Tracking the curing process of automotive paint by moving-window two-dimensional infrared correlation spectroscopy and principal component analysis

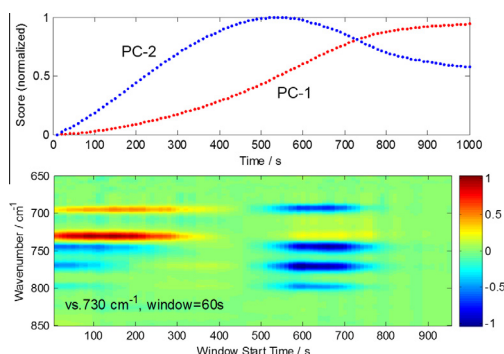Jian-bo Chen [a], Su-qin Sun [a], Jing Yu [b], Qun Zhou [a,*]

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HIGHLIGHTS

- MW2DCOS and PCA were combined for the first time to interpret time serial spectra.
- Three stages of the curing process of a paint sample were found by MW2DCOS and PCA.
- Time-resolved spectral changes are shown in AP-MW2D correlation spectra.
- The time-resolved relationship of spectral peaks is revealed by PP- and PL-MW2DCOS.

GRAPHICAL ABSTRACT

ABSTRACT

Moving-window two-dimensional correlation spectroscopy (MW2DCOS) and principal component analysis (PCA) were combined to interpret the time serial infrared spectra. The curing process of an automotive paint sample was tracked by attenuated total reflection Fourier transform infrared spectroscopy. Score plots of the first and second principal components showed that the curing process contained three stages. Meanwhile, the loading spectra indicated that the solvent was a mixture of aromatic compounds. Absorption peaks which changed significantly in each stage were revealed by auto-peak MW2DCOS. Furthermore, point-line and point-point MW2DCOS demonstrated the time-resolved relationship between absorption peaks from toluene, xylene and resin. In summary, the evaporation of toluene was the first stage of the curing process of this automotive paint sample. Next, the mixture of *o*-xylene, *m*-xylene and *p*-xylene began to evaporate in the second stage. After the evaporation of the solvent, the solid paint membrane was formed. For the interpretation of the time serial spectra, PCA is useful to estimate the number of significant chemical components and to find out the important turning points of the process, while MW2DCOS can show the changes of the spectral peaks and the relationship between them step by step. The combination of PCA and MW2DCOS is very interesting to extract and display the time-resolved information in the time serial spectra.

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1. Introduction

The features of direct, nondestructive and label-free make infra-red (IR) spectroscopy an ideal in situ analytical method to monitor various reaction processes. A large number of time serial spectra will be obtained when a reaction process is followed by IR

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spectroscopy. Manual interpretation of these spectra one by one may be a hard work even for an experienced spectroscopist sometimes. Therefore, some chemometrics techniques are necessary to interpret the time serial spectra objectively and quantitatively. Principal component analysis (PCA) is one of the most used methods [1,2]. It is possible to know about the molecular structures and concentration profiles of some components from the loading spectra and score plots of the principal components (PCs). The score plots can indicate the stages contained in the whole process. However, the spectral changes showed by the loading spectrum are the overall results of the whole process. Neither the time-resolved spectral changes nor the relationship between different spectral peaks can be revealed.

Two-dimensional correlation spectroscopy (2DCOS) may be a good option to show the relationship between different spectral peaks during the reaction process. 2DCOS was first proposed and developed by Noda [3–6]. Synchronous and asynchronous 2D correlation spectra are calculated from the dynamic spectra of the sample under the applied perturbation and show the extent and sequence of the spectral changes, respectively. In this way, chemical components and the interactions between them under the perturbation can be revealed [7–12]. Although the conventional 2D correlation spectrum can show the relationship between different spectral peaks, it is still the overall result of the whole process. To obtain the time-resolved spectral changes, the moving-window method was introduced into 2D correlation spectroscopy [13–16].

In the auto-peak moving-window two-dimensional correlation spectroscopy (AP-MW2DCOS), the auto-peak spectrum, i.e., the diagonal of the synchronous 2D correlation spectrum, of each window is arranged along the perturbation [13]. Spectral peaks which change at different stages are evident in this way. Subsequently, Zhou et al. [17] proposed the point-point and point-line moving-window two-dimensional correlation spectroscopy to reveal the stepwise variation of the relationship between different peaks during the process. The point-point moving-window two-dimensional correlation spectroscopy (PP-MW2DCOS) shows the change of the correlation between two specific peaks along the perturbation, while the point-line moving-window two-dimensional correlation spectroscopy (PL-MW2DCOS) displays the time-resolved correlation between a specific peak and all peaks in a spectral region. This method has been applied successfully in the study of the phase transition of phospholipid and the molecular interaction of lysine–lactose mixture [17].

Principal component analysis can estimate the number of significant components and indicate the stages contained in the time serial spectra. As a complementary method, MW2DCOS can show the time-resolved changes of spectral peaks and the relationship between them. Therefore, the mutual support of the above two methods should be expected to mine the information hidden in the time serial spectra. As an example, PCA and MW2DCOS is combined for the first time to interpret the infrared spectra of the curing process of an automotive paint sample.

2. Experimental

2.1. Materials

The automotive paint used in this research was taken out from the paintwork-repairing pen (ColorEasy, Wenzhou, China) designed for the do-it-yourself repair of minor scratches of the pearl white paint of Toyota 070 GTA-2. The stated components were acrylic resin, solvents and pigments. The paint was measured without any further processing. Reference infrared spectra of toluene, o-xylene, m-xylene and p-xylene were extracted from the LUB1 spectral library (PerkinElmer, Waltham, MA, USA).

2.2. Data collection

Infrared spectra of the automotive paint during the drying process were measured by a Frontier FT-IR/NIR spectrometer (Perkin-Elmer, Waltham, MA, USA) with a universal attenuated total reflection (ATR) sampling accessory (PerkinElmer, Waltham, MA, USA). The internal reflection element (IRE) was a diamond/ZnSe crystal and the angle of incidence was 45°. IR spectra were immediately and continuously recorded when the paint was dropped on the surface of the crystal. The starting-time interval between two successive IR spectra are 10 s. The whole measurement last for 2000 s and was controlled by the software Timebase v3.1.2 (PerkinElmer, Waltham, MA, USA). A total of 200 spectra in the range of 4000–650 cm^{-1} with a spectral resolution of 4 cm^{-1} were obtained and each spectrum was the average of 8 scans. The interval between two successive data points was 1 cm^{-1}.

2.3. Data processing

The original infrared spectral data was stored in a single file (*.spp) by Timebase. All IR spectra were exported out as separate files (*.sp) after the ordinate was transformed into absorbance and the baseline was corrected by the auto-flat function of the Timebase software. PCA and MW2D correlation analysis of the time serial IR spectra were performed by the software MATLAB v7.0 (The MathWorks, Natick, MA, USA). The singular value decomposition (SVD) function in MATLAB was used for the PCA decomposition. The MW2D correlation spectra was calculated according to the algorithm proposed by Zhou et al. [17]. The selected infrared spectra measured at specific time were processed by the software Spectrum v6.3 (PerkinElmer, Waltham, MA, USA). ATR correction with a zero contact factor and automatic baseline correction were applied successively on the original spectra. The second derivative infrared spectra were calculated with a window of 13 points.

3. Results and discussion

3.1. Stages of the curing process determined by PCA

According to the cumulative infrared spectra of the paint during the curing process shown in Fig. 1, the main spectral changes occurred in the region of 1800–650 cm^{-1}. Therefore, the time serial spectra in this region were used for the PCA decomposition. The first two principal components contained 97.2% and 2.5% of the
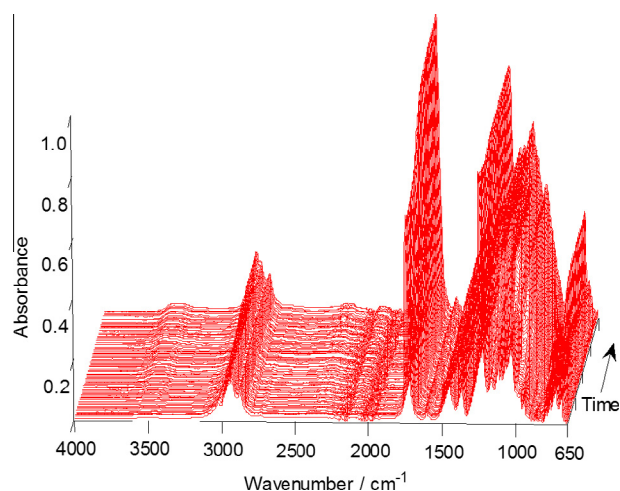

Fig. 1. Time serial infrared spectra of the paint during the curing process. Significant changes locate in the spectral region of 1800–650 cm^{-1}.