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Unraveling the mechanism of thermal and thermo-oxidative degradation of tannic acid

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ABSTRACT

The thermal and thermo-oxidative degradation of hydrolysable tannin, i.e. tannic acid is reported. The study on thermal and thermo-oxidative degradation mechanism of tannic acid was carried out by using several advanced thermal characterization techniques such as Thermogravimetric analysis (TGA) coupled with Fourier-Transform Infrared (FTIR) Spectroscopy (TGA–FTIR), pyrolysis–gas chromatography–mass spectroscopy (Py–GC–MS) and Attenuated Total Reflectance (ATR)–FTIR. The condensed phase and gaseous phase degradation studies were combined to deduce a probable degradation pathway for tannic acid molecule at high temperature under nitrogen and air atmosphere.

1. Introduction

Tannins are a type of polyphenols concentrated in the barks of trees. Tannin is one of the important ingredients in the bark of the trees that have been reported to provide thermal and antimicrobial protection [1,2]. Tannins are traditionally used as chemical agents for the conversion of animal hides to leather. Bate-Smith and Swain defined tannins [3] as "water soluble phenolic compounds having molecular mass between 500 and 3000 giving the usual phenolic reactions and having special properties such as ability to precipitate alkaloids, gelatin and other proteins". These polyphenols contain a large number of hydroxyl or other functional groups (1–3 per 100 D), and therefore are capable of forming cross-links with proteins and other macromolecules. Tannins can be classified into two categories: hydrolysable and non-hydrolysable or condensed tannins [4]. Hydrolysable tannins (as shown in Fig. 1) contain a central core of polyhydric alcohol such as glucose, connected partially or entirely to gallic acid (gallotannins) or hexahydroxydiphenic acid (ellagitannins) through ester linkages. The structures of condensed tannins are far more complicated than hydrolysable tannins. The structural unit of condensed tannin consists of polymerized forms of flavan-3-ols and flavan-3,4-diols or a mixture of the two [5].

Apart from providing numerous reactive hydroxyl groups, tannins can also impart good thermal stability. For example tannin-based rigid foams have been reported to exhibit good thermal insulating characteristics and can be used in cavities of hollow-core wooden doors. Thermosets based on tannin extract, formaldehyde and furfuryl alcohol have been used for producing these foams [6]. The thermal insulation capacity of these tannin-based foams are comparable to those of synthetic foams, such as polyurethanes, but with the added advantage of being non-combustible, and exhibiting intumescence upon burning. Grigsby et al. have modified the condensed tannin through esterification and used it as an additive for polylactic acid [7]. Tannin copolymers can be blended with polyesters (polyethylene terephthalate, 'PET', and polybutylene terephthalate, 'PBT') and polycarbonate to improve thermal stability and lower melt dripping upon ignition [8]. It has been reported that as low as 100 ppm of tannin copolymer (condensation product of tannin with polyvinyl alcohol, 'PVA', or polyethylene glycol, 'PEG') reduces flame sustenance time by more than 50%. Thermal

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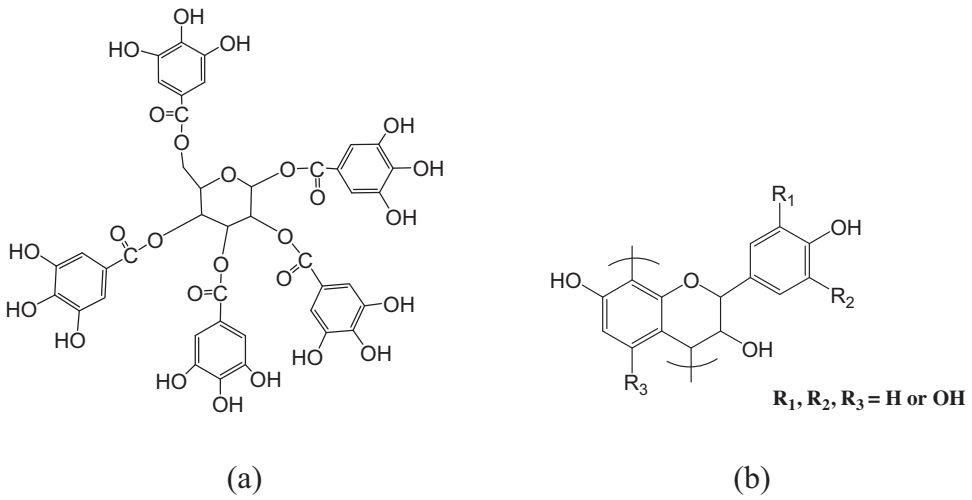

Fig. 1. Typical structures of (a) hydrolysable tannin and (b) condensed tannin.

degradation behavior of condensed tannin extracted from Radiata pine bark is reported in literature [9]. In their work, Gaugler and Grigsby suggest that condensed tannin extracted from Radiata pine is stable for processing at temperatures below 200 °C. However there are very few reports on the thermal degradation of hydrolysable tannin [1,10–12]. Considering the fact that hydrolysable tannin is a processable type of tannin, the study of its thermal stability and thermal degradation behavior is important from an application standpoint. In this paper we present a detailed study of thermal and thermo-oxidative degradation of a hydrolysable tannin (tannic acid).

2. Experimental

2.1. Materials

Technical grade tannic acid (ACS reagent, CAS Number 1401-55-4, formula: $C_{76}H_{52}O_{46}$, molecular mass: 1701.20 g/mol, loss on drying: <7.5%) was purchased from Sigma-Aldrich. The material was used as received. No further purification or drying was performed.

2.2. Degradation study of tannic acid

2.2.1. Thermal and thermo-oxidative degradation studies

Thermogravimetric analysis (TGA) of samples was done using a TGA Q50 (TA Instruments) under nitrogen or air purge of 30 mL/min to study thermal stability of materials. Approximately 10 mg of samples was weighed and heated from room temperature to 750 °C at a constant heating rate of 20 °C/min. Three runs were carried out for each sample to ensure consistency of the results. The samples were also tested at multiple heating rates of 5, 10, 20 and 25 °C/min under nitrogen or air purge of 30 mL/min to study the effect of heating rates on degradation profile.

2.2.2. Mechanistic study of thermal and thermo-oxidative degradation using evolved gas analysis

Evolved gas analysis (TGA–FTIR) was used to monitor the degradation products of tannic acid. In the experiment, TGA equipped with appropriate gas purge was connected with a TGA–FTIR interface (Thermo Electron Corporation) installed inside the infrared spectrometer (Nicolet 4700, Thermo Electron Corporation). Nitrogen or air was typically purged at 50 mL/min. About 12 mg of tannic acid was used in each test. The thermal and thermo-oxidative degradation was studied under nitrogen and air, respectively at a heating rate of 20 °C/min from room temperature to 750 °C. The temperature of the transfer pipe was set at 215 °C while the TGA–FTIR sample cell was set at 245 °C to prevent the condensation of volatiles in the sample chamber. The data from infrared spectrometer comprises a series of IR spectra measured at average of 16 scans with 4 cm^{-1} resolution. Four spectra were obtained every minute. The IR spectra were compared with standard spectra of organic species reported in NIST (National Institute of Standard and Technology) standard reference database and the OMNIC's spectral library.

2.2.3. Comparative study of degradation using pyrolysis–gas chromatography–mass spectroscopy (Py–GC–MS)

The Py–GC–MS analysis of tannic acid was carried out in a CDS 5200 pyrolyzer coupled to an Agilent GC–MS instrument (GC Model 7890A, MS Model-5975C). 1 mg of tannic acid was heated rapidly to decompose into volatile monomers or smaller fragments. The volatile products of pyrolysis were transferred to the gas chromatograph. Subsequently the volatiles were separated and identified by the mass spectrometer. The pyrolysis was done under helium carrier gas at a flow rate of 54 mL/min. In this experiment, the pyroprobe temperature was raised to 400 and 750 °C, respectively. The interface and thermally insulated transfer line temperature were set at 300 °C to keep the chemicals volatilized during transport from the pyrolyzer to the GC column. The GC column was a DB-5ms low bleed, (5%-phenyl)-methylpolysiloxane column (30 m × 0.25 mm × 0.25 μm). The GC temperature was initially held at 40 °C for 2 min, and was increased to 300 °C at 10 °C/min ramp, and then held at 300 °C for 10 min. The mass spectra were measured using electron impact ionization energy of 70 eV. The mass detector was scanned from 35 to 400 m/z at scan rate of 4 scans per second. The data were searched using the NIST 2008 MS library and the CDS's pyrolysis library.

2.2.4. Spectroscopic analysis of condensed phase at various temperatures for detailed investigation of degradation residue

The thermal degradation of tannic acid was conducted with a TGA Q50. Approximately 10 mg tannic acid was loaded into a ceramic TGA pan. Then the sample was heated to 100 °C, 200 °C, 300 °C, 400 °C, 500 °C, 600 °C, 700 °C and 800 °C, respectively at a heating rate of 20 °C/min with 30 mL/min nitrogen purge on both balance and samples. Fourier-Transform Infrared (FTIR) Spectroscopy measurement was carried out for tannic acid char collected at those temperatures on a Nicolet 4700 FTIR spectrometer with a