Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

for

Understanding the Crystallization Behavior of Polyamide6/Polyamide66 Alloys from the Perspective of Hydrogen Bonds: Projection Moving-Window 2D Correlation FTIR Spectroscopy and the Enthalpy

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1. Theory of Projection-MW2D based on auto-correlation

1.1. Spectral data matrix

Entire infrared spectrum is actually a large matrix *A*, a region of spectroscopy or a series of spectral correlation spectroscopy is called sub-matrix which is also considered as a window.

A is supposed to be an $M \times N$ matrix of entire infrared spectral data with *M* rows and *N* columns. The *v* and *I* represent the spectral variables (e.g., wavenumber) and external perturbation variables (e.g., temperature), respectively. Each row of *A* corresponds to the discrete data points of a spectrum.

$$A=\begin{pmatrix} y(v,I_1) \\ \vdots \\ y(v,I_j) \\ \vdots \\ y(v,I_M) \end{pmatrix} \tag{1}$$

The sub-matrix A_j is extracted from the main matrix *A*. At this point, the serial number of the perturbation variable *I* ranges from $j-m$ to $j+m$. Obviously, the sub-matrix A_j has $2m+1$ rows, whose column number is the same as the main matrix *A*. The $2m+1$ is called the window size.

$$A_j=\begin{pmatrix} y(v,I_{j-m}) \\ \vdots \\ y(v,I_j) \\ \vdots \\ y(v,I_{j+m}) \end{pmatrix} \tag{2}$$

In general, the reference spectrum and the dynamic spectrum of the *j*th sub-matrix are calculated by the following formulas.

$$\bar{y}(v)= \frac{1}{2m+1}\sum_{J=j+m}^{j+m} y(v,I_J) \tag{3}$$

$$\tilde{y}(v,I_J)=y(v,I_J)-\bar{y}(v) \tag{4}$$

where *J* is a row number within a sub-matrix.

The mean-centered *j*th sub-matrix can be described as follows:

$$\tilde{A}_j = \frac{1}{\sqrt{2m}} \begin{pmatrix} \tilde{y}(v, I_{j-m}) \\ \vdots \\ \tilde{y}(v, I_j) \\ \vdots \\ \tilde{y}(v, I_{j+m}) \end{pmatrix} \quad (5)$$

1.2. Projection matrix

Then, we select a matrix Y from $\tilde{A}_j$, and its rows should be the same as those of $\tilde{A}_j$. So, Y has $2m+1$ rows and k columns, but it reduces to a single vector y when Y has only one column.

The singular value decomposition (SVD) of matrix Y is defined as follows:

$$Y = U_Y S_Y V^T{}_Y + E_Y \quad (6)$$

U_Y is a matrix of $(2m+1)\times(2m+1)$. $V^T{}_Y$ is a square matrix of $k\times k$. S_Y is a $(2m+1)\times k$ matrix, and its diagonal elements of $\sigma_1, \sigma_2, \ldots, \sigma_k$ are the singular values of the matrix Y. E_Y is the residual matrix. In general, it is small enough to be negligible. Here, we give an index r, which makes the value of $(\sigma_1 + \sigma_2 + \ldots + \sigma_r)/(\sigma_1 + \sigma_2 + \ldots + \sigma_r + \ldots + \sigma_k)$ greater than or equal to 0.9 (90 %), and the 1, … , $(2m+1)$ rows and the 1,..., r columns of U_Y are used for the subsequent calculations.

Then, the projection matrix R_Y from Y can be calculated as:

$$R_Y = U_Y U^T{}_Y \quad (7)$$

R_Y is a $(2m+1)\times(2m+1)$ matrix. The used $(2m+1)\times r$ part of U_Y avoids R_Y transform to an identity matrix. The corresponding null-space projection matrix is defined as:

$$(I - R_Y) = I - U_Y U^T{}_Y \quad (8)$$

where I is the $(2m+1)\times(2m+1)$ identity matrix, Both R_Y and $I-R_Y$ are the symmetric matrix.

1.3. Positive projection transformation

According to Noda's proposal, the loading matrix L of $\tilde{A}_j^P$ is defined as:

$$L = \tilde{A}_j^T U_Y \quad (9)$$

Then, $\tilde{A}_j^P$ can be expressed as:

$$\tilde{A}_j^P = U_Y L_T \tag{10}$$

Here, we introduce a positive loading matrix L_+, which comes from L by data processing. L_+ retains the elements of ≥0 in L, and the elements of <0 are replaced by 0. After positive projection transformation, we obtain a new projection matrix $\tilde{A}_j^{P+}$. $\tilde{A}_j^{P+}$ only reserves the columns in $\tilde{A}_j^P$ that have the same change (or orientation) direction as in matrix Y.

$$\tilde{A}_j^{P+} = U_Y L_+^T \tag{11}$$

The corresponding null-space projection matrix is:

$$\tilde{A}_j^{N+} = \tilde{A}_j - \tilde{A}_j^{P+} \tag{12}$$

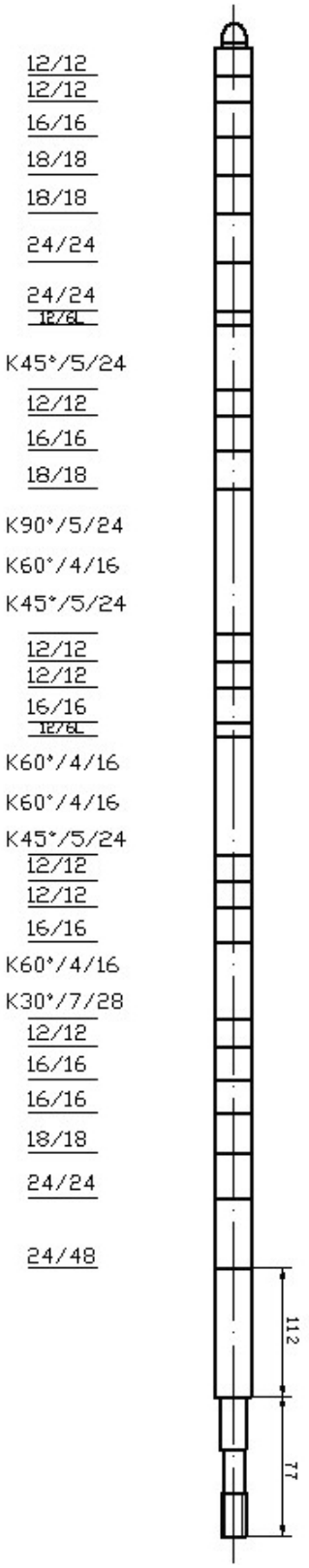

Figure S1. The detail screw elements of the twin-screw extruder (Φ20 mm) used in our work.

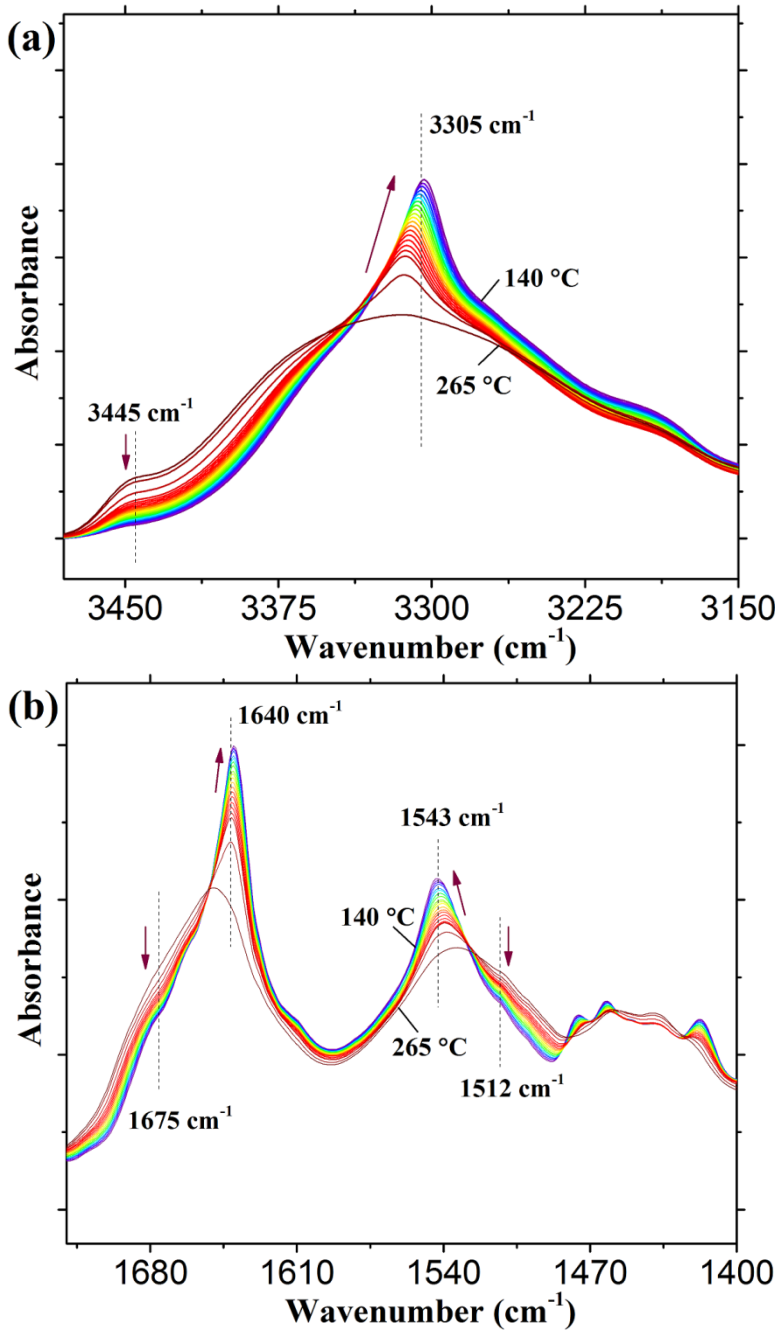

Figure S2. The *in situ* FTIR spectra of neat PA6 upon cooling from 265 °C to 140 °C. **(a)** 3500−3150 cm^{-1}; **(b)** 1700−1400 cm^{-1}.

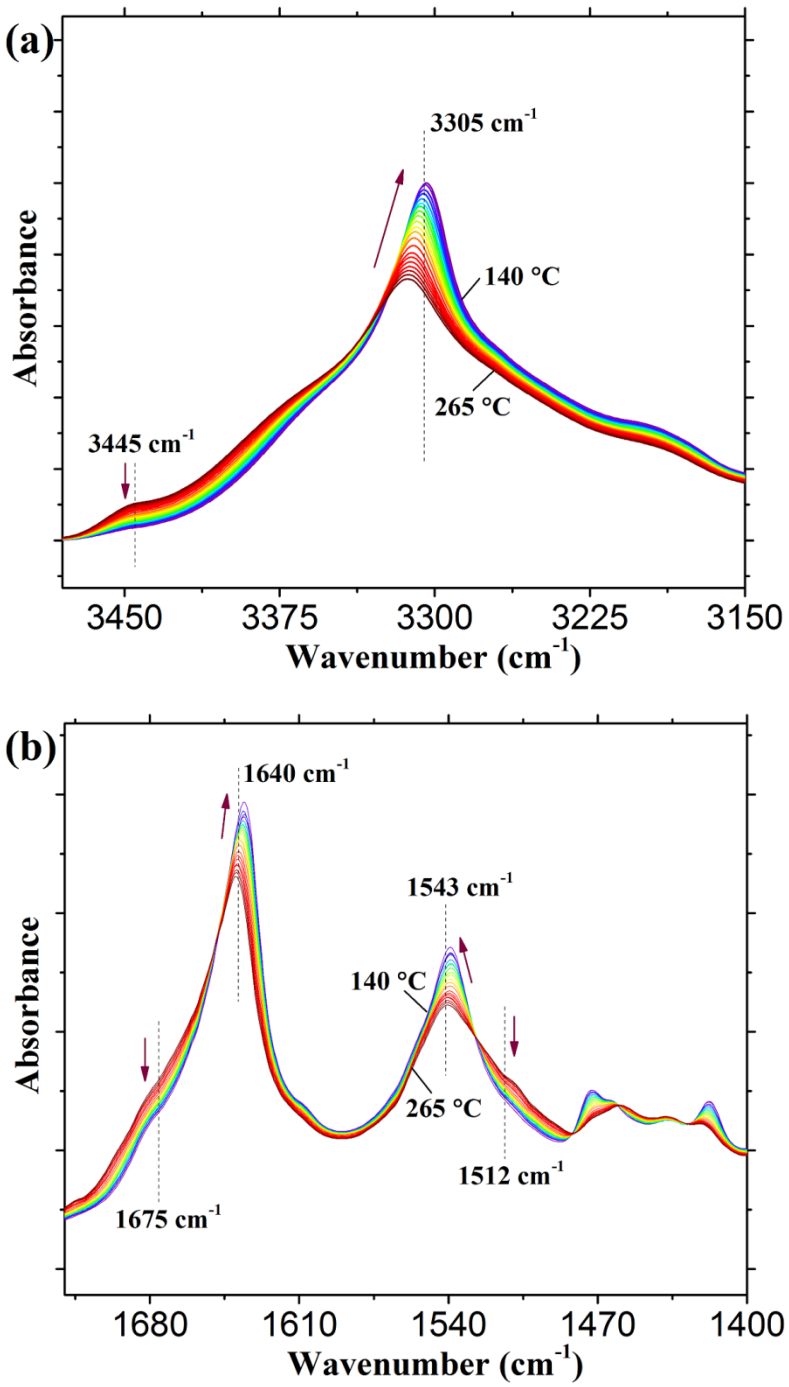

Figure S3. The *in situ* FTIR spectra of neat PA66 upon cooling from 265 °C to 140 °C. **(a)** 3500−3150 cm^{-1}; **(b)** 1700−1400 cm^{-1}.

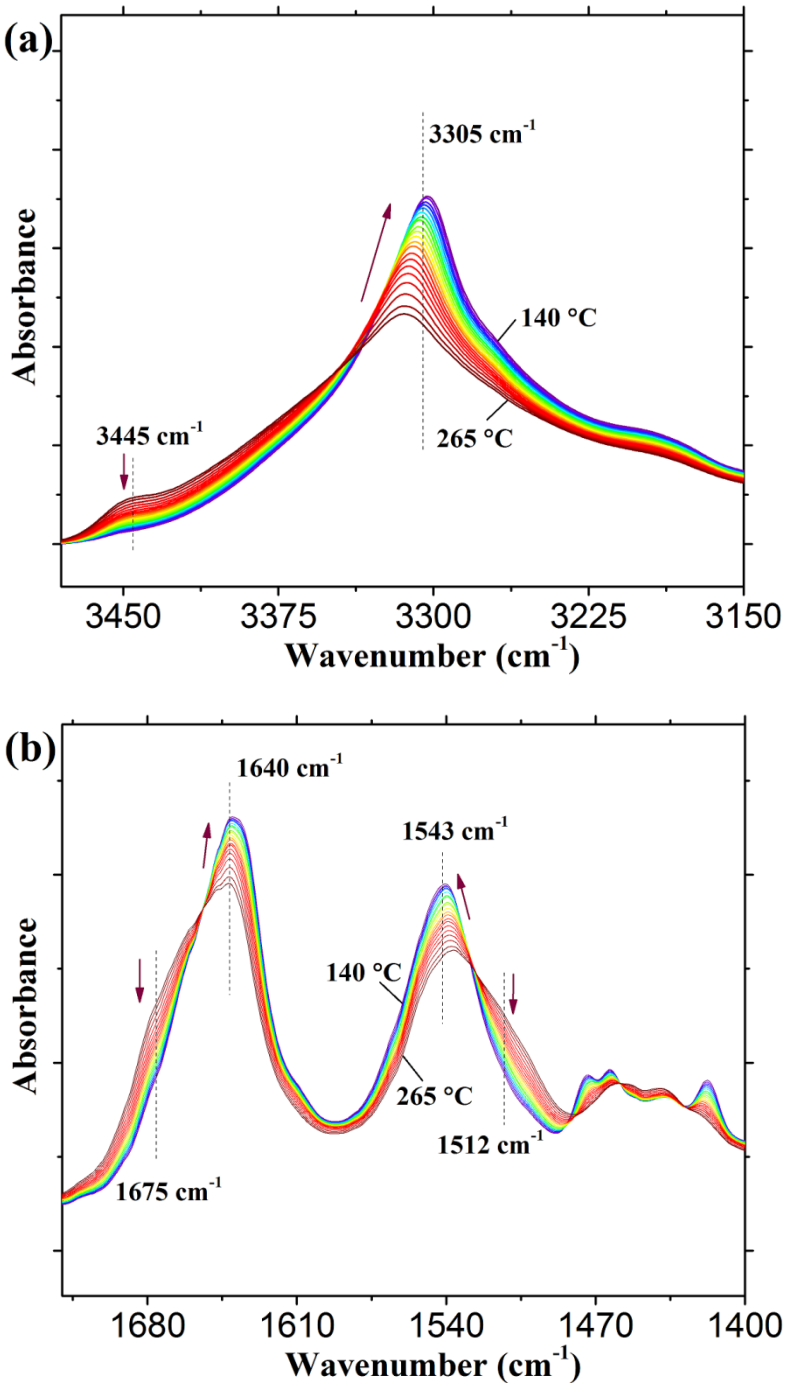

Figure S4. The *in situ* FTIR spectra of PA6/PA66 (60:40) alloy upon cooling from 265 °C to 140 °C. **(a)** 3500−3150 cm^{-1}; **(b)** 1700−1400 cm^{-1}.