attractive force of 17.6 nN and 18.4 nN for P35 and P60, respectively. Force curves recorded on block copolymer HOMEs infused by ILs (ILs-P35 and ILs-P60) as shown in Figure 7c exhibit stronger attractive forces, i.e., 36.8 nN at a distance of ~114 nm and 37.5 nN at ~286 nm, respectively.

The force curves obtained in Gr/ILs-P35 and Gr/ILs-P60 are significantly different, as shown in Figure 7b. The [BMIM] cation of ILs ([BMIM][PF6]) adsorbed on graphene through the π–π stacking interaction of the imidazolium ring with the conjugated structures of graphene layers, leading to the change in electrostatic attractions between the ions, and thus residual charges in Gr/ILs membranes. So the approaching part of force curves in Gr/ILs membranes, different from ILs membrane and bare membranes, displays a long-range attraction, and could be explained by an electrostatic force because of residual charges. At a large distance, the AFM tip did not interact with the Gr/ILs hybrid film (position A). As the tip was moved toward the liquid hybrid film, a sudden jump was observed at a defined position (B). We interpret this jump to be caused by capillary forces. As soon as the tip touched the liquid, a meniscus was formed (C). The meniscus causes an attractive capillary force. Directly after the jump, the tip was not yet in contact with the surface but remained a certain distance away (C). Upon further approach, a steep linear increase in the force was observed (D), indicating that contact had been established between the tip and the block copolymer HOMEs surface.

As the tip was retracted, it was released from the copolymer surface once the force due to cantilever deflection exceeded the contact adhesion force between the tip and the surface (68 and 75 nN, respectively, for Gr/ILs-P35 and Gr/ILs-P60). The attraction increased with increasing distance to 93.8 nN at ~446 nm for Gr/ILs-P35, and 107.3 nN at ~484 nm for Gr/ILs-P60. The strengthened adhesion force observed in Gr/ILs-P60.
P60 may be due to electrostatic force and diversity of ionic charge from graphene–ionic liquid hybrids. After this point, there was a gradually decreasing attractive force between the tip and the Gr/ILs film with increasing distance (F,G) to 49 nN at ~1345 nm in Gr/ILs-P35 case, 61 nN at ~1375 nm in Gr/ILs-P60 case. At this point, the meniscus became unstable and ruptured (marked in gray circles), and the tip was thus completely released from the film and jumped to zero force (H). The largest ruptured distance observed in Gr/ILs-P60 at 1375 nm with the strongest attractive force suggests that the pore features on P60 surfaces provide a larger capillary force to support a stable overcoating of the lubricant of graphene/ILs hybrid than the other systems, i.e., Gr/ILs-P35, and pure ILs infused block copolymer HOMEs surface, reducing the friction coefficient. The force–separation curve upon retraction, specifically the pull-off force, gives information about the interfacial energy, which includes the contribution of van der Waals, oscillatory entropic solvation and electrostatic forces.46 The pull-off force on Gr/ILs membranes (~93.8, 107.3 nN for Gr/ILs-P35, Gr/ILs-P60) is ~2–3 times larger than on ILs (~36.6 and 37.5 nN for ILs-P35 and ILs-P60) and ~5–6 times larger than on bare membranes (~17.6 and 18.4 nN for P35 and P60). The shape of Gr/ILs retraction curves is different from ILs and bare substrates, attributed to a twisting of the end of the cantilever37 caused by the stronger capillary effects in Gr/ILs systems.

The supported stable Gr/ILs hybrid liquid films on P60 surfaces can be further confirmed by the smaller residual indentation depth (Figure 8), while the other liquid-infused HOMEs systems, including Gr/ILs-P35, ILs-P35, and ILs-P60, exhibit larger values in both indentation displacements and residual indentation depth. As shown in representative load–displacement curves measured by a nanoindenter in Figure 8, both the residual indentation depth (231 nm) and peak indentation depth (i.e., penetration depth at peak load, 294 nm) were presented to be much smaller on Gr/ILs-P60 surfaces, indicating possible shallower wear track. No significant plastic deformation was observed on the surfaces, which could be attributed to the synergistic lubrication effect by the combination of the solid lubrication effect of the graphene-based film and the boundary lubrication of the ionic liquid lubricant. Noting that the indentation depth continues to increase during the 5s peak holding segment, likely due to a viscoelastic or viscoplastic response. The residual indentation in the other systems, however, are apparently deeper (255, 321, and 273 nm, respectively, for Gr/ILs-P35, ILs-P35, and ILs-P60). These systems also exhibit larger peak indentation depth under peak loading (323, 368, and 352 nm, respectively, for Gr/ILs-P35, ILs-P35, and ILs-P60). The lubricant at Gr/ILs-P35, ILs-P35, and ILs-P60 interfaces can thus be easily lost, which leads to the thinning of the lubricant layer and exposure of the underlying block copolymer HOMEs,38 and this aids in increments of the friction coefficient. Therefore, much smaller residual indentation depth and peak indentation depth confirm the stably supported Gr/ILs hybrid liquid films on P60 and thus the better lubricating properties of graphene–ILs hybrids infused on 60 nm-pore size block copolymer HOMEs, i.e., Gr/ILs-P60.

4. CONCLUSIONS

We have shown that Gr/ILs-infused block copolymer HOMEs provide lower friction coefficient compared to bare block copolymer HOMEs. The infusion of Gr/ILs hybrid enables a reduction in the friction coefficient due to the compact, dense and continuous Gr/ILs hybrid lubricating layer at interfaces. The parallel alignment of the cation of ILs on graphene by the π–π stacking interaction of the imidazolium ring with the laminated-structured graphene layer, loosens the lattice spacing of Gr in Gr/ILs. The Gr in Gr/ILs hybrids thus reveals a larger lattice spacing of 0.36 nm, than the pristine Gr (0.33 nm). The loose Gr layers caused by the coexistence of Gr and ILs, would make the sliding easier, and favor the lubrication. In comparison with Gr/ILs-infused block copolymer HOMEs, an increase in the friction coefficient observed on ILs-infused ones, attributable to the absence of Gr and the unstably formed ILs film. Especially, the cylindrical features on P60 surfaces, i.e., HOMEs with ~60 nm homogeneous pore structures, provide a larger capillary force to hold a stable overcoating of the lubricant of Gr/ILs hybrid (Gr/ILs-P60) than any other systems. This was confirmed by the largest ruptured distance together with the strongest attractive force observed from AFM force–separation curves in Gr/ILs-P60. Much smaller residual indentation depth and peak indentation depth obtained in Gr/ILs-P60 measured by nanoindenter, agreed well with AFM results. Stably supported Gr/ILs hybrid liquid films on P60, prevent the thinning of the lubricant layer and exposure of the underlying block copolymer HOMEs, to aid the reduction of the friction coefficient. The employment of block copolymer HOMEs to hold stable lubricating hybrid films of graphene/ionic liquids, presents opportunities to further explore the potential of membrane lubrication technology.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b01973.

Optical microscopy images for Gr/ILs- and ILs-infused P35 and P60 (PDF)

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