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A study of radiation effects on polyester urethane using two-dimensional correlation analysis based on thermogravimetric data

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ABSTRACT

Polyester-urethane adhesive was irradiated by gamma rays at various radiation doses. Thermogravimetric analysis (TGA) and infrared attenuated total reflection (ATR) spectroscopy were used to study the radiation effects. Particularly, 2D correlation techniques were employed to study the derivative thermogravimetry (DTG) data. The results of the synchronous and asynchronous 2D correlation spectra are analyzed and discussed. Three decomposition pathways in the urethane linkages, and two decomposition mechanisms of the polyester in soft segments were proved. Besides, we obtained the sequential order of several polyester-urethane adhesive decomposition ranges along the perturbation variable (radiation dose), which showed the soft segments in polyester-urethane were affected by gamma radiation first, whilst the hard segments latest. These results could not be obtained only from the DTG data. In addition, we summarized the gamma radiation effects on polyester-urethane adhesive based on the results we observed.

1. Introduction

2D spectroscopy was firstly used in the area of NMR spectroscopy [1,2], which would spread peaks over two dimensions making complex spectra consisting of many overlapped peaks visible. In 1993, Noda expanded the concept of 2D vibrational correlation spectroscopy and established the theory of generalized 2D correlation spectroscopy. Then, the 2D correlation method became virtually limitless, ranging from Raman, UV–vis [3], X-ray scattering [4], fluorescence [5,6] and IR [7], even to the fields outside of spectroscopy, such as chromatography [8] and molecular dynamics [9]. 2D correlation techniques possess the following main advantages [10]: (i) simplification of many overlapping peaks, and enhancement of spectral resolution by spreading peaks over the second dimension; (ii) illustrating the sequential order of spectral intensity changes taking place during the changes of perturbation variables. The 2D correlation techniques are truly of universal applicability, and can be used in any form of analytical technique. In this paper, we tried using 2D correlation techniques to deal with DTG data.

TGA is a powerful technique that measures the weight of a small sample as a function of temperature or time. A derivative weight curve named DTG analysis can be used to study onset decomposition temperature, the maximum decomposition rate temperature, end decomposition temperature, the number and content of steps involved in the thermal degradation of the sample. Polymers usually have a complex structure. Different molecular chains usually have different degradation temperatures. Thus, DTG curves usually have more than one peak. But DTG peaks sometimes are too wide to separate from each other. These overlapping peaks often persuade us finding more information on polymer structure.

The thermal degradation of polyurethanes usually occurs in two or three steps [11–17]. The first step is caused by the degradation of the hard segments, which would produce isocyanate, alcohol, primary or secondary amine, olefin and carbon dioxide. The second or third steps are due to the degradation of the soft segments. The first step is well known to contain three main degradation pathways to lose weight shown in Schemes 1–3 [18–22]. So, is there some method that could distinguish these three pathways? We haven't seen any reports to deal with it. Maybe 2D correlation techniques can be available.

Polyurethane radiation effects have been studied widely. Guignot et al. [23] investigated electron radiation effects on segmented polyetherurethane, finding that both soft segment and hard segment exhibited significant chain scission and they showed the appearance of oxidation localized mainly on soft segments. Since radiation can change the structure of soft and hard segments,

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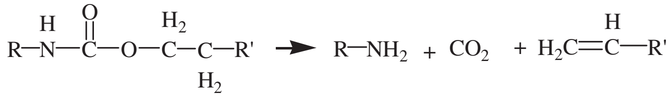
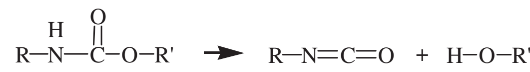


Scheme 1. Pathway 1: formation of the primary, olefin and carbon dioxide.



Scheme 3. Pathway 3: formation of isocyanate and alcohol.

DTG curves would be changed by radiation. Thus, in this work, gamma radiation was used to irradiate the polyesterurethane with different radiation doses, and then the irradiated samples were measured by thermogravimetric analysis. Finally, we used 2D correlation techniques to analyse the DTG data, hoping to find some novel information that we could not derive only from DTG data.

2. Experiment

2.1. Materials

Polyesterurethane adhesive was synthesized using two basic components (A and B) of Tie Mao 101-F adhesive from Shanghai XinGuang Chemical Plant. Component A contains polyethyleneglycol adipate in ethyl acetate solution, and component B with a concentration of 11–13% free isocyanate group was the modified toluene diisocyanate (TDI) by trimethylolpropane (TMP). Component A was mixed with B uniformly in a glass beaker. The mass ratio of the used components was A:B = 10:4. Then the admixture was poured onto a clean horizontal glass plate. When it was cured at room temperature for 7 days, a vacuum oven was used to remove remaining solvents (ethyl acetate and acetone) for 1 month at 30 °C. Finally polyesterurethane sheet samples were prepared.

2.2. Gamma radiation

A ^{60}Co source was used to irradiate the samples in air at various radiation doses up to 1000 kGy (at an approximate dose rate of 5 kGy/h) at room temperature at Institute of Nuclear Physics and Chemistry in China. All the samples were placed in polyethylene bags.

2.3. Characterization

Thermal stability was analyzed in the range of 25–700 °C with a TGA instrument (TGA 2050, America) using a heating rate of 10 °C/min under nitrogen. The weight of the samples used was controlled in the range of 3–4 mg.

Chemical structures were examined by infrared attenuated total reflection (ATR) spectroscopy using a NICOLET 6700 FTIR instrument. ATR spectra were measured with a resolution of 4 cm^{-1} in the range of 400–4000 cm^{-1}. All the spectra were the results of 32 co-added scans.

2.4. 2D correlation analysis

The theory used is Noda's method to deal with unevenly spaced data [24]. In this paper, the perturbation variable is radiation dose t_i (t_1, t_2, $t_3 \dots t_m$), and the raw data is DTG data $y_i(T)$. T represents heating temperature in TGA.

Scheme 2. Pathway 2: formation of the secondary and carbon dioxide.

For unevenly spaced data, the reference spectrum $\bar{y}(T)$, is given by

$$\bar{y}(T) = \frac{\sum_{i=1}^{m} y_i(T)\cdot(t_{i+1} - t_{i-1})}{\sum_{i=1}^{m}(t_{i+1} - t_{i-1})} \tag{1}$$

Here, two additional points in radiation doses t_0 and t_{m+1} must be defined as

$$t_0 = 2t_1 - t_2 \tag{2}$$

$$t_{m+1} = 2t_m - t_{m-1} \tag{3}$$

The dynamic spectrum $\tilde{y}_i(T)$ induced by a perturbation is formally defined as

$$\tilde{y}_i(T) = y_i(T) - \bar{y}(T) \tag{4}$$

The synchronous and asynchronous 2D correlation spectrum calculated for unevenly spaced data are respectively given by

$$\Phi(T_1, T_2) = \frac{1}{2(t_m - t_1)} \sum_{i=1}^{m} \tilde{y}_i(T_1)\cdot\tilde{y}_i(T_2)\cdot(t_{i+1} - t_{i-1}) \tag{5}$$

$$\Psi(T_1, T_2) = \frac{1}{2(t_m - t_1)} \sum_{i=1}^{m} \tilde{y}_i(T_1)\cdot\tilde{z}_i(T_2)\cdot(t_{i+1} - t_{i-1}) \tag{6}$$

$\tilde{z}_i(T_2)$ is the discrete Hilbert transform, which can be obtained from equation (7).

$$\tilde{z}_i(T_2) = \frac{1}{2\pi} \sum_{j=1}^{m} \frac{\tilde{y}_j(T_2)}{t_j - t_i}\cdot(t_{j+1} - t_{j-1}) = \sum_{j=1}^{m} N_{ij}\cdot\tilde{y}_j(T_2) \tag{7}$$

where N_{ij} is the element of the Hilbert–Noda transformation matrix

$$N_{ij} = \begin{cases} 0 & i = j \\ \dfrac{t_{j+1} - t_{j-1}}{2\pi(t_j - t_i)} & \text{otherwise} \end{cases} \tag{8}$$

From the above theory, generalized 2D correlation DTG were calculated by a computer program written in MATLAB 7.0. The 6% autocorrelation intensity of correlation spectra was considered to be noise and was cut off. In 2D correlation spectra, blue represented negative correlations and red or yellow indicated positive correlations. In a printed, journal, grey represents negative correlations and white represents positive correlation. 40 contour lines were drawn in synchronous correlation spectra and 30 in asynchronous correlation spectra.

3. Results and discussions

3.1. DTG data

DTG curves of polyester-urethane irradiated by different radiation doses are shown in Fig. 1. It seems that there are three pyrolysis steps. The first (250–320 °C) is due to the degradation of the hard