Polymer Degradation and Stability 96 (2011) 2010–2018

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Effect of urea additive on the thermal decomposition of greige cotton nonwoven fabric treated with diammonium phosphate

Sunghyun Nam[a], Brian D. Condon[a,*], Dharnidhar V. Parikh[a], Qi Zhao[b], Michael Santiago Cintrón[a], Crista Madison[a]

[a] USDA ARS Southern Regional Research Center, 1100 Robert E. Lee Blvd., New Orleans, LA 70124, USA
[b] Department of Chemistry, Tulane University, 6400 Ferret Street, New Orleans, LA 70118, USA

ARTICLE INFO

Article history:
Received 2 June 2011
Received in revised form
22 August 2011
Accepted 25 August 2011
Available online 5 September 2011

Keywords:
Greige cotton nonwoven fabric
Flame retardant
Urea
Diammonium phosphate
Carbamate
Thermogravimetry

ABSTRACT

This study showed that greige cotton nonwoven fabric can effectively be flame retardant by applying the phosphorus of diammonium phosphate (DAP) as low as 0.8 wt% with the addition of urea. At such a low content of phosphorus, the char length and limiting oxygen index (LOI) were continuously decreased and increased, respectively, as the concentration of urea increased. The effect of urea additive on the thermal decomposition of flame retardant greige cotton nonwoven fabric was investigated by thermogravimetry, ATR-FTIR, XRD, $^{1}H \rightarrow {}^{13}C$ CP/MAS NMR, and SEM. The results indicated that, upon heating, urea not only facilitated the phosphorylation reaction of DAP but also introduced carbamate groups into cellulose to decrease the degree of crystallinity prior to the decomposition of the crystalline cellulose. Compared with DAP treatment alone, the addition of urea accelerated the decomposition of glycosyl units, which resulted in a slight increase of weight loss and decrease of char yield. The char morphology observed after LOI tests indicates that urea released nonflammable gases, which blew the carboneous char layer to protect the underlying substrate.

Published by Elsevier Ltd.

1. Introduction

As most fatal residential fires originate in bedrooms [1], fire blocking by textile materials is critical. In 2005–2007, annual residential fires in the U.S. involving mattress/bedding were estimated to be 9900 and resulted in 370 deaths, 1230 injuries, and $344 million in property loss [2]. In order to reduce fire rates, many flammability regulations for textile products have been adopted, e.g. 16 CFR 1633 for mattresses, put into effect in 2007. Recent our studies [3–5] have shown potential benefit of using greige (raw) cotton to produce a fire-barrier for mattresses and furniture upholstery. Greige cotton is prepared without wet processing that consumes a large amount of chemicals, water and energy. The utilization of greige cotton, therefore, is beneficial in reducing costs and supporting the environment. Currently, highly efficient mechanical cleaning system lowers the trash content in greige cotton. Pre-cleaned cotton, e.g., UltraClean® cotton is commercially available for the intended end-use application that is not likely to require scouring and bleaching. To be used as a fire barrier, the greige cotton fiber can directly be treated with flame retardants (FRs) and subsequently converted into a fabric by nonwoven fabrication (i.e., high-loft), or FR treatment can be applied after the nonwoven or woven fabrications.

Phosphorus-based FRs (P-FRs) are widely used for cotton-based materials due to their effectiveness in FR performance. Their action mechanism involves a phosphorylation reaction with cellulose, which inhibits the formation of flammable levoglucosan, and consequently reduces the fuel supply necessary for combustion [6]. The catalyzation of a dehydration reaction by P-FRs themselves or by the Bronsted acids they produce also accounts for the flame-retarding action. It is well known that the efficacy of P-FRs can be further enhanced by the addition of nitrogen (N) compounds, although these additives have limited FR function. For example, an earlier study showed that in a phosphoric acid/urea system, the fixation of 2.2% of N reduced the amount of P in almost half, from 4.5 to 2.4%, in imparting similar flame resistance to scoured and bleached cotton-woven fabric [7]. This P–N synergism was found to increase with the contents of P and N rather than to predominate at a specific N/P ratio [8, 9]. N additives that have shown the synergistic function include cyanamide [10], guanidine carbonate [7,11,12], and guanylurea [7]. Recently, chitosan was demonstrated to have synergism with DAP [13]. Many researchers have tried to

* Corresponding author. Tel.: +1 504 286 4540; fax: +1 504 286 4390.
E-mail address: brian.condon@ars.usda.gov (B.D. Condon).

0141-3910/$ – see front matter Published by Elsevier Ltd.
doi:10.1016/j.polymdegradstab.2011.08.014

explain how and why N additives enhance the efficiency of P-FRs, and their theories may be outlined as follows: 1. N additives facilitate the phosphorylation reaction of P-FRs [14]. 2. N additives and P-FRs interact to form P–N bonds, which have better thermal stability than P–O bonds [12] and thus increase the retention of P and N in char [15,16]. The intermediate products containing P=N or P–NH_2, which are formed during pyrolysis, efficiently phosphorylate cellulose [17] and catalyze a dehydration reaction [18]. 3. N additives release non-combustible gases, contributing to the vapor-phase flame retardation [15,19,20]. These existing theories, however, may not apply to all P and N compounds because, depending on the kinds of N additive and P-FR, different physical and chemical reactions are involved. As a result, new explanations are continuously being proposed. For example, Gaan et al. attributed the synergism of tributyl phosphate and three N additives including urea, guanidine carbonate, and melamine formaldehyde to the formation of protective polymeric coating [21].

In an effort to utilize greige cotton nonwoven fabric in fire barrier products, we applied DAP and urea. These compounds are less expensive and environmentally friendly. As a non-durable or semi-durable FR, DAP has been widely used on infrequently washed or disposable products [22]. As compared in the literature, DAP was the most effective among non-durable and durable FRs in imparting FR properties to cellulosic materials and in yielding char [23–26]. Upon curing, the phosphorylation of DAP takes place on the hydroxyl groups of cellulose to produce cellulose phosphate. This reaction yield is above 90% in the presence of urea [27]. The durability test showed that the cotton modified with DAP and urea had good alkaline hydrolytic stability to stand ten laundering cycles, but got affected by hard water launderings that cause ion exchange [27]. Since the synergetic action of urea on the DAP function was recognized in 1940s, several action mechanisms have been proposed, and some of them were rejected. The mechanism generally accepted is that urea is molten during curing to act as a solvent medium for the phosphorylation reaction and as a swelling agent for cellulose [14]. A powerful swelling capability of urea on cotton was demonstrated by several researchers [28,29], who explained that the polar nature of urea disturbs the hydrogen-bonded crystalline region of cellulose. Other work, however, showed that the action of urea is limited to the amorphous region [30] or the surface of cellulose [31]. On the other hand, Segal and Eggerton reported some evidence for the formation of reaction product when cellulose and an aqueous solution of urea were heated [32].

Motivated by the incomplete understanding the action of urea and its possible effect on the thermal decomposition of crystalline and amorphous regions of cotton, we have applied different ratios of urea to DAP onto cotton without curing and examined the chemical and physical changes of cellulose during thermal decomposition and combustion processes. Another motivation is the desire to characterize the synergistic FR performance of DAP and urea for greige cotton nonwoven fabric on a quantitative basis. In general, the flammability of textiles is influenced by surface characteristic and construction of fabric [9]. According to our previous study, greige cotton experienced more stable thermal decomposition, generating four times greater char than scoured cotton [33]. Considering the fact that most studies on FR cotton have been conducted using scoured/bleached cotton woven fabrics, a systematic study on FR greige cotton nonwoven fabric will lead to a new understanding the effectiveness of greige cotton in the FR application. In this study, the FR properties of greige cotton nonwoven fabrics were evaluated by char length and limiting oxygen index (LOI). The thermal decomposition of greige cotton fabrics was monitored by thermogravimetric (TG) and differential thermogravimetric (DTG) analyses, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), X-ray diffraction (XRD), and $^{1}H \rightarrow {}^{13}C$ CP/MAS NMR. The char structure and morphology left in LOI tests were examined by scanning electron microscopy (SEM).

2. Experimental

2.1. Material

Greige cotton needle-punched nonwoven fabric was fabricated in the pilot plant at Southern Regional Research Center. Two randomly selected American Upland cotton fibers were mechanically cleaned and opened by traditional textile equipment. A continuous fiber web ($\sim$12 g/m^2) produced by a tandem card was introduced to a cross-lapper and subsequently to a needle-punching machine equipped with two boards of 4000 needles. The density of the obtained nonwoven fabrics was 100 g/m^2. DAP and urea were purchased from Magnolia Chemical and Solvents Inc. The percentages of P and N for DAP were determined to be 21.8% and 20.5%, respectively, and the percentage of N for urea was determined to be 46.1% by elemental analyses. Triton® X-100 was purchased from Fisher. All chemicals were used as received from suppliers.

2.2. Sample preparation

Greige cotton nonwoven fabric was immersed in a FR aqueous solution containing DAP and urea, which was formulated to provide different %P and %N (Table 1). Triton® X-100 (0.1 wt%) was also added into the formulation to expedite wetting of greige cotton fabric that contains hydrophobic surface compounds such as waxes and pectins. The fabric was passed through a laboratory padder to reach an average wet pick-up of 100 $\pm$ 5% and air dried. The samples were then kept under standard conditions (65% relative humidity and 21 °C) for 24 h. The percentages of P and N on treated fabrics were determined using, respectively, an inductively-coupled plasma emission spectrophotometer (ARCOS, Spectro Analytical Instruments) and a combustion analyzer (VarioMax, Elementar Americas, Inc.) in the agriculture diagnostic laboratory at the University of Arkansas, Fayetteville. The average value of two measurements is presented in Table 1. The selected samples were heated in a bench furnace (Lindberg Blue M Electric) under nitrogen with a flow rate of 1.6 L/min. The temperature was elevated from room temperature at a rate of 18 °C/min. When the furnace reached the desired temperature, samples were removed from the furnace and cooled to room temperature.

Table 1
The percentages of P and N in the treatment of DAP (D) and urea (U) and their measured values on treated greige cotton nonwoven fabrics by elemental analysis.

Sample name	Concentration in padding bath (%)		Predicted content on fabric		Content on fabric by elemental analysis	
	DAP	Urea	%P	%N	%P	%N
D1	4.3	0	0.9	0.9	0.9	0.6
D1U1		1.9	0.9	1.8	0.9	1.7
D1U2		5.8	0.9	3.4	0.8	3.4
D1U3		9.6	0.8	5.0	0.8	5.0
D1U4		13.5	0.8	6.6	0.8	6.7
D2	8.5	0	1.8	1.6	1.7	1.1
D2U2		3.8	1.8	3.3	1.6	3.0
D2U3		7.7	1.8	4.9	1.6	4.7
D2U4		11.6	1.7	6.5	1.5	6.1
U4	–	15.5	–	6.6	–	7.0