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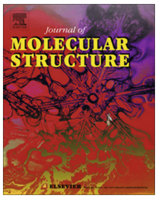

Near-infrared (NIR) imaging analysis of polylactic acid (PLA) nanocomposite by multiple-perturbation two-dimensional (2D) correlation spectroscopy

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HIGHLIGHTS

- Two-dimensional (2D) correlation analysis for spectroscopic imaging data.
- UV-induced variation of polylactic acid including nanoparticles.
- Identification of similar or dissimilar intensity variation on image plane.

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ABSTRACT

Multiple-perturbation two-dimensional (2D) correlation spectroscopy was applied to sets of near-infrared (NIR) imaging data of polylactic acid (PLA) nanocomposite samples undergoing UV degradation. Incorporation of clay nanoparticles substantially lowers the surface free energy barrier for the nucleation of PLA and eventually increases the frequency of the spontaneous nucleation of PLA crystals. Thus, when exposed to external stimuli such as UV light, PLA nanocomposite may show different structure alternation depending on the clay dispersion. Multiple-perturbation 2D correlation analysis of the PLA nanocomposite samples revealed different spatial variation between crystalline and amorphous structure of PLA, and the phenomenon especially becomes acute in the region where the clay particles are coagulated. The incorporation of the clay leads to the cleavage-induced crystallization of PLA when the sample is subjected to the UV light. The additional development of the ordered crystalline structure then works favorably to restrict the initial degradation of the polymer, providing the delay in the weight loss of the PLA.

Introduction

This paper extends our work on the spectroscopic imaging data analysis based on multiple-perturbation two-dimensional (2D) correlation spectroscopy [1–3]. We have recently reported several novel concepts on the multiple-perturbation two-dimensional (2D) correlation spectroscopy which can handle more than two perturbations in the correlation analysis [1–3]. By using multiple-perturbation 2D correlation technique, it becomes possible to effectively sort out key information underlying spectroscopic imaging data. For example, in a separated article, we demonstrated the central idea of imaging data analysis based on multiple-perturbation 2D correlation spectroscopy with a simple example of Raman imaging data of polymer blends [4]. The chemically meaningful variation of spectral feature depending on two spatial variables (e.g., *x*- and *y*-coordinates) was readily elucidated as a form of 2D correlation spectra.

In this communication, we will explore a practical case of imaging data analysis based on the multiple-perturbation 2D correlation technique. An examples is provided with near-infrared (NIR) imaging data of polylactic acid (PLA) nanocomposite films undergoing UV-induced variation to show how the multiple-perturbation 2D correlation technique can be utilized in analyzing the real-world material. Poly(lactic acid) (PLA) is a novel class of bio-based biodegradable plastics that can be produced from renewable feed stocks without directly depending on petroleum [5,6]. The inclusion of nanoparticles in PLA matrix often induces molecular-level interaction with polymer matrix and eventually offers improvement of physical or chemical property of the polymer [7,8]. Such polymer

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nanocomposites are generally formed by the addition of a small amount of nanoclay dispersion. Typical form of the nanocomposite is intercalated nanocomposite, in which the unit cells of clay structure are expanded by the insertion of polymer into the interlayer spacing, while the periodicity of the clay crystal structure is maintained [9,10]. The development of the intercalated structure often brings additional variation of supermolecular structure of PLA. For example, the clay substantially lowers the surface free energy barrier for nucleation and eventually increases the frequency of the spontaneous nucleation of the PLA crystals. When exposed to external stimuli, such as UV light, PLA noacomposite may show different structure variation (e.g., degradation) depending on the clay dispersion. Thus, the analysis of the NIR spectra of PLA nanocomposite may reveal effects of the clay on the UV-induced variation, which in turn brings pertinent background information on polymer deformation systems in terms of molecular level structure.

Methods

Doubly 2D correlation spectra

We assume that a set of spectra $A(\nu, p, q)$ of a system under multiple perturbations are collected as a function of an appropriate spectral variable, like wavenumber ν. The two additional variables, $p = 1, 2, \ldots, P$ and $q = 1, 2, \ldots, Q$, represent different perturbation variables, e. g., x- and y-axis coordinates, respectively. Multiple-perturbation 2D correlation spectra can be derived from the three way data matrix $A(\nu, p, q)$ by lumping two perturbation variables p and q [4]. Collective 2D correlation spectra are derived directly from the three way data matrix $A(\nu, p, q)$ by lumping two perturbation variables p and q together. Reference and dynamic spectra over p and q are described as

$$\bar{A}(\nu) = \frac{1}{PQ}\sum_{p=1}^{P}\sum_{q=1}^{Q} A(\nu, p, q) \tag{1}$$

$$\tilde{A}(\nu, p, q) = A(\nu, p, q) - \bar{A}(\nu) \tag{2}$$

Doubly synchronous and asynchronous correlation spectra for p and q planes can be described as

$$\Phi_{pq}(\nu_1, \nu_2) = \frac{1}{PQ-1}\sum_{p=1}^{P}\sum_{q=1}^{Q} \tilde{A}(\nu_1, p, q) \cdot \tilde{A}(\nu_2, p, q) \tag{3}$$

$$\Psi_{pq}(\nu_1, \nu_2) = \frac{1}{PQ-1}\sum_{p=1}^{P}\sum_{q=1}^{Q} \tilde{A}(\nu_1, p, q) \cdot \tilde{A}^{\neq}_{pq}(\nu_2, p, q) \tag{4}$$

where $\tilde{A}^{\neq}_{pq}(\nu_2, p, q)$ represents the Hilbert–Noda transformation given by

$$\tilde{A}^{\neq}_{pq}(\nu_2, p, q) = \sum_{r=1}^{P} N_{pr} \sum_{s=1}^{Q} N_{qs} \tilde{A}(\nu_2, r, s) \tag{5}$$

$$N_{pr} = \begin{cases} 0 & \textit{for } p = r \\ 1/(r-p)\pi & \textit{otherwise} \end{cases} \tag{6}$$

In the spatial 2D correlation analysis, the intensity of a synchronous 2D correlation spectrum $\Phi_{pq}(\nu_1, \nu_2)$ represents the simultaneous or coincidental changes of spectral intensity variations at ν_1 and ν_2 caused by the increase in distance from a reference point on image [4,12,13]. On the other hand, the intensity of an asynchronous spectrum $\Psi_{pq}(\nu_1, \nu_2)$ indicates the sequential or successive changes of spectral intensities at ν_1 and ν_2, caused by the change of the spatial coordinate [4,11–13]. In other words, the doubly correlated 2D correlation spectra derived from imaging data reveal the difference in the change of pattern on the images constructed with ν_1 and ν_2. The determination of the sequential order is generally less significant in actual practice of the 2D correlation analysis of spectroscopic imaging data. There are several options in the selection of reference point on the microimage. If the reference point is switched to the point on the opposite side of the image, the sign of asynchronous correlation becomes opposite providing the different sequential order of the events. It is thus convenient to estimate the disrelation spectrum as an approximation for the doubly asynchronous spectrum by circumventing the Hilbert–Noda transformation, which is computationally somewhat demanding [1,11–13].

$$\Lambda^2_{pq}(\nu_1, \nu_2) = \Phi_{pq}(\nu_1, \nu_1)\Phi_{pq}(\nu_2, \nu_2) - \Phi^2_{pq}(\nu_1, \nu_2) \tag{7}$$

The disrelation intensity can be seen as a portion of the total joint variance of signal fluctuations measured at ν_1 and ν_2 that is not accounted for by covariance. In other words, it corresponds to the disvariance component of the total variance, where fluctuations are not coincidental with each other but occur separately along with perturbation directions, i.e., asynchronousity [1,13,14]. The intensity of a disrelation correlation spectrum $\Lambda^2_{pq}(\nu_1, \nu_2)$ can be used as an index to estimate dissimilar change of the patterns on the images constructed with ν_1 and ν_2, while it provides only positive value.

Experimental procedure

Material

A commercial PLA ($M_n = 11{,}000$, $M_w = 65{,}000$, $T_m = 170$ °C, $T_g = 70$ °C) supplied by Mitsui Chemicals Company and organically modified clay (S-BEN W®, Hojun, Aichi, Japan) were used. The PLA and clay were thoroughly dried in vacuum at 80 °C overnight before the manipulation. The PLA pellets of 1 g and the clay of 3 wt% were dissolved into 100 ml chloroform and sonicated with an ultrasonic homogenizer USS-1 (Nihonseki Kaisha Ltd., Tokyo, Japan) for 5 min. The solutions were then dried in vacuum at 30 °C overnight to remove the chloroform. Total 0.5 g nanocomposite samples were first hot-pressed at 190 °C for 10 min under 5 MPa pressure and quenched in the ice water. The sample was finally aged at 25 °C for 12 h. The thicknesses of the films were approximately 80 μm. A part of the PLA film was exposed to UV light with a UV-irradiator for 30 h. In our geometry, the UV light intensity was approximately 2.0 mW/cm^2. Change in the haze induced by the UV irradiation was measured by a Haze meter NDH5000 (Nippon Denshoku Industries Co., Ltd., Tokyo, Japan).

NIR spectra

Sets of NIR imaging spectra of the PLA films were collected in transmittance mode with a PerkinElmer Spotlight 400 by co-adding 32 scans. NIR spectra were collected approximately over the 500 × 400 μm region with a spatial resolution 6 μm per pixel. Visible images of the samples are illustrated in Fig. 1.

Results and discussions

Sample opacity

Fig. 2 shows the opacity of the PLA films measured by the haze meter. The obvious change in the opacity of the samples caused by the UV irradiation can be observed. Measuring the haze involves separating scattered light from directly transmitted light. For example, the transmitted light which deviates more than 2.5° from the incident beam by forward scattering is considered to be haze. Indeed, such phenomenon is characteristic of semicrystalline