Friction-induced electroactive $\beta$ polymorph of poly(vinylidene fluoride)

Fanglin Xu, Yuanshi Xin, Tongsheng Li
State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, China
Correspondence to: T. Li (E-mail: lits@fudan.edu.cn)

INTRODUCTION
Poly(vinylidene fluoride) (PVDF) has been extensively explored due to the excellent electric properties (i.e., dielectric, pyroelectric, and piezoelectric), high mechanical performance, resistance to chemicals, and remarkable thermal stability.\(^1\) As a semicrystalline polymer, the crystallinity and crystallite morphs have an important effect on its properties.\(^1,2\) Commonly, PVDF possesses five polymorphs at least, i.e., nonpolar $\alpha$ [form II, trans-gauche-trans-gauche (TGTG)] and $\epsilon$ [form V, TTTGTTTG] phases, and polar $\beta$ (form I, TTT), $\delta$ (form IV, TGTG), and $\gamma$ (form III, TTTGTTTG) forms. As PVDF chains are packed to form parallel molecular conformation, the crystal shows the net dipole moment, associated with polar $\beta$, $\gamma$, and $\delta$ polymorphs. However, nonpolar $\alpha$ and $\epsilon$ forms are obtained under anti-parallel alignment conformation.\(^3-8\) Nonpolar $\alpha$ phase is thermodynamically stable polymorph with crystal lattice of orthorhombic, and is frequently obtained under directly cooling crystallization from melt. In contrast, polar $\beta$ polymorph displays the most noticeable pyroelectric and piezoelectric properties arising from an all-trans planar zigzag conformation with crystal unit of orthorhombic.\(^8\) Therefore, polar $\beta$ polymorph is preferential from the industrial viewpoint. Usually, it is prepared by the mechanical drawing or rolling of $\alpha$ polymorph, quenching from melt, shear-induced crystallization, poling under high electric fields, and crystallization from the polar solvents. Besides, high electric fields also accelerate the formation of $\delta$ crystal, while $\gamma$ and $\epsilon$ phases are observed through annealing of $\alpha$ polymorph and crystallization at high pressures and temperatures.\(^8\)

Among those polymorphs, promotion of polar $\beta$ phase attracts more interest due to the most noticeable pyroelectric and piezoelectric properties. With respect to the formation of $\beta$ phase from $\alpha$ polymorph ($\alpha\rightarrow\beta$) through uniaxial drawing, $\beta$-phase content was obviously enhanced with rising drawing rate and ratio.\(^6\) In particular, $\beta$-phase content increased to 86.5% under elongation of 550% and stretching rate of 50 cm/min at 87°C. Moreover, the authors pointed out that necking region showed higher $\beta$-crystal content. Under drawing, lamellae in PVDF spherulites are frequently pulled out to form fibrils as applied stress is higher than the critical stress. As a consequence, PVDF chain segments align along stretching direction, which induces formation of all-trans (TTT) planar zigzag conformation for polar $\beta$ polymorph. At higher drawing ratio, the domains of fibrillation increase. Consequently, more $\beta$ crystals are formed. In general, alignment and relaxation of PVDF chains simultaneously occur during drawing. As to rising drawing rate, thus, PVDF chains have no enough time to undergo relaxation. Hence, alignment of PVDF chains is enhanced to give rise to polar conformation for polar $\beta$ polymorph. Besides, the effect

Additional Supporting Information may be found in the online version of this article.

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of drawing temperature on $\alpha \rightarrow \beta$ was revealed. At 90°C, $\beta$-crystal content reached the highest value under all drawing ratios. The authors attributed it to $\alpha_{r}$-relaxation of PVDF chain segments in the crystalline part. Commonly, the temperature of PVDF $\alpha_{r}$-relaxation ($T_{a}$) ranges from 70 to 100°C. Below $T_{a}$, chain mobility of PVDF is too low to undergo chains conformation alignment. As drawing temperature is apparently higher than $T_{a}$, however, improving chain mobility leads to orientation of entire crystalline portion, rather than planar zigzag conformation. Consequently, oriented $\alpha$ phase is obtained, instead of $\beta$ crystal. Moreover, higher temperature will accelerate relaxation of PVDF chains to hinder the formation of $\beta$ polymorph.

On the other hand, the shear history exhibited a noticeable influence on direct formation of $\beta$ phase by crystallization from melt. Under the quiescent condition, $\beta$-crystal content was only $\sim$38% by crystallization. As shear was imposed at 220°C and 10 s$^{-1}$, $\beta$-crystal content increased up to about 83%. Moreover, the rate of crystallization was obviously enhanced with rising shear temperature and shear rate. During isothermal crystallization, correspondingly, the higher shear rate and temperature gave rise to higher nucleation density and smaller spherulites. As a general trend, extension and orientation of chain segments assist to overcome energy barrier of nucleation and crystallization under shear. As shear rate is lower than $1/\tau_d$ ($\tau_d$ is chains disentanglement time), shear has no obvious effect on crystallization. While shear rate is higher than $1/\tau_p$ but lower than $1/\tau_c$ ($\tau_c$ refers to chains stretch time), the enhanced point nucleation occurs. Furthermore, fibrillation nucleation is observed to generate shish–kebab crystallization under shear rate larger than both $1/\tau_d$ and $1/\tau_c$. With respect to shear rate of 10 s$^{-1}$, the plausible interpretation was occurrence of point nucleation, prompting crystallization of PVDF. Higher shear rate and temperature led to improving extension and orientation of chains, associated with enhancement of point nucleation.

As a flexible and cost-effective engineering plastic, PVDF of polar $\beta$ phase is widely used as electrodes binder, barrier coating, sensors, actuators, electrostriction, etc. In other words, electroactive $\beta$ phase will obviously affect the performance of PVDF, especially at the electroactive aspect. As mentioned earlier, $\beta$ phase could be obtained from $\alpha$ polymorph or induced by melting shear–crystallization. However, the effect of friction on formation of $\beta$ phase is rarely explored. Indeed, friction at interfaces is inevitable in many applications. Besides, PVDF was recently reported as friction layer in triboelectric nanogenerator (TENG) to improve energy output performance of TENG. On the other hand, friction is expected to be a promising approach with respect to formation of $\beta$ phase at interfaces of electric devices. Hence, it is necessary to probe the effect of friction on $\beta$ phase in detail from the viewpoints of both application and theory. In this article, PVDF with rich $\alpha$ polymorph was subjected to friction. By exploring friction surfaces and wear debris, formation of $\beta$ phase was unveiled. Overall, friction plays a crucial role in the formation of $\beta$ phase through plastic strain (PS) and shear crystallization.

**EXPERIMENTAL**

**Material and Preparation**

PVDF (FR902) was supplied by 3F Company (Shanghai, China) and the essential properties are provided in Table I. PVDF was processed into discs through compression mold utilizing a hydraulic press at 220°C and 10 MPa for 5 min, and then cooled at 20°C and 10 MPa. PVDF was pre-dried at 90°C for 12 h prior to processing.

**Friction Procedure**

Friction procedure was conducted on a linear reciprocating ball-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 is illustrated in Supporting Information Figure S1. The counterface was a stationary stainless steel ball (9Cr18, diameter: 6 mm and roughness: 20 nm). The stroke length and normal load were fixed at 6 mm and 20 N, respectively. The procedure was performed at sliding frequency of 10 Hz with total sliding time of 30 min. Prior to tests, samples and steel ball were cleaned with ethanol. Friction coefficient ($\mu$) was calculated as $\mu = \beta F_n$ where $f$ is friction force and $F_n$ is normal load.

**Characterization**

To investigate crystalline phase in unworn PVDF, the sample was assessed by Fourier transform infrared (FTIR) (Thermo Scientific, NICOLET 6700, Waltham, MA) with a DTGS detector. The measurement was conducted under an attenuated total reflection mode with a wavenumber range from 525 to 4000 cm$^{-1}$, 64 scans and a resolution of 2 cm$^{-1}$. The samples were laid on the diamond crystal. The crystallization and melting behaviors of unworn PVDF and wear debris were investigated through a differential scanning calorimetry (DSC) on a TA Instruments Q2000. The used specimens were fixed at $\sim$3.5 mg. The analysis was conducted from 40 to 200°C at a rate of 10°C min$^{-1}$ and held at 200°C for 5 min. Then, samples were cooled to 40°C at a rate of 10°C min$^{-1}$. The average of three tests was presented. Prior to further characterization, the friction surfaces were dipped into ethanol and cleaned under ultra-sonication at room temperature for 15 min to remove residual wear debris. The frequency of ultrasonic transducer was 30 kHz and power was 0–200 W. The selected domains for following characterization are shown in Supporting Information Figure S2. Then friction surfaces were observed through the polarized-light optical microscope (POM) (Leica, DM2500P, Germany). Raman spectroscopy of friction surfaces were recorded utilizing an XploRA spectrometer (HORIBA JobinYvon, France). 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm$^3$)</th>
<th>MFI (g/10 min)</th>
<th>$T_d$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>Tensile strength (MPa)</th>
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<tbody>
<tr>
<td>PVDF</td>
<td>1.77</td>
<td>10</td>
<td>-45</td>
<td>160</td>
<td>44</td>
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</tbody>
</table>

MFI: melt flow index; $T_d$: glass transition temperature; $T_m$: melting temperature.
detected on each specimen. The statistics analysis of values is conducted through ASTM Standard E 691. Here, average values, standard deviation, and relative standard deviation are provided.

RESULTS AND DISCUSSION
Friction Surfaces
The online friction coefficient as a function of sliding time is shown in Figure 1. Apparently, entire sliding of PVDF consists of two regimes, i.e., running-in and steady-state. The first 4 min belongs to running-in, at which friction coefficient increases linearly with time due to ball-on-disc contact configuration and rising contact area. After friction coefficient is enhanced up to about 0.5, steady-state is dominated. During steady-state sliding, friction coefficient is always in the vicinity of around 0.5. Besides, friction gives rise to obvious stick–slip oscillation, accompanying periodic saw-tooth pattern at the trace of friction coefficient. Commonly, the upper spikes refer to the stick, while the lower spikes correspond to the slip. It is noteworthy that although possessing similar chain configuration with high-density polyethylene and polytetrafluoroethylene (PTFE), PVDF exhibits higher friction coefficient. The possible interpretation is the discrepancy of chains conformation and crystalline structure.

Figure 2 reveals corresponding friction surfaces of PVDF. In the first 1 min, friction surface, covered with mechanical shearing bands, is apparently rough and lumpy due to direct fatigue-tearing process during sliding. Correspondingly, the contact area rises linearly with time, associated with increasing friction coefficient. As to 2 and 3 min, the sizes of shearing bands tend to decrease. Moreover, visible shearing bands at friction surface is almost absent at 4 min, with slight melting-flow (MF) domains as marked by the circle. The MF domains are attributed to generation of friction heat under sliding.

Figure 1. Online friction coefficient for PVDF. Inset: stick–slip oscillation. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 2. The POM micrographs of friction surfaces on PVDF as a function of sliding time. Sliding direction is vertical and each image has the same scale as shown. Regime I: running-in period, regime II: steady-state period. [Color figure can be viewed at wileyonlinelibrary.com]
It is well established that friction is resistance to relative slide at contact interfaces.\(^{16}\) As to polymers, friction is always correlated with energy dissipation mainly arising from plastic deformation. On the one hand, friction energy is almost converted into heat through visco-elastic hysteresis losses at friction interface. Owing to low thermal conductivity, maximum surface temperature of polymer is often comparable to melting temperature under some friction conditions, irrespective of low bulk temperature.\(^{16}\) Therefore, MF domains are frequently observed at friction surfaces of polymer. As a result, friction surfaces tend to be softened and smoothened. At 20 min, the area of MF dominates friction surface of \(\sim 50\%\). As to 30 min, area of MF has been predominant at the friction surface. On the other hand, PS and MF frequently lead to chains disentanglement and orientation parallel to sliding direction.\(^{17–21}\) As a consequence, chains conformation and crystal polymorphs will be correspondingly changed.

**Temperature Rise at Friction Surfaces**

In Figure 2, MF gradually dominates friction surface due to increasing surface temperature. Considering the vital role of surface temperature, it is necessary to evaluate temperature rise at friction surfaces during friction. However, exactly measuring transient temperature rise through experimental techniques is commonly quite difficult as to a sliding contact. Among various measurement approaches, the infrared radiation techniques come closer to true transient temperature, but the requirement is that one of contact surfaces must be transparent to infrared. Apparently, infrared radiation is unavailable in this situation. Besides, theoretical analysis is also another frequently used method to assess transient temperature. Here, we explored the temperature evolution during sliding through theory mode.

At first, mechanics analysis for frictionless contact was performed.\(^{16}\) With respect to the contact between the hard steel ball and soft PVDF, the situation could be simplified as an individual asperity contact.

The composite modulus \(\left( E^* \right)\) is obtained by

\[
\frac{1}{E^*} = \frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2}
\]  

(1)

The parameters \(v\) and \(E\) are the Poisson’s ratio and elastic modulus, respectively. The subscripts 1 and 2 refer to the steel ball and the PVDF, respectively and elsewhere in the following texts. Here, \(E_1 = 200\) GPa, \(v_1 = 0.3\), \(E_2 = 2\) GPa, and \(v_2 = 0.4\). Therefore,

\[E^* = 2.36\text{ GPa}\]

The composite radius is given by

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

(2)

The \(R_1\) and \(R_2\) denote the radii of steel ball and the PVDF flat surface, respectively. Here, \(R_1 = 3\) mm, and \(R_2 = \infty\).

Therefore,

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

The load \(W_y\) to initiate yield is written as

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

(3)

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

Therefore,

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

The load \(W\) of 20 N was applied in this friction procedure. Thus, the elastic limit was exceeded, which leads to some plastic deformation.

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

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

(4)

\[= 0.267\text{ mm}\]

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

\[A_r = \pi a^2
\]  

(5)

\[= 0.222\text{ mm}^2\]

As a general trend, the impact of friction on the real area of contact and normal pressure is relatively small, particularly when the friction coefficient is lower than 1.\(^{16}\) Therefore, the deformation and stresses due to the tangential and normal forces are commonly assumed to be independent of each other and the real area of contact sustains a constant value in this friction tests.

Once sliding begins, wear occurs and contact plane is approximately a rectangular outline with an arched profile of radius \(R = 3\) mm, rather than a circular outline at the static state. The length \((l)\) of rectangle is written as

\[l = 2R \arcsin \frac{d/2}{R_1}
\]  

(6)

where \(d\) is width of the worn track and rises with friction. Thus, the width \((b\) along the sliding direction) of rectangle is denoted by

\[b = A_r / l
\]  

(7)

Regarding a rectangular heat source analysis,\(^{16}\) the \(Pe\) number \((L)\) is given as

\[L = \frac{Vb}{2\alpha} = \frac{Vbp_cR}{2k}
\]  

(8)

\(V\) refers to sliding velocity, \(\alpha\) is the thermal diffusivity \((\text{m}^2/\text{s})\), \(\rho\) is mass density \((\text{kg}/\text{m}^3)\), \(c_p\) is specific heat \([\text{J}/(\text{g K})]\), and \(k\) refers to the thermal conductivity \([\text{W}/(\text{m K})]\). It is hypothesized that thermal properties of the friction surface are constant under friction. In our friction 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 assessed at the onset and end of sliding, respectively.

\[L_{\text{max}} = 116\]

\[L_{\text{min}} = 81\]
$L > 10$ during entire sliding and it is the high speed situation. Hence, the maximum temperature rise ($\theta_{\text{max}}$) is illustrated as

$$\theta_{\text{max}} = 1.6 \frac{q}{\rho c_p V} \left( \frac{Vb}{2\alpha_s} \right)^{1/2} = 1.6 \frac{\mu W}{k^2} \left( \frac{Vb}{2b} \right)^{1/2}$$  \hspace{1cm} (9)$$

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

$$Q = \mu PV_A = \mu WV$$  \hspace{1cm} (10)

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

$$r = \left[ 1 + \frac{k_e}{k_c} \left( \frac{2\alpha_s}{Vb} \right) \right]^{-1}$$  \hspace{1cm} (11)

The time needed to reach steady temperature during one sliding stroke could be approximated to be

$$t_s = \frac{1.25b}{V}$$  \hspace{1cm} (12)

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

$$E_i = Q t_s = 1.25 \mu WB \left[ 1 + \left( \frac{k_e}{k_c} \left( \frac{2\alpha_s}{Vb} \right) \right) \right]^{-1}$$  \hspace{1cm} (13)

And it is assumed that rising temperature is concentrated uniformly on a PVDF plate with an area $A$, and a thickness $H$. The $H$ is stated as

$$H = \frac{E_i}{A \rho c_p \theta_{\text{max}}}$$  \hspace{1cm} (14)

The corresponding $H$ and $\theta_{\text{max}}$ as a function of time are listed in Table II. As to the reciprocating sliding, it must be pointed out that heat source repeats over the same point at the friction surface. The heat produced in the first sliding stroke does not leave out completely, which leads to the residual heat as the next sliding proceeds. Thus, an extra temperature rise ($\theta_r$) should be considered. As the simplified consideration, a central zone with one unit of contact area ($A_c$) is chosen to be analyzed. This heat loss problem at the friction surface could be equivalent to a transient heat transport of infinite plate considering the extremely small $H$ compared with $A_c$. To identify a theory mode, the dimensionless parameter referred to as the Biot number ($Bi$) is applied and stated as

$$Bi = \frac{hH}{2k_c}$$  \hspace{1cm} (15)

$h$ [W/(m$^2$ K)] is the heat transport coefficient. The varying $Bi$ with time is listed in Table II. The lumped system formulation is applicable since $Bi \ll 0.1$, and it is written as

$$\frac{t_r - t_{\infty}}{t_0 - t_{\infty}} = e^{-BiFo}$$  \hspace{1cm} (16)

$t_r$ is the temperature after time $\tau$, $t_0$ is the initial temperature, and $t_{\infty}$ is the equilibrium temperature. In other words, $t_r - t_{\infty}$ is the residual temperature rise at the time $T (\theta_r)$, that is

$$\theta_r = t_r - t_{\infty}$$  \hspace{1cm} (17)

Here, $\tau = 0.05$ s according to the sliding frequency (10 Hz) and $t_{\infty} = 20^\circ C$. $Fo$ is Fourier number and is expressed as

$$Fo = \frac{\alpha_s \tau}{(H/2)^2}$$  \hspace{1cm} (18)

Due to relatively 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, the end $\theta_{\text{max}}$ at 10 min is 302.2$^\circ$C and is given as the average $\theta_{\text{max}}$ from 9 to 10 min. The initial $h$ is given as 120 W/(m$^2$ K). It is assumed that the $h$ is a constant value during friction. Besides, considering that the current situation belongs to a three-dimensional heat conduction, the $\theta_r$ should be corrected through a factor of 1/3 to attain more reasonable data. Hence, maximum surface temperature at the sliding time $T (\text{min})$ is expressed as

$$t_{\text{max},T} = t_e + \frac{1}{3} \sum_{0}^{T} \theta_r + \theta_{\text{max}}$$  \hspace{1cm} (19)

$t_e$ is the environmental temperature (20$^\circ$C), and $t_{\text{max},T}$ are listed in Table II.

According to Table II, $t_{\text{max}}$ shows a rising tendency with sliding time. In particular, $t_{\text{max}}$ at 1 min has exceeded the melt temperature of PVDF, which demonstrates the feasibility of shear-flowing. Moreover, the stick-slip behavior during friction (as shown in Figure 1) leads to obvious oscillation of rising temperature. Besides, heat generated in first sliding stroke almost leaves out completely before the next sliding proceeds, and the additional temperature rise ($\theta_r$) is just $\sim 10^{-5}$ $^\circ$C. Although the real area of contact is approximated to be a constant value, the apparent area of contact gradually increases during friction, and accelerates heat loss. Hence, $\theta_r$ has little contribution to $t_{\text{max}}$.

It should be noted that $t_{\text{max}}$ just exhibits the local temperature at friction surface, rather than the mean surface temperature. Although mean surface temperature is considered to increase with friction, it is apparently lower than $t_{\text{max}}$ during friction. As the evidence, the $t_{\text{max}}$ at 30 min has been high up to 346$^\circ$C, but the PS and MF areas still coexist at friction surface. Besides, the above analysis does not consider the variation of all heat transport parameters with increasing temperature, and the energy dissipation of friction is not entirely presented by the form of heat, this is, others have been neglected in above analysis. Hence, the rising tendency of $t_{\text{max}}$ with sliding time does not mean that the $t_{\text{max},T}$ would continually increase with time after 30 min. Overall, the high $t_{\text{max}}$ at friction surface illustrates that shear-flowing of PVDF is considerable, as shown in Figure 2.

**Polymorphs at Friction Surfaces**

To probe the evolution of polymorphs under friction, friction surfaces of PVDF were assessed utilizing Raman spectroscopy, as shown in Figure 3. Figure 3(a,b) exhibits the representative Raman spectra of PS domains at the friction surfaces and corresponding intensity ratios between 839 and 797 cm$^{-1}$ peak at various sliding time, respectively. The 797 cm$^{-1}$ peak is associated with $\alpha$ polymorph, and 839 cm$^{-1}$ peak corresponds to $\beta$ and $\gamma$ phase crystals. With respect to unworn PVDF, intensity of $\alpha$ polymorph is apparently dominant compared with that of polar phases. At 1 min, however, intensity of polar phase is overwhelming compared with that of $\alpha$ polymorph, as shown...
Correspondingly, intensity ratio in Figure 3(b) obviously rises, compared to that of unworn PVDF. Moreover, enhancement of 839 cm\(^{-1}\) peak at 1 min almost arises from increasing fraction of \(\beta\) polymorph. In the first 1 min, the friction surface is covered by shearing bands without visible MF tracks, implying that PS is dominant. PS prefers formation of \(\beta\) polymorph than \(\gamma\) phase, therefore, formation of \(\beta\) polymorph contributes to enhancement of 839 cm\(^{-1}\) peak. However, a clear drop of intensity ratio is observed at 2 min. As a general trend, temperature plays a crucial role as to the formation of \(\beta\) phase through the PS. Commonly, formation of \(\beta\) phase is preferred in vicinity of \(\alpha\)-relaxation temperature (\(T_a\)) ranging from 70 to 100°C. At 2 min, slight MF tracks are visible, manifesting rising mean surface temperature comparable with melting temperature (160–170°C). In fact, the \(t_{\text{max}}\) at 2 min has been high up to 301.5°C, and MF is considerable. Hence, fraction of \(\beta\) polymorph decreases. With sliding proceeding, intensity ratios are gradually lowered. Since 20 min, MF domains almost have covered friction surface. Under this situation, the dominant formation mechanism of \(\beta\) crystal has been shear-induced crystallization,\(^9\) rather than PS. However, the nucleation and growth of \(\alpha\) phase is also accelerated to depress crystallization of \(\beta\) polymorph, arising from high shear rate (10\(^5\)–10\(^8\) s\(^{-1}\)).\(^{9,16}\) As a consequence, fraction of \(\beta\) polymorph obviously decreases in comparison with that under PS.

Figure 4 shows corresponding relative standard deviation of intensity ratio as a function of sliding time. From 0 to 4 min, decreasing tendency of relative standard deviation is observed, which is well consistent with gradually coming steady-state. Besides, unworn PVDF exhibits a high variation of 19.1%, might arising from the discrepancy of cooling rate, pressure, and interfacial properties of mold during processing. At 10 min, the deviation sharply rises to 11.9% and then gradually drops. According to the discussion above, formation mechanism of \(\beta\) crystal has gradually involved shear-induced crystallization since 10 min, besides of PS. Thus, the mixture of two mechanisms

**Table II. Varying Temperature Parameters with Friction Time by Theory Analysis**

<table>
<thead>
<tr>
<th>(T) (min)</th>
<th>(\theta_{\text{max}}) (°C)</th>
<th>(H \times 10^7) (m)</th>
<th>(Bi \times 10^4)</th>
<th>(\Sigma\theta, \tau \times 10^5) (°C)</th>
<th>(t_{\text{max}}, \tau) (°C)</th>
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<tr>
<td>1</td>
<td>229.1</td>
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</tr>
<tr>
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<td>2</td>
<td>0.92</td>
<td>2.05</td>
<td>330.9</td>
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<tr>
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<td>0.92</td>
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</tr>
<tr>
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<td>0.92</td>
<td>2.06</td>
<td>334.2</td>
</tr>
<tr>
<td>25</td>
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<td>1.96</td>
<td>0.91</td>
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<tr>
<td>26</td>
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<td>2.06</td>
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<tr>
<td>27</td>
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<td>0.9</td>
<td>2.06</td>
<td>343.1</td>
</tr>
<tr>
<td>28</td>
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<td>1.92</td>
<td>0.88</td>
<td>2.06</td>
<td>347.6</td>
</tr>
<tr>
<td>29</td>
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<td>0.88</td>
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<tr>
<td>30</td>
<td>326</td>
<td>1.87</td>
<td>0.86</td>
<td>2.06</td>
<td>346</td>
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</table>
leads to high variation. Moreover, the decreasing variation is observed with shear-induced crystallization being dominant formation mechanism of β crystal. As to the high deviation at 30 min, the possible interpretation is that the nucleation and growth of α phase is accelerated to depress crystallization of β polymorph.

As the evidence, Figure 5 shows the contrast of β polymorph fractions between the PS and MF domains. Apparently, the fractions of β form at PS domains are higher than that at the MF domains. Besides, fractions of β phase at both PS and MF domains simultaneously decrease with time, attributed to the increasing mean surface temperatures.

The corresponding relative standard deviation of intensity ratio is listed in Table III. The variation of PS domains has been discussed as above. As to MF domains, both α and β polymorph are generated under shear-induced crystallization. However, the nucleation and growth of α phase is predominantly accelerated to depress crystallization of β polymorph with friction proceeding according to Figure 5. Hence, deviation correspondingly increases.

**Wear Debris**

As a crucial hint of friction, the morphology and structure of wear debris were explored in detail, as illustrated in Figure 6. The fatigue-tearing process of PVDF surface under sliding gives rise to the large plate-like debris in Figure 6(a), clarifying PS at running-in period. Correspondingly, the rough and lumpy morphology at friction surface further evidences this behavior, as

<table>
<thead>
<tr>
<th>Sample</th>
<th>20 min</th>
<th>25 min</th>
<th>30 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastic strain</td>
<td>10%</td>
<td>6.4%</td>
<td>12.7%</td>
</tr>
<tr>
<td>Melting-flow</td>
<td>4.9%</td>
<td>8.1%</td>
<td>12.3%</td>
</tr>
</tbody>
</table>
shown in Figure 6(b). In contrast, MF domain is very smooth. Besides, the presence of microfibrils debris manifests noticeable fibrillation process, leading to deformation of lamellae in PVDF spherulites.7,8 Figure 7 displays FTIR spectra of unworn PVDF and wear debris. The peak at 762 cm\(^{-1}\) corresponds to \(\alpha\) polymorph, and \(\beta\) crystals are at 839 cm\(^{-1}\). The unworn PVDF exhibits the presence of \(\beta\) phase, arising from pressure and temperature during preparation.7,8 IR absorption peaks at 762 cm\(^{-1}\) (\(\alpha\) polymorph) and 839 cm\(^{-1}\) (\(\beta\) polymorph) are selected to determine relative portion of \(\beta\) phase \([F(\beta)]\) based on the following equations6–8

\[
A_a = \log \left(\frac{T_a}{I_b}\right) = K_a C X_a L
\]

\[
A_b = \log \left(\frac{T_b}{I_b}\right) = K_b C X_b L
\]

\[
F(\beta) = \frac{X_b}{(X_a + X_b)} = \frac{A_b}{(K_b/K_a) A_a + A_b}
\]

In the equations above, \(A\) corresponds to IR absorbance, \(I\) and \(P\) are associated with transmission and incident intensity, respectively. \(K\) corresponds to absorption coefficient at corresponding peak \((K_a = 6.09 \times 10^4\) and \(K_b = 7.7 \times 10^4\) cm\(^{-2}\)mol\(^{-1}\)). \(L\) and \(C\) are thickness of sample and concentration of average total monomer, respectively. \(X\) is degree of crystallinity.

With respect to unworn PVDF, content of \(\beta\) phase \([F(\beta)]\) is 39.6% according to the above equations, while \(F(\beta)\) of wear debris is enhanced to 91.1%. When we consider that \(\beta\)-phase content at friction surface is approximately equal to \(F(\beta)\) of wear debris, the average \(F(\beta)\) for friction surface would be enhanced up to above 91.1% during entire friction.

Corresponding DSC data of unworn PVDF and wear debris are shown in Figure 8, and the overview is illustrated in Table IV. The crystallization degree \((X_c)\) was calculated as following equation: \(X_c = \Delta H_m / \Delta H_m^0\), where \(\Delta H_m\) is fusion enthalpy and \(\Delta H_m^0\) corresponds to fusion enthalpy of neat PVDF 100% crystallized \((X_c = 1)\), \(\Delta H_m^0 = 104.6\) J/g.23,24 The crystallization half-time \((t_{1/2})\) was determined as follows: \(t_{1/2} = (T_0 - T_{1/2})/\phi\), where \(T_0\) is the onset crystallization temperature, \(T_{1/2}\) is the temperature where the relative degree of crystallinity is 0.5, and \(\phi\) is cooling rate.25

According to Table IV, peak melting temperature \((T_m)\) of wear debris is slightly higher than that of unworn PVDF. Due to all-trans planar zigzag conformation and denser packing, melting temperature of \(\beta\) polymorph is commonly higher than that of \(\alpha\) polymorph.23–26 Hence, increasing \(F(\beta)\) leads to higher \(T_m\). However, heating curves of both unworn PVDF and wear debris only exhibit single melting peaks at 167.4 and 167.9 °C, respectively, regardless of \(F(\beta)\). The plausible interpretation is that melting temperatures of \(\beta\) and \(\alpha\) polymorph are too close to be distinguished under present characterization.7,8 But fusion enthalpy and crystallinity degree of wear debris display noticeable increase in comparison with that of unworn PVDF, which illustrates that the friction not only assists formation of \(\beta\) phase but also enhances crystallization.

Besides, crystallization ability of wear debris is clearly improved, based on the cooling curves. The onset crystallization temperature \((T_{onset})\), crystallization temperature \((T_c)\), and crystallization enthalpy \((\Delta H_c)\) of the wear debris show a noticeable tendency of increase. In particular, \(T_c\) increases from 136.8 to 138.6 °C by ~2 °C. Moreover, the rate of crystallization is also improved in terms of crystallization half-time \((t_{1/2})\). It seems that some nucleating agent is introduced into wear debris to enhance crystallization. The relative standard deviation of DSC data is concluded in Supporting Information Table S1. In conclusion, the wear debris exhibits higher deviation. This is due to the complexity of friction process.
The tribochemical reactions have been found in PTFE, polyimide, etc. Correspondingly, those reactions give rise to many polar groups.16 As regards PVDF, a O peak at 1749 cm\(^{-1}\) is observed in FTIR spectra of unworn PVDF. It is suggested that friction-induced reaction of PVDF occurs with introduction of polar groups. Thus, the polar groups are able to act as nucleating agent to enhance crystallization of PVDF.6–8 Besides, another possible interpretation is that entanglement density of chains for wear debris decreases, arising from break of chains and disentanglement under high shear rate (10^5–10^8 s).16 Consequently, formation and growth of nucleus are improved. Overall, F(β), crystallization degree, and crystallization ability of wear debris are obviously promoted under friction, compared to that of unworn PVDF. As an acceptable anticipation, on the other hand, friction should have similar effect on friction surface with wear debris as to polymorph and crystallization.

Formation Mechanism of β Phase

In conclusion, the friction is able to induce the formation of β phase. At initial running-in period, mean surface temperature is below the PVDF melting temperature, although \( t_{\text{max}} \) at 1 min has been high up to 249.1 °C. Thus, PS, as shown in Figure 2, plays a crucial role as to the formation of β phase. When applied shear stress is higher than the critical stress, PVDF chain segments are extended and oriented, which leads to the formation of TTT conformation for polar β polymorph from TGTG' conformation for α polymorph.7,8 Moreover, the lamellae in PVDF spherulites are pulled out to form microfibrils of wear debris, further prompting α→β.6–8 With mean surface temperatures increasing, however, the fractions of β are gradually lowered. During friction, alignment and relaxation of PVDF chains simultaneously occur. Higher surface temperatures prefer relaxation than extension and orientation, which leads to the depression of β polymorph. Besides, improving chain mobility under rising mean surface temperatures favors orientation of entire crystalline portion, rather than planar zigzag conformation.7,8 Consequently, oriented α phase is obtained, instead of β crystal.

With sliding proceeding, increasing mean surface temperatures are comparable to melting temperature of PVDF, accompanying existence of MF domains. At this time, dominant formation mechanism of β crystal is shear-induced crystallization, rather than PS. Under friction, crystallization of PVDF is accelerated by shear-induced point nucleation, assisting to overcome energy barrier of nucleation and crystallization for β polymorph. However, high shear rate (10^5–10^8 s) prefers the nucleation and growth of α phase and inhibits crystallization of β polymorph.16 As a consequence, fraction of β polymorph is obviously suppressed in comparison with that under PS.

In general, β polymorph are obtained through other processing conditions, such as rolling, drawing, annealing, poling, and their combinations.27 However, the poling and annealing only produced F(β) of about 60% and 46%, respectively, lower than friction-induced average F(β) of 91.1%. Although rolling and their combinations are able to improve F(β), the process is too complex. Besides, those methods have little availability at interfaces. Hence, friction is expected to be a promising approach with respect to formation of β phase at interfaces of electric devices.

CONCLUSIONS

In this article, we obtain some insight into the effect of interfacial friction on formation of β phase by spectroscopy and

![Table IV. Overview of DSC Curves of Unworn PVDF and Wear Debris](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_m ) (°C)</th>
<th>( \Delta H_m ) (J/g)</th>
<th>( X_c ) (%)</th>
<th>( T_{\text{onset}} ) (°C)</th>
<th>( T_c ) (°C)</th>
<th>( \Delta H_c ) (J/g)</th>
<th>( t_{1/2} ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unworn PVDF</td>
<td>167.5 ± 0.35</td>
<td>42.9 ± 0.25</td>
<td>41.1 ± 0.17</td>
<td>145.1 ± 0.17</td>
<td>136.8 ± 0.15</td>
<td>47.3 ± 0.31</td>
<td>75.5 ± 0.35</td>
</tr>
<tr>
<td>Wear debris</td>
<td>167.9 ± 0.21</td>
<td>58.2 ± 0.25</td>
<td>55.5 ± 0.31</td>
<td>146 ± 0.23</td>
<td>138.6 ± 0.35</td>
<td>51.5 ± 0.35</td>
<td>72.8 ± 0.51</td>
</tr>
</tbody>
</table>

\( T_m \): peak melting temperature; \( \Delta H_m \): fusion enthalpy; \( X_c \): degree of crystallinity; \( T_{\text{onset}} \): onset crystallization temperature; \( T_c \): peak crystallization temperature; \( \Delta H_c \): crystallization enthalpy; \( t_{1/2} \): crystallization half-time.
thermal analysis. In terms of friction coefficient, entire sliding of PVDF consists of two regimes, i.e., running-in and steady-state period. Correspondingly, striking PS and MF domains are observed at friction surfaces, respectively. Dominant PS highly accelerates $\alpha \rightarrow \beta$ at initial running-in period. In particular, the average $F(\beta)$ for friction surface would be enhanced up to above 91.1% during entire friction. Under PS, extension and orientation of PVDF chain segments lead to the formation of TTT conformation for $\beta$ polymorph from TGTG$^b$ conformation for $\alpha$ polymorph. At subsequent steady-state period, formation of $\beta$ crystal is almost attributed to shear-induced crystallization. Due to shear, occurrence of point nucleation assists to overcome energy barrier of nucleation and crystalization for $\beta$ polymorph. However, fractions of $\beta$ form at MF domains are obviously lower than that at PS domains. Moreover, with friction proceeding, the fraction of $\beta$ phase gradually decreases owing to rising mean surface temperature. Besides, the friction-induced $\beta$ phase is further confirmed by evaluation of wear debris.

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REFERENCES