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TG/DTG/DTA evaluation of flame retarded cotton fabrics and comparison to cone calorimeter data

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ABSTRACT

Unbleached cotton fabrics (UCF) with 12.5% polypropylene scrim treated with two phosphate–urea based fire-retardant (FR) formulations were evaluated for FR properties using thermogravimetry/differential thermogravimetry/differential thermal analysis (TG/DTG/DTA) method. In addition to testing the two FR-treated unbleached cotton fabrics (CF-FR1 and CF-FR2), bleached cotton fabric (BCF) treated with the two FR formulations (BCF-FR1 and BCF-FR2) was evaluated. Both formulations were washable with add-on of FR chemicals at 18.7% (FR1) or 17.4% (FR2) for UCF and 22.5% (FR1) or 24.9% (FR2) for BCF. The decreasing order of sums at maximal rates of samples degradation in air environment according to DTG method was: BCF (21.40%/min) > UCF (12.91%/min) > BCF-FR2 (12.83%/min) > BCF-FR1 (11.68%/min) > CF-FR2 (10.20%/min) > CF-FR1 (9.73%/min). It indicates that both formulations cause the decrease of thermooxidation of the products at slower rates than the starting material. Several endo- and exothermic peaks observed by DTA in inert and oxidative environment gives additional information about the degradation process. The order of decreasing thermal responses of the studied samples based on sums of DTA peak values of endothermic and exothermic peaks in air environment is: UCF (0.597 °C/mg) > BCF (0.120 °C/mg) > CF-FR1 (0.089 °C/mg) > BCF-FR1 (0.077 °C/mg) > CF-FR2 (0.062 °C/mg) > BCF-FR2 (0.053 °C/mg). This is in agreement with the cone calorimeter results according to which the flammability properties are improving with the decreasing heat release rates or ignition time prolongation in order: UCF > CF-FR1 > CF-FR2. The advantage of TG/DTG/DTA method is slower linear heating rate, which allows the more detailed evaluation of the light and flammable cotton fabric.

1. Introduction

At the present time, it is more and more evident that flammable materials like cotton fabrics need to be tested by several independent methods to properly evaluate effectiveness of the flame retardancy formulations (Alongi, Ciobanu, & Malucelli, 2012; Gao, Wu, & Wu, 2009; Hagen, Hereid, Delichatsios, Zhang, & Bakitzis, 2009; Mostashari & Baie, 2010). Cone calorimeter testing is less sensitive when flammable and low density materials are tested in small quantities and high heat fluxes. In such cases, the heat release rate values are not giving the complete picture. Thermogravimetry is a predominant and important analytical method to evaluate the thermal processes of cotton. Also the use of limited oxygen index (LOI) method brings a difference picture due to atmosphere manipulation, but could be misleading at high FR add-on. It is also informative to know the temperature of the studied sample during the course of degradation, which is dependent upon the architecture of the burning chamber. This can be better achieved on thermobalance than with cone calorimeter. The effectiveness of flame retardant could then be evaluated on the basis of volatiles formed with increasing temperature, which is related to amount of residue produced. Also the effect of thermooxidation during the process could be observed with TG/DTG/DTA when comparing the degradation process in inert and oxidative environment (Šimkovic, Antal, Balog, Košík, & Plaček, 1985). A more effective flame retarded material exhibits smaller differences during the course of degradation for inert in comparison to oxidative conditions (Chang et al., 2011; Tian et al., 1999). The problem of residue behavior is especially important when large amounts of flame retardants are added (Chang et al., 2007; Parikh et al., 2003). When evaluating the residue behavior of fabric samples with initial mass of 2 g, the cone calorimeter might provide unreliable data due to the low sensitivity of a balance with a 0–500 g range (White, Nam, & Parikh, 2012). For such applications TG/DTG/DTA should be used for comparison.

The future of flame retardants is in a more environmental approach, and especially for cotton, less plastic containing and more polysaccharide containing composites need to be studied (Horrocks, 2011; Šimkovic, 2008). Examples of the use of

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the cone calorimeter for light composite sample evaluation are known (Šimkovic, Martvoňová, Maníková, & Grexa, 2005; Šimkovic, Martvoňová, Maníková, & Grexa, 2007; Šimkovic, White, & Fuller, 2012; Šimkovic, 2012). It indicates that at lower heating levels the shape of heat release rate (HRR) curve is broadening due to slower increasing of temperature in the heating chamber. Under these circumstances the heating conditions of cone calorimeter and TG/DTG/DTA are closer and might be complementary for the study of flame retarding conditions. In this way it could be learned if the samples could be tested properly with cone calorimeter due to several times smaller thicknesses used than for UCF sample. This series of TG/DTG/DTA tests is a follow-up to an evaluation of the FR fabrics in a cone calorimeter (White, Nam, & Parikh, 2012).

The goal of the present work was to use a TG/DTG/DTA system to understand the behavior and to evaluate the effectiveness of two phosphate–urea flame retardants in improving the fire performance of UCF and compare the results with cone calorimeter tests on the same materials. Additionally BCF samples modified with the same formulations were evaluated with TG/DTG/DTA. These formulations were developed for mattresses applications and tested on different settings (Nam, Parikh, & Condon, 2010; Parikh et al., 2003; Uppal, Mercemik, Sunghayun, Parikh, & Condon, 2010). Similar concepts were studied by other authors with the help of thermogravimetry (Liodakis, Fetsis, & Agiovlastis, 2009). This method was already used before (Šimkovic, Antal, Balog, Košík & Plaček, 1985) when DTG and DTA are used for evaluation of cellulose thermooxidation. Problems related to textile or decreasing the sample size when tested by cone calorimeter are also known (Limdholm, Brink, & Hupa, 2012; Schartel & Hull, 2007).

2. Experimental

2.1. Materials

Gray cotton blend NW fabric: Gray cotton needle punched nonwoven (NW) fabric (UCF; 87.5% cotton with 12.5% polymer scrim of polypropylene; N, 0.14; C, 46.69; H, 7.23; S, 0; P, 0.33), 1.3–2.5 mm thick, 150 g/m^2 was donated by the Warm Company, Lynnwood, WA.

Bleached cotton NW fabric: Bleached cotton spunlaced nonwoven fabric (BCF; 220–240 g/m; N, 0; C, 43.60; H, 6.67; S; 0; P, 0.19), 0.25 mm thick was developed at SRRC from bleached cotton fiber and bleached cotton comber oil fiber at 1:1 (w/w) ratio.

2.2. FR formulations

The non-durable FR formulations were the phosphate-nitrogen based formulations SRRC-1 and SRRC-2 as described previously (White, Nam, & Parikh, 2012). FR formulations were applied at the Southern Regional Research Center (SRRC) to the fabrics with two immersions and two nips on a Mathis padder. The thoroughly wetted and saturated fabrics were passed through the first padding at a nip pressure of 90 PSI at a speed of 2 m/min to obtain a low wet pick-up of about 60%. Fabrics were again saturated in the formulation, and passed through a nip pressure of 10 PSI at 2 m/min to obtain a wet pick-up of about 95–100%. The samples were placed on a pin frame and dried thoroughly in the Mathis forced-air dryer at 135 °C for 2 min 45 s. The technique of double immersion and double padding was used to obtain good penetration of FR chemicals into the fiber and uniform saturation of FR chemicals in gray fabrics. The add-on of FR chemicals was 18.7% for SRRC-1 (CF-FR1) and 17.4% for SRRC-2 (CF-FR2). The elemental composition of CF-FR1 specimen was: N, 3.08; C, 42.99; H, 7.13; S, 0; P, 2.51, while for CF-FR2 it was: N, 3.84; C, 43.18; H, 7.13; S, 0; P, 3.60. On BCF sample treated with SRRC-1 (BCF-FR1) it was: N, 3.27; C, 38.73; H, 6.18; S, 0; P, 2.31, while for BCF modified with SRRC-2 (BCF-FR2) it was: N, 3.89; C, 38.29; H, 6.54; S, 0; P, 2.31. The add-on of FR chemicals for sample treated with SRRC-1 formulation (BCF-FR1) was 22.5%, while for BCF-FR2 sample it was 24.9%.

Fig. 1. UCF sample in sample holder before testing on cone calorimeter.

2.3. Analytical methods

The elemental composition of specimens was performed on Macro Analyzer (Elementar Analysensystem GmbH, Donauestr, 7, 63452 Hanau, Germany) at detection ranges for C, 0–150 mg (or 100%); H, 0–15 mg (or 100%); N, 0–100 mg (or 100%); S, 0–18 mg (or 100%). Phosphorus was determined colorimetrically by calibration on phosphate.

Thermogravimetric measurements were run on SDT 2960 (TGA-DTA module; TA Instruments) thermobalance at 90 cm^3/min nitrogen or air flow and 10 K/min heating rate from 20 to 1000 °C using 6–7 mg sample amounts in platinum pan.

The conditions used for cone calorimeter testing demonstrated in Figs. 1–4 were discussed previously in the earlier publication (White, Nam, & Parikh, 2012).

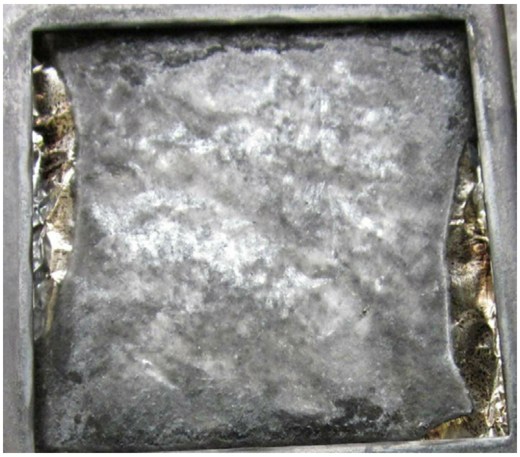

Fig. 2. UCF sample after cone calorimeter testing at 10 kW/m^2 flux.

Table 1
Thermal analysis features of samples.[a]

Sample	Atmosphere	DTA (°C)	Peaks (°C mg)	DTG (°C)	Peaks (%/min)	Residue (%)				
						200	300	400	500	1000 (°C)
UCF	Nitrogen	160	−0.001							
		339	−0.012	339	10.57	95	85	31	18	2
		369	−0.017	451	1.13					
		451	−0.017							
			Σ −0.047		Σ 11.70					
	Air	243	0.026	319	8.96	95	69	15	1	0
		334	0.065	414	3.95					
		407	0.100							
		439	0.406							
			Σ 0.597		Σ 12.91					
CF-FR1	Nitrogen	193	−0.004	281	7.93	91	50	35	26	0
		261	−0.001	576	1.26					
		397	0.016							
			Σ 0.011		Σ 9.19					
	Air	195	−0.004	275	7.73	93	48	34	17	3
		245	0.018	495	2.00					
		322	0.048							
		495	0.027							
			Σ 0.089		Σ 9.73					
CF-FR2	Nitrogen	195	−0.007	258	7.60	92	48	39	32	8
		268	−0.007	421	1.00					
			Σ −0.014		Σ 8.60					
	Air	197	−0.006	253	8.87	91	43	33	19	2
		316	0.043	500	1.33					
		493	0.025							
			Σ 0.062		Σ 10.20					
BCF	Nitrogen	348	−0.046	364	18.00	94	93	10	8	0
			Σ −0.046		Σ 18.00					
	Air	259	−0.002	339	19.17	95	91	15	0	0
		327	0.002	471	2.23					
		351	0.077							
		482	0.041							
			Σ 0.118		Σ 21.40					
BCF-FR1	Nitrogen	193	−0.007	281	8.80	92	48	38	33	14
		283	−0.012							
			Σ −0.019		Σ 8.80					
	Air	239	−0.004	276	9.63	91	45	32	15	1
		315	0.054	500	2.05					
		500	0.027							
			Σ 0.077		Σ 11.68					
BCF-FR2	Nitrogen	196	−0.009	256	9.33	91	43	36	33	14
		260	−0.011							
			Σ −0.020		Σ 9.33					
	Air	197	−0.008	251	11.00	91	38	27	14	0
		307	0.038	502	1.83					
		502	0.023							
			Σ 0.053		Σ 12.83					

[a] The abbreviations are listed in the text.

Fig. 3. BCF sample in sample holder before testing on cone calorimeter.

3. Results and discussion

3.1. Untreated cotton fabric

All six samples were run in inert and oxidative environment using TG/DTG/DTA equipment to learn about their thermolysis and thermooxidation processes (Table 1). This tabular presentation of the data was considered more useful than producing figures with overlapping curves when the exact values at certain temperatures could not be listed. As seen from elemental analysis (see Section 2), UCF contains some traces of protein in addition to the cellulose and polypropylene (PP). There is an endotherm at 160 °C due to melting of PP (Horrocks, 2011). Under the nitrogen environment, the first DTG maximum was observed at 339 °C. This peak is related to glycosidic bond thermolysis of the cellulose macromolecule to degradation products (Šimkovic, 1986). It is accompanied with an endotherm on DTA curve at the same temperature and another smaller endotherm with peak at 369 °C

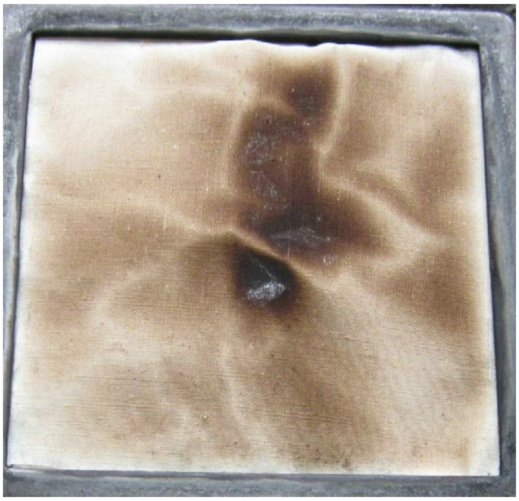

Fig. 4. BCF sample after cone calorimeter testing at 10 kW/m^2 flux.

follows. The second DTG maximum at 451 °C is accompanied with endotherm with maximum at the same temperature. These peaks are probably related to the formation of gaseous products from PP degradation, because they were not observed on poor cotton when analyzed with TG (Hirata & Nishimoto, 1991). According to the flat shape of DTA and TG curves it could be concluded that the rest of the process up to 1000 °C is related to slow volatilization of the carbonized residue.

When tested in the presence of air there was no endotherm observed. There were four exotherms present at 243, 334, 407, and 439 °C. Two exotherms at 366 and 468 °C were observed in a TG test of cotton using a 20 K/min heating rate in air environment (Gao, Wu, & Wu, 2009). According to another source (Tian et al., 1999) using TG at 10 K/min heating rate and static air environment, the reported peak temperatures were 365 and 461 °C. The exotherm at 365 °C is considered to be related to cotton depolymerization, while the peak at 461 °C is ascribed to rapid volatility of degradation products and levoglucosan formation. According to ignition studies on cotton cellulose by DTA, the ignition temperature is at the peak of the exotherm, which is around 350 °C and only one exotherm was observed at the conditions used (10 mg of sample; 20 K/min heating rate, and 200 cm^3/min air flow; Davies, Horrocks, & Greenhalgh, 1983). It indicates that with increasing heating rate and excess of oxygen the thermolysis and thermooxidation processes are overlapping and could not be exactly evaluated. Due to the presence of PP in UCF this process is more complicated than for BCF. According to the value at the peak and its sharpness the flaming took place at 439 °C (Table 1).

3.1.1. *Flame retarded cotton fabric treated with the SRRC-1 formulation*

On sample prepared using the SRRC-1 formulation (CF-FR1; 2.19 mm thick) the thermolysis in inert environment starts with an endotherm already at 193 °C due to 18.7% FR add-on (Table 1). It is due to the dehydration and it was not observed on UCF sample (Šimkovic, 1986). Then a small exotherm at 261 °C is observed, followed by broad exotherm with peak at 397 °C, which is responsible for all the overlapping condensation reactions taking place during the residue formation and its degradation resulting in gasification between 800 and 1000 °C (Hirata & Nishimoto, 1991). It is assumed that the first DTG peak at 281 °C is related to glycosidic bond cleavage and is shifted to much lower temperature in comparison to UCF. The second broad DTG peak with maximum at 576 °C is due to the residue degradation.

Because the sample pretreatment was done at 135 °C, which is above the melting point of urea, it is probable that all the urea condensed toward the polymeric structures (Chen & Isa, 1998). On the other hand diammonium phosphate (DAP) degrades in three stages at 150, 170, and 260 °C (Nam et al., 2012). This process is probably related to the first endotherms observed at 193 °C. Beside cellulose carbamates and phosphates, formaldehyde is condensing, after formation from dimethyloldihydroxyethyleneurea (DMDHEU), with other components of the mixture. Because there is no formaldehyde forming from urea, and also due to its formation from SRRC-1 formulation, SRRC-1 was replaced by SRRC-2 formulation where DMFHEU was omitted.

In the air environment, the peak of first endotherm is almost at the same temperature (195 °C) as in inert environment, being not affected with oxygen presence. The following exotherm at 245 °C is due to cleavage of glycosidic bonds and is at similar temperature as on UCF sample analyzed in the presence of air. The maximal speed of 7.73%/min was determined at DTG peak at 275 °C. The peak is shifted to lower temperature due to the FR formulation. The sum of values of all four exotherms at 195, 245, 322 and 495 °C at the peak are giving less intense responses than the peaks at 243, 334, 407 and 495 °C observed on UCF (Table 1). It indicates the difference in the reaction course caused by the treatment. The first DTG peak at 275 °C is between the two DTA peaks and the second DTG peak follows the last DTA peak. The residues in both environments are much smaller at 300 °C than on UCF, while at 400 and 500 °C the opposite is observed. This confirms that the phosphorylation of cotton with DAP takes place in presence of urea during the treatment and subsequent gasification of the formed residue occurs during the thermooxidation process (Hirata & Nishimoto, 1991).

3.1.2. *Flame retarded cotton fabric using the SRRC-2 formulation*

On the sample modified with SRRC-2 preparation (CF-FR2; 2.46 mm thick; Table 1) two endotherms at 195 and 268 °C were observed in inert environment. The first one, which is probably related to dehydration, is at similar temperature to that observed with the CF-FR1 specimen. The second endotherm is assumed to be related to depolymerization. After the two peaks no exothermic effect is observed, like it was on CF-FR1. The first DTG peak is related to the second endotherm due to depolymerization and is at lower temperature in comparison to two previous samples (UCF and CF-FR1). The TG curve has a course up to 300 °C that is similar to CF-FR1, but slightly higher residue is observed at the higher temperatures (e.g. 8% at 1000 °C). There is also a second DTG maximum at 421 °C which might be related to PP gasification as this peak was also observed with the UCF under similar circumstances (Table 1).

Under oxidative conditions the dehydration endotherm at 197 °C occurs similar to that for CF-FR1 sample. Subsequently the process becomes strongly exothermic with maximum at 316 °C with a shoulder at temperature lower than 300 °C. This indicates similarity in the degradation course with CF-FR1 where the additional exotherm at 245 °C was observed. We might ascribe that peak to the presence of DMDHEU and related formaldehyde condensation. The exotherm observed at 316 °C has slightly smaller value at peak than the value of the DTA peak under similar conditions for CF-FR1 at 322 °C. Analogically, a smaller value at the peak at 493 °C was observed for CF-FR2 sample than for the value at 495 °C of CF-FR1 was observed. This confirms greater exothermic response for SRRC-1 formulation than for SRRC-2 preparation. The two DTG maxima are also at similar temperatures for both CF-FR1 and CF-FR2 samples. Also the residues at 400, 500 and 1000 °C are slightly greater in inert environment for CF-FR2 than for CF-FR1 and similarly also in the air presence. Due to the larger TG residues, one could conclude that CF-FR2 is more thermally stable and also more fire resistant than CF-FR1 sample when UCF was used as a starting material. It is probably due to higher nitrogen and phosphorus content resulted from formation of polymer network producing smaller amount of flammable degradation products. Also the smaller exothermic responses at DTA peaks at 316 and 493 °C for CF-FR2 specimen than for CF-FR1 when compared to peaks at 322 and 495 °C indicates more suitable FR properties of CF-FR2 formulation.

3.1.3. Untreated bleached cotton fabric

The untreated bleached cotton fabric (BCF) is up to ten times thinner (0.25 mm) than UCF (1.30–2.50 mm) and does not contain PP and traces of proteins. This fabric consists of two types of bleached cotton fibers which results in higher metric weight at 220–240 g/m^2, than obtained on UCF (150 g/m^2). When analyzed in inert environment only one endotherm was observed. It is at lower temperature (348 °C) than for UCF sample. Similar behavior was observed on purified cotton linters studied by other authors (Hirata & Nishimoto, 1991). The residue for BCF is 8% greater at 300 °C than for the UCF sample; 21% smaller at 400 °C; 10% smaller at 500 °C; reaches 0% at 1000 °C. The shape of the DTA curve is flat and horizontal after reaching 400 °C. There is also only one DTG peak at 364 °C observed on BCF in inert environment in comparison to two peaks for UCF.

In the air environment, there is one endotherm at 259 °C and the three exotherms at 327, 351 and 493 °C. The endotherm observed with the BCF sample is probably related to dehydration of hydroxyls and carboxyls introduced by bleaching. The first exotherm at 327 °C might be related to random oxidation on the surface, while the second exotherm at 351 °C is close to ignition temperature (Davies, Horrocks, & Greenhalgh, 1983) and the third exotherm with peak at 482 °C might be due to residual glowing (Shafizadeh & Sekiguchi, 1985). The process is completed before 500 °C as indicated by no residue observed at this temperature. While at 300 °C the residues in both environments are greater for BCF than for UCF, at 400 and 500 °C the opposite is observed. The DTG peaks are at higher temperatures for BCF in both environments than for UCF.

3.1.4. Bleached cotton fabric treated with the SRRC-1 formulation

In the inert environment, BCF-FR1 sample degrades in a course consisting of two endotherms at 193 and 283 °C. At higher temperatures, the DTA curve is flat without exothermic effect. The dehydration due to additive presence is taking place between 112° and 209 °C, which is related to the first endotherm. The second endotherm is accompanied with DTG peak at 281 °C. The residues at 500 and 1000 °C are greater than observed on CF-FR1 with larger amount of incorporated FR additive (22.5% in comparison to 18.7% for CF-FR1). The residue at 300 °C is 2% less, while it is 3% greater at 400 °C and 7% greater at 500 °C than for CF-FR1. This is probably related to the PP gasification in the CF-FR1.

In oxidative environment an endotherm at 239 °C was observed, followed by two exotherms at 315 and 500 °C. According to the TG curve, the dehydration related to the endotherm results in 4.6% of sample balance decrease. In comparison to CF-FR1 (Table 1) there is an exotherm missing at 245 °C, which might be related to PP absence. This means the BCF-FR1 specimen responded with less exothermic effect than CF-FR1. The first DTG maximum (276 °C) is before the first exotherm, while the second DTG peak is accompanied with the second DTA maximum. The residue at 1000 °C is only 1%, while in inert environment it was 14%.

3.1.5. Bleached cotton fabric treated with the SRRC-2 formulation

The bleached cotton sample treated with SRRC-2 formulation (BCF-FR2) when analyzed in inert environment gives two endotherms at 196 and 260 °C and a flat response at temperatures higher than 346 °C. The first endotherm is related to dehydration observed on all FR samples. The second endotherm is accompanied with the DTG peak at 256 °C and is due to glycosidic bonds cleavage. The peak is at slightly lower temperature than for BCF-FR1 with slightly higher maximal rate of degradation observed at DTG peak. The residues at 200, 300, 400, 500 and 1000 °C are close to values observed on BCF-FR1 and the value observed at 1000 °C is the greatest in comparison to all studied samples under identical conditions (Table 1).

In oxidative environment, the endotherm at 197 °C remains and the courses at higher temperatures are also very similar to the one for BCF-FR1. The peak of first exotherm is at 307 °C with a shoulder bellow 300 °C, similarly like it was observed on CF-FR2 and the second exotherm at 502 °C. The first DTG maximum (249 °C) is before the first exotherm, while the second DTG peak is accompanied with the second exotherm. In inert environments the amount of residues at 500 and 1000 °C is identical for both modifications. In the air environment, slightly smaller amounts of residues are observed for BCF-FR2 than for BCF-FR1.

3.2. Ranking of all samples

The decreasing order of temperatures at maximal rates of sample degradation in air environment is: BCF (339 °C/19.17%/min) > UCF (319 °C/8.93%/min) > BCF-FR1 (276 °C/9.63%/min) > CF-FR1 (275 °C/7.73%/min) > CF-FR2 (253 °C/8.87%/min) > BCF-FR2 (251 °C/11.00%/min). This order changes when decreasing rates of sample degradation/thermooxidation are considered as the criteria (BCF > BCF-FR2 > BCF-FR1 > UCF > CF-FR2 > CF-FR1). It indicates that both formulations cause thermooxidation of cellulose at lower temperatures than on starting material. When the overall order of decreasing fire resistance is based on decreasing sums of maximal rates at DTG peaks measured in air environment, the ranking is as followed: BCF (21.40%/min) > UCF (12.91%/min) > BCF-FR2 (12.83%/min) > BCF-FR1 (11.68%/min) > CF-FR2 (10.20%/min) > CF-FR1 (9.73%/min). On the other hand, when evaluating the decreasing sums of values of endothermic and exothermic peaks in air, the rankings decreases in order: UCF (0.597 °C/mg) > BCF (0.120 °C/mg) > CF-FR1 (0.089 °C/mg) > BCF-FR1 (0.077 °C/mg) > CF-FR2 (0.062 °C/mg) > BCF-FR2 (0.053 °C/mg). This method could be used for calculation of heats of reaction covered by individual peaks when run in oxygen environment. But the heat values determined in this way could not be compared with the results obtained by cone calorimeter because they were obtained at different conditions (Šimkovic, Antal, Balog, Košík, & Plaček, 1985). Additionally for experiments in oxygen environment 100 mg amounts of the fabric would be needed. This is impossible to achieve on the used fabrics. That is why, only temperature differences between sample and the reference cell at DTA peaks were listed for simplified evaluation. The first criterion is affected by gasification and smoke production, while the second one is related only to the thermal response of the process. According to both criteria all the flame retarded samples are evaluated as better behaving than the starting materials. On the other hand the differences in listed values between individual FR samples are much smaller than differences between UCF and BCF. This might be related to the statistical insignificance of the differences between the two used FR formulations (White, Nam, & Parikh, 2012). Production of smoke was higher for CF-FR2 than for CF-FR1 according to cone calorimeter tests. It is in the agreement with the DTG evaluation, when greater sum of maximal rates of thermooxidation was observed for CF-FR2 than for CF-FR1.

3.2.1. Comparison with cone calorimeter testing

The situation is much more complicated when analyzed by cone calorimeter where only one HRR peak related to all the burned degradation reactions was observed (White, Nam, & Parikh, 2012). Temperature of the cone calorimeter heater could be set to required temperature by using the proper heat flux. For fire situations where the heating rate of fabric is slow, the lower heat fluxes might be more appropriate. In Fig. 1 there is the UCF sample before testing. After the treatment at 10 kW/m^2 flux the cotton component of UCF sample is decomposed and only charred residue remained in partially shrunk form (Fig. 2). According to measurements on the surface of ceramic plate it indicates that at 10 kW/m^2 the operation temperature reaches the value around 300 °C (Schartel & Hull, 2007). This is lower temperature than the estimated ignition of cotton at 350 °C (Davies, Horrocks, & Greenhalgh, 1983). Under the conditions when the UCF sample at the thickness of 2.46 mm and 2.03 g initial mass was tested at fluxes 20–50 kW/m^2, due to higher temperatures reached which could be estimated to be between 300 and 610 °C, the values of time of sustained ignition (TSI) measured on cone calorimeter becoming shorter with increased heat applied. They might be shorter than the 4 s criterion for sustainable ignition. On the other hand the delay is also tied to the amount of volatile mass generated by pyrolysis. The measured value at 50 kW/m^2 flux was 4.7 s for UCF (White, Nam, & Parikh, 2012). When the poor cotton with metric density of 214 g/m^2 was tested using 35 kW/m^2 flux, the 14 s TSI value was determined (Alongi, Brancatelli, & Rosace, 2012).

When BCF specimen (Fig. 3) was tested at 10 kW/m^2 flux on the cone calorimeter the surface of the sample did not reach the flaming temperature as could be assumed from partially charred surface on the treated sample (Fig. 4). Under these conditions the sustainable ignition could not be observed. When comparing the samples of UCF and BCF in Figs. 2 and 4, the UCF sample is much more degraded, although both samples were tested at the same applied heat. To find out the optimal testing conditions for light and fire sensitive samples, the cone calorimeter data should be obtained under special arrangement (Dietenberger, 2011).

4. Conclusions

Gray cotton blend NW fabric and bleached cotton fabric treated with two phosphate–urea-based FR formulations, SRRC-1 and SRRC-2, were evaluated with TG/DTG/DTA method. According to the DTG peak sums, the rates of thermooxidation in air environment are decreasing in order: BCF (21.40%/min) > UCF (12.91%/min) > BCF-FR2 (12.83%/min) > BCF-FR1 (11.68%/min) > CF-FR2 (10.20%/min) > CF-FR1 (9.73%/min). It indicates that both formulations are more thermally stable when applied on UCF as a starting material than on BCF. But on the basis of decreasing sum of values of endothermic and exothermic peaks in air the fire resistance decreases in order: BCF-FR2 (0.053 °C/mg) > CF-FR2 (0.062 °C/mg) > BCF-FR1 (0.077 °C/mg) > CF-FR1 (0.089 °C/mg) > BCF (0.120 °C/mg) > UCF (0.597 °C/mg). It is due to increasing values of temperature effects measured by DTA. These results are in agreement with cone calorimeter tests.

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