Thermal Degradation Properties of Urushi Film: Thermogravimetric Analysis (TGA) & Total Ion Chromatogram (TIC) Pyrogram

Toshiya SATO, Seiji, TAKAHASHI, Yuki KITAHARA, Márti JUHÁSZ, Toshihiro FUJIIm
Meisei University, Department of Chemistry, Faculty of Sciences and Engineering, Hodokubo 2-1-1, Hino, Tokyo 191-8506 JAPAN, E-mail: fujii@chem.meisei-u.ac.jp

ABSTRACT

The kinetics of thermal degradation of Japanese lacquer (Urushi) films containing Urushiin in nitrogen and in air were studied with thermogravimetry analysis (TGA) and evolved gas analysis (EGA) mass spectrometry. Both derivative thermogravimetric (DTG) traces and total ion chromatogram (TIC) indicates that the degradation takes place in three stages. The activation energy ($E_a$), obtained by the TGA curve of the first decomposition event, were 19.12 kJ/mol (N$_2$) and 10.19 kJ/mol (Air), and preexponential factor (A) were 6.18 x 10$^5$ min$^{-1}$ (N$_2$) and 1.24 x 10$^{14}$ min$^{-1}$ (Air) for one-year-old Urushi.

INTRODUCTION

Thermal Stability of Urushi Films

The thermal stability of a polymeric composite material is one of the most important properties for both processing and application. It is also true for oriental lacquer, a natural polymeric material with a beautiful surface and high durability, which has been used for decorative and protective coatings since the fifth century B.C. Indeed, thermal degradation can pose major problems in preservation and conservation of ancient lacquer samples. This can lead to significant decays in preservation and conservation. Therefore, it is necessary to obtain information on the thermal stability of ubiquitous oriental lacquer materials.

Previous Study (including method; TGA & Pyrogram) :

As a conventional stability assessment, thermogravimetry analysis (TGA) and evolved gas analysis/mass spectrometry (EGA/MS) in nonisothermal mode are commonly employed. TGA measures to determine changes in weight in a material as a function of temperature (or time) under a controlled atmosphere. Its principal uses are measurement of a composite's thermal stability and estimation of the degradation kinetics for lifetime prediction. TGA is now well-established to obtain the Arrhenius kinetic parameters of activation energy ($E_a$) and pre-exponential factor $A$ through a weight loss during thermal degradation.

EXPERIMENTAL

Sample Materials:

Preparation of Japanese lacquer films was made such that Japanese lacquer was coated on slide glass substrates (thickness: 50 micron m) and was kept for a week at room temperature and at 75 ± 5% RH. The Urushi sample used in this work was an aged lacquer film. These were obtained by aging the above films for more than one year in a glass-windowed cabinet placed in dark area.

Thermogravimetric analysis (TGA) :

A Shimadzu micro thermogravimetric analyzers TGA-50 was used to determine the thermal stability of the Urushi films. Experiments were performed on about 2 mg sample placed in platinum crucibles under nitrogen at a flow rate of 80 mL/min and a heating rate of 20 °C/min, up to 600 °C. The TG & DTG curves were recorded; using a Shimadzu C-R6A data processing unit. Fig. 1 and Fig. 2 show the TG and DTG curves of Urushi films in the nitrogen and air environments. The temperature of maximum degradation corresponds to the temperature at which the DTG curves reach their maximum.

RESULTS AND DISCUSSION

1. TGA analysis:

The TG and DTG curves of Japanese lacquer film obtained under nitrogen atmosphere, are drawn in Fig. 1. The scanned temperature range was from ambient temperature to 600 °C. It was revealed that this film experiences weight loss in a very complex way, starts decomposing considerably at about 250 °C and yields the second maximum rate of decomposition temperature at about 470 °C. This maximum is followed by a more marked decomposition step in the higher temperature range of 500-600 °C. At 600 °C about 2.4% of charred residue is left. The figure also indicates that the degradation takes place in three main stages via three main decomposition steps. Apparent activation energies ($E_a$) and pre-exponential factor ($A$) have been calculated from the curves of each step (Table I). For instance, from the maximum DTA curve in the initial degradation stage, was calculated $E_a$ = 19.12 kJ/mol for TGA nitrogen, indicating the production rate of decomposition product and $A$ = 6.18 x 10$^5$ min$^{-1}$, respectively.

2. Degradation Kinetics:

We used TGA system to study the kinetics of Urushi pyrolysis. A DTA (program) obtained from the TGA system gives the relative number of decomposition product molecules, indicating the production rate. In TGA, the degree of conversion ($\alpha$) at any temperature ($T$) is equal to the integrated area under the DTA curve between the temperature at the start ($T_s$) and ($T$). The DTA plot acquired from real-time weight loss due to chemicals released from a thermally decomposed specimen was used to obtain the functional forms of the kinetic rate expression. When the reaction is assumed to be first-order (i.e., a unimolecular decomposition reaction), the functional forms of the following kinetic rate equation is given,

$$\ln(\operatorname{d}[\text{mol}]/\operatorname{dt}) = \ln(\beta)/A - E_a/RT + \ln(1 - \alpha)$$

where $\alpha$ is the degree of yield of the decomposed specimen, $A$ is the frequency factor, $E_a$ is the apparent activation energy, $T$ is temperature, and $R$ is the gas constant. With the addition of the heating rate ($\beta = \text{dT/dt}$), Arrhenius parameters such as activation energy and pre-exponential factor can be determined from plots of ln(du/dT) versus 1/T.

We investigated the degradation kinetics over the temperature range in nitrogen and in air to obtain the rate expressions for Urushi degradation. The slopes of the plots of temperature versus signal intensity were constant for all the main decomposition steps. Apparent activation energies ($E_a$) with the pre-exponential factor $A$ were calculated from the curves of each step (Table I). For instance, from the maximum DTA curve in nitrogen and in air (Fig. 1 & 2), $E_a$ = 63.05 kcal/mol with $A = 3.38 \times 10^{16}$ min$^{-1}$, and $E_a$ = 63.69 kcal/mol with $A = 1.66 \times 10^{16}$ min$^{-1}$, respectively.

CONCLUSION

In conclusion, TGA from which the thermal degradation kinetics has been studied, was validated in the thermal degradation properties of Japanese lacquer Urushi. Some preliminary conclusions may be drawn from the present results.

1. Urushi films containing water and urushiol moieties showed a main three-stage thermal degradation process both in nitrogen and in air.

2. The apparent activation energy ($E_a$) of Urushi films for the three main decomposition steps is given.

3. It is revealed that the atmospheric environment has an influence on those $E_a$ values.

Table 1. Thermal degradation kinetic parameters for Japanese lacquer Urushi degradation determined by TGA in nitrogen.

<table>
<thead>
<tr>
<th>Method (atmosphere)</th>
<th>Degradation Step</th>
<th>$E_a$ (kcal/mol)</th>
<th>$A$ (min$^{-1}$)</th>
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<tr>
<td>TGA (Nitrogen)</td>
<td>1st</td>
<td>19.12</td>
<td>6.18 x 10$^5$</td>
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<tr>
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<td>2nd</td>
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</tr>
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Fig. 1 TG and DTG Curves of Japanese Urushi film in nitrogen.  Fig. 2 TG and DTG Curves of Japanese Urushi film in air.  Fig. 3 Typical Arrhenius Plots of ln(du/dT) (1 – $\alpha$) vs. 1/T for urushi Films: From the DT curve due to the first degradation step in the nitrogen conditions [see Fig. 1].

Fig. 2 Typical Arrhenius Plots of ln(du/dT) (1 – $\alpha$) vs. 1/T for urushi Films: From the DT curve due to the first degradation step in the nitrogen conditions [see Fig. 1].

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Acknowledgements:

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