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

Fanglin Xu, Yuanshi Xin, Tongsheng Li[*]

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai, 200433, China

A B S T R A C T

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

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 friction force on sliding velocity corresponds well to that of viscoelastic loss factor on frequency, and thereby is often employed to explore surface relaxation behavior of polymers [15]. Under friction, the most direct and predominant responses of polymers are chains disentanglement and orientation parallel to sliding direction at friction interfaces [16—18], but accompanying chains relaxation. Thus, high orientability, weak chains relaxation and low entanglement density favor to depress friction [19]. On the other hand, the wear resistance is correlated with strength and stiffness. During sliding, adhesion bonds are commonly observed at contact interfaces [9,20]. The fragments detachment and wear of bulk polymers are triggered if shear strength of adhesion bonds is comparable to that of bulk polymers. Therefore, both enhancing strength of polymers and lowering strength of adhesion bonds are able to suppress wear.

As regards LCP, the noticeable steric interference effects among rigid rodlike chains show low entanglement, high orientation and long relaxation time [21,22]. On the other hand, LCP possesses high stiffness and strength. Moreover, apparent anisotropic property of LCP leads to weak strength of adhesion bonds at contact interfaces [23], which is easier to be ruptured than bulk LCP. From the viewpoints of theory, hence, LCP is able to simultaneously reduce coefficient of friction and wear when introduced into polymer blends as lubricants, which has been evidenced by our investigations. Furthermore, LCP nanoplates on friction PVDF domains played a crucial role with respect to decreasing friction and wear. In this paper, we explore the evolution of LCP nanoplates in more detail, obtain some insight into the lubricating mechanism of LCP, and provides guide for further tribological applications of LCP in the polymeric systems. Based on our present results, LCP nanoplates are gradually merged into nanocoatings to cover the friction PVDF domains as friction proceeds. Morphology evolution of LCP nanocoatings with time is observed under friction through atomic force microscopy (AFM), and visualized distribution of LCP nanocoatings is assessed via Raman spectroscopy. Besides, interfacial microscopic hardness on friction PVDF domains with nanocoatings is probed by nanoindentation tests.

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: $50 \pm 10\%$). 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 $\mu = f/F_n$, where f is friction force and F_n is normal load. Wear rate (k) was obtained by the following equation:

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

(1)

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 μm^2. Surface mechanical properties were evaluated utilizing an ultra
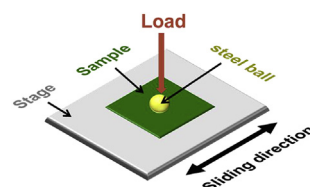

Fig. 1. Configuration of ball-on-disc tribometer.