Friction-induced lubricating nanocoatings of main-chain thermotropic liquid crystalline polymer

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ABSTRACT

The main-chain thermotropic liquid crystalline polymer (LCP) has been reported to be able to simultaneously lower friction coefficient and wear rate when introduced into poly (vinylidene fluoride) (PVDF) as the lubricant. In this investigation, we aim to obtain some insight into the lubricating mechanism of LCP. Through atomic force microscopy (AFM) and Raman spectroscopy, friction-induced in-situ nanocoatings of LCP are observed on friction PVDF domains, which arises from increasing surface temperatures and high shear thinning properties of LCP. Consequently, LCP nanocoatings obviously enhance microscopic hardness of friction PVDF domains. In other words, LCP nanocoatings could be treated as a type of protective lubricant to prevent the direct contact between counterface and PVDF domains, promote wear resistance and lower friction coefficient. To our best knowledge, such an interesting lubricating mechanism is rarely reported. Overall, this investigation not only proposes the novel lubricating mechanism of LCP, but also provides support for further tribological applications in the polymeric systems.

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1. Introduction

The thermotropic liquid crystalline polymer (LCP) has attracted more and more interest owing to the high strength, low melt viscosity, high orientability properties, and superb chemical resistance [1–4]. Conventionally, LCP is classified into two groups—main chain LCP and side chain LCP—in terms of the sites of liquid crystalline moieties. Due to highly anisotropic properties and high cost, main-chain LCP is commonly applied as a minor component to enhance polymer blends. In this case, there are two advantages.1 On one hand, the LCP obviously reduces melt viscosity of blends during processing. On the other hand, LCP microfibrils self-reinforcing composites are often achieved under suitable conditions, mainly attributed to high long-range order of rigid rodlike chains in mesogenic phase [3,4]. In this respect, the poly (l-lactide) (PLLA)/LCP blends were studied by injection [3]. As regards blend containing 30 wt % LCP, the dynamic storage modulus (E’) even surpassed that of pure LCP at the room temperature. Moreover, the striking decrease of E’ for PLLA in the vicinity of α-relaxation temperature also disappeared. According to the authors, the enhancement behavior was attributed to self-reinforcement of LCP microfibrils generated in the blend.

The complexity, cost, and environmental constraints of systems preclude alternative lubrication strategies, e.g. fluid and grease lubrication. Thus, polymeric lubricants are increasingly necessary in many tribological applications—gears, compressor, microelectromechanical systems (MEMS) and bearing components—attributed to the low coefficient of friction [5–9]. The low shear strength of lamellae enables polytetrafluoroethylene (PTFE) to be a type of superb self-lubricant [10]. Besides, high-density polyethylene (HDPE) also exhibits low coefficient of friction duo to obvious chains orientation under friction [11]. However, the striking disadvantage of polymers is high wear rate in tribological applications, which is attributed to low strength and stiffness. Commonly, the reinforcing fillers (e.g. carbon fiber, glass fiber) are frequently introduced to enhance polymers [12]. But, friction coefficient correspondingly increases at this time. Hence, the additional lubricants (e.g. graphite, PTFE) are often needed to lower friction coefficient [13].

In our recent investigations, we reported that LCP was able to simultaneously lower friction coefficient and wear rate when introduced into representative matrix poly (vinylidene fluoride) (PVDF) as the lubricant. In particular, the friction coefficient, wear rate and oscillation amplitude of blend at 20 wt % LCP

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simultaneously decreased by 80.7%, 97.7% and 80.2%, respectively. Besides, frequency-enhancement phenomenon was observed. Through atomic force microscopy (AFM), various frozen nanometer-level textures and striking orientation were presented on friction surfaces of LCP particles, which implied the presence of shear-flow under friction. Moreover, friction PVDF domains exhibited the LCP nanoplates, acting as a type of protective layer to prevent direct contact of counterface-PVDF domains and promote wear resistance. In other words, LCP underwent interfacial shear-flow under increasing surface temperatures and high shear rate to form LCP nanoplates on friction PVDF domains, owing to high shear thinning properties.

As a general trend, friction is always associated with energy dissipation almost arising from viscoelastic relaxation behavior with respect to polymers [9, 14, 15]. In this regard, the dependence of dissipation almost arising from viscoelastic relaxation behavior to form LCP nanoplates on friction PVDF domains, owing to high shear-flow, provide direct contact of counterface-PVDF domains and promote wear resistance. In other words, LCP underwent interfacial shear-flow under increasing surface temperatures and high shear rate to form LCP nanoplates on friction PVDF domains, owing to high shear thinning properties.

2. Experimental section

2.1. Materials

PVDF (FR902) was supplied by 3F Company (Shanghai, China). Main-chain LCP (Vectra A950) was purchased from Hoechst Celanese Company. This random copolyester consisted of p-hydroxybenzoic acid (HBA) of 73 mol % and 2, 6-hydroxynaphthoic acid (HNA) of 27 mol %. The essential properties of PVDF and LCP are provided by suppliers and listed in Table S1.

2.2. Blends preparation

The blend of 90 wt % PVDF and 10 wt % LCP was prepared by melt mixing in an internal batch mixer (Thermo scientific, HAAKE PolyLab OS) at 290 °C and 70 rpm for 10 min and then quenching in an ice water bath to maintain the dispersion state of LCP during melt mixing. Subsequently, the blend was hot pressed into discs utilizing a hydraulic press at 220 °C (below LCP melting temperature) and 10 MPa for 5 min, and then cooled at 20 °C and 10 MPa. All samples were predried at 90 °C for 12 h prior to process.

2.3. Friction procedure

The friction measurement was conducted on a linear reciprocating ball-on-disc tribometer (HS-2M, Lanzhou Zhongke Kaihua Technology Development Co., Ltd., China) under ambient conditions (temperature: 20 ± 2 °C, relative humidity: 50 ± 10%). The contact configuration was illustrated in Fig. 1. A stationary stainless steel ball (9Cr18, diameter: 6 mm and roughness: 20 nm) was used as the counterface. The stroke length and normal load were fixed at 6 mm and 20 N, respectively. A fixed sliding frequency of 10 Hz was applied and the total sliding time was 30 min. Prior to tests, the samples and steel ball were cleaned with ethanol. Coefficient of friction (μ) was calculated as μ = f/Fn, where f is friction force and Fn is normal load. Wear rate (k) was obtained by the following equation:

\[
K = \frac{l \times \left[ R^2 \arcsin(d/2R) - R^2 \sin(2 \arcsin(d/2R))/2 \right]}{(F_n s)}
\]

In the equation above, l is stroke length, R corresponds to radius of steel ball and d is width of worn track and s corresponds to sliding distance.

2.4. Characterization

The morphology of PVDF/LCP blend was observed by scanning electron microscopy (SEM) (TESCAN, VEGA 3 XMU). The characterization was conducted at an accelerating voltage of 20 kV. Prior to SEM characterizations, the specimens were cryogenically fractured and then coated with a thin Au layer. Prior to further characterization, the friction surfaces were cleaned using ethanol under ultra-sonication for 20 min to remove residual wear debris. The selected domains for following characterization are shown in Fig. 2. The friction surfaces were observed through the polarized-light optical microscope (POM) (Leica, DM2500P). Raman spectroscopy of friction surfaces was recorded utilizing an XploRA spectrometer (HORIBA JobinYvon). Measurements were carried out with a laser wavelength of 785 nm and a spectral range from 200 to 2000 cm⁻¹. A 50 × objective was used. At least five points were detected on each specimen. Atomic force microscopy (AFM) was used to evaluate the surface morphology at tapping mode (Bruker, Multimode 8). The scan size was 2 × 2 μm². Surface mechanical properties were evaluated utilizing an ultra
nanoindentation tester (CSM Instruments, Switzerland) with a Berkovich diamond indenter. After approaching the surface, the indenter was pressed into specimen with a constant load rate of 5 mN/min until a maximum load of 0.25 mN, and then withdrawn with the same rate as loading. At least 10 indents were performed on each specimen, and the average values were presented.

3. Results and discussion

3.1. Time evolution of friction surfaces

To obtain some insight into lubrication effect of LCP, the time variations of friction surfaces were investigated in detail, as exhibited in Fig. 3.

As to PVDF/LCP blend, the entire wear behavior corresponds to three regimes—running-in, transition and steady state—compared with neat PVDF (Fig. S4). At 1 min, the friction surface is apparently rough with high initial wear rate of $2.49 \times 10^{-4}$ mm$^3$/N m arising from brittle fatigue-shearing process and adhesion wear (as highlighted by the red circles in Fig. 3(a)). This is due to the ball-on-disc contact configuration during sliding, leading to extremely high initial contact pressure. Besides, LCP particles are stick up out and then removed from friction surface. Moreover, the average wear rate is high up to $1.16 \times 10^{-4}$ mm$^3$/N m at entire running-in period (Fig. 3(b)), however, which is obviously lower than $4.9 \times 10^{-3}$ mm$^3$/N m of neat PVDF (Fig. S4). With sliding, the friction surfaces gradually tend to be regular and smooth, similar to neat PVDF. During transition period, besides, large LCP particles are still stick up out and then removed from friction surfaces, suggesting relatively higher average wear rate than that at steady-state period. It should be noted that the smearing behavior of melting LCP occurs at 10 min, attributed to increasing surface temperature and high shear rate. In general, friction heat is an important dissipation form of energy, accounting for rising temperature of friction surface often comparable to the melting temperatures of polymers. The melting LCP is self-coated on friction PVDF domains to form dispersed coatings under friction (white zones indicated by red arrows in Fig. 3(a)).

Under steady-state period, large LCP particles are observed at greatly smooth friction surfaces, accompanying rising portion of coated domains and obviously depressed wear rate ($5.85 \times 10^{-6}$ mm$^3$/N m). Interestingly, LCP particles approximately sustain the original droplet shapes though occurrence of smearing behavior. Considering total wear rate, it is greatly lowered from $68.8 \times 10^{-5}$ to $2.6 \times 10^{-5}$ mm$^3$/N m by 96% at the existence of LCP. On the other hand, the coefficient of friction is obviously lowered in the absence of running-in and transition periods, compared with neat PVDF (Fig. S4). It is worth mentioning that melting-flow tracks of neat PVDF occur at 4 min, while that of LCP at 10 min. On one hand, melting temperature of LCP (280 °C) is apparently higher than that of PVDF (160 °C). Besides, friction heat is in proportion to coefficient of friction. With respect to PVDF/LCP blend, stable coefficient of friction of 0.11 is obviously lower than 0.5 of neat PVDF, correspondingly leading to suppressed friction heat.

![Fig. 2. Schematic illustrating selecting strategy for characterization.](image1)

![Fig. 3. (a) POM micrographs of friction surfaces for PVDF/LCP blend with sliding time. Sliding direction is horizontal and each image has the same scale as shown. (b) Corresponding wear volume and coefficient of friction with sliding time. The labels are referred to micrographs in (a) and solid lines are the guide for seeing. Regimes: running-in, regime II: transition and regime III: steady-state. The assignment of regimes is based on wear volume. The further evolution of friction surfaces and wear volume under longer friction times are provided in Figs. S1–S3 and Table S2.](image2)
In conclusion, with respect to PVDF/LCP blend, the evolution of wear is greatly similar to that of neat PVDF. As an exception, the transition period of PVDF/LCP blend is distinguished with appearance of LCP coatings and medium wear rate. With friction proceeding, melting LCP is self-coated on friction PVDF domains to form coatings, giving rise to striking lubrication effect on PVDF, i.e. hindered friction and wear rate. On the other hand, the evolution of wear volume greatly differs from that of friction coefficient. As to coefficient of friction, running-in and transition periods are obviously negligible in comparison with the steady-state period. In the other words, the wear volume is more sensitive to lubrication effect than coefficient of friction.

3.2. Friction-induced nanocoatings of LCP

AFM has been widely applied to analyze the surface [24–26]. In this paper, the appearance of LCP coatings is a crucial hint of lubrication effect, leading to decreasing friction and wear rate. To further explore potential interpretations, AFM was utilized to visualize time evolution of LCP coatings at nanometer-scale, as shown in Fig. 4. In principle, the brighter region corresponds to harder domain [26].

At 1 min, irregular pits and ridges apparently cover the rough and lumpy friction surface, owing to brittle fatigue-shearing process and adhesion wear. Besides, the alignment of microscopic shearing-bands is approximately perpendicular to sliding direction, accounting for large fragments [27–31]. It should be noted that no visible melting-flow behaviors are observed. This is due to extremely higher initial wear rate, corresponding to continuously refreshed friction surface. As a consequence, the deformed contact asperities could be immediately removed in every cycle. With sliding proceeding, the local pits and ridges are coarsened and gradually disappear since 2 min, and visual shearing-bands are also absent at 3 min. In addition, the friction surfaces exhibit noticeable discrepancy of brightness, suggesting variation of interfacial stiffness. Obviously, the stiffness at ridges and asperities is remarkably lower than that at other zones. During sliding, the ridges and asperities endure most of load, leading to plastic deformation or melting-flow at contact interfaces. Consequently, the interfacial stiffness is depressed. The portion of depressed zone apparently increases at 5 min, accompanying smoothed friction surface. Besides, no PVDF wear debris is visible at friction surfaces, owing to cleaning treatment prior to characterization.

Apparently, some dispersed nanoplates are observed at 10 min, with a diameter of 50–100 nm and a thickness of around 10 nm (Fig. S6). At first, the presence of wear debris is excluded. Besides, interfacial stiffness of nanoplates is obviously higher in comparison with surrounding PVDF domains. Thereby, LCP is the only interpretation, well in agreement with situation in Fig. 3(a). As mentioned above, rigid rodlike molecules of LCP enable high

![AFM images of friction PVDF domains of PVDF/LCP blend with various sliding times.](image-url)
orientability and shear thinning properties owing to noticeable steric interference effects. Thus, LCP is easy to undergo interfacial shear-flowing under increasing surface temperatures and high shear rate, prompting formation of in-situ nanoplates at friction PVDF domains. Besides, covering area of nanocoatings gradually rises. At 30 min, around 70% of friction PVDF domains are covered to construct a framework of nanocoatings. Intriguingly, thickness variation of nanocoatings is very slight, with a desirable thickness of about 10 nm. It is noteworthy that surface textures of LCP are not observed under shear-flowing. The possible assumption is that due to intermolecular interactions, LCP chains are involved in rod-coil network with PVDF chains, disturbing mesogenic phase of LCP.

Corresponding Raman spectra of friction PVDF domains are shown in Fig. 5. The 1600 cm\(^{-1}\) peak corresponds to 1,4 para-substituted benzene ring of HBA segments, further proving existence of LCP nanocoatings. Intensity ratio between 1600 and 797 cm\(^{-1}\) is associated with the relative content of LCP on friction PVDF domains. In Fig. 5(a), the increasing intensities of benzene ring are striking as sliding proceeds, implying enhancing self-coated behavior of LCP. Although no LCP coatings are visible at running-in periods, the existence of LCP is still observed. In particular, the LCP contents show noticeable increments at 15 and 20 min (Fig. 5(b)), consistent with evolution of wear in Fig. 3. The visualized distribution of LCP nanocoatings on friction PVDF domains is displayed in Fig. 5(c). The deep red domains correspond to LCP particles. At 10 min, LCP particles begin to be surrounded by green domains, implying that LCP is self-coated on PVDF domains to form dispersed nanocoatings. The coating behavior is apparently enhanced with sliding time. At 30 min, the friction surface has been dominated by LCP nanocoatings. Thus, LCP nanocoatings act as a type of protective layer on PVDF domains, responsible for hindered wear rates. It is worth noting that LCP are not detected at PVDF domains of frictionless PVDF/LCP blend, demonstrating that existence of LCP at PVDF domains is due to sliding friction.

As regards polymorphs of PVDF, intriguingly, the gradually increasing trend of polar crystal is revealed with sliding time, clearly opposite to the situation of neat PVDF. The possible interpretation is the noticeable intermolecular interactions between PVDF and LCP, as evidenced through IR and DSC. As pronounced driving force, the intermolecular interactions prefer formation of polar crystals [32–34], accounting for enhancement of polar crystals in PVDF/LCP blend.

To shed insight into effect of LCP nanocoatings on wear resistance, the nanoindentation tests were conducted to assess interfacial microscopic hardness of friction PVDF domains. Nanoindentation tests are an effective method to assess interfacial microscopic hardness [35]. Conventionally, there are two modes, i.e. quasi-static mode of load-controlled and dynamic mode of displacement-controlled. They are distinguished by the analysis way of elastic contact stiffness (S). With respect to quasi-static mode, S is only obtained by slope of load-displacement curve at maximum indentation depth. But, the S is continuously determined as a function of displacement under dynamic mode, that is, continuous stiffness measurement (CSM). In our investigation, the dynamic mode was used.

As to load-displacement curve, the following equation is applied:

\[ P = \left(h - h_f\right)^m \]  

\[ S = \frac{dP}{dh} \left(h = h_{\text{max}}\right) \]  

Thus, the reduced elastic modulus (\(E_r\)) is shown by following equations:

\[ E_r = \frac{S}{h_{\text{max}}} \]  

\[ E_r = \frac{S}{h_{\text{max}}} \]  

Fig. 5. (a) Representative Raman spectra on friction PVDF domains of PVDF/LCP blend with sliding time. The spectra have been shifted upward for clarity. Raw data are provided in Fig. S7. (b) Corresponding intensity ratios. The 797 and 839 cm\(^{-1}\) peaks correspond to \(\alpha\) and polar \(\beta\) and \(\gamma\) polymorphs of PVDF, respectively. The 1600 cm\(^{-1}\) peak is associated with the 1,4 para-substituted benzene ring of HBA segments. (c) Distribution of LCP nanocoatings on friction PVDF domains. The scale bar of color corresponds to relative content of LCP and each image has the same scale as shown.
where \( n_1 \) and \( E_1 \) are the Poisson's ratio and elastic modulus of the indenter, respectively. As to diamond indenter, correspondingly, they are 0.07 and 1141 GPa. The \( n_2 \) and \( E_2 \) refer to the Poisson's ratio and elastic modulus of sample, respectively. \( \beta \) is a constant, which is 1.034 as Berkovich diamond indenter is used. The contact area \( (A) \) under load is obtained by shape function of Berkovich diamond indenter. Besides, the hardness of sample is denoted by:

\[
H = \frac{P}{A}
\]  

\( P \) is the peak load and \( A \) is contact area under \( P \). 

The microscopic hardness displays a tendency of decreasing at first, and then increases. In Fig. 6(b), depressed interfacial hardness is observed from 2 to 5 min, due to plastic deformation and melting-flow at contact interfaces. At 3 min, the hardness drops to the minimum value. Then, the rising tendency is observed since 5 min and the hardness approximates to the saturation point at 15 min. To be more specific, the hardness shows a remarkable increase by 160% at 15 min, in comparison with that at 3 min. Moreover, the hardness at 15 min even exceeds that of frictionless PVDF domains. 

Besides, in Fig. 6(a), the indentation displacements at the maximum load exhibit a noticeable bias at 1 min, suggesting inhomogeneous interfacial strength at friction surface. 

Correspondingly, the bias of hardness exceeds 35%, remarkably higher than 6.6% of frictionless surface. According to Fig. 4, friction surface is rough and lumpy covered with irregular pits and ridges at 1 min. Obviously, the interfacial hardness is inconsistent between pits and ridges, which leads to large bias. With sliding proceeding, the discrepancy of displacements gradually decreases, attributed to regular and smooth friction surfaces.

As pointed out previously, interfacial properties during friction are temperature-dependent. In general, most of the input frictional energy is associated with plastic and viscoelastic deformation, which is converted into heat at friction interface. However, it is commonly very difficult to exactly measure transient temperature rise in a sliding contact. Among various measurement techniques, the infrared radiation comes closer to the true transient temperature, but requires that one of contact surfaces is transparent to infrared. Obviously, infrared radiation technique is unavailable in our situation. Besides, theoretical analysis is another frequently used approach to evaluate transient temperature. Here, we analyze the temperature evolution during friction by theory mode.

At first, the mechanics analysis of frictionless contact is conducted [9]. Considering the contact between the soft PVDF and hard steel ball, the situation is simplified to be an individual asperity contact, and the effect of LCP is negligible. 

The composite modulus \( (E^*) \) is given by

\[
1 \frac{1}{E^*} = \frac{1-n_2^2}{E_2} + \frac{1-n_1^2}{E_1}
\]  

\( 1 \frac{1}{E^*} = \frac{1-n_2^2}{E_2} + \frac{1-n_1^2}{E_1} \)  

The parameters \( E \) and \( \nu \) are the elastic modulus and Poisson's ratio, respectively. The subscripts 1 and 2 refer to steel ball and PVDF sample, respectively and elsewhere in following texts. Here, \( E_1 = 200 \text{ GPa}, \nu_1 = 0.3, E_2 = 2 \text{ GPa} \) and \( \nu_2 = 0.4 \). Therefore, 

\( E^* = 2.36 \text{ GPa} \)

The composite radius is obtained by

\[
1 \frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}
\]  

\( 1 \frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} \)  

The \( R_1 \) and \( R_2 \) are the radii of the steel ball and PVDF flat surface, respectively. Here, \( R_1 = 3 \text{ mm}, \) and \( R_2 = \infty \). Therefore, 

\[ R = 3 \text{ mm} \]

The load to initiate yield \( W_y \) is given by

\[
W_y = 21.17R^2Y \left( \frac{Y}{E^*} \right)^2
\]  

\[ W_y = 21.17R^2Y \left( \frac{Y}{E^*} \right)^2 \]  

Here, \( Y \) is yield stress and the hardness \( H = 2.8Y \). Hardness of PVDF is about 150 MPa according to nanoindentation test. Therefore, 

\[ W_y = 5.25 \text{ N} \]

The applied load \( W \) was 20 N in our friction procedure, so elastic limit was exceeded and some plastic deformation occurred. 

Besides, the radius of the contact \( (a) \) is denoted by

\[
a = \left( \frac{3W}{4R^2E^*} \right)^{1/3}
\]  

\[ a = \left( \frac{3W}{4R^2E^*} \right)^{1/3} \]

\[ a = \left( \frac{3W}{4R^2E^*} \right)^{1/3} = 0.267 \text{ mm} \]

As to the pair of soft polymer and hard steel, the real area of contact \( (A_r) \) is approximated to be the apparent area of contact.

---

**Fig. 6.** (a) Representative load - displacement traces on friction PVDF domains of PVDF/LCP blend at a maximum load of 0.25 mN. The other traces are shown in Fig. 5B. (b) Microscopic hardness of friction PVDF domains at various sliding times.
Thus, the real area of contact is obtained by

$$A_r = \pi d^2 = 0.222nm^2$$  \hspace{1cm} (11)

In most general, the effect of friction on normal pressure and real area of contact is generally small, particularly when the coefficient of friction is less than 1 [9]. Therefore, the stresses and deformation due to the normal and tangential forces are generally assumed to be independent of each other and real area of contact keeps a constant value in our friction tests.

With friction proceeding, wear occurs and the contact plane approximately is a rectangular outline with an arched profile having a radius $R = 3$ mm, instead of the circular outline at the static state. The length ($l$) of the rectangle is given by

$$l = 2R_1 \arcsin \frac{d/2}{R_1}$$  \hspace{1cm} (12)

where $d$ refers to the width of worn track and increases with friction proceeding. Thus, the width ($b$, in the sliding direction) of the rectangle is denoted by

$$b = \frac{A_r}{t}$$  \hspace{1cm} (13)

As to a rectangular heat source analysis [9], the $Pe$ number ($L$) is written as

$$L = \frac{V b}{\sigma} = \frac{V b \rho c_p}{2k}$$  \hspace{1cm} (14)

$V$ is sliding velocity, $\alpha$ is thermal diffusivity ($m^2/s$), $\rho$ is the mass density ($kg/m^3$), $c_p$ is the specific heat ($J/(g K)$) and $k$ is the thermal conductivity ($W/(m K)$). It is assumed that thermal properties are constant during sliding. In our tests, $V=0.12$ m/s, $\alpha_1=12.5 \times 10^{-6} m^2/s$, $\alpha_2=0.64 \times 10^{-7} m^2/s$, $k_1=45$ W/(m K), and $k_2=0.13$ W/(m K). The maximum and minimum $L$ is obtained at the onset and end of friction, respectively.

$L_{max}=786$

$L_{min}=236$

$L > 10$ during entire friction and it is a high speed situation. Hence, the maximum temperature rise ($\theta_{max}$) is written as

$$\theta_{max} = 1.6 \frac{q}{\rho c_p V} \left( \frac{V b}{2 \alpha_2} \right)^{1/2} = 1.6 \frac{\mu W}{k_2 t} \left( \frac{V b}{2 \alpha_2} \right)^{1/2}$$  \hspace{1cm} (15)

$\mu$ is friction coefficient and $q$ ($W/m^2$) is heat flux. $Q$ ($W$) is total heat generated in friction and is illustrated as

$$Q = \mu P V A_r = \mu W V$$  \hspace{1cm} (16)

The friction heat will go into both steel ball and PVDF sample, and the portion ($r$) of the heat going into PVDF sample is stated as

$$r = \left[ 1 + \frac{k_1}{k_2} \left( \frac{2 \alpha_2}{V b} \right)^{1/2} \right]^{-1}$$  \hspace{1cm} (17)

The time it takes to reach the steady temperature in one sliding stroke is approximated to be

$$t_s = \frac{1.25b}{V}$$  \hspace{1cm} (18)

Hence, the energy ($E_i, J$) inputting PVDF surface is

$$E_i = q r t_s = 1.25 \mu W b \left[ 1 + \left( \frac{k_1}{k_2} \right) \left( \frac{2 \alpha_2}{V b} \right)^{1/2} \right]^{-1}$$  \hspace{1cm} (19)

And it is assumed that the rising temperature is uniformly concentrated at a PVDF plate with area $A_r$ and thickness $H$. $H$ is defined as

$$H = \frac{A_r \rho c_p \theta_{max}}{\alpha_t}$$  \hspace{1cm} (20)

The corresponding $\theta_{max}$ and $H$ with time are listed in Table 1. As to reciprocating sliding, it should be pointed out that the heat source repeats over the same point on the surface. The heat generated in first sliding stroke does not leave out completely and there is still residual heat as the next sliding proceeds. Thus, an additional temperature rise ($\theta_t$) should be included. As a simplified consideration, the central zone with one unit of contact area ($A_r$) is selected to be analyzed. The heat loss problem from friction surface is equivalent to a transient heat transport of infinite plate due to the extremely small $H$ compared with $A_r$ [38]. To determine the theory mode, a dimensionless parameter referred to as the Biot number ($Bi$) is used and given as

$$B_i = \frac{h H}{2k_2}$$  \hspace{1cm} (21)

$h$ is the heat transport coefficient with units $W/(m^2 K)$. The varying $Bi$ with time are given in Table 1. Since $Bi \ll 0.1$, the lumped system formulation is applicable and is expressed as

$$\frac{t_r - t_\infty}{t_0 - t_\infty} = e^{-BiFo}$$  \hspace{1cm} (22)

$t_0$ is initial temperature, $t_r$ is temperature after time $t$ and $t_\infty$ is

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<th>Table 1</th>
<th>Varying temperature parameters with friction time by theory analysis.</th>
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equilibrium temperature. In other words, \( t_e - t_\infty \) is residual temperature rise at time \( T (t) \), that is

\[
\theta_f = t_e - t_\infty
\]  

(23)

Here, \( \tau = 0.05 \text{s} \) according to the sliding frequency and \( t_\infty = 20 \text{°C} \). \( F_0 \) is Fourier number and is written as

\[
F_0 = \frac{a q T}{(H/2)^2}
\]  

(24)

Due to small \( \theta_{\text{max}} \) Variation with time, the end \( \theta_{\text{max}} \) in every minute is set as the average \( \theta_{\text{max}} \) in this minute. As an example given, the end \( \theta_{\text{max}} \) at 10 min is 115.5 °C and is set as the average \( \theta_{\text{max}} \) from 9 to 10 min. The initial \( h \) is given as 120 W/(m² K) [36]. It is assumed that \( h \) is constant during friction. Besides, considering that current situation is a 3-dimensional heat conduction, the \( \theta_{\text{f}} \) should be corrected by a factor of 1/3 to obtain more reasonable data. Hence, the maximum surface temperature at sliding time \( T \) (min) is given as

\[
t_{\text{max,T}} = t_e + \frac{1}{3} \sum_{0}^{T} \theta_f + \theta_{\text{max}}
\]  

(25)

\( t_e \) is environmental temperature (20 °C). The \( t_{\text{max,T}} \) are given in Table 1. According to Table 1, \( t_{\text{max,T}} \) has reached the melt point of PVDF, which implies the possibility of PVDF shear-flowing and severe wear. At 30 min, \( t_{\text{max,T}} \) is high up to 225.1 °C. It should be noted that the maximum surface temperature just denotes the average surface temperature as to one unit of contact area, and the flash temperature at contact asperity is greatly higher than \( t_{\text{max,T}} \). Hence, shear-flowing of LCP is still considerable, and leads to the corresponding friction surfaces in Figs. 3–5, although the maximum surface temperature does not exceed the melt point of LCP during current friction. Besides, the \( t_{\text{max,T}} \) increases with time in a period of 30 min, and following interesting question rise: “Would the \( t_{\text{max,T}} \) continually increase with time after 30 min?” We think that it would be a negative answer.

At first, the above analysis does not consider the variation of all heat transport parameters with increasing temperature. Actually, heat loss rises at higher temperature. Besides, the energy dissipation of friction is not entirely presented by the form of heat, and others have been neglected in above analysis. Moreover, as pointed out above, the \( t_{\text{max,T}} \) just shows the local mean temperature at one unit of contact area, rather than the mean temperature of entire friction surface. Commonly, the mean temperature is apparently lower than \( t_{\text{max,T}} \) during friction [9].

On the other hand, the continually increasing surface temperature at friction leads to the eventual failure of PVDF/LCP blend. We have varied the friction time with increasing up to 120 min. The wear data were collected in a time interval of 3 min and shown in Figs. S1–S3 and Table S2 (Supplementary data).

According to Fig. S1, the regime of steady-state is sustained before 39 min. From 39 to 45 min, the variation of wear volume is very slight and this period could be approximately seen as a zero-wear regime (regime IV). Since 45 min, however, the wear volume begins to obviously increase with friction time. Moreover, a sharper increase of wear volume is shown after 81 min. It seems that the friction is under running-in. The period from 45 to 81 min is labeled as regime V, and that from 81 to 99 min is regime VI. Then, wear volume per minute gradually decreases after regime VI, and regime VII refers to this period ranging from 99 to 120 min. As to friction coefficient, there are no obvious variation in regime IV and V, compared with that in the first 30 min. Since regime VI, however, the friction coefficient increases gradually. In particular, the friction coefficient rises up to 0.135 at 120 min. According to Table S2, the average wear volume per minute in regime VI increases up 0.046 mm³/min, even greatly higher than that in regime I (0.0092 mm³/min). As to regime VII, the average wear volume per minute is lowered to 0.0064 mm³/min. Besides, the standard deviation of wear volume in regime VI and VII are obviously higher than that in other regimes, implying the higher instability of friction and wear.

Fig. S2 exhibits representative friction surfaces at various regimes. As the continue of regime III, the friction surface at 36 min is still very smooth. Besides, it is worth noting that LCP particles have deformed into bars under increasing surface temperature and high shear rate, as marked by red arrows. Under polarized-light mode, the bars are more striking in Fig. S3, compared with friction surface at 30 min. With friction proceeding, a large amount of LCP smearing track are displayed at 42 min due to continually increasing surface temperature. Correspondingly, a zero-wear regime (regime IV) is observed. However, some crack appears at friction surface during regime V (51 min), and is highlighted by red arrow. Moreover, at 69 min, a large volume of PVDF is directly detached from friction surface and a large pit is visible (denoted by red arrow), associated with the obviously rising wear volume. Very rough friction surface implies severe wear with a sharper increase of wear volume in regime VI (90 min). Interestingly, the friction surface gradually become smooth after regime VI, as shown at 105 and 120 min (regime VII).

Based on the friction surfaces at 36 and 42 min, the continually increasing surface temperature is verified. Commonly, the friction heat not only leads to the temperature rise at friction surface, but also affects temperature gradient perpendicular to friction surface (Z axis). Under friction, both temperature rise and thermal penetration depth along Z axis are enhanced with continually increasing surface temperature. As a consequence, the mechanical properties beneath friction surface gradually decrease. Moreover, the distribution of temperature along XY plane is not uniform, which leads to the “phase separation” of mechanical properties. Under reciprocating friction, the surface fatigue occurs. Hence, crack appears at the friction surface, and portion with lower mechanical strength is directly detached. Subsequently, severe wear is initiated at regime VI. However, the wear is depressed after most of softened portion are removed. Although interfacial strength are also weakened with rising surface temperature at regime III and IV, LCP nanocoatings could be seen as a type of protective lubricant to obviously enhance interfacial strength. Besides, the inhomogeneity of interfacial properties could be weakened by “mixing” effect of friction. As a consequence, the wear is relatively slight.

In conclusion, the suppressed wear and friction are attributed to lubrication effect of LCP in-situ nanocoatings induced by friction. Due to rigid rodlike molecules and low entanglement, relaxation time of LCP chains is obviously larger than the rearrangement time, leading to high orientability and shear thinning properties. With increasing surface temperatures, shear-flowing of LCP occurs at high shear rate. Thus, flowing LCP is self-coated on friction PVDF domains to form in-situ lubricant with high wear resistance. As a consequence, the friction and wear predominantly undergo at the interfaces between counterface and lubricant, responsible for hindered wear rates. Moreover, high orientation of LCP along sliding direction is easy to leads to friction anisotropies. As a consequence, the coefficient of friction parallel to sliding direction obviously decreases compared with other directions.

4. Conclusion

In this paper, we investigate friction-induced lubrication nanocoatings of main-chain thermotropic LCP. At initial running-in
period, the plastic deformation is dominant on friction PVDF domains accompanying high initial wear rates, due to low surface temperature and high contact pressure. With friction proceeding, increasing surface temperatures lead to occurrence of shear-flowing for LCP at transition state. Thus, LCP is self-coated on friction PVDF domains to form in-situ nanoplates under friction, arising from high shear thinning. Moreover, as to steady state, LCP nanoplates are gradually merged into nanocoatings to cover the friction PVDF domains. Consequently, LCP nanocoatings obviously enhance microscopic hardness of friction PVDF domains, and average wear rates gradually decrease. Besides, friction coefficient is lowered due to high orientability of LCP. In other words, LCP nanocoatings could be used as a type of protective lubricant to prevent the direct counterface-PVDF domains contact, and hinder stick-slip oscillation, coefficient of friction and wear rate. In conclusion, this investigation sheds some insight into the lubricating mechanism of LCP, and provides support for further tribological applications in polymeric systems.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.polymer.2018.02.049.

References