

The Crystallization Behavior Regulating Nature of Hydrogen Bonds Interaction on Polyamide 6,6 by Poly(vinyl pyrrolidone)

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Electronic Supplementary Information

Abstract The crystallization behavior of polyamide 6,6 (PA66) under complex flow field is of great importance for its final mechanical properties. Poly(vinyl pyrrolidone) (PVP) was applied as crystallization modifying agency to improve processability of PA66. The regulation nature on hydrogen bonds (H-bonds) interaction of PVP was studied upon cooling process. As revealed by *in situ* FTIR, the sample with 5 wt% PVP displays decreased enthalpy change (ΔH) for both the generation of H-bonds and the transition of H-bonds from “disordered” to “ordered” state, which illustrates the molecular mechanism for the regulation of crystallization behavior. Moreover, 2D-WAXD is applied to reveal the evolution of microstructure for sample under external injection field. Hermans orientation factor (f_H) decreases obviously with the addition of PVP, because the relaxation of chain segments is promoted as well the crystallization is retarded. The above crystallization and microstructure changes during the processing provokes the improvement of processability without the apparent sacrifice of mechanical properties.

Keywords Polyamide 66; Poly(vinyl pyrrolidone); Hydrogen bonds interaction

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INTRODUCTION

The crystallization behavior with the synergistic effect of external field, such as injection molding,^[1–4] extrusion,^[5–8] film blowing,^[9–11] is of great significance for the industrial application of semicrystalline polymer. Among them, injection molding is an efficient and economic method for the mass fabrication of industrial parts, and their application performance exhibit great dependence on the microstructure formed during the mold-filling process.^[2,3,12,13] Thus, specific external field are finely designed to explore the flow induced crystallization (FIC) of polymer melt that subjected to different flow conditions, *i.e.*, shear or extension rate, pressure, temperature, *etc.*^[14–17] Herein, non-Newtonian flow and non-isothermal crystallization behavior is acknowledged and crystalline structure shows polymorphism that depends on the external field for diverse polymer, such as polyolefin,^[18,19] polyester, polyamide (PA),^[4] and so on. Meanwhile, computational simulation has been well established to depict the flow pattern inside the mold channel,

and the fountain flow, which is characterized by a mushroom pattern at the flow front, is therefore supposed.^[20,21] The most prominent feature is the multilayer microstructure formed with the orientation of chains.^[22–24] According to early experiments,^[4] a complex flow field, which coupled extensional “pulse” and following shear flow effects, is designed and the anisotropic microstructure evolves across both parallel and perpendicular to the flow direction (FD). It is revealed that shish-kebab structure exists in the core layer and the lamellae twists as approaching the wall due to the transverse tumble of fountain flow.

As aforementioned, temperature field is also an important component of external field.^[25–27] The polymer melt usually undergoes the non-isothermal crystallization process during the processing. Thus, it is necessary to investigate the non-isothermal crystallization behavior for a better understanding of the original question. Herein, polyamide ranks the polymer with strong interchain interaction.^[28] The crystallization behavior of polyamide is mainly affected by the hydrogen bonds (H-bond) interaction formed between the amide groups that attributes to the regular arrangement of molecular chains.^[29,30] Among polyamides, polyamide 6,6 (PA66) has high density of amide group and therefore exhibits high crystallization temperature as well as crystallization rate.^[31] Vari-

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able temperature FTIR is a useful method to investigate the non-isothermal crystallization behavior for the strong inter-chain interaction system.^[29,32,33] According to previous reports for polyurethane, the act of H-bonds dominates the initial crystal formation process.^[28] However, the overquick crystallization rate leads to hardship for the industrial processing of PA66. In order to improve the processability of PA66, it is valid to hinder the crystallization behavior by regulating the formation of H-bonds. For example, Lewis acid, such as GaCl_3 , AlCl_3 , LiCl ,^[34–36] could embeds inside the lamellae sheets and act as molecular zip by complexing with carbonyl group. In addition, some kinds of polymer, *i.e.*, poly(vinyl alcohol),^[37] poly(vinyl pyrrolidone),^[38–40] poly(*p*-vinyl phenol),^[41] *etc.*, which could be a proton acceptor, could act as a strong Lewis base and compose with other Lewis acid polymer. That is, the regulation of H-bonds is the prerequisite for the decrease of crystallization temperature.

In this work, poly(vinyl pyrrolidone) (PVP) is used to regulate the crystallization behavior of PA66. PVP is an amorphous polymer that could form thermodynamically stable miscible mixture with polyamide over the melt temperature. The corresponding interaction between PVP and PA6 is verified by FTIR, and the carbonyl of PVP could form stronger H-bonds with N—H of PA6.^[38] Additionally, the nucleation stage could be depressed by the addition of PVP, which is proposed for both the PA66/PVP blends and PA66-PVP-fiber system.^[40] However, the mechanism of the regulation effect of H-bonds during non-isothermal crystallization process is still indistinct.

Therefore, the aim of present study is to investigate the regulation nature of PVP on H-bonds interaction for PA66 during crystallization, which determines the microstructure and fluidity of PA66 within processability. For this purpose, temperature-dependent FTIR is applied here to study the H-bonds regulation mechanism, and combined with thermal and X-ray analysis, the interaction between PVP and PA66 is investigated. Moreover, injection flow field is introduced to explore the effect of PVP on microstructure for the injection parts, which is associated with the H-bonds interaction in system.

EXPERIMENTAL

Materials and Samples Preparation

The materials used in this research were provided by Kingfa Sci. & Tech. Co., Ltd. The melt flow index of PA66 was 58 g/10min, as determined at 275 °C according to ASTM D1238 (2.16 kg). Poly(vinyl pyrrolidone) (PVP) with the weight-average molecular weight $M_w=1.3 \times 10^6 \text{ g} \cdot \text{mol}^{-1}$ was used in this research.

PA66-PVP blends were prepared by melt compounding using a single screw extruder set up with medium shear configuration modular screw. The temperature of extruder was maintained at 260 °C with a rotating speed of 500 r/min. The neat PA66 was also submitted to the extrusion process to ensure the same thermomechanical history. Hence polymer blends based on PA66 and containing different amounts of PVP (0 wt%, 1 wt%, 3 wt%, 5 wt%, 8 wt%, 10 wt%, 15 wt%), were prepared. And these prepared samples were named as PA66, PA66_PVP1, PA66_PVP3, PA66_PVP5, PA66_PVP8, PA66_PVP10 and PA66_PVP15, respectively. The pellets of neat PA66 and PA66-PVP blends were dried in a vacuum oven

at 100 °C for 8 h before experiments.

The pellets were injected into rectangular plates with dimension of 400 mm × 280 mm × 3 mm on a 440T injection molding machine. The mold had a V-shaped runner of 3 mm thickness and an entrance of 280 mm × 3 mm, which is equal to the cross section of the plate cavity and the V-shaped runner enable the melt to flow uniformly along the width of the cavity. The injection temperature and flow rate were set as 275 °C and 40 mm·s^{−1}, respectively, while holding pressure was 15 bar for 3 s.

Differential Scanning Calorimetry (DSC)

DSC instruments (TA Q200) was employed for the thermo analysis in this research. About 3 mg of samples was sealed in aluminum crucible. The crystallization and melting behaviors were recorded from 30 °C to 300 °C, with a ramp rate of 10 °C/min after the elimination of thermal history at 300 °C for 3 min, and the melting enthalpy (ΔH_m) were integrated with the second heating traces.

Temperature-Dependent FTIR Measurements

FTIR spectral were acquired by using a Nicolet 6700 FTIR spectrophotometer (Thermo Fisher Scientific) equipped with a mercury cadmium telluride (MCT) detector in transmission mode. The specimens were first compression molded at 280 °C and 5 MPa for 3 min, then quickly cooled to room temperature by cool compression. Films with thickness of ~40 μm sandwiched in between potassium bromide thin slice and mounted onto a Linkam FTIR 600 hot stage in the test chamber of FTIR to record *in situ* spectra. The specimens were isothermal at 280 °C for 3 min and cooled to 180 °C at a rate of 4 °C/min, and the spectrum of cooling process were recorded every 30 s. For each spectrum, 16 scans were collected from 4000 cm^{−1} to 650 cm^{−1} at a resolution of 4 cm^{−1}. The spectral correction was carried out according to the total area of both symmetric and asymmetric methylene stretching mode band ($\nu_a(\text{CH}_2)$, 2936 cm^{−1}, $\nu_s(\text{CH}_2)$, 2852 cm^{−1}).

X-ray Measurements

The *ex situ* WAXD/SAXS measurements were carried out on a Xeuss 2.0 equipment operating at 50 keV with Cu-Kα radiation ($\lambda=1.54 \text{ \AA}$). The sample-to-detector distance were 137 and 2500 mm, respectively.

(a) The specimens were compression molded at 280 °C and 5 MPa for 3 min, then cooled slowly to room temperature. Films with thickness of 1 mm were set on the sample stage and the exposure time was 300 s for WAXD and 600 s for SAXS.

(b) The injection rectangular plates were used to investigated the skin-core structure of samples under complex flow field. The specimens were cut along the flow direction and numbered according to their position from the cavity entrance (as shown in Fig. 1). The skin (~60 μm) and core (~700 μm) of the specimens were separated by using a Leica RM2235 ultra microtome.

The Herman's orientation factor (f_H) is applied to quantified the orientation behavior of neat PA66 and PA66-PVP blends that subject to the injection field. For (*hkl*) plane, the definition of f_H could be expressed as:^[42]

$$f_H = \frac{3\langle \cos^2 \phi \rangle_{hkl} - 1}{2} \quad (1)$$

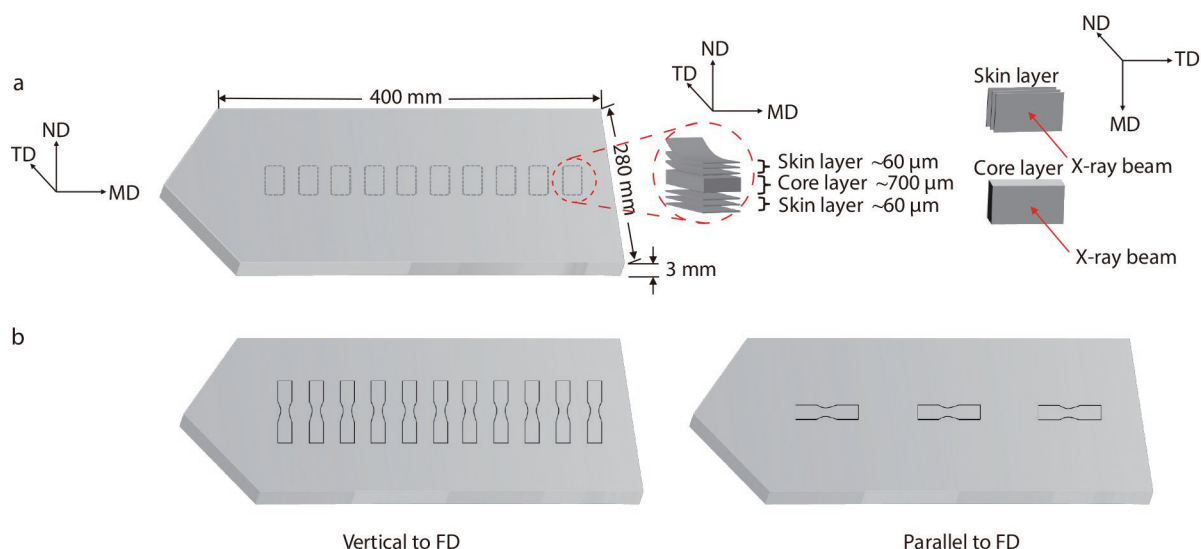


Fig. 1 Schematic of the cut positions of specimens for (a) WAXD measurements, (b) tensile measurements.

where $\cos^2\phi$ is defined as:

$$\langle \cos^2\phi \rangle_{hkl} = \frac{\int_0^{\pi/2} I(\phi) \cos^2\phi \sin\phi d\phi}{\int_0^{\pi/2} I(\phi) \sin\phi d\phi} \quad (2)$$

where ϕ is the azimuthal angle between orienting and reference direction, while $I(\phi)$ is the scattered intensity along ϕ . In this study, the reference direction is assigned to be flow direction.

Small Amplitude Oscillating Shear Measurements

Rheological experiments were performed with a Discovery Hybrid rheometer (TA DHR-2) using parallel plates with diameters of 25 mm. Small amplitude oscillating shear (SAOS) measurements were performed with frequency ranging from 100 rad/s to 0.1 rad/s at 280 °C, with an amplitude of 1% in the linear viscoelastic regime and with a continuous purge of nitrogen.

Mechanical Performance

Tensile properties of injected specimens were tested by Instron 3365 instruments, and the dumbbell shaped specimens were cut from the injected rectangular plates along both the parallel and vertical directions to the FD, as shown in Fig. 1(b).

RESULTS AND DISCUSSION

Regulating Mechanism of PVP on Hydrogen Bonds Organization under Thermal Field

It is well established that H-bonds dominate the crystallization behavior of polyamide 6,6. Herein, thermal behaviors of PA66-based resin are explored by DSC method, as displayed in Figs. 2(a) and 2(b). The plots of T_c and T_m as a function of PVP content are shown in Fig. 2(c). The incorporation of 1 wt% PVP causes a sharp reduction in T_c from 233.1 °C to 230.0 °C, and further increase to 8 wt% causing a linear decrease of T_c with a slope of -0.367 . However, the reduction of T_c slows down and deviated from the linearity. The explanation for this phenomenon will be discussed in next section. Fig. 2(a) displays a typical dual-endothemic behaviors for neat PA66, that has been intensively studied in previous literature.^[43] It corresponds to the melting of two morphological crystalline, forms I and II. Form I is kinetically

preferred and represents a less perfect crystal, which can melt and recrystallizable into more perfect morphology upon heating, while form II is thermodynamically preferred and its T_m is attributed to crystal size and perfection.^[44,45] But the incorporation of PVP leads to the disappears of form I at high PVP concentration, that is, this kinetically controlled crystalline is impeded by PVP. Notably, there is hardly change for T_m of form II. Thus, the lamella thickness and perfection are considered to remain unchanged with the addition of PVP. Herein, SAXS/WAXD is applied to verified the effect of PVP on microstructure. As shown in Fig. 3(a), there is no significant change for the positions of reflection peaks.

That is, the d -spacings for (010)/(110), (100) lattices of α phase are independent of PVP. On the other hand, SAXS is an effective means to analyze the effects of PVP on microstructure (as shown in Fig. S1 in the electronic supplementary information, ESI), and $L/I_a/I_c$ value is estimated by the 1-D electron density correlation function (as displayed in Fig. S2 in ESI).^[46,47] The effect of PVP on I_c and I_a is shown in Fig. 3(b). With the increasing of PVP, I_a increased first and remain unchanged at high PVP concentration (>8 wt%), however the value of I_c is independent of PVP. These results are as expected with T_m of these samples, which illustrate that PVP exist in amorphous region and has no effects on the structure of lattice. Considering the plateau in I_a plot, it can be deduced that a macro phase separation between PA66 and PVP is logical regarding the compatibility at room temperature. And it matches the variation of T_c at high PVP concentration.

For a better understanding of the regulation nature for H-bonds interaction of PVP, temperature-dependent FTIR is applied to study the crystallization behavior. Fig. 4 shows the effect of PVP on characteristic bands of PA66-based resin at room temperature. Hydrogen-bonding interaction was verified in neat PA66 by sharped amide A, amide I and amide II bands, which are assigned to $\nu(\text{N}-\text{H})_{\text{bond}}$ (3302 cm^{-1}), $\nu(\text{C}=\text{O})_{\text{bond}}$ (1638 cm^{-1}) and $\nu(\text{C}-\text{N})_{\text{bond}}$ (1540 cm^{-1}), respectively. Here, PVP is ranked as a Lewis base with nucleophilic carbonyl on its side group, while the $\text{C}=\text{O}$ can hinder the H-bonds interaction of PA66 according to literatures. Currently,

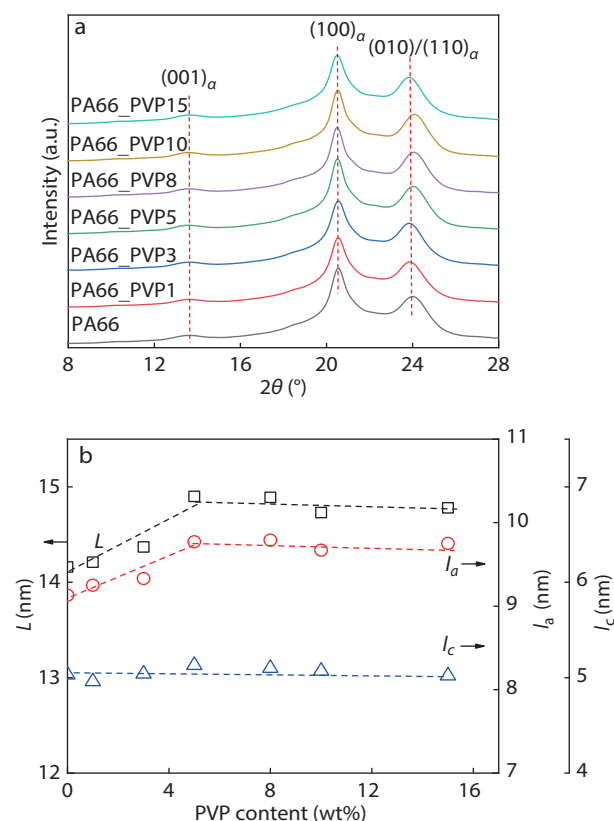


Fig. 2 The (a) heating and (b) cooling curves of PA66 and PA66-PVP blends in DSC measurements; (c) The plots of T_m/T_c versus PVP content according to DSC results.

ous domain, and with higher PVP mass fraction, the absorption at 1680 cm^{-1} emerges that is attributed to free C=O. Hence, it has been verified that PVP can regulate H-bonds interaction of PA66. That is, the regulation nature of PVP on crystallization can be explored *in situ* by temperature-dependent FTIR based on the evolution of amide I band. (The measurements results are displayed in Fig. S3 in ESI)

Accordingly, the amide I bands are sensitive to the local arrangement of C=O groups with respect to the differences in

the ordering of hydrogen bonds.^[29,32] Referring to the previous literature,^[32] the three components of amide I bands can be discerned by second-derivative spectral, and the relative contribution to amide I bands can be quantified by curves deconvolution. Combined the published studies on polyamide,^[30,32] the following restrictions should be obeyed for the deconvolution: (1) the band shape is set as Gaussian-Lorentz type, which shows the best approximated with the initial curves; (2) The base line is separately adjusted from 1720 cm⁻¹ to 1590 cm⁻¹ (i.e., amide I band) to obtain more reliable fitting results; (3) The positions of three components are initially affirmed by second derivative spectrum of amide I bands at room temperature. As previous studies on polyamide 11 by Coleman,^[32] as well as polyurethane by Hsu,^[28] the frequency of those fitted C=O components is dependent on temperature due to the variation of strength for H-bonds. However, this dependence is not remarkable, and only minor red shift happened upon each temperature interval. Herein, we fine tune the position of fitted C=O components upon cooling stage based on the initial position to obtain a better fitted result; (4) The breadth of resolved C=O bands is determined according to literatures, which shows little dependence on temperature. Figs. 5(a) and 5(b) display the outcome of deconvolution at selected temperatures (190 °C, 224 °C, 264 °C, 280 °C) for neat PA66 and PA66_PVP5. The output fitted curves (blue pentagrams) shows good regression compared with the origin curves (red circles) with the $r^2 > 0.999$ (r , coefficient of determination). For both cases, there exit two components of free (pink downward triangles) and disordered hydrogen bonded C=O groups (green upward triangles) at 280 °C, while the ordered hydrogen-bonded C=O emerges at 264 °C and increases in intensity at lower temperature.

The absorption coefficient (ϵ) of amide I band is insensitive to hydrogen bond strength.^[28,32] Thus, amide I is appropriate for quantitative analysis. The formation and dissociation of H-

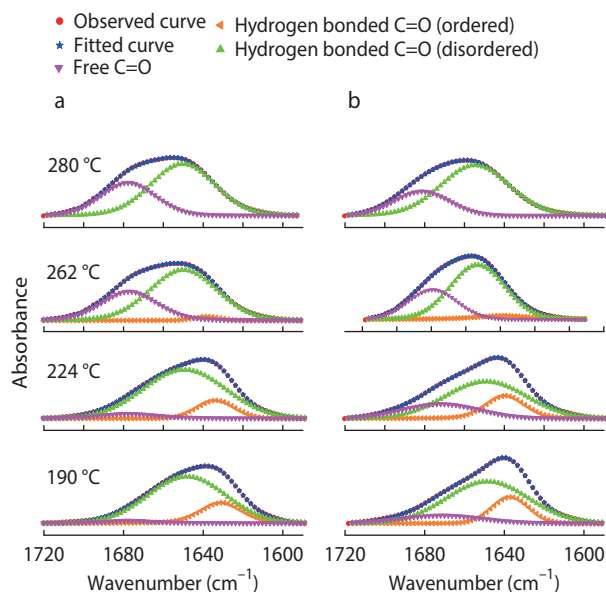
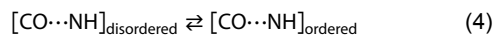
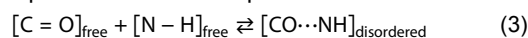


Fig. 5 Deconvolution curves of C=O stretching vibration band at 190, 224, 264 and 280 °C for samples: (a) PA66, (b) PA66_PVP5.

bonds, as well as the reorganization of H-bonds from disordered to ordered state, are being kinetic equilibrium.^[29] Therefore, these two process upon crystallization can be expressed as Eqs. (3) and (4). Herein, we presume that it has arrived the equilibrium at each temperature.



The total molar concentration of C=O group in the system is set as C_0 , which exist equivalence relationship with N-H group, and the fraction of each component is assigned as a_{free} , $a_{\text{disordered}}$, and a_{ordered} , respectively. According to the Lambert-Beer law, the infrared absorbance of specific group is proportional to the product of absorption coefficient, thickness and molar concentration. Due to the absorption coefficient of C=O is insensitive to the strength of hydrogen bonds, the equilibrium constant of the above reactions (K_1 and K_2) can be calculated as follows, respectively.

$$K_1 = \frac{C_{[CO \cdots NH]_{\text{disordered}}}}{C_{[C=O]_{\text{free}}} \cdot C_{[N-H]_{\text{free}}}} = \frac{a_{\text{disordered}}}{C_0 \cdot a_{\text{free}}^2} \quad (5)$$

$$K_2 = \frac{C_{[CO \cdots NH]_{\text{ordered}}}}{C_{[CO \cdots NH]_{\text{disordered}}}} = \frac{a_{\text{ordered}}}{a_{\text{disordered}}} \quad (6)$$

Eqs. (5) and (6) can be further expressed as Van't Hoff form:

$$\ln \frac{a_{\text{disordered}}}{a_{\text{free}}^2} = -\frac{\Delta H_1}{R} \frac{1}{T} + \frac{\Delta S_1}{R} + \ln C_0 \quad (7)$$

$$\ln \frac{a_{\text{ordered}}}{a_{\text{disordered}}} = -\frac{\Delta H_2}{R} \frac{1}{T} + \frac{\Delta S_2}{R} \quad (8)$$

where T is the absolute temperature and R is ideal gas constant (8.314 J·mol⁻¹·K⁻¹). The ΔH_1 and ΔS_1 represent enthalpy and entropy change for the generation of disordered H-bonds, while the ΔH_2 and ΔS_2 represent the change of enthalpy and entropy during the conformational transition of H-bonds from disordered to ordered state, respectively.

As a result, Fig. 6(a) shows the plots of $1/1000RT$ versus $\ln(a_{\text{disordered}}/a_{\text{free}}^2)$. It can be discerned three linear regions in 280–190 °C for both neat PA66 and PA66_PVP5. The ΔH of corresponding process can be calculated through the slope of fitted straight lines for the Van't Hoff plots. Table 1 summarizes the results of ΔH for the two samples, where negative value signifies a typical exothermic process.

As aforementioned, there are disordered H-bonds in system within 280–264 °C and the increasing of H-bonds is slowly. Thus, ΔH_1 is merely –25.5 kJ·mol⁻¹, and no significant effect of PVP is observed; because the thermodynamic factor dominates the generation of disordered H-bonds at high temperature. When temperature is lower than 264 °C, there is an apparently turning points in Van't Hoff plots and ΔH_1 jumps to –222.8±21.0 kJ·mol⁻¹ for neat PA66, indicating a greater tendency for the generation of H-bonds. As contrasts, the ΔH_1 of PA66_PVP5 significantly reduced to –117.1±6.0 kJ·mol⁻¹, that demonstrates the interaction between PVP and PA66 hinders the generation of H-bonds. Zhou *et al.* studied the crystallization behavior of PA66-PA6 blends and verified that the generation enthalpy of hydrogen bonds is reduced compared with neat PA66.^[29] While in their opinion, the addition of second component occupied the position of origin PA66 molecular chains, which retarded the generation of H-bonds. In this research, there exist H-bonds interaction

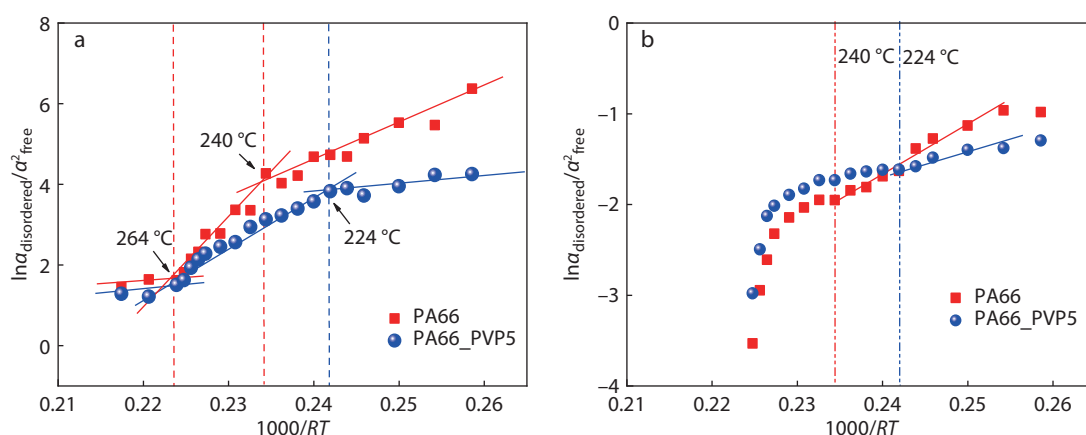


Fig. 6 Van't Hoff plots calculated from amide I bands that represents all three types of C=O groups of the successive two reaction: (a) the formation of disordered hydrogen bonds, (b) the conformational transition from disordered to ordered hydrogen bonds.

Table 1 the enthalpy of PA66 and PA66_PVP5 calculated from Van't Hoff plots during crystallization process.

samples	Generation enthalpy of disordered hydrogen bonds, ΔH_1 (kJ·mol ⁻¹)			Conformational transition enthalpy, ΔH_2 (kJ·mol ⁻¹)
PA66	280–264 °C –25.5	264–240 °C –222.8±21.0	240–190 °C –93.7±8.9	–52.7±3.0
PA66_PVP5	280–264 °C –33.9	264–224 °C –117.1±6.0	224–190 °C –33.6±10.1	–20.4±3.8

between PVP and PA66, while it is much more unstable than that of PA66, as judged from the reduced ΔH_1 .

Furthermore, the second turning points appear at low temperature for both the cases, and the ΔH_1 drastically decreases within this region. It mainly reflects that the disordered H-bonds is unstable and rearrange into ordered state, just as illustrated in Eq. (4). The plots of $\ln(a_{\text{ordered}}/a_{\text{disordered}}) \sim 1/1000RT$ is shown in Fig. 6(b) and the slope of fitted linear regions indicates the conformational transition enthalpy (ΔH_2) from disordered to ordered. While it should be pointed out that this ordered domain represents short range order domain rather than crystalline domain. As for the neat PA66, Fig. 6(b) shows that the linear region starts from 240 °C with the ΔH_2 equals -52.7 ± 3.0 kJ·mol⁻¹. That is, the molecular chains are more liable to reorganized as local ordered conformation at temperature lower than 240 °C, which suggests the unstable of disordered H-bonds and logically lead to the reducing of ΔH_1 to -93.7 ± 8.9 kJ·mol⁻¹. In contrast, an obviously decrease in the turning point (224 °C) can be recog-

nized for PA66_PVP5, and the ΔH_1 reduces to -33.6 ± 10.1 kJ·mol⁻¹. Meanwhile, the ΔH_2 reduced to -20.4 ± 3.8 kJ·mol⁻¹. In consequence, it demonstrates that PVP can effectively suppressed the rearrangement of PA66 chain segments. Considering the interaction between PVP and PA66, it mainly reflect the restriction effects of PVP on the mobility of PA66 molecular chains.

Effect of PVP on Isothermal Crystallization Kinetics

The isothermal crystallization behavior is examined at several annealing temperatures. The relative crystallinity, χ_t , can be obtained by the integral of the heat flow curves according to Eq. (9):

$$\chi_t = \frac{\int_0^t (dH/dt) dt}{\int_0^\infty (dH/dt) dt} \quad (9)$$

where dH/dt is the rate of heat evolution. Fig. 7(a) displays the relationship between χ_t versus t , which illustrates the

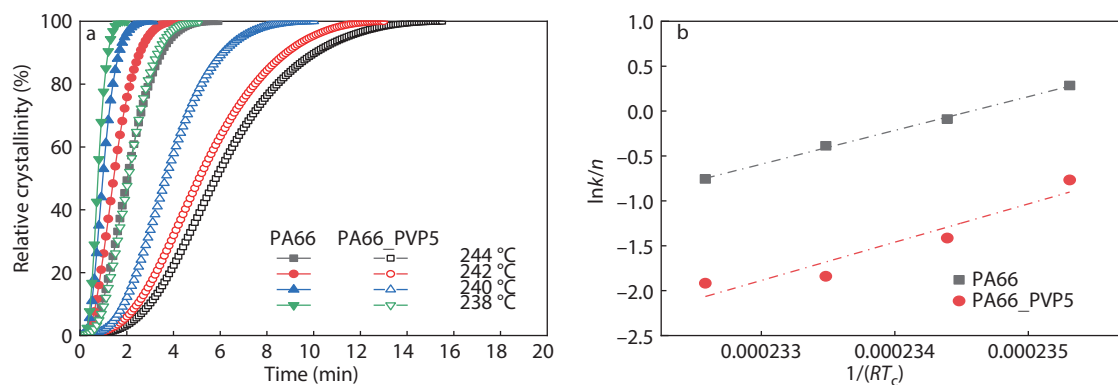


Fig. 7 Isothermal crystallization kinetic results: (a) relationship between relative crystallinity versus isothermal time for PA66 and PA66_PVP5, and (b) Arrhenius plots for PA66 and PA66_PVP5.

crystallization rate of PA66_PVP5 is significantly lower than PA66. In order to quantitatively describe the isothermal crystallization behavior, the Avrami equation is applied here to deal with the obtained data:^[48]

$$\chi_t = 1 - \exp(-kt^n) \quad (10)$$

where n represents the Avrami exponent that describes the dimensionality of the nucleation and growth of crystals, and k is the Avrami rate constant. The values of k and n can be obtained by fitting χ_t and t according to Avrami equation and the results are summarized in Table S1 (in ESI). It can be seen that the values of n are around 2.7–3.0 for PA66 and PA66_PVP5 and independent of the annealing temperature, suggesting the incorporation of PVP has little effects on the dimensionality of nucleation and growth of PA66. Meanwhile, the incorporation of PVP leads to the reduction of k , which represents the crystallization rate. The Lauritzen-Hoffman theory, that establishes the relationship between the rate of crystal growth and nucleation, is usually applied to describe the isothermal crystallization behavior of polymers. However, the crystal growth rate is hard to be obtained through POM due to the spherulite being fragmented and irregular-shaped for PA66. Thus, the Arrhenius equation is applied here by assuming that the crystallization process is thermally activated.^[49,50] Apparent activation energy (ΔE), which reflects the ability of segments to transport to the surface of lamella, can be calculated according to Eq. (11):

$$\frac{1}{n} (\ln k) = \ln k_0 - \frac{\Delta E}{RT_c} \quad (11)$$

where k_0 is temperature dependent pre-exponential factor, T_c is the isothermal temperature and R is gas constant (8.314 J·mol⁻¹·K⁻¹). The plots of $(1/n)\ln k$ versus $(1/RT_c)$ are displayed in Fig. 7(b) and the value of ΔE can be obtained by fitting the curves. The results are also listed in Table S1 (in ESI). The ΔE of PA66_PVP5 is 426.3 kJ·mol⁻¹, which is significantly higher than PA66 (376.0 kJ·mol⁻¹). Therefore, it confirms that PVP can hinder the transport of PA66 chain segments towards the growing surface of lamella due to the H-bonds interaction with PA66.

Evolution of Microstructure under External Injection Field

2D-WAXD technique can provide microstructure information of the sample under injection flow field. As previous literature reported, the thermoplastic melt experiences fountain flow during mold-filling process,^[4] which shows mushroom-shaped tracer line at the front of flow.^[20,21] Thus, the injection part is characterized by multi-layered microstructure across the direction perpendicular to MD. Mavridis *et al.* proposed the evolution mechanism of fountain flow at the section of injection runner by numerical simulation method.^[21] When fluid element is near to flow front, it decelerates and stretches in the direction vertical to FD, whereas as it reaches the wall in a curved path, the fluid element deforms and orients along FD. Thus, the lamella orientation is supposed to depend on the distance away from centerline.

The evolution of multilayered microstructure has been well established in several polymer systems, *i.e.*, polyolefin^[22,51,52] and polyamide.^[3,4] Herein, we focus on the effect of PVP on the microstructure under injection flow field. Fig. 8 displays the evolution of diffraction pattern from gate to end for both skin and core layer. The typical diffraction patterns of α -phase

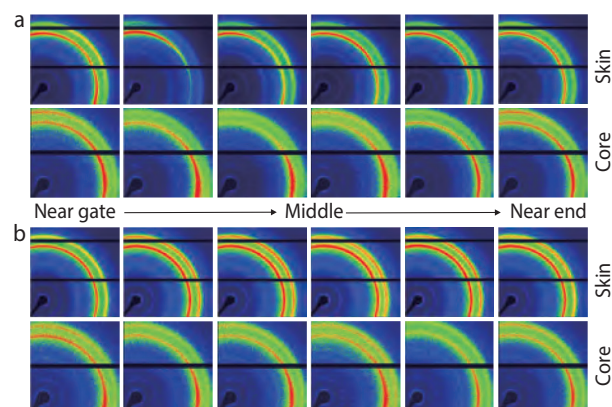


Fig. 8 2D-WAXD patterns of the injection rectangular spline of (a) PA66 and (b) PA66_PVP5. The skin and core layer microstructure were characterized respectively and samples at different locations were cut according to Fig. 1.

crystal with diffraction arcs of $(100)_\alpha$ and $(010)_\alpha/(110)_\alpha$ planes shows clearly intensity inhomogeneity along the azimuthal. As shown in Fig. 8(a), the diffraction pattern of $(100)_\alpha$ plane displays arc-shaped reflection maximum about the meridian in core layer. It demonstrates that the c -axis of unit cell oriented perpendicular to flow field. The diffraction rings become nearly isotropic near the end position. The reduction of orientation is reasonable considering the relaxation behavior of oriented chain segments. The azimuthal intensity scans of $(100)_\alpha$ planes and $(010)_\alpha/(110)_\alpha$ are shown in Figs. S4 and S5 (in ESI), respectively. The diffraction intensity of $(100)_\alpha$ increases obviously around meridian at the positions near gate. The peak intensity of $(010)_\alpha/(110)_\alpha$ plane shows a 20° offset away from the equator, which is derived from the disorientation or more prominently, twisting lamellae of α -phase. At the end position, the orientation behavior is weakened with homogeneous intensity along the azimuth, which indicates random orientation after relaxation process. However, the skin layer displays a distinct different diffraction pattern, as shown in Fig. 8(a). There is a strong diffraction arc for $(100)_\alpha$ plane around the equator, which is identified by azimuthal intensity distribution. It can be deduced that the c -axis of unit cell oriented along the flow field under the shear effect of mold wall at skin layer, and it is in accordance with the predicts of fountain flow mode. Meanwhile, there is an arc emerged around meridian of $(010)_\alpha/(110)_\alpha$ plane, and it is further identified by the azimuthal integral curves in Fig. S5 (in ESI). The diffraction intensity decays slightly from meridian to equator, representing the twisting of lamella at skin layer.

The regulation effect of PVP on microstructure is confirmed by 2D-WAXD. As shown in Fig. 8(b), the diffraction pattern is approximately isotropic for $(100)_\alpha$ and $(010)_\alpha/(110)_\alpha$ plane at core layer, which indicates isotropic microstructure. It indicates that PVP impedes the orientation behavior under external flow field. At skin layer, a $(100)_\alpha$ diffraction arc emerges around equator, representing slightly degree of orientation occurred under the shear effect of the wall. In order to quantify the orientation degree, we calculated the Herman's orientation factor (f_H) of $(100)_\alpha$ plane according to Eq. (1). If the lamellae are random distribution, the f_H yields zero, and if the normal direction of lamellae completely vertical to the

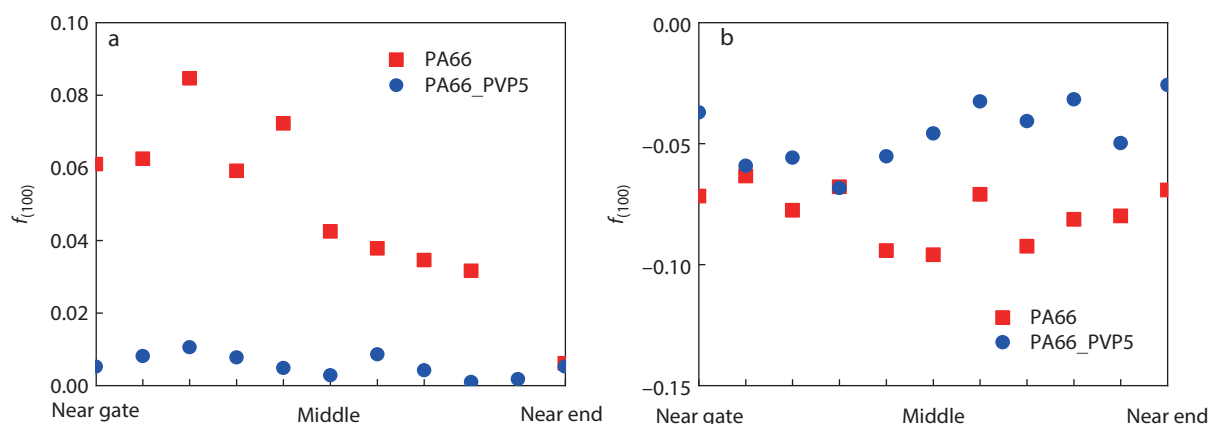


Fig. 9 Herman's orientation factors (f_H) of (a) core and (b) skin layer which were separated from PA66 and PA66_PVP5, respectively.

flow direction, *i.e.*, the molecular chains orient along the flow direction, $f_H = -0.5$. However, if parallel to the flow direction, *i.e.*, the molecular chains orient opposite to the flow direction, $f_H = 1$.

As shown in Fig. 9, the f_H yields positive value at core layer, and first increase with the evolution of fountain flow at the initial stage after entering the runner, whereafter, f_H experiences stepwise decrease as the relaxation of oriented chain segments. At skin layer, the negative f_H represent the parallel alignment of chain segments along the flow direction. The f_H value undergoes V-shape tendency just as core layer. Notably, PVP causes the overall reduction of f_H compared with neat PA66, in especial the f_H is near zero at core layer.

Herein, the viscoelasticity is combined to explain the effect of PVP on microstructure under injection flow field. As shown in Fig. 10, the storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) of PA66_PVP5 obviously decrease compared with neat PA66, which indicates improved mobility of chain segments and accelerated relaxation process. As dis-

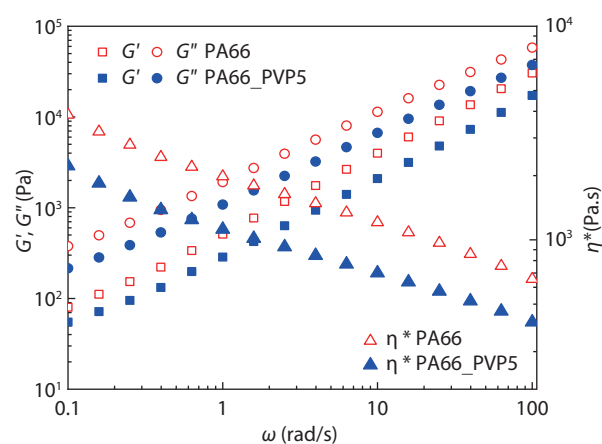
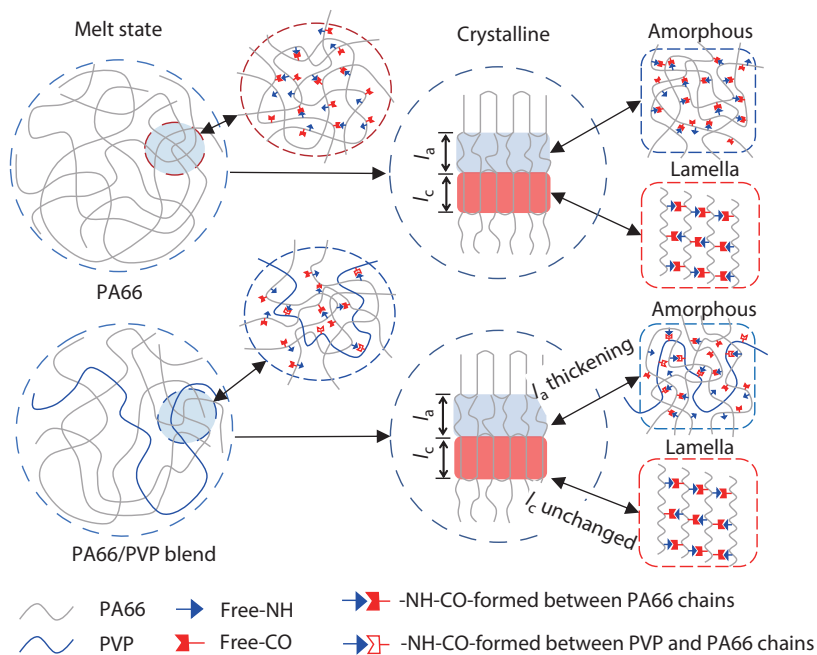


Fig. 10 storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) versus angular frequency of PA66 and PA66_PVP5.



Scheme 1 Schematic diagram of the regulation effect of PVP on microstructure.

cussed above, the H-bonds in the molten state of PA66 is disturbed due to the interaction between PA66 and PVP, thus PVP can act as plasticizer for PA66 and promotes the fluidity of PA66.

Therefore, the regulation nature of PVP on crystallization behavior of PA66 is depicted by Scheme 1. In the melt state, the exist of PVP occupies the position of PA66, and forms H-bond with amino group of PA66. This interaction restricts the overall formation of H-bonds between PA66, which decrease the $G'/G''/\eta^*$ of the system. Upon the cooling process, the formation of disordered H-bonds of PA66 is retarded due to the existed interaction with PVP. Moreover, the transition of H-bonds from disordered to ordered state by the rearrangement of chain segments is impeded, which hence lead to the decrease of T_c . Notably, the exist of PVP has no effect on the lamellae structure, while l_a thicken obviously. Thus, it indicates that PVP is expelled out of the lamellae during crystallization, and mainly exists in amorphous domain.

Effects of Poly(vinyl pyrrolidone) on Mechanical Properties of Polyamide 6,6

We further examined the effect of PVP on mechanical properties as the variation of microstructure. The specimens were cut from the injection-molded rectangular plates along two directions, as shown in Fig. 1(b).

The tensile measurements are carried out for PA66 and PA66_PVP5, and the mechanical properties of specimens that

are parallel and perpendicular to the flow direction are analyzed respectively. Fig. 11 compares the tensile modulus of the PA66 and PA66_PVP5 samples at different flow field position. As shown in Figs. 11(a) and 11(b), the evolution of microstructure from gate to end position has hardly effects on the mechanical properties for both cases. Notably, the incorporation of PVP, which effectively regulate the crystallization behavior, exhibits limited influence on the tensile properties of the PA66, especially for the specimens that cut perpendicular to flow direction.

Hence, PVP offers a resultful way to improve the processibility of PA66 by regulate the interchain interaction without sacrificing the mechanical properties of the materials.

CONCLUSIONS

In the present work, the regulation effects of PVP on the crystallization behavior and microstructure of PA66 under the external field have been systematically investigated. The crystallization behavior is investigated *via* temperature dependent FTIR and the crystallization process can be separated into two stages: the formation of disordered H-bonds and the transition of H-bonds from disordered to ordered state. The enthalpy of crystallization process has been calculated according to Van't Hoff plots, and it is revealed that PVP decrease the ΔH for both the two stages. It illustrates that the interaction between PA66 and PVP can suppress the formation of H-bonds and impede the rearrangement of chain segments. Therefore, the crystallization behavior is retarded and shows linear dependence on the concentration of PVP. However, the efficiency decreases when PVP exceed 8 wt% due to the phase separation between the two components. As for the microstructure under injection flow field, the skin and core layer show quite the opposite orientation behavior due to the fountain flow pattern, while the evolution of f_H along the flow direction can be attributed to the relaxation process. With the incorporation of PVP, the relaxation is promoted with an enhanced fluidity of the melt. Thus, it turns out that the f_H at both skin and core layer decreased compared with neat PA66. Notably, the mechanical properties are basically unchanged.

Above all, this study probes the regulation mechanism of PVP on the crystallization behavior of PA66 when subject to external field, and the crystallization temperature and microstructure can be finely designed by adjusting the interchain interaction. It offers a new insight into the correspondence between interchain interaction and microstructure under external flow field.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2852-8>.

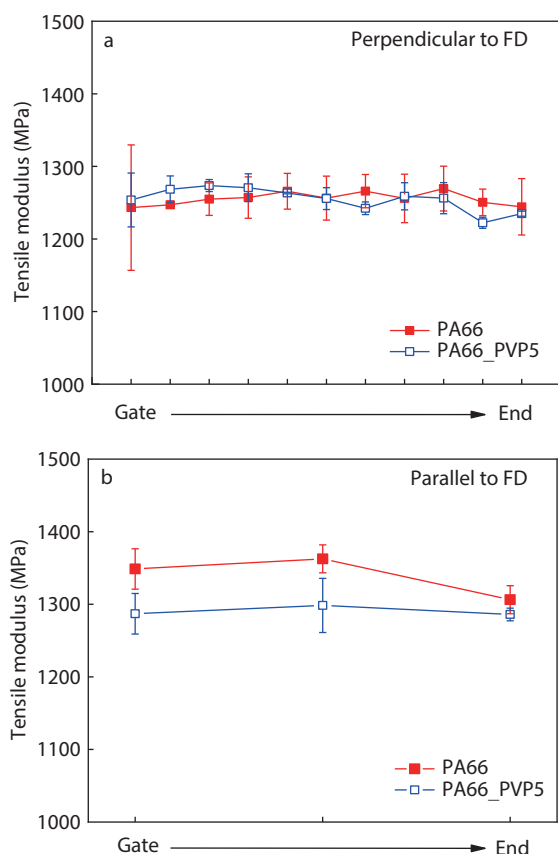


Fig. 11 Tensile modulus of specimens that were cut along (a) perpendicular direction; (b) Parallel direction to FD for samples PA66 and PA66_PVP5 at different flow field position.

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