EFFECT OF PHOSPHORUS AND NITROGEN ON THERMAL DECOMPOSITION KINETICS OF FLAME RETARDANT COTTON

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Abstract

Four kinetic methods, Kissinger, Friedman, Flynn-Wall-Ozawa, and modified Coats-Redfern, were used to study the activation energy, E_a, of the thermal decomposition of greige cotton nonwoven fabric treated with diammonium phosphate (DAP) and urea. The results show that the E_a is significantly influenced by phosphorus (P) and nitrogen (N). The E_a for the fabric treated with DAP alone continuously increased throughout the conversion (i.e. decomposition) process, while the E_as for those treated with mixtures of DAP and urea became constant at high conversions. The overall E_a increased with the addition of urea, and decreased by a further increase of urea. These effects of P and N on the E_a were explained by the enhanced thermal stability and the facilitated decomposition of cellulose chains in crystalline region.

Introduction

In continuing our study (Nam *et al*., 2010) on the synergism of DAP and urea in "green" fire barrier of greige cotton nonwoven fabric, the kinetic study of its thermal decomposition was undertaken. Since the thermal decomposition of flame retardant (FR) cotton is involved with a variety of physical and chemical reactions, E_a is considered to be an important factor in understanding the flame-retarding mechanism. Several researchers have measured the E_a values of cellulose materials treated with various FRs, but their results are contradictory. For example, the E_a of phosphorylated cellulose was smaller than that of cellulose (Jain *et al*., 1985), whereas the E_as of cotton fabrics treated with phosphorus FRs were greater than that of untreated fabric (Gaan and Sun, 2007). Furthermore, no information has been reported about the effect of N additives, which have the synergistic action with phosphorus FRs, on the E_a. Motivated by the insufficient data on E_a in relation with flame-retarding action, we have conducted thermogravimetric analysis of greige cotton nonwoven fabrics treated with varying the N content at a fixed P level. The E_a of the sample was determined by Kissinger method and three iso-conversion methods: Friedman, Flynn-Wall-Ozawa, and modified Coats-Redfern methods.

Background

The rate of conversion or decomposition, $d\alpha/dt$, is described as:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

In this study, the conversion, α, is: $\alpha = (W_0 - W_t)/(W_0 - W_f)$, where W_0, W_t, and W_f are initial weight, weight at time, t, and final weight, respectively. The reaction rate constant, k, has been given by the Arrhenius expression:

$$k = A\exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

where A is the pre-exponential factor, E_a, is the apparent activation energy, R is the gas constant (8.314 $JK^{-1}mol^{-1}$), and T is the absolute temperature. The combination of Eqs. (1) and (2) gives:

$$\frac{d\alpha}{dT} = Af(\alpha)\exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

The introduction of heating rate, $\beta = dT/dt$, in the thermogravimetric analysis into Eq. (3) gives:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}f(\alpha)\exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

Based on above equations, four different kinetic methods used in this study are presented in Table 1.

Table 1. Kinetic methods for the determination of activation energy of thermal decomposition.

Method	Equation	Ref.
Kissinger	$\ln(\beta/T_p^2) = \ln(AR/E_a) - E_a/RT_p$	Kissinger, 1956
Friedman	$\ln(d\alpha/dt) = \ln[Af(\alpha)] - E_a/RT$	Friedman, 1964
Flynn-Wall-Ozawa	$\log\beta = \log[AE_a/Rg(\alpha)] - 2.315 - 0.4567E_a/RT$	Flynn and Wall, 1966 Ozawa, 1965
Modified Coats-Redfern	$\ln[\beta/T^2(1 - 2RT/E_a)] = \ln[-AR/E_a \ln(1 - \alpha)] - E_a/RT$	Brown, 2000

Materials and Methods

Materials 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 (~12 g/m^2) was produced by a tandem card and was subsequently lapped by a cross-lapper. The obtained multi-lap was then needle-punched by a machine equipped with two boards of 4000 needles at a speed of 5 m/min. The density of the nonwoven fabrics was 100 g/m^2. DAP and urea were purchased from Magnolia Chemical and Solvents Inc., and Triton® X-100 was purchased from Fisher.

FR treatment Greige cotton nonwoven fabric was immersed in a FR aqueous solution containing DAP and urea, which were formulated to provide different P and N concentrations (Table 2). To improve the absorbance of greige cotton, 0.1 wt% of Triton® X-100 was included. The fabric was passed through a laboratory padder to reach an average wet pick-up of 100 ± 5% and naturally 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 by inductively-coupled plasma spectrometry and combustion analyzer, respectively, in the agriculture diagnostic laboratory at the University of Arkansas, Fayetteville. The average value of two measurements is presented.

Measurements TGA, DTG, and D^{2}TG were measured using a TGA Q500 thermal gravimetric analyzer (TA Instrument). Five samples (2.5 cm in diameter) were randomly taken from each fabric, and ground in a Wiley Mill (Arthur H. Thomas Co.) with a 40 mash (0.42 mm). 5-6 mg of the powders were heated from room temperature (25 ± 3 °C) to 600 °C at four different heating rates, 2, 5, 10, and 15 °C/min, under nitrogen. The obtained thermograms were analyzed using Universal Analysis 2000 software. Three runs were performed to obtain average thermal decomposition parameters.

Table 2. The percentages of P and N in the treatment of DAP (D) and urea (U) and their measured values on the fabric by the elemental analysis.

Sample name	Conc. of treatment		Conc. by elemental analysis	
	%P	%N	%P	%N
D2	2	1.8	1.66 (0.03)[a]	1.10 (0.09)
D2U1		3.6	1.60 (0.02)	2.98 (0.03)
D2U2		5.4	1.57 (0.02)	4.69 (0.19)
D2U3		7.2	1.52 (0.03)	6.09 (0.03)
U3	-	7.2	-	6.94 (0.05)

[a]: Standard deviation of two measurements.

Results and Discussion

The contents of P and N on greige cotton fabrics determined by the elemental analyses were found to be lower than those applied in the treatment (Table 1). This incomplete absorption may be resulting from the hydrophobic surface nature of greige cotton. Figure 1 presents a typical thermogravimetric decomposition process of greige cotton nonwoven fabric treated with a mixture of DAP and urea at a heating rate of 5 °C/min. Several thermally induced reactions are observable: the decomposition of urea at around 160 °C, the phosphorylation of cellulose at around 250

°C, and the major decomposition of cellulose at around 280 °C. The thermal decomposition parameters for the measurement of E_a were obtained from the TG, DTG, and D^{2}TG curves. The onset temperature of decomposition, T_0, was obtained by extrapolating the slope of the DTG curve in correspondence with the first maximum in D^{2}TG curve and down to the zero level of the DTG axis. The shift temperature, T_s, where the decomposition of cellulose ends, was obtained by the same way used for T_0, but using the minimum point in D^{2}TG curve. The peak temperature, T_p, was determined from the maximum weight loss rate in DTG curve. The weight losses corresponding to these three temperatures and char contents remained at 600 °C for all samples are presented in Table 3.

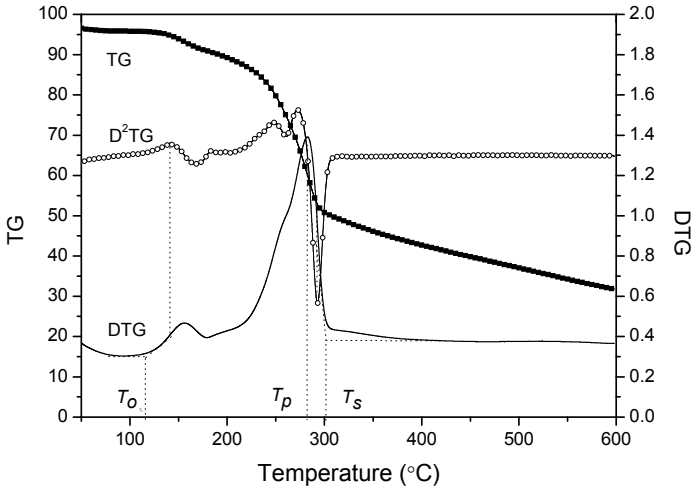

Figure 1. Thermal decomposition process of greige cotton nonwoven fabric treated with DAP and urea (D2U2) at a heating rate of 5 °C/min under nitrogen, and determination of thermal decomposition parameters.

Table 3. Thermal decomposition characteristics of the greige cotton nonwoven fabrics untreated and treated with DAP, urea, and mixtures of DAP and urea.

Sample	T_0 [a] (°C)	WL_0 (%)	T_p (°C)	WL_p (%)	T_s (°C)	WL_s (%)	Char [b] (%)	E_a [c] (kJ/mol)
Untreated	277.5 (0.6)[d]	11.2 (0.2)	336.0 (0.3)	49.4 (0.5)	362.4 (0.3)	69.0 (0.4)	15.9 (1.2)	177.7 (1.0)
D2	173.0 (2.7)	6.4 (0.7)	276.8 (0.5)	38.4 (0.8)	291.5 (1.1)	46.0 (0.4)	33.4 (0.5)	292.8 (1.1)
D2U1	125.8 (0.3)	6.9 (0.6)	284.3 (0.3)	40.9 (0.3)	298.5 (0.1)	48.7 (0.5)	32.4 (0.4)	303.1 (2.9)
D2U2	122.5 (0.2)	6.6 (3.1)	281.6 (1.0)	41.1 (2.1)	299.1 (0.4)	50.5 (1.8)	31.1 (1.0)	304.0 (4.7)
D2D3	119.7 (0.1)	6.5 (3.3)	279.4 (0.1)	42.1 (2.5)	295.3 (0.6)	51.4 (1.4)	30.3 (0.1)	269.0 (6.1)
U3	131.8 (0.2)	5.7 (0.7)	348.5 (1.0)	59.2 (0.1)	368.2 (0.6)	78.1 (0.2)	11.8 (0.6)	210.0 (6.9)

[a]: T = temperature; WL= weight loss; $_0$ = onset; $_p$ = peak; $_s$ = shift.
[b]: Char amount measured at 600 °C.
[c]: Activation energy obtained by Kissinger method.
[d]: Standard deviation of three measurements.

By Kissinger method, the E_a was calculated from the slope of the linear plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ (Figure 2) and the values for untreated and treated samples are presented in Table 3. The E_a of untreated greige cotton nonwoven fabric was determined to be 178 kJ/mol, which is higher than the reported value (150 kJ/mol) of scoured and bleached cotton woven fabric (Gaan and Sun, 2007). The treatment of DAP alone significantly increased the E_a to 293 kJ/mol. With the addition of urea, the E_a slightly increases with increasing N content and decreases with further increase of N content to 6.1%. Since Kissinger method determines the E_a from one conversion, α, at T_p, it may not represent the overall trend of E_a during the thermal decomposition.

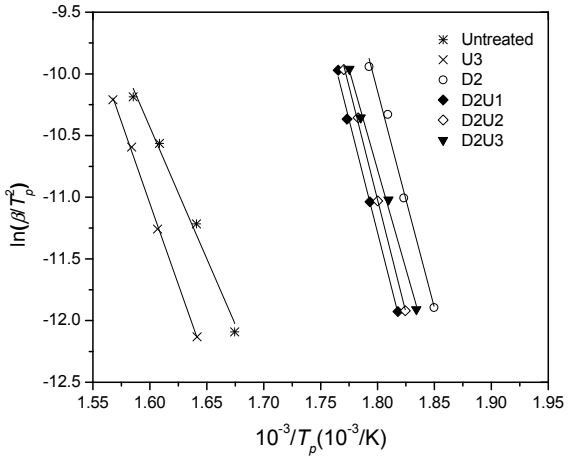

Figure 2. Plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ for greige cotton nonwoven fabrics untreated and treated with DAP, urea, and mixtures of DAP and urea by Kissinger method.

To better understand how P and N affect E_a, the iso-conversion methods, by which the variation of E_a can be observed at different steps of thermal decomposition, were employed. All iso-conversion plots showed good correlation coefficients (> 0.99) for the entire range of α from 0 to 1. The plots by Friedman method are shown in Figure 3 as an example. In Figure 4, the E_a is plotted as a function of α using three iso-conversion methods. The E_a determined by Friedman method is slightly higher than those by other two methods, but their trends are similar. The E_a of untreated fabric is almost constant with α. The initial E_as of treated fabrics are smaller than those of untreated fabric due to easily decomposable DAP and urea. For DAP alone, the E_a was found to continuously increase with α. This ascending behavior may be attributed to the enhanced thermal stability resulting from the formation of polyphosphoric acid inside fiber during pyrolysis. The addition of urea increases E_as, and a further increase of urea yields lower E_a values than DAP alone. It is also noted that the E_as of fabrics treated with mixtures of DAP and urea become constant above $\alpha = 0.6$. This effect of urea is probably associated with the formation of thermally stable P-N bonds with DAP and with the facilitated decomposition of cellulose at low temperatures by breaking the hydrogen bonds in crystalline region.

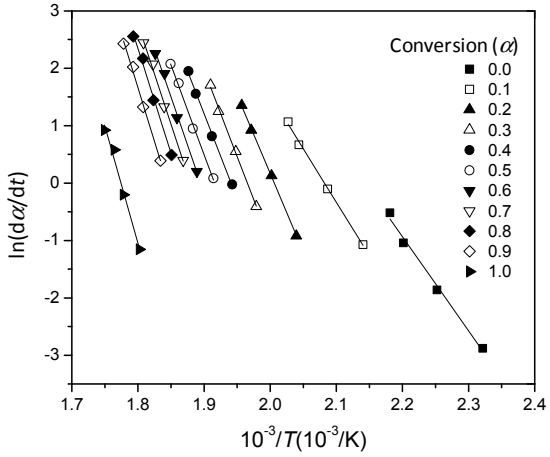

Figure 3. Iso-conversion plots of $\ln(d\alpha/dt)$ versus $1/T$ for greige cotton nonwoven fabric treated with DAP (D1) by Friedman method.

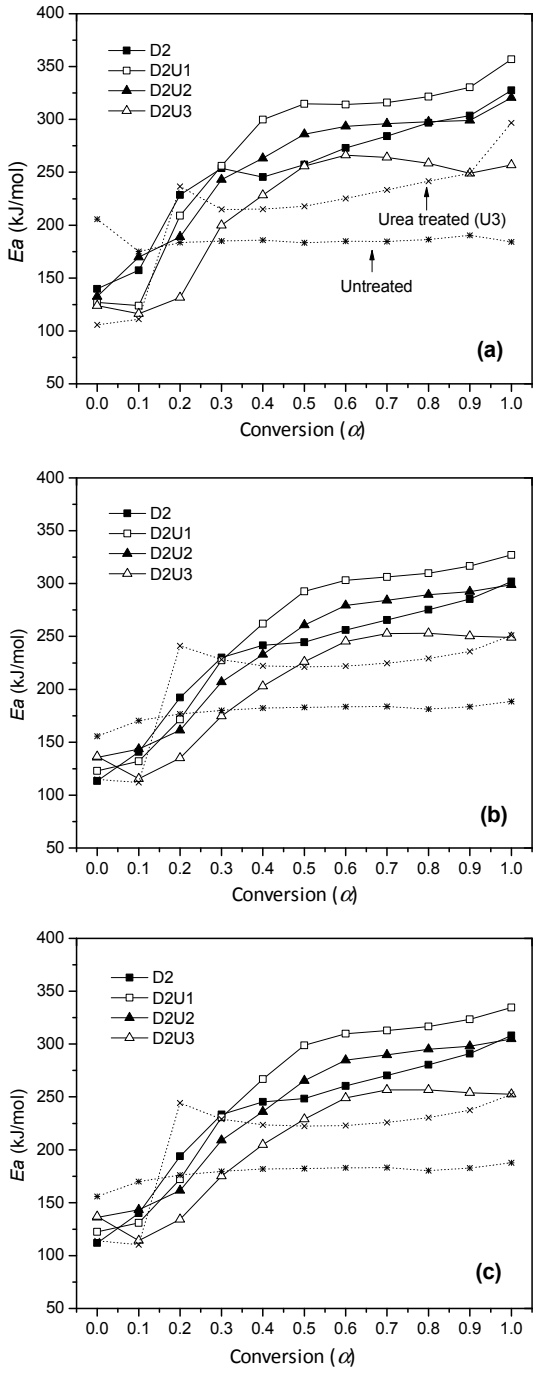

Figure 4. A variation of activation energy, *Ea*, as a function of conversion, α, for untreated and treated greige cotton nonwoven fabrics: (a) Friedman method, (b) Flynn-Wall-Ozawa method, (c) modified Coats-Redfern method.

Summary

This study shows that DAP and urea, which have synergism in enhancing the flame-retarding function, affect the E_a throughout the thermal decomposition of greige cotton nonwoven fabric. The E_a of the fabric was significantly increased by the treatment of DAP alone. The addition of urea induced higher E_a, but its further addition resulted in lower E_a than DAP alone. Such results indicate that FR greige cotton fabric decomposes with greater difficulty than the untreated one. Urea additive increases the thermal stability and enhances the efficiency of DAP in decomposing cellulose chains in crystalline region.

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