PHOSPHORUS-NITROGEN SYNERGISM IN THE FIRE BARRIER OF GREIGE COTTON NONWOVEN FABRICS

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Abstract

The phosphorus-nitrogen (P-N) synergism of diammonium phosphate (DAP) and urea was studied to determine their optimum ratio in the flame retardant (FR) greige cotton nonwoven fabrics. Compared with the treatment of DAP alone, the addition of urea at %P:%N = 2.5:4.6 enhanced the flame resistance of FR greige cotton nonwoven fabric, showing the increase of limited oxygen index in 13% and decrease of char length in 54%. This synergistic flame retardance was attributed to the increased activation energy of thermal decomposition and the formation of nonflammable insulative coating on the fiber surface. Further increase of %N, however, did not show any improvement of flame retardance.

Introduction

With worldly recognized climate change, the sustainability in textile production and processing that involve large consumption of energy, water, and raw materials is desired more than ever. For example, consumers are now demanding natural, organic, no synthetic, no regenerated, and no bleached textile products. Greige cotton fiber that is mechanically cleaned without using any chemicals is the most natural form, and thus one of the greenest candidates. Compared with scoured/bleached cotton, the greige cotton not only has unique characteristics such as smooth surface and natural creamy color, but also exhibits different thermal decomposition to generate more than 4 times of char at 600 °C (Figure 1). Through the energy-efficient nonwoven processing, the greige nonwoven fabric can find many applications to benefit the low cost and green fabrication.

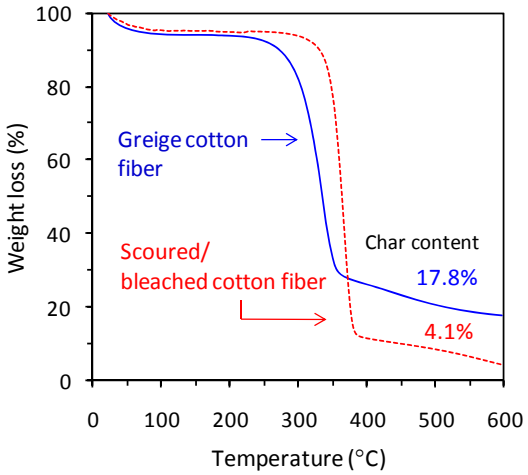


Figure 1. TGA thermograms for greige and scoured/bleached cotton fibers obtained at a heating rate of 5 °C/min under nitrogen.

Recent studies at Southern Regional Research Center have shown that greige cotton nonwoven fabric can be utilized as a fire barrier for mattresses to comply with the flammability regulation (16 CFR 1633) with the treatment of flame retardant (FR) (Parikh *et al.*, 2003, 2009). Although many new FRs have been developed, diammonium phosphate (DAP) is still considered to be an effective FR among phosphorus based FRs (Gaan and Sun, 2007) as well as environmentally favored and cheap. For inexpensive textile products of mattress and upholstered furniture to meet flammability regulations, the systematic studies on the efficacy of cost-effective FRs are required. The synergism on the flame retardance of DAP in the presence of urea is well known (Preston *et al.*, 1954), but its effect

has not been clearly explained other than the swelling of cotton and decrease of cellulose degradation. In this work, the kinetic study of thermal decomposition and observation of char morphology were carried out to explain the phosphorus-nitrogen (P-N) synergism induced by urea. Based on the limited oxygen index (LOI) and the open flame test in vertical direction, the optimum ratio of DAP and urea was determined.

Materials and Methods

Materials. Needle punched greige cotton nonwoven fabric was fabricated in the nonwovens laboratory at Southern Regional Research Center. Randomly selected two American Upland cotton fibers were mechanically cleaned, and passed through a carding and subsequently cross-lapper machine to produce a 16-lap assembly. This multi-lap was transported to a double-board needle machine, where 3-barb needles (ca. 9 cm in length) generated a light needling impact. The density of the nonwoven fabrics was 85 g/m^2. Diammonium phosphate and urea were purchased from Magnolia Chemical and Solvents Inc. Triton® X-100 was purchased from Fisher and used as a wetting agent.

Sample preparation. Cotton nonwoven fabrics were immersed in the FR solution containing different P and N concentrations with 0.1% of a wetting agent, padded through a laboratory padder to produce 100% wet pick-up, and dried at 80 °C for 5 min. Before the analysis, all samples were conditioned under the standard condition for 24 h.

Measurements. Thermal gravimetric analysis (TGA) and differential thermal gravimetry (DTG) were obtained using a TGA Q500 thermal gravimetric analyzer (TA Instrument), where ultrapure nitrogen was introduced into the furnace at a flow rate of 60 mL/min. The temperature was increased from room temperature to 600 °C with a heating rate of 5 °C/min. To measure the activation energy of decomposition by Kissinger method, three additional heating rates, 2, 10, and 15 °C/min were used. Vertical flame test was conducted according to ASTM standard method D6413-99 with 12 sec of flame exposure, and after-flame time, afterglow time, and char length were determined. Limiting oxygen index (LOI) was measured according to ASTM standard method D2863-00 using a Limiting Oxygen Index Chamber (Dynisco Polymer Test). The samples treated with DAP and mixture of DAP and urea showed a burst of flame rather than candle-like combustion when measuring their LOIs. The chars obtained after LOI test was examined under a Scanning Electron Microscope (SEM) (Philips, XL 30).

Results and Discussion

The greige cotton needle-punched nonwoven fabrics were treated with varying %N and fixed P (2.5%). Table 1 shows the contents of P and N on cotton fabrics calculated from add-ons.

Table 1. Concentrations of phosphorus (P) and nitrogen (N) on treated greige cotton nonwoven fabrics.

Sample	Concentration (%) in solution		Add-on (%)[a]	% calculated from add-on	
	DAP	Urea		P	N
DAP	10.7	0	10.2 [0.1]	2.5	2.3
DU1	10.7	5	15.5 [0.8]	2.5	4.6
DU2	10.7	8	18.2 [0.4]	2.5	6.0
DU3	10.7	11	21.0 [0.5]	2.5	7.4
Urea	0	11	11.3 [0.4]	0	7.4

[a] Average value of four samples and standard deviation.

Before examining the synergistic effect by the addition of urea, the effect of single treatment of DAP and of urea on the greige cotton nonwoven fabric was first examined. Figure 2 presents TGA (a) and DTG (b) thermograms of these fabric obtained under nitrogen at a heating rate of 5 °C/min. Compared with untreated fabric, DAP treated fabric decomposed at lower temperature with a slight slope change. The temperatures determined at the maximum decomposition rate in DTG, T_{max}, of DAP treated and of untreated fabrics were 263 and 334 °C, respectively. This reduction of T_{max} is attributed to the catalyzed dehydration of cellulose by DAP. The urea treated fabric exhibits a two-stage decomposition process: a small initial decomposition at 167 °C resulting from the decomposition of urea and the major cellulose decomposition at 356 °C. The T_{max} of urea treated sample was found to be slightly greater

than that of untreated sample. It can be seen that the shape of DTG curve is significantly changed by either DAP or urea treatments. For DAP treated fabric, a shoulder peak generated by the slope change at TGA made the decomposition peak broad, indicating a slow and moderate thermal decomposition reaction, whereas the deep and narrow curve by urea treatment reflects a fast and drastic reaction. Consequently, the weight loss of greige cotton fabric was decreased by DAP, and increased by urea. The amount of char/residue at 600 °C for untreated, DAP treated, and urea treated cottons were 17.8, 36.2, and 8.7%, respectively.

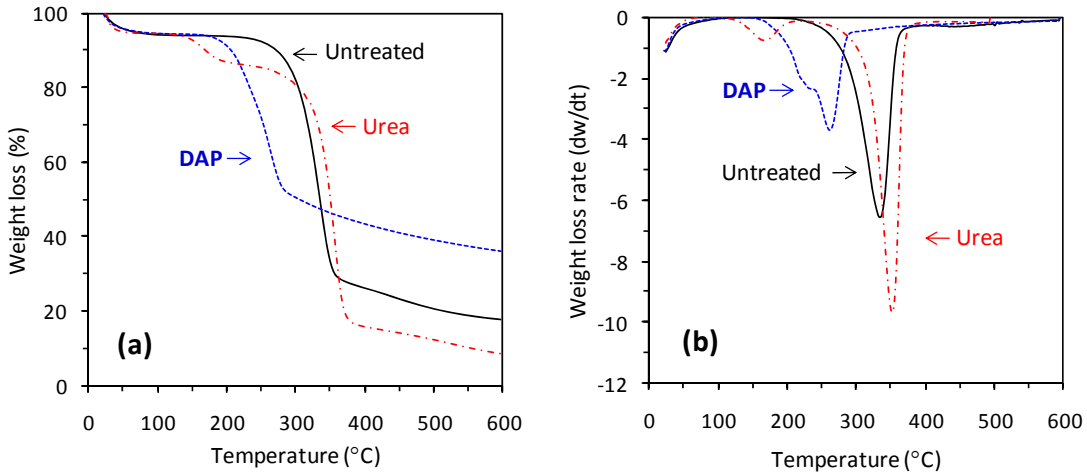


Figure 2. Thermal gravimetric decomposition of the greige cotton nonwoven fabrics untreated and treated with DAP, or urea alone: (a) TGA and (b) DTA. Heating rate was 5 °C/min under nitrogen.

Figure 3 shows TGA and DTG of the greige cotton nonwoven fabrics treated with varying the %N by addition of urea to DAP. The initial decomposition by urea became larger as increasing %N. The T_{max} of major cellulose decomposition slightly increased with the addition of urea, but the overall decomposition process did not significantly change with %N. Similar amount of char/residue was obtained for different %Ns.

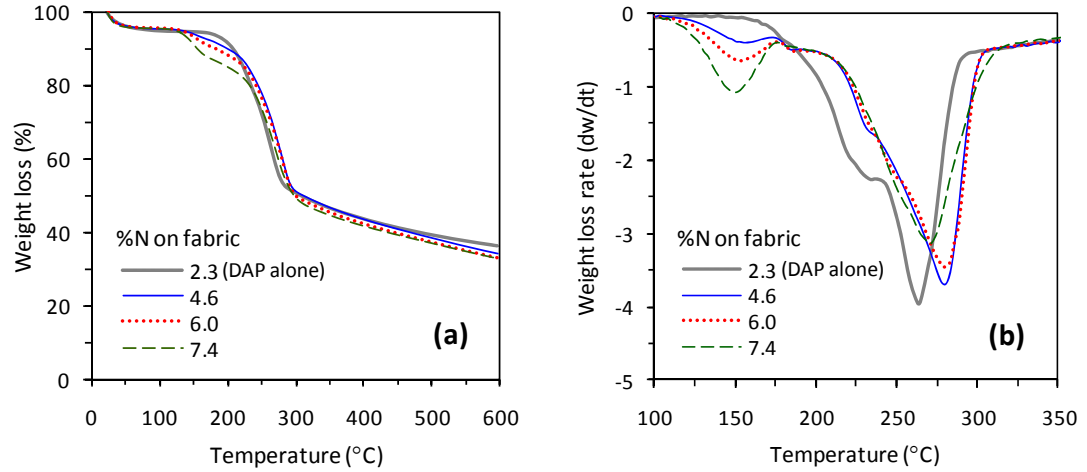


Figure 3. Thermal gravimetric decomposition of the greige cotton nonwoven fabrics treated with different %N and fixed 2.5% P: (a) TGA and (b) DTA. Heating rate was 5 °C/min under nitrogen.

To better understand the effect of %N on the thermal decomposition, the apparent activation energy of decomposition was determined using the Kissinger's equation (Kissinger, 1956):

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \left(\frac{E_a}{RT_{\max}}\right)$$

where E_a is the apparent activation energy, β is the heating rate (K/min), T_{max} is the temperature at the maximum decomposition rate (K), A is the pre-exponential factor (min^{-1}), and R is the gas constant (8.314 $JK^{-1}mol^{-1}$). From the linear plot of $\ln(\beta/T^2_{max})$ as a function of $1/T_{max}$ for different heating rates (Figure 4), the E_a was calculated from the slope and presented in Table 2 along with other thermal decomposition characteristic values. It was found that the E_a significantly increased by the addition of urea, showing the synergistic effect from the N of urea. The highest value was obtained at %P:%N = 2.5: 4.6, and further increase of %N lowered the E_a.

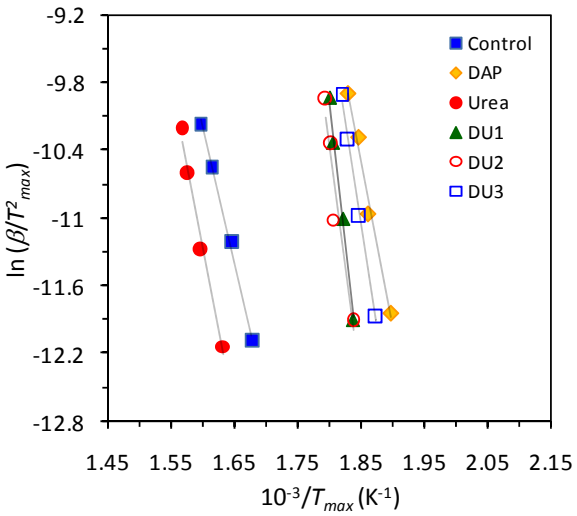


Figure 4. Linear plots of $\ln(T^2_{max}/\beta)$ versus $1/T_{max}$ of the greige cotton nonwoven fabrics untreated and treated with DAP, urea, and mixtures of DAP and urea by Kissinger equation.

Table 2. Thermal decomposition characteristics of the greige cotton nonwoven fabrics untreated and treated with DAP, urea, and mixtures of DAP and urea.

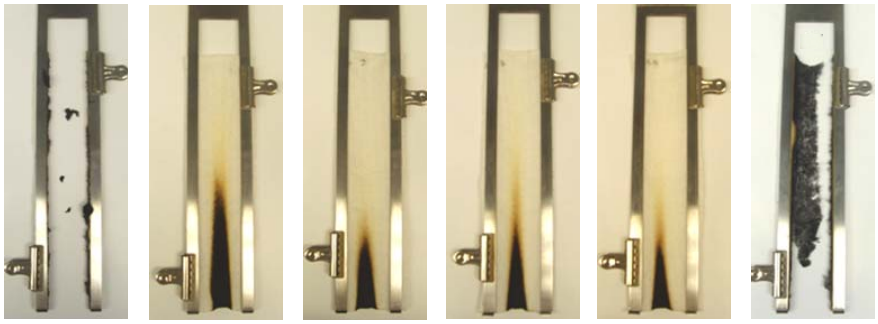
Sample	%P:%N	T_i (°C)	T_{max} (°C)	WL_{max} (%)	Residue/char (%)	E_a (kJ/mol)
Untreated	-	-	334	48.1	17.8	196
DAP	2.5:2.3	-	263	36.5	36.2	243
DU1	2.5:4.6	160	280	39.2	34.3	429
DU2	2.5:6.0	154	280	40.5	33.1	348
DU3	2.5:7.4	151	270	37.5	32.8	306
Urea	0:7.4	167	356	61.2	8.7	244

T_i = temperature of initial decomposition in DTG; T_{max} = temperature of major cellulose decomposition in DTG; WL_{max} = weight loss at T_{max}; Residue = char content measured at 600 °C; E_a = activation energy obtained by Kissinger method.

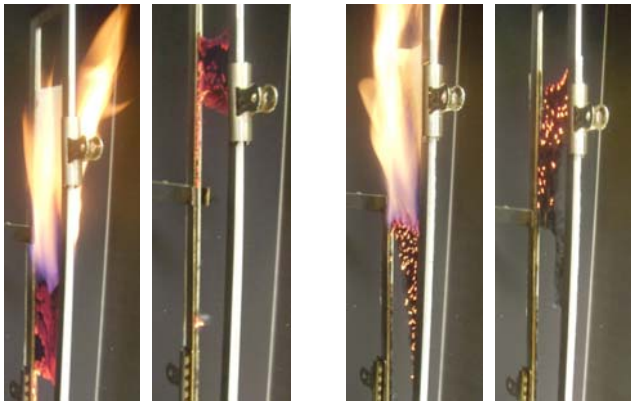
The measurement of LOI and open flame test in vertical direction were carried out to evaluate the flame retardance (FR) of treated greige cotton nonwoven fabrics (Table 3). The LOI of untreated greige cotton was measured to be 20.0%, which is a little greater than the reported values (17.5-18.5%) (Chang *et al*., 2007) of bleached cotton textiles. The DAP treatment alone increased the LOI to 32.3%, showing good FR effectiveness for its P and N, but the urea treatment yielded similar LOI with untreated fabric. By the addition of urea at %P:%N = 2.5:4.6, the LOI was increased to 36.6%, signifying the synergistic reaction with the N of urea. The higher content of N, however, did not show further enhancement of the LOI. In the vertical flame test, both untreated and urea treated fabrics completely burned, consuming almost all fabric. The urea treated fabric exhibited longer after-flame time, but shorter afterglow time than untreated fabric. As can be seen in Figure 5, the smaller size of afterglow was generated on the urea treated fabric than on untreated fabric. The samples treated with DAP and the mixture of DAP and urea exhibited char lengths less than half of the sample length with no observable after-flame and afterglow. In excellent

agreement with LOI data, the char length obtained from %P:%N = 2.5:4.6 decreased in 54% compared to DAP alone, and no significant further reduction was observed for higher %N.

Table 3. LOI and results of vertical flame test for greige cotton nonwoven fabrics untreated and treated with DAP, urea, and mixtures of DAP and urea.[a]

Sample	untreated	DAP	DU1	DU2	DU3	Urea
%P:%N	0:0	2.5:2.3	2.5:4.6	2.5:6.0	2.5:7.4	0:7.4
Samples after vertical flame test						
After-flame time (s)	0.8 [0.2]	0	0	0	0	3.4 [0.3]
Afterglow time (s)	31.5 [2.1]	0	0	0	0	11.5 [1.1]
Char length(cm)	-	10.9 [1.0]	7.1 [0.9]	8.1 [1.1]	7.1 [0.9]	-
LOI (%)	20.0 [0.0]	32.3 [0.8]	36.6 [1.1]	36.2 [1.3]	37.0 [1.0]	21.0 [0.0]

[a] Average value of five samples and standard deviation.



(a) Untreated (b) Urea treated

Figure 5. The afterglows in the vertical flame test after the flame was removed a) untreated and b) urea treated.

During the LOI test, all samples formed chars. The surface morphology of the chars left after LOI test was observed using the SEM (Figure 6). For untreated and urea treated cottons, although they maintain the fiber morphology, all fibers were severely damaged to become porous. Unlike untreated fiber, most of the urea treated fibers was found to remain in twisted form after the burning. By the DAP treatment, cotton fibers were not damaged and showed the intact microfibrilla structure on the fiber surface. The formation of polyphosphoric acid may be resulted in the protection of fiber structure (Gaan and Sun, 2007). In the treatment of %P:%N = 2.5:4.6, it was observed that a smooth coating layer formed on the fiber surface, which was absent on the DAP treated cotton fiber. This result indicates that nonflammable polymeric coating was generated by the addition of urea, contributing to the synergistic flame retardance. It is noted that some part of this insulative coating was protruded like a balloon, which may be attributed to the non-combustible gas released from urea. As seen in Figure 6, with increasing the concentration of urea, more balloons were observed and some of them had burst.

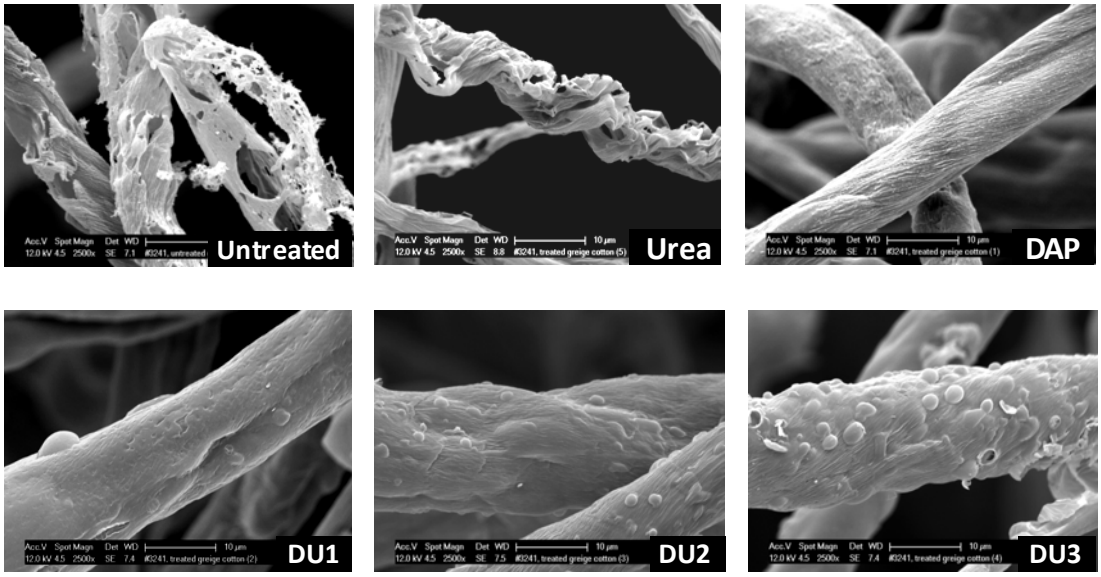


Figure 6. SEM images of chars left LOI test for greige cotton nonwoven fabrics untreated and treated with DAP, urea, and mixtures of DAP and urea.

Summary

The optimum flame retardance was obtained in greige cotton nonwoven fabrics by the addition of urea at %P:%N = 2.5:4.6, showing the increase of LOI to 36.6% from 32.3% and reduction of the char length to 7.1 cm from 10.9 cm compared with the treatment of DAP alone. This P-N synergism was explained by the increased activation energy of thermal decomposition and the formation of an insulative coating on the fiber surface.

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References

Chang, S., Sachinvala, N. D., Sawhney, P., Parikh, D. V., Jarrett, W., Grimm, C., 2007. Epoxy phosphonate crosslinkers for providing flame resistance to cotton textiles. *Polym. Adv. Technol*., 18, 611-619.

Gaan, S., Sun G., 2007. Effect of phosphorus flame retardants on thermo-oxidative decomposition of cotton. *Polym. Degrad. Stab*., 92, 968-974.

Kissinger, H. E., 1956. Variation of peak temperature with heating rate in differential thermal analysis. *J. Res. Natl. Bur. Stand*., 57, 217-221.

Parikh, D. V., Sachinvala, N. D., Sawheny, A. P. S., Roberts, K. Q., Graves, E. E., Calamari, T. A. 2003. Flame retardant cotton blend highlofts, *J. Fire Sci*. 21, 383-395.

Parikh, D. V. *et al*., 2009. A study of FR greige cotton barrier nonwovens for mattresses, In preparation.

Preston, J. M., Clark, J. F., Beath, W. R., Nimkar, M. V., 1954. Swelling powers of urea solutions on cellulose, *J. Text. Inst*., 45, 504-509.