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Primary thermal degradation effects on the polyurethane film

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ABSTRACT

Primary thermal degradation effects on polyurethane at 175 °C are studied by time-dependent IR spectra and two-dimensional (2D) correlation spectra. It was observed that the hard segments in polyurethane would degrade first, and the urethane group with the bonded C=O was more stable than that with the free C=O. The main structure changes at 175 °C were caused by the degradation of urethane linkages. Urethane linkages firstly experienced two pathways to degrade resulting in the formation of isocyanate, alcohol, secondary amine and carbon dioxide. The produced isocyanates were highly reactive, and would react with the secondary amine forming urea which was more stable than polyurethane.

1. Introduction

Polyurethanes usually possess segmented structure: Hard segments (HS) are formed by diisocyanates and chain extenders, while the soft segments (SS) are composed of polyols (polyether or polyester) [1]. Polyurethanes have gained attention due to their fascinating hydrogen-bond behavior, and have been widely used as car paints, flexible foams, rigid foams, adhesives and other commercial goods. The investigation of degradation allows for the determination of optimum conditions for designing and processing polyurethanes as well as obtaining high performance polymers with the improved stability [2]. The thermal degradation of polyurethanes usually occurs in two or three steps [2–8]. The first step is caused by the degradation of HS at the temperature range of 180–300 °C [2], which would produce isocyanate, alcohol, primary or secondary amine, olefin and carbon dioxide. The second or third steps are due to the degradation of SS. Among the steps, the primary degradation step is the most important because the polymer chains start to break at this step and this step decides the highest molding or processing temperature. The first step is well known containing three main degradation pathways shown in Scheme 1 [9–14].

The main methods to analysis the thermal degradation mechanisms on polyurethanes are pyrolysis–GC/MS, TG–FTIR and TG–MS [2,3,12,13]. All these methods need high enough temperature to ensure the obvious degradation to test and the thermal degradation mechanisms are ratiocinated through the volatile products. Whereas, time or temperature-dependent FTIR spectra are aimed to directly study the structure changes of the condensed matter with increasing the time or temperature. It is sensitive to phase transition and molecular structure degradation. Thus, Time or temperature-dependent spectra have gained advantages to study the polymer degradation.

Usually, the degradation rate of polymer increases with increasing the temperature, and the degradation mechanism becomes more complicated. With increasing the temperature, polyurethanes will firstly experience the physics structure changes, i.e. hydrogen-bond interaction changes or phase mixing effects [15] or forming more ordered structure [16]. Teo and his partners [15] studied the hydrogen bonding interaction of polyurethane using FTIR at a temperature range of 30–200 °C, and observed that the hydrogen bonding of the polyurethanes persisted up to 200 °C. Yen and his partners [16] studied the hydrogen-bond interactions for polyester–urethane using FTIR in a temperature range of 25–235 °C. Five types of hydrogen-bond were observed, and the polyurethane formed a more ordered domain at temperatures 130–200 °C. Although both Teo and Yen did not claim any degradation mechanism below 200 °C, we believe that the degradation effects will be accompanied with the physics structure changes at a little lower temperature than that of the polyurethane begin to degrade obviously in TG. As far as we know, the polyurethane degradation mechanism at a lower temperature (lower than 180 °C) has not been ever studied and this mechanism is closer to the applications.

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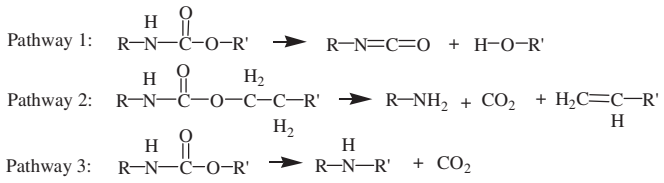

Scheme 1. Three pathways for urethane linkages degradation.

Generalized 2D correlation infrared spectroscopy proposed by Noda in 1993 is an important method that can provide the sequential order of the spectral variables from the dynamic infrared spectra, which is convenient to investigate the mechanism of polymer structure transitions [17]. Particularly, this method is powerful for studying the overlapped bands that usually appear in most polymer IR spectra. In polyurethane, different types of C=O stretching vibration (i.e. free C=O in HS and SS, hydrogen-bonding C=O in HS) are usually overlapped, which increases the difficulty to study the structure changes.

In this paper, in order to obtain the primary degradation mechanism of polyurethane, firstly we used TG analysis to decide the initial degradation temperature for the polyurethane film, and then employed time-dependent IR spectroscopy to study the structure evolvement at the obtained initial degradation temperature from TG. Specially, 2D correlation infrared spectroscopy was used for determining the sequential order of the spectral intensity changes of different types of C=O groups, which is important in polyurethane degradation mechanism studies.

2. Experimental section

2.1. Materials

Polyurethane was synthesized by two components (A and B) of Tie Mao 101-F adhesive from Shanghai XinGuang Chemical Plant. Component A contains polyethyleneglycol adipate, and component B with a concentration of 11 ~ 13% (mass ratio) free isocyanate groups was the modified tolylene diisocyanate (TDI) by trimethylolpropane (TMP). Component A was mixed uniformly with B as a mass ratio of A:B = 10:4 in a glass beaker. A vacuum oven was used to remove the gas bubbles. Then a little mixture was poured onto a horizontal silicon slice which was fixed in a spin coater KW-4A made by Microelectronice of Chinese Academy of Science. Then, let the slice circumrotate with a speed of 900 revs for 3 min. After 7 days, polyurethane film with a thickness of about 10 μm was prepared.

2.2. TG analysis

Thermal degradation temperature was analyzed in the range of 25–600 °C by Thermo-gravimetric Analyzer Instrument (TGA 2050, America) using a heating rate of 2 °C/min under nitrogen. The weight of the sample was 2.85 mg.

2.3. Time-dependent IR spectra analysis

KBr powder was ground in a mortar and pestle for several minutes. Transferred the powder to a mold and made the surface of KBr flat gently. Laid the polyurethane film in the center of the surface of KBr. After that, polyurethane film was covered with another quality of KBr powder. A pressure of 10 MPa was used to press the sample to disc.

The disc sample was placed in a sample fixer of a heating device shown in Fig. 1. The sample heating device was placed in NICOLET 6700 FT–IR ensuring that the IR beam could transmit through the whole device. The heating tube could heat the sample according to the temperature control's order. Before heating, a background spectrum was collected, and all spectra at different temperatures were auto-subtracted this background spectrum. 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 16 co-added scans. We used three steps to heat the sample to 175 °C: A, heating the sample to 150 °C at a heating rate of 10 °C/min; B, heating the sample to 175 °C at a heating rate of 2 °C/min; C, keeping the temperature constant at 175 °C for 220 min. IR spectra were begun to record when the temperature is up to 175 °C and one spectrum was recorded at intervals of 5 min.

2.4. 2D correlation IR analysis

Generalized 2D correlation spectra were calculated by a computer program written by MATLAB 7.0 using Noda's theory [19]. The 2% autocorrelation intensity was considered to be noise and was cut off. In 2D correlation spectra, the negative correlation peaks were marked with blue and the positive correlation peaks were marked with red or yellow. If you see this paper in a printing journal, white represents positive correlation and gray represents negative correlations. 40 contour lines were drawn in both synchronous correlation spectrum and asynchronous correlation spectrum.

3. Results and discussion

3.1. TG results

TG can yield important information on a polymer system, such as the volatile content and decomposition temperature. The DTG curve of the polyurethane film is shown in Fig. 2. It is observed that the polyurethane experience three steps to degrade, which likes most thermal degradation studies on other polyurethanes [2]. The first step occurs at the range 150–250 °C. Since we aim to study the primary thermal degradation, 175 °C is chosen for time-dependent IR spectra.

3.2. Changes in the time-dependent IR spectra

Fig. 3 shows the normalized time-dependent IR spectra at 175 °C in the region 1800–1000 cm^{-1}. The band in the region 1620–1800 cm^{-1} is due to the C=O stretching vibrations. In polyurethane (especially in polyester–urethane), C=O is complicated because C=O in SS and C=O (free and bonded) in HS usually overlap with

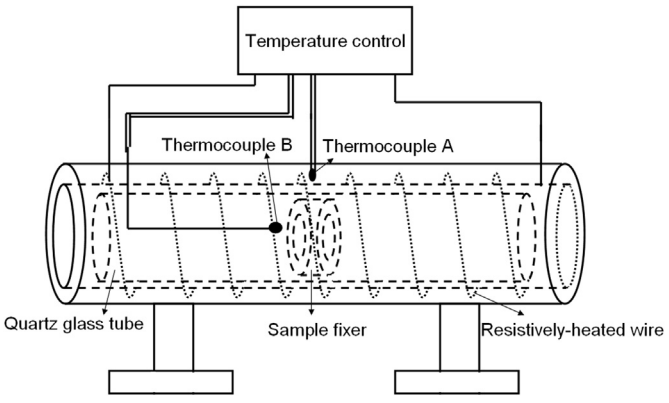

Fig. 1. The special sample heating device [18].