

Effect of urea additive on the thermal decomposition kinetics of flame retardant greige cotton nonwoven fabric

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ABSTRACT

Urea is well known to have a synergistic action with phosphorus-based flame retardants (FRs) in enhancing the FR performance of cellulosic materials, but the effect of urea on the thermal decomposition kinetics has not been thoroughly studied. In this study, the activation energy (E_a) for the thermal decomposition of greige cotton nonwoven fabrics treated with various amounts of urea at fixed contents of diammonium phosphate (DAP), was measured using the Kissinger, Friedman, and Flynn-Wall-Ozawa methods. The three methods produced consistent results revealing a dual function of urea additive in the kinetics depending on the concentration. Those functions were correlated with the synergistic FR action of urea. Up to a certain concentration, the addition of urea raised the overall E_a . The steeply increasing trend of E_a observed in the low conversions indicates that urea enhanced the multiple reactions of DAP, which were confirmed by ³¹P MAS NMR and ATR-FTIR. Higher concentrations of urea additive, however, significantly lowered the E_a values for both the DAP reactions and the decomposition of cellulose. As evidenced by a slight reduction in char yield, the decrease in E_a suggests that the excess of urea acted to facilitate the diffusion of volatiles and heat transfer in the cotton structure, resulting in catalyzing the decomposition of cellulose at low temperatures. The latter function was predominant when the greater synergistic FR action of urea was achieved.

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1. Introduction

Shortly after reporting how urea additive influences the thermal decomposition of greige cotton nonwoven fabric in the treatment of diammonium phosphate (DAP) [1], we have examined the effect of urea on the thermal decomposition kinetics. Since the previous study showed that urea influenced the thermal decomposition and combustion behaviors of greige cotton, this kinetics study is expected to improve our understanding of the role of urea in synergistically improving the flame retardancy of cotton. There have been several theories proposed to explain the synergistic action of urea [2–6], but the generally accepted explanation is it promotes DAP reactions by being a solvent medium for DAP. This simple action, however, does not completely explain our previous observation, in which the extent of improvement of flame retardancy of cotton was prominent when urea was combined with a low concentration of DAP. A similar dependence of the urea effect on

the amount of phosphorus flame retardant (FR) was also reported by other researchers [5], but no clear explanation has been made.

A kinetics study based on thermogravimetric analysis (TGA) and differential thermal analysis (DTA) is known to be helpful in understanding the thermal decomposition of solid materials. These analyses can be done with a simple preparation of a small quantity of sample under variable experimental conditions. Numerous kinetics studies, therefore, have been conducted for natural fibers, synthetic polymers, and their composites. Traditionally, the reaction model has been chosen from a list of well-known reaction models by fitting the experimental data with aid of statistical analyses. This model-fitting method mostly uses single heating rates so that it produces a single set of kinetic parameters, i.e., activation energy (E_a) for a whole process. Moreover, the model-fitting method is not effective in producing consistent E_a values from non-isothermal data [7]. As an alternative approach, the model-free method has been demonstrated to produce reliable and consistent kinetic information from both isothermal and non-isothermal experiments [7–9]. The non-isothermal experiment has the advantage of resolving the problem of the isothermal experiment, which is some undesirable reactions of the sample

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possibly occur during the time needed to reach the set temperature. Unlike the model-fitting method, the model-free method, which is based on isoconversional principle, can measure the E_a as a function of the degree of conversion. Thus, isoconversional model free methods [10–13] adequately reveal the multi-step process of materials without making any assumptions about the reaction models, and consequently help understand the underlying kinetic schemes.

The presence of FRs and/or their decomposed byproducts affects the kinetics of the thermal decomposition of the substrate materials. Smith et al. [14] treated cotton cellulose with about twenty FR and non-FR compounds and obtained the E_a values based on first-order kinetics. They found a relation between the E_a values and the match-test angle data: a decrease in E_a observed for a greater flame retardant property. Jain et al. [15] compared the E_a values of pure cellulose and phosphorylated cellulose products using model-free non-isothermal methods and reported a decrease of E_a after the treatment of phosphorus compounds. This reduction of E_a was observed throughout the pyrolysis process including dehydration, decomposition, and char formation. On the other hand, Gaan and Sun [16] observed 13–82% increases in E_a for the thermal decomposition of cotton fabric treated the fabric with commonly used organophosphorus FRs. Nakanishi and coworkers [17], using the Ozawa's method, noticed two trends, ascending and descending, in the variation of E_a as a function of conversion depending on FR components. These behaviors of E_a were attributed to the different FR mechanisms and correlated with LOI values and char amounts. Such noticeable changes in E_a resulting from the incorporation of FRs have also been observed for other synthetic polymers [18–20].

As for the effect of additives, which are frequently used to improve the FR function, on the thermal decomposition kinetics of the substrate, very limited reports are available. Nakanishi et al. [21] found that when applying tetrakis hydroxymethyl phosphonium sulfate monomer to cotton fabric, the addition of urea raised E_a , while the additions of a catalyst and a nonionic surfactant lowered E_a . Gaan et al. [22] also observed a similar effect of nitrogen additives. The E_a for the thermal decomposition of the cotton fabric treated with a combination of three nitrogen additives: urea, guanidine carbonate, and melamine formaldehyde with tributyl phosphate was higher than the E_a of the fabric treated with tributyl phosphate alone. The reason for the increase of E_a by nitrogen additives, however, has not been agreed upon. Nakanishi et al. attributed the observed increase to the extra E_a required for the decomposition of the nitrogen additive, whereas Gaan et al. attributed it to the formation of more thermally stable char by the nitrogen additives. All of these results were based on using a single concentration of additives and relied on one kinetic method.

In this work, two model-free isoconversional methods, the Friedman and Flynn-Wall-Ozawa methods, along with the Kissinger method were used to examine how a combination of urea with DAP affects the E_a at various stages of the thermal decomposition of greige cotton needle-punched fabric. A wide range of urea concentrations were applied at two fixed contents of DAP: 1) ~0.8 wt% P that was too low to provide FR property and 2) ~1.6 wt% P, which provided an FR property with cotton. The effect of urea on the dependence E_a on conversion was correlated with its synergistic FR action. The thermal decomposition processes were monitored using ^{31}P MAS NMR and ATR-FTIR.

2. Experimental

2.1. Material

Greige cotton needle-punched nonwoven fabric was fabricated in the pilot plant at the Southern Regional Research Center. Two

randomly selected American Upland cotton fibers were processed through a commercial-grade cotton opening/cleaning system. A continuous fiber web (~12 g/m²) was produced by a tandem card and was subsequently lapped by a cross-lapper. The obtained multi-lap was then needle-punched at a speed of 5 m/min by a machine equipped with two boards of 4000 needles. The density of the nonwoven fabric was 100 g/m². DAP (%P: 21.8%; %N: 20.5%) and urea (%N: 46.1%) were purchased from Magnolia Chemical and Solvents Inc. Triton[®] X-100 was purchased from Fisher. All chemicals were used as received from suppliers.

2.2. Flame retardant treatment

Ten padding bath solutions were prepared by dissolving DAP, urea, or a mixture of DAP and urea in water at different weight concentrations as shown in Table 1. Triton[®] X-100 (0.1 wt%) was included in the formulation to facilitate wetting of greige cotton fabric. Greige cotton nonwoven fabric (30 cm × 30 cm) was immersed in a bath solution (500 mL) and then passed through a laboratory padder (Werner Mathis U.S.A Inc.). The loading of FRs on the fabric was controlled by the padding pressure and speed. A pressure of 68.9 kPa and a speed of 2 m/min were tested to produce an average wet pick-up of 100 ± 5%. The treated fabric was then air dried. The weight percentages of P and N on the fabric were measured using, respectively, an inductively-coupled plasma emission spectrophotometer (ARCOS, Spectro Analytical Instruments, Inc.) and a combustion analyzer (VarioMax, Elementar Americas, Inc.) in the agriculture diagnostic laboratory at the University of Arkansas, Fayetteville. The measured percentage values of P and N, which are presented in Table 1, were close to the calculated values based on the wet pick-up. The samples treated with ten formulations were denoted using D and U corresponding to DAP and urea, respectively, along with numbers indicating the increment of their concentrations.

The selected samples were heated in a bench furnace (Lindberg Blue M Electric) at six different temperatures, 200, 250, 275, 300, 325, and 350 °C, under nitrogen. The flow rate of a nitrogen stream was 1.6 L/min and the heating rate was about 18 °C/min.

2.3. Thermal analysis

Thermogravimetric analysis was carried out using a TGA Q500 thermal gravimetric analyzer (TA Instrument) under nitrogen atmosphere. Five disk 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 mesh (0.42 mm). About 5 mg of the powdered samples were evenly placed on the bottom of an aluminum pan. The temperature was increased from room

Table 1
Treatment of cotton nonwoven fabrics with DAP, urea, or a mixture of DAP and urea.

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

temperature (23 ± 3 °C) to 600 °C at four different heating rates, 1, 2, 5, and 10 °C/min. The nitrogen flow into the furnace was maintained at a rate of 90 mL/min. The data sampling interval was 0.5 s per point. TGA, DTG, and D²TG thermograms were analyzed using Universal Analysis 2000 software. Three runs were performed to obtain an average of the thermal decomposition parameter.

2.4. E_a determination

The E_a for the thermal decomposition of greige cotton nonwoven fabrics was determined by the Kissinger, Friedman, and Flynn-Wall-Ozawa methods from non-isothermal experiments. These methods are based on the following fundamental kinetic equation combined with the Arrhenius expression of the temperature-dependent rate constant.

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (1)$$

where α is the conversion of reaction, $(W_0 - W_t)/(W_0 - W_f)$ (where W_0 , W_t , and W_f are the initial, time t , and final weights of the sample, respectively), T is the absolute temperature, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and $f(\alpha)$ is the reaction model.

In a non-isothermal experiment, introducing the heating rate, $\beta = dT/dt$, into Eq. (1) gives

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (2)$$

Integration of the both sides of Eq. (2) gives

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (3)$$

The Kissinger method [23] is based on the fact that the derivative of Eq. (1) is equal to zero at the maximum reaction rate. After differentiation, taking its logarithm form gives

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{-AR}{E_a} f'(\alpha_p)\right) - \left(\frac{E_a}{RT_p}\right) \quad (4)$$

where T_p is the temperature at the maximum weight loss rate and α_p is the conversion at T_p . Because $f'(\alpha_p) = n(1-\alpha_p)^{n-1}$, where n is the reaction order, is approximated to be a constant, the E_a can be obtained from the slope of the plot $\ln(\beta/T_p^2)$ against $1/T_p$ for a series of experiments at different β s.

The Friedman method [10] is an iso-conversion method, consisting of taking the logarithm of Eq. (1)

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E_a}{RT} \quad (5)$$

Plotting $\ln(d\alpha/dt)$ as a function of $1/T$ at a given α leads to a straight line, the slope of which provides the E_a .

Unlike the Friedman method, which is derivative $d\alpha/dt$, the Flynn-Wall-Ozawa method [11,12] is based on the integration of Eq. (2) using Doyle's approximation [24]. Taking the logarithm of the integrated results gives

$$\log\beta = \log\left(\frac{AE_a}{Rg(\alpha)}\right) - 2.315 - \frac{0.457E_a}{RT} \quad (6)$$

Since it is assumed that the reaction rate at a given α is a function of only temperature, the E_a can be obtained from the slope of a linear fit to the plot $\log\beta$ against $1/T$.

2.5. Other characterization

³¹P solid-state NMR experiments were carried out on a Bruker DSX 300 MHz NMR instrument at 298 K ³¹P MAS NMR spectra with proton decoupling were acquired at a frequency of 121.5 MHz under 8 kHz spinning rate using a 4 mm ZrO₂ rotor. 1 μs of pulse width (ca. $\pi/8$ pulse) and 10 s of recycle delay were used. The recycle delay of 10 s was enough to recover the magnetization to equilibrium state. Aqueous 85% H₃PO₄ was taken as an external reference of ³¹P chemical shift.

The ATR-FTIR spectra were measured via a Bruker Vertex 70 spectrometer equipped with a MIRacle ATR accessory (Pike Technologies) that used a diamond crystal plate as the reflector. All spectra were recorded with a resolution of 4 cm⁻¹ and 64 scans.

3. Results and discussion

3.1. E_a by the Kissinger method and flammability

To study E_a in relation with flammability, the previous results [1] of the char lengths and limiting oxygen index (LOI) values of greige cotton nonwoven fabrics untreated and treated with different concentrations of DAP and urea are summarized in Table 2. The char length was measured by the vertical flame test, where a flame is applied to the bottom of the vertically placed specimen (7.6 × 30.0 cm) for 12 s. LOI value is the minimal oxygen concentration in the mixture of oxygen and nitrogen that either maintains flame combustion of the fabric (6.4 × 12.7 cm) for 3 min or consumes a length of 5 cm of the vertically placed fabric. The higher LOI value indicates the better FR property. When urea, which has a negligible FR function, was applied onto the fabric with a fixed amount of DAP, the char length and LOI value continuously decreased and increased, respectively, as the urea concentration was increased. This synergistic action of urea in improving the FR property was found to be greater at a smaller amount of DAP.

Typical TG, DTG and D²TG curves of the fabric treated with a mixture of DAP and urea are presented in Fig. 1. Urea decomposes at low temperatures in the range of 130–170 °C. The phosphorylation reaction of DAP was recognized as a shoulder peak at around 250 °C in the DTG curve. The cellulose decomposed between 250 and 310 °C depending on the concentration of DAP or urea. Three decomposition parameters were determined for the calculation of E_a . As shown in Fig. 1, the onset decomposition temperature, T_o , was determined by the intersection of the zero level of the DTG axis and the tangent line extrapolated from the point of the DTG curve corresponding to the first maximum point in the D²TG curve [25]. The end decomposition temperature, T_e , was determined by the same way, but using the minimum point in the D²TG curve. The

Table 2
Char length and LOI of untreated and treated greige cotton nonwoven fabrics [1].

Sample name	Char length (cm) ^a	LOI (%) ^b
Untreated	–	21.6 (0.5) ^c
D1	29.7 (1.7) ^c	26.0 (0.3)
D1U1	19.5 (2.4)	27.0 (0.3)
D1U2	10.4 (0.7)	30.3 (0.5)
D1U3	8.6 (1.0)	33.3 (0.5)
D1U4	8.5 (0.5)	35.7 (0.7)
D2	9.7 (0.8)	31.8 (0.8)
D2U2	8.8 (0.8)	33.3 (0.6)
D2U3	7.6 (0.7)	35.5 (0.8)
D2U4	7.1 (0.6)	37.0 (1.0)
U4	–	22.6 (0.5)

^a Obtained by vertical flammability test (ASTM D6413-99).

^b Measured according to ASTM D2863-00.

^c Standard deviation of six samples.

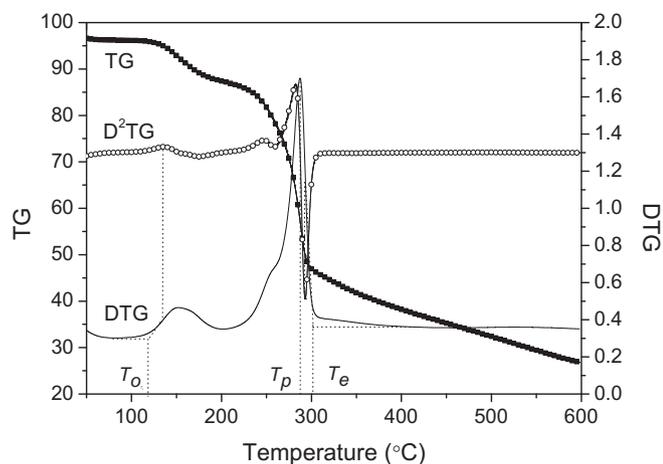


Fig. 1. Typical thermal decomposition process of greige cotton nonwoven fabric treated with a mixture of DAP and urea (D1U4) at a heating rate of 5 °C/min under nitrogen and determination of thermal decomposition parameters for the calculation of E_a .

maximum decomposition rate temperature, T_p , was defined as a maximum point in the DTG curve. The T_p was used in the determination of E_a by the Kissinger method. The variation of E_a between T_0 and T_e was determined by the Friedman and Flynn-Wall-Ozawa methods. Since heating rate influences decomposition characteristic temperatures, the T_0 , T_p , and T_e values obtained from the four heating rates were extrapolated to a zero heating rate. The resulting $T_{0,\beta \rightarrow 0}$, $T_{p,\beta \rightarrow 0}$, and $T_{e,\beta \rightarrow 0}$ are presented in Table 3. The char yield at 600 °C was not significantly changed by heating rate. The average value of the char yields at different heating rates is presented. DAP treatment, due to its dehydration, significantly lowered the $T_{p,\beta \rightarrow 0}$ of cellulose and consequently increased the char yield. It is noticed that urea additive had a more modest effect on $T_{p,\beta \rightarrow 0}$ and char yield. Higher concentrations of urea resulted in a decrease of char content. The presence of urea increased the $T_{p,\beta \rightarrow 0}$, but the effect decreased slightly for the higher concentrations of urea, particularly for the high DAP treated samples. Increased char yield is generally associated with improved flammability. The increased char yield for the DAP treatment is consistent with the shorter char lengths and higher LOI in the flammability tests (Table 2). The correlation between lower $T_{p,\beta \rightarrow 0}$ /higher char yield and lower flammability was not observed in the data at different concentrations of urea.

The E_a values of untreated and treated fabrics were calculated using the Kissinger method. According to Eq. (4), $\ln(\beta/T_p^2)$ is plotted against $1/T_p$ in Fig. 2. All samples exhibit the fitted straight lines.

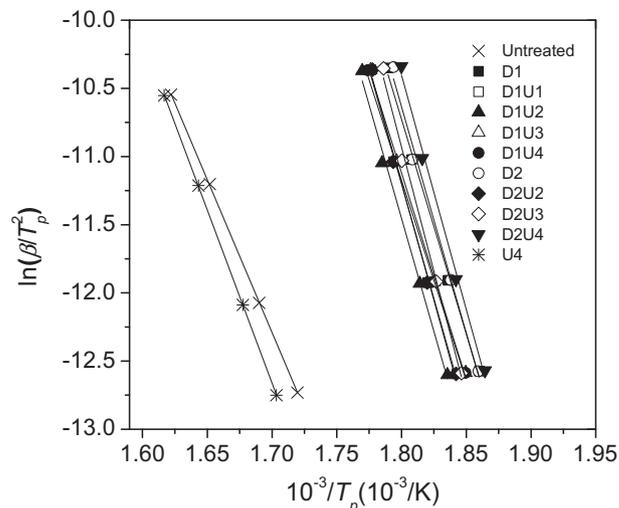


Fig. 2. Plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ for greige cotton nonwoven fabrics untreated and treated with DAP, urea, and mixtures of DAP and urea.

The E_a values calculated from the slopes are presented with correlation coefficients (r) in Table 3. The E_a of untreated greige cotton nonwoven fabric was 187 kJ/mol, which falls in the range of 150–190 kJ/mol reported for cotton in literature [16,17,26,27]. Urea treatment slightly increased the E_a to 222 kJ/mol, whereas DAP treatment greatly increased the E_a to 267 kJ/mol at ~0.8 wt% P and to 286 kJ/mol at ~1.6 wt% P. An increase in E_a by DAP agrees with the result by Gann and Sun [16], who reported 273 kJ/mol at 2 wt% P for scoured and bleached cotton woven fabric. Fig. 3 shows the effect of urea additive on E_a at a fixed wt% P. For both P contents, a similar effect of urea was observed. The addition of urea raises the E_a , but a further increase of urea concentration significantly reduces the E_a . These results clearly show that urea additive affects the thermal kinetics. In terms of the flammability results, the higher LOI values for the DAP treatment was correlated with higher E_a values. But at the higher concentrations of urea, higher LOI values and shorter char lengths for constant DAP content were correlated with lower E_a values. Higher LOI values and shorter char lengths reflect reduced flammability.

3.2. Analysis of decomposed cotton

The samples of D2 and D2U4 treated without urea and with urea, respectively, were heated at elevated temperatures and analyzed. Fig. 4 shows the ^{31}P MAS NMR spectra of D2 and D2U4.

Table 3

Thermal decomposition characteristic values and E_a determined by the Kissinger method for greige cotton nonwoven fabrics untreated and treated with different percentages of DAP and urea.

Sample	$T_{0,\beta \rightarrow 0}$ (°C)	$T_{p,\beta \rightarrow 0}$ (°C)	$T_{e,\beta \rightarrow 0}$ (°C)	Char yield (%) ^b	E_a (kJ/mol)	Correlation coefficient (r)
Untreated	261.1 (1.2) ^a	302.4 (0.9)	321.9 (1.1)	15.5 (0.1)	186.9 (0.4)	0.9999
D1	136.5 (1.2)	260.2 (0.1)	273.1 (0.2)	29.6 (0.8)	267.1 (7.3)	0.9986
D1U1	146.6 (2.6)	265.9 (0.7)	278.5 (0.8)	29.8 (0.9)	279.5 (4.7)	0.9987
D1U2	102.7 (1.3)	267.6 (0.9)	279.8 (1.2)	30.0 (0.7)	277.8 (1.2)	0.9998
D1U3	101.4 (1.4)	263.8 (1.1)	275.9 (4.4)	27.7 (0.6)	260.1 (11.9)	0.9997
D1U4	101.4 (0.1)	263.6 (0.9)	274.5 (1.3)	27.6 (1.1)	251.7 (9.8)	0.9988
D2	145.0 (1.4)	261.5 (2.1)	275.2 (1.4)	32.4 (0.3)	286.1 (11.2)	0.9979
D2U2	105.6 (0.8)	265.5 (0.1)	278.0 (0.1)	31.3 (0.5)	307.8 (9.2)	0.9982
D2U3	103.0 (0.1)	265.5 (1.8)	279.4 (1.7)	30.7 (1.1)	302.6 (0.2)	0.9979
D2U4	102.1 (0.2)	263.4 (1.0)	276.6 (1.1)	30.6 (0.7)	292.7 (7.4)	0.9993
U4	108.9 (1.2)	307.8 (1.3)	323.7 (3.5)	12.3 (0.6)	222.2 (8.3)	0.9998

^a Standard deviation of three samples.

^b Obtained at 600 °C.

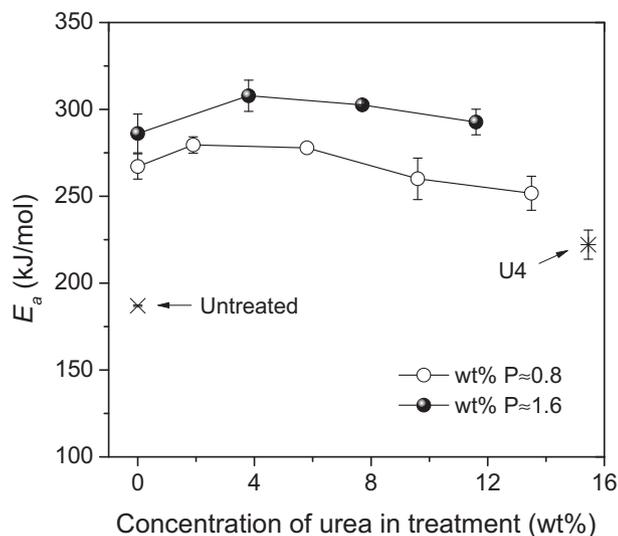
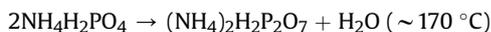


Fig. 3. E_a determined by the Kissinger method for fabrics untreated and treated with different concentrations of urea at fixed contents of P.

Before heating, the diammonium orthophosphate peak appears as a single narrow peak at about 0 ppm. When the samples were heated at 200 °C, a new peak at -10 ppm develops for both samples. This peak is assigned to the formation of ammonium pyrophosphate [28]. According to the decomposition scheme of DAP below [29,30], after the loss of 1 mol of ammonia at ~150 °C,

the endothermic reaction takes place at ~170 °C to produce diammonium pyrophosphate and release 1 mol of water.



Comparison of the peak intensities for D2 and D2U4 clearly shows that the formation of pyrophosphate was greater in the presence of urea. Urea becomes liquid at 140–160 °C and acts as solvent or medium for DAP [3,4] to assist the formation of pyrophosphate. Pyrophosphate is an efficient FR and active in cellulose esterification [3]. The broad peak at about 0 ppm observed for D2U4 at 200 °C indicates the presence of a mixture of orthophosphates and pyrophosphates or intermediates of pyrophosphate ester. Upon further heating, the pyrophosphate peak for D2 quickly disappears at 250 °C, whereas the peak for D2U4 slowly declined up to 300 °C. This is because the esters of pyrophosphate decomposed to orthophosphate ester [3] and free pyrophosphate decomposed to form ammonium metaphosphate by the following reaction [29,30].



At 300 °C, D2 sample exhibits a broad peak at around 20 ppm, which corresponds to polyphosphoric acid and its possible cross-linking.

Figs. 5 and 6 show the ATR-FTIR spectra of the heated samples of D2 and D2U4, respectively. Upon heating, the cellulose characteristic bands for both samples: 3333 cm^{-1} (O–H stretching), 2898 cm^{-1} (C–H stretching), 1428 cm^{-1} (C–H wagging), 1160

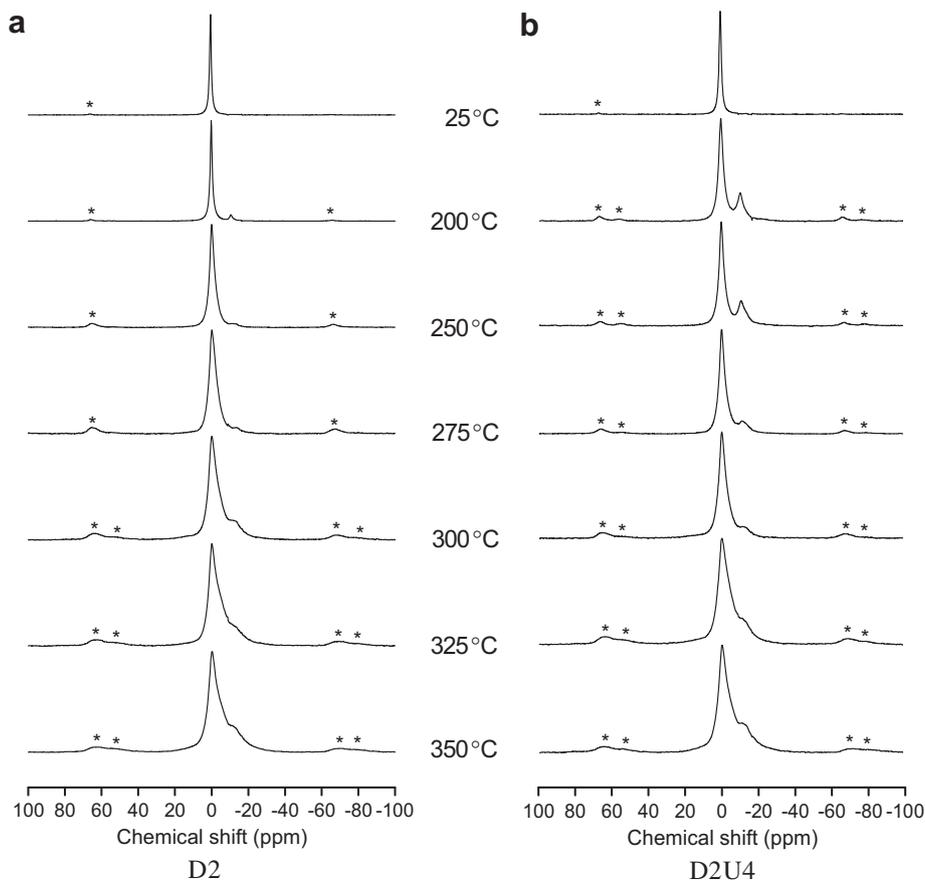


Fig. 4. ^{31}P MAS NMR spectra of treated greige cotton nonwoven fabrics, (a) D2 and (b) D2U4, heated at elevated temperatures. Asterisks denote spinning sidebands.

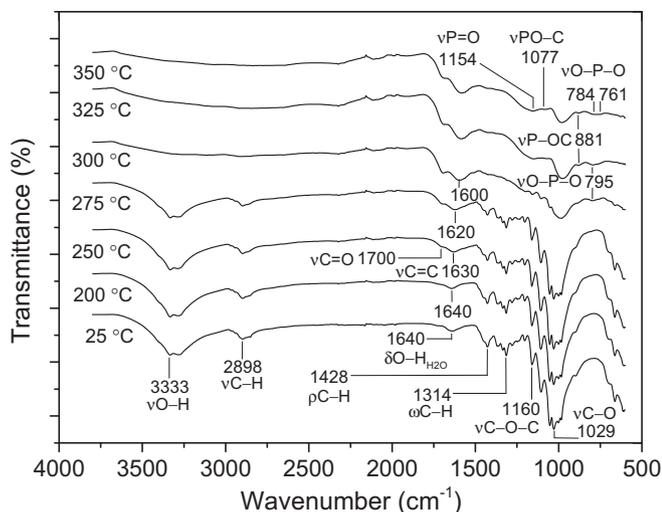


Fig. 5. ATR-FTIR spectra of greige cotton nonwoven fabric treated with DAP alone (D2) and heated at elevated temperatures.

(C–O–C stretching) and 1029 cm^{-1} (C–O stretching) [31] gradually decrease due to dehydration. For D2, new bands at 1700 and 1630 cm^{-1} corresponding to C=O stretching of unsaturated aldehyde and C=C stretching of alkenes [32], respectively, appear at 250 °C , indicating that the decomposition of cellulose begins to occur. For D2U4, the bands from urea [33,34]: 1449 (N–C–N stretching), 1659 (C=O stretching), and 3407 cm^{-1} (N–H₂ stretching) disappears at 200 °C . At the same temperature, several new bands develop. Agreeing with the ^{31}P MAS NMR result, the band at 834 cm^{-1} , which is barely detectable for D2, is assigned to P–O–P stretching of pyrophosphate [35,36], and it diminishes on further heating. Another new band at 1712 cm^{-1} , which is assigned to C=O stretching in the base of urethane [37], appears and becomes intense as the temperature increases to 275 °C . The previous study [1] showed that urea treatment produced cellulose carbamate upon heating. With further heating to 300 °C , the cellulose characteristic bands for D2 disappear, while the band at 1700 cm^{-1} becomes intense, and the band at 1630 cm^{-1} shifts to 1600 cm^{-1} due to conjugation of C=C bonds. It is noticeable that

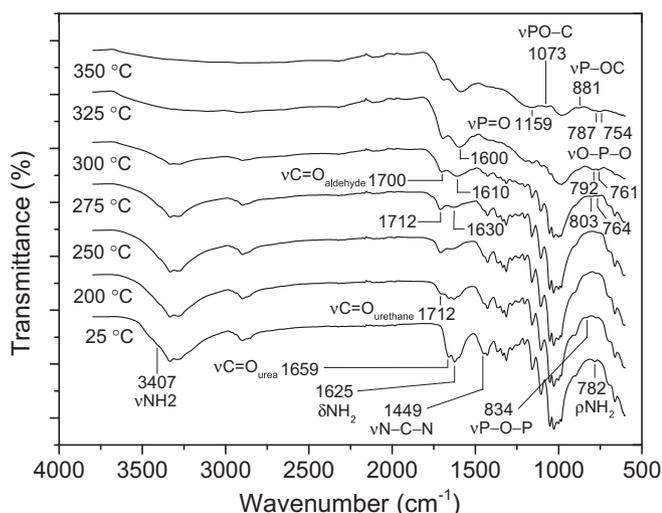


Fig. 6. ATR-FTIR spectra of cotton nonwoven fabric treated with a mixture of DAP and urea (D2U4) and heated at elevated temperatures.

the temperature, where the cellulose bands disappear, shifts to 325 °C for D2U4. The polymerization of phosphoric acid for D2 and D2U4 was recognized by the appearance of bands in the range of $803\text{--}754\text{ cm}^{-1}$ corresponding to O–P–O stretching [38] at around 300 °C . Consistent with the ^{31}P MAS NMR result, the presence of C–O–P linkage in char of both samples was evidenced by PO–C stretching (1077 and 1073 cm^{-1} , respectively) and P–OC stretching (881 cm^{-1}).

The amounts of P and N that remained on the charred fabrics after LOI tests were measured by elemental analysis. All charred fabrics, D1, D1U1, D1U1, D1U3, and D1U4, had about 2.3 wt\% P . This P amount is a factor of 2.9 greater than that for the unburned samples. For D2, D2U2, D2U3, and D2U4, which originally contained $\sim 1.6\text{ wt\% P}$, about 4.2 wt\% P was measured on the charred samples. There was no significant change in the P amount on char by the addition of urea. It has been suggested that the synergistic action of N additives in improving FR performance can be attributed to the higher retention of P in char by forming P–N bonds during combustion [5,39]. An examination of the charred fabrics suggests that urea does not have such a function. The wt% N values for the charred fabrics, D1, D1U1, D1U1, D1U3, and D1U4, were determined to be 2.3, 3.9, 4.6, 5.4, and 6.1, respectively. The wt% N values for D2, D2U2, D2U3, and D2U4 were 3.1, 4.5, 5.4, and 6.5, respectively. The calculated N/P atomic ratios were compared before and after burning in Fig. 7. After burning, the N/P ratio in the charred fabric decreases considerably with respect to the ratio in the original fabric. Fabrics with a higher N/P lost more N, most of which had escaped in the vapor phase, i.e., ammonia. It is notable that the N/P ratios in the char for $\sim 0.8\text{ wt\% P}$ are greater than those for $\sim 1.6\text{ wt\% P}$. If P–N bonds form during the combustion, more N will be retained for $\sim 1.6\text{ wt\% P}$. The comparison of N/P ratios confirms the absence of P–N formation.

3.3. Dependence of E_a on conversion

The analysis of the decomposed fabrics showed that urea did not chemically react with DAP, but it enhanced the DAP reactions. To understand how urea additive affects the E_a for the reactions of DAP and the decomposition of cellulose, the dependence of E_a on conversion throughout the whole pyrolysis process was examined using two isoconversional methods, the Friedman and Flynn-Wall-

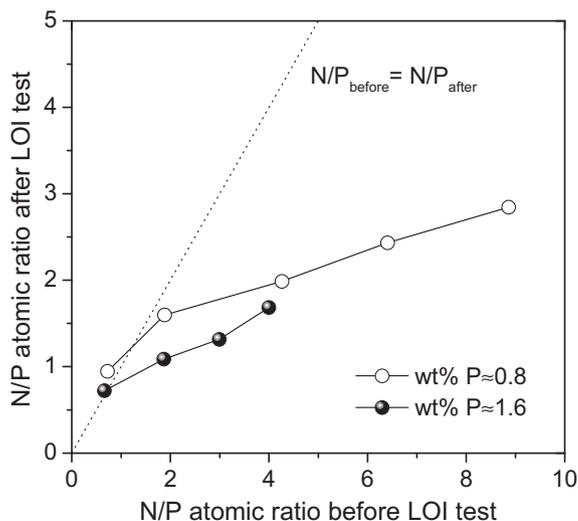


Fig. 7. The comparison of N/P atomic ratios on fabrics obtained from elemental analysis before and after combustion.

Ozawa methods. The Kissinger method generally produces E_a consistent with isothermal kinetic information [40], but since a single E_a is obtained based on the maximum decomposition rate temperature, this method has a weakness when it comes to identifying the kinetic scheme. On the other hand, the isoconversional methods can measure the dependence of E_a on conversion in the whole process. In this study, the E_a was measured in the conversion (α) range of 0.05–0.95. According to Eq. (5), the Friedman plot of $\ln(d\alpha/dt)$ vs. $1/T$ for the selected sample (D1) is shown in Fig. 8 (a). According to Eq. (6), the Flynn-Wall-Ozawa plot of $\log \beta$ vs. $1/T$ for D2 is shown in Fig. 8 (b). All samples exhibited straight lines ($r > 0.99$) in the entire conversion range studied, signifying the feasibility of these methods. The E_a values determined by the Friedman and Flynn-Wall-Ozawa methods are plotted against conversion in Figs. 9 and 10, respectively. The E_a for untreated cotton remains mostly constant over the conversion. Contrary to this monotonous behavior of E_a , the pyrolysis of cotton, which is mainly comprised of cellulose, is known to be multi-step processes. According to the Broido–Shafizadeh model, the first step of the decomposition of cellulose is the formation of active cellulose followed by two parallel steps, the formation of volatiles and the formation of gas/char [41,42]. The initial decreasing trend in E_a is

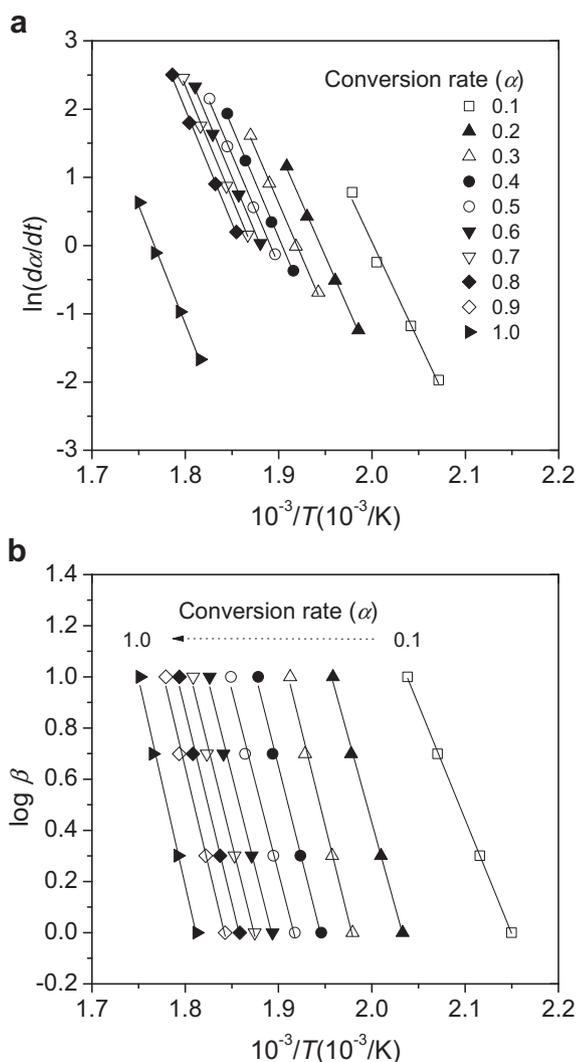


Fig. 8. Typical iso-conversion plots: (a) $\ln(d\alpha/dt)$ versus $1/T$ by the Friedman method for D1 and (b) $\log \beta$ versus $1/T$ by the Flynn-Wall-Ozawa method for D2.

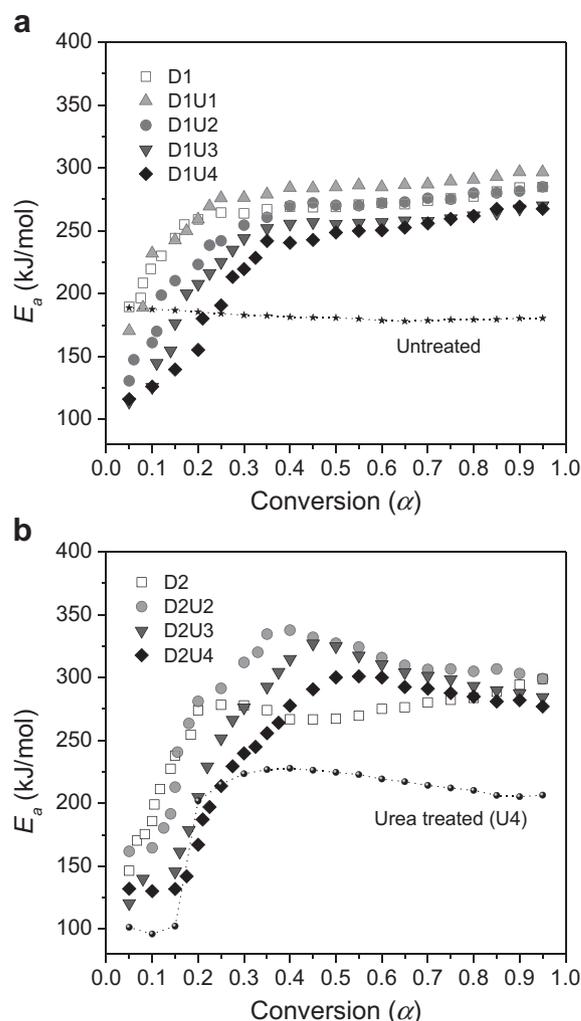


Fig. 9. Dependence of E_a on conversion (α) for untreated and treated greige cotton nonwoven fabrics by the Friedman method: (a) ~ 0.8 wt% P and (b) ~ 1.6 wt% P.

probably due to the reversible reaction that produces active cellulose [43,44]. However, the overall constant behavior of E_a implies that the E_a is governed by the rate-determining step. Studies using isothermal and non-isothermal conditions are in agreement that the main kinetics of cellulose pyrolysis involves nuclei-growth process [40,45,46]. The defects in the crystalline cellulose, which are generated by the initially decomposed substances, become merged into a larger porous structure [46]. The average value of E_a for untreated fabric is 196.3 ± 4.3 kJ/mol by the Friedman method, which agrees well with 193.6 ± 7.4 kJ/mol obtained by the Flynn-Wall-Ozawa method. These values are a little higher than 186.9 kJ/mol determined by the Kissinger method.

For the cotton fabrics treated with urea, DAP, or mixtures of urea and DAP, noticeable changes in the variation of E_a were observed, indicating that the thermal decomposition kinetics of cotton was influenced by the treatments. The E_a from the Friedman method was a little higher ($\sim 6\%$) than that from the Flynn-Wall-Ozawa method, but these two methods produced the consistent results on the dependence of E_a on conversion. All treated samples show an increasing dependence of E_a before a conversion of 0.4 for ~ 0.8 wt% P and 0.5 for ~ 1.6 wt% P. This increasing function is characteristic of complex reactions involving competitive or consecutive reactions [47,48]. In the beginning stage, urea and DAP started to decompose with the E_a values lower than the value of

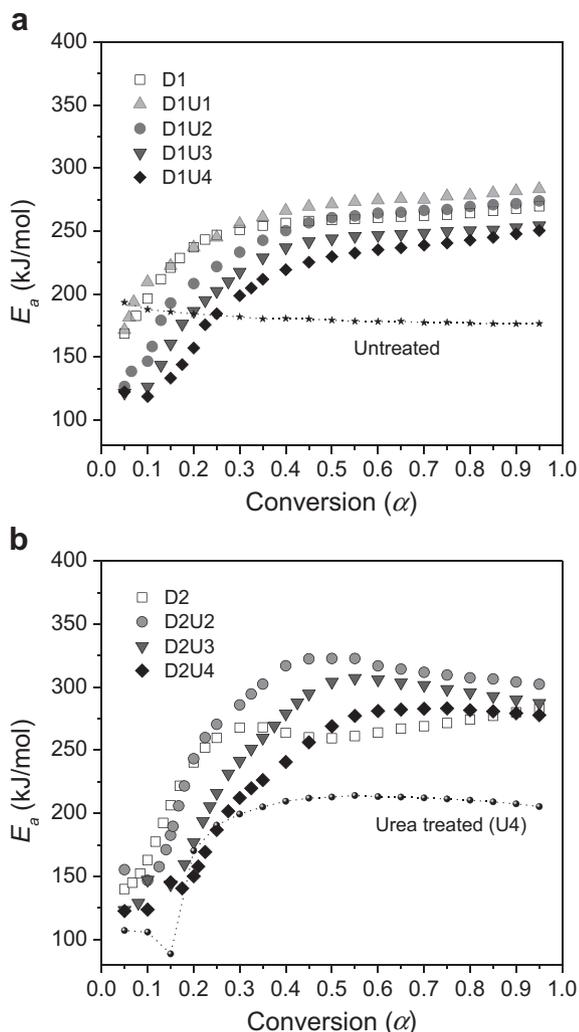


Fig. 10. Dependence of E_a on conversion (α) for untreated and treated greige cotton nonwoven fabrics by the Flynn-Wall-Ozawa method: (a) ~ 0.8 wt% P and (b) ~ 1.6 wt% P.

untreated cotton, followed by the phosphate and phosphorylation reactions. Above these conversions, where cellulose decomposed and char formed, the E_a approaches the constant level. Agreeing with the result from the Kissinger method, the overall E_a was significantly increased by the DAP treatment. According to Farooq and Milnes's kinetic study [49], the rate-determining step for the thermal decomposition of cotton fabric under nitrogen was changed to a three-dimensional diffusion mechanism after the treatment of condensed phase FRs (Amgard TR and Pyrovatex CP). The E_a in this mechanism was related with the evolution of volatile species, which diffuse into the solid char. The higher E_a for FR treated cotton fabric was attributed to the formation of thermally stable char, which acted as a barrier to slow down the diffusion of volatiles escaping from the fabric. This effect on the decomposition process was correlated with the higher char yields.

Urea additive significantly influenced the variation of E_a depending on the amount of P. For ~ 0.8 wt% P shown in Fig. 9 (a) and Fig. 10 (a), the overall E_a is slightly increased by the addition of urea, but, as increasing the concentration of urea, the E_a is gradually decreased. The trends of E_a variation for all these samples remain the same. For ~ 1.6 wt% P shown in Fig. 9 (b) and Fig. 10 (b), the addition of urea significantly raises the E_a in the conversion range of

0.3–0.4 corresponding to the temperature range of 230–260 °C. This steeply increasing behavior indicates that the multiple reactions of DAP were promoted by urea additive, which was confirmed earlier by ^{31}P MAS NMR and ATR-FTIR. However, higher concentrations of urea reduce the E_a values for both the DAP reactions and the decomposition of cellulose. The decrease in E_a for the decomposition of cellulose is indicative of a rapid evolution of volatiles. The excess of urea, having polar nature, opened the cotton structure not only to allow good contact with DAP, but also induce the efficient diffusion of volatile species and thus enhance heat transfer during the charring process. The catalyzed decomposition of cellulose at low temperatures was evidenced by a slight reduction in char yield (Table 3). It is worth to note that the catalyzing function was predominant for the samples containing ~ 0.8 wt% P, which exhibited a greater synergistic FR action of urea additive than the samples containing ~ 1.6 wt% P.

4. Conclusion

Two isoconversional methods, the Friedman and Flynn-Wall-Ozawa methods, were used to identify the role of urea additive in the reactions of DAP and in the decomposition of cellulose. These methods produced consistent results on the dependence of E_a on conversion, and their overall E_a was in good agreement with that obtained from the Kissinger method. The examination of E_a for the thermal decomposition of greige cotton nonwoven fabric treated with different concentrations of urea at fixed contents of DAP showed a dual, contradictory function of urea additive. Up to a certain amount, the addition of urea resulted in a steeply increasing trend of E_a in the conversion range corresponding to the temperatures for the DAP reactions, indicating that urea additive promoted the DAP function. The resulting formation of FR active products was confirmed by the analysis on the decomposed fabrics using ^{31}P MAS NMR and ATR-FTIR. On the other hand, higher concentrations of urea lowered the E_a values to catalyze not only the DAP reactions, but also the decomposition of cellulose at low temperatures. A larger reduction in E_a was observed for the sample that exhibited a greater improvement in the FR property by urea additive. This kinetics study helped better understand the synergistic FR action of urea.

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