Intumescent flame-retardant cotton produced by tannic acid and sodium hydroxide

Sunghyun Nam[a,*], Brian D. Condon[a], Zhiyu Xia[b], Ramaswamy Nagarajan[b], Doug J. Hinchliffe[a], Crista A. Madison[a]

[a] Southern Regional Research Center, Agricultural Research Service, USDA, 1100 Robert E. Lee Blvd., New Orleans, LA 70124, USA
[b] Department of Plastics Engineering, University of Massachusetts, Lowell, MA 01854, USA

ARTICLE INFO

ABSTRACT

Tannins, natural phenolic compounds abundant in many plants, exhibit low thermal conductivity and low flammability and have inspired bionic approaches in the development of flame-retardant materials. Still, tannins have been used as a dyeing fixative for cotton, and their potential contribution to developing flame-retardant cotton has not yet been examined. This study shows that tannic acid with the aid of sodium ions can produce intumescent flame-retardant cotton. Treatment with tannic acid alone altered the thermal patterns of the pyrolysis and combustion of cotton and increased the char yield, but the limiting oxygen index (LOI) was not improved significantly. The addition of low concentrations of sodium hydroxide enhanced the adsorption of tannic acid onto cotton and catalyzed the decarboxylation of tannic acid and the dehydration of cotton cellulose at lower temperatures. Such modified thermal reactions as well as the formation of intumescent char led to a reduction in heat release capacity of 82% (from 278 to 51 J/g K) and an increase in the LOI by as much as 30.2% as compared with that for control cotton.

1. Introduction

Tannins, natural phenolic compounds found in a number of plants, have many special properties, such as antibacterial and antioxidant effects [1,2], the ability to precipitate proteins [3], and a reducing capability (as an electron donor) [4]. Moreover, concentrated in the bark of trees, tannins are naturally fire resistant – during a fire, tannins efficiently reduce oxidants and radicals to maximize the unburned solid and charred remain, aiding tree survival [5]. Due to their thermal stability and similar reactivity to phenol, tannins have been combined with hardeners to produce functional polymers such as adhesives and resins [6,7] and have been used to generate porous materials such as aerogels and foams [8–10]. These tannin-based products have exhibited low thermal conductivity and low flammability comparable to those of fossil-based compounds. As a result, the use of tannins appears to be serving as a new bio-inspired basis for the development of thermal insulation or/and fire-resistant additives and building materials.

There have been some efforts to elucidate the thermal properties of tannins. The thermal degradation of tannins depends on composition, structure, the degree of polymerization, and the nature of the inter-flavonoid bonds [11]. For example, tannins with lower concentrations of carbohydrates and higher tannin purity exhibited enhanced thermal

stability [11,12]. The glass transition of (non-hydrolysable) condensed tannin occurred at around 140 °C, and acetylation of the hydroxyl groups decreased the glass transition temperature [13]. The thermal degradation of condensed tannin is distinctive from that of hydrolysable tannin (i.e., tannic acid). Condensed tannins exhibited two degradation stages with the formation of 55% char, whereas tannic acid exhibited five degradation stages with the formation of 28% char [14]. The main gaseous product from the pyrolysis of condensed tannins at 600 °C was catechol [15]. On the other hand, tannic acid consisting of two layers of gallic acid units and a core glucose ring released 1,2-benzene diol and 1,2,3-benzene triol as main fragments from the disintegration of the outer layer of gallic acid units [16]. The outer layer disintegrated below 400 °C, but the inner layer was stable to higher temperatures and crosslinked to produce intumescent carbonaceous char at above 700 °C [16].

Tannins, which are responsible for the color of brown cotton, have been linked to superior thermal resistance of the fiber, i.e., lower heat release capacity and slower burning, as compared with white cotton fiber [17]. Besides their inherent thermal stability, tannins can adsorb metal ions, playing an important role in improving the thermal resistance of the fiber [17]. Inorganic salts naturally occurring in raw cotton were found to suppress the depolymerization of cellulose at high

---

temperatures and consequently reduced the production of levoglucosan, which is a major constituent of flammable tar [18,19]. Regarding inorganics, the concentration of sodium exhibited significant correlations with the heat release capacity and LOI of cotton [17]. Inspired by such a natural fire-protecting strategy, intumescent flame-retardant cotton nonwoven fabric has been produced in this study by applying tannic acid and sodium hydroxide. The thermal degradation and combustion properties modified by tannic acid and sodium ions were demonstrated using thermogravimetric and microscale combustion calorimetric analyses. The formation of intumescent char was examined using scanning electron microscopy.

2. Experimental

2.1. Materials and sample preparation

American Upland raw cotton fiber was acquired from the national registry. Tannic acid ($C_{76}H_{52}O_{46}$), sodium carbonate ($NaCO_3$), hydrogen peroxide solution (H_2O_2, 30 wt.% in H_2O), and Triton X-100 were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH) and sodium silicate solution (42° Be) were purchased from J. T. Baker and Columbus Chemical Industries, Inc., respectively. All chemicals were used as received.

Hydroentangled nonwoven cotton fabrics were fabricated using traditional cotton processing and pilot-scale nonwoven production equipment at the Southern Regional Research Center [20]. Cotton fiber passed through a feed hopper, a step cleaner, a fine opener/cleaner, and an automatic chute-feed system. The opened fiber was fed to a 1 m wide card specially designed to process cotton. The carded web (12 g/m) was crosslapped to produce a batt, which was continuously fed into a needle-punch machine equipped with one needle board. The lightly needle-punched substrate was subsequently hydroentangled using a pre-wet water pressure of 50 bar and a bonding water pressure of 135 bar at a process speed of 5 m/min. The area density of the fabric measured according to ASTM D 6242-98 was 50 $\pm$ 3 g/m^2.

The scouring and bleaching of cotton nonwoven fabrics were carried out according to a published procedure [21]. Briefly, using an overflow-jet dyeing apparatus (Werner Mathis USA Inc., Concord, NC), fabric was immersed in an aqueous solution containing sodium hydroxide (4.0 g/L), sodium carbonate (0.7 g/L), sodium silicate solution (1.8 g/L), hydrogen peroxide solution (7.0 g/L), and Triton X-100 (0.125 g/L) with a liquid-to-fabric ratio of 22.4:1 and circulated at 100 °C for 90 min. Following treatment, the fabric was rinsed with cold water for 20 min three times and circulated in 100 °C water for 20 min and subsequently in cold water for 20 min. The fabric was neutralized with a solution of acetic acid (0.25 g/L) in water for 10 min and rinsed with cold water. The fabric was then passed through a continuous hot air dryer (Werner Mathis USA Inc., Concord, NC).

For treatment, the weighed nonwoven fabric was immersed in an aqueous solution containing various concentrations of tannic acid and NaOH (Table 1) and passed through a laboratory padder (Werner Mathis USA Inc., Concord, NC) with a pressure of 68.9 kPa (10 psi) and a padder speed of 2 m/min. The fabric was then air-dried and weighed to calculate a percentage dry add-on.

2.2. Characterization

The content of sodium on the fabric was measured at Elemental Analysis, Inc. in Lexington, KY, using an Element 2TM high-resolution inductively coupled plasma mass spectroscope (ICP-MS, Thermo Fisher Scientific, Waltham, MA).

The UV/Vis spectra were obtained in a wavelength range of 220–900 nm using a UV/Vis/NIR spectrometer (UV-2600 ISR-2600, Shimadzu). Photographs of samples were taken using a digital camera (rx100, Sony).

Thermogravimetric (TG) and differential thermogravimetric (DTG)

Table 1
Treatment summary of cotton nonwoven fabrics with tannic acid and NaOH.

Sample name	Concentration in padding bath (wt.%)		Dry add-on (wt.%)	Content of Na on fabric (wt.%)
	Tannic acid	NaOH		
T5N0	5	0	5.7 (0.2)[a]	–
T5N025	5	0.25	5.8 (0.4)	0.16
T5N05	5	0.50	18.6 (1.1)	0.91
T5N075	5	0.75	12.6 (1.5)	0.88
T5N1	5	1.00	10.3 (1.4)	0.85
T20N0	20	0	30.5 (4.0)	–
T20N025	20	0.25	36.8 (3.1)	0.22
T20N05	20	0.50	55.1 (0.9)	0.55
T20N075	20	0.75	65.1 (3.9)	0.88
T20N1	20	1.00	87.5 (6.3)	1.40

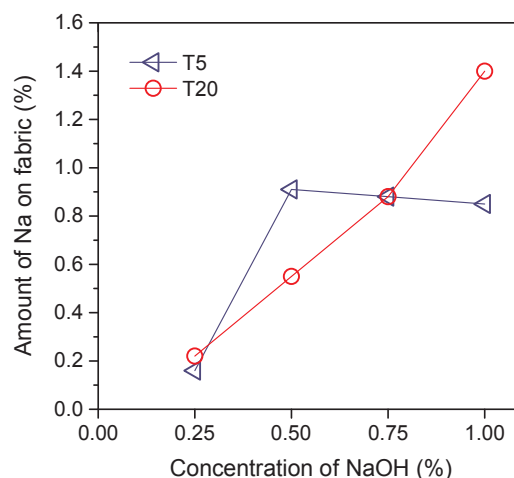[a] Standard deviation of three measurements.

Fig. 1. Amount of sodium on the fabric treated with various concentrations of tannic acid and NaOH.

analyses were carried out using a TGA Q500 thermal gravimetric analyzer (TA Instruments, New Castle, DE) under a nitrogen atmosphere. The nitrogen flow into the furnace was maintained at a rate of 90 mL/min. Approximately 5 mg of the sample placed in a platinum pan was heated from 30 $\pm$ 5 °C to 900 °C with a heating rate of 10 °C/min. TG and DTG thermograms were analyzed using Universal Analysis 2000 software (TA Instruments). Three measurements were performed. Deconvolution of the DTG curve was conducted based on the application of Gaussian and/or Fraser-Suzuki (asymmetric) type signals and Marquardt's non-linear optimization using AKTS-Thermokinetics software.

Microscale combustion calorimetric (MCC) analysis was conducted using an MCC-2 (Deatak, McHenry, IL) according to ASTM D 7309-13. Approximately 5 mg of the ground fiber sample were placed in an MCC ceramic cup and weighed on an Excellence Plus XP205 analytical balance (Mettler-Toledo Inc., Columbus, OH). The sample was then heated to 650 °C at a heating rate of 1 °C/s in a stream of nitrogen flowing at 80 cm^3/min. The volatile thermal decomposition products formed in a pyrolyzer were swept by the gas stream of nitrogen and fully mixed with an oxygen stream at 20 cm^3/min in a combustor, where the decomposed products were completely oxidized at 900 °C for 10 s. The oxygen depletion involved in the combustion was determined by the oxygen concentration and flow rate of the combustion gases to measure a heat release rate (HRR). The parameters obtained by the MCC Curve Fit v.2 software (Deatak) are as follows: the specific HRR (W/g) obtained by dividing the HRR by the initial sample mass; the peak heat release rate (PHRR, W/g), which is the maximum specific HRR;