

Use of DMDHEU with novel FR chemical for CO/PET blends

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Abstract. In present study, DMDHEU (dimethylol dihydroxyethyleneurea), which has been used for wrinkle-resistant finishing in textile, was used in FR finishing of CO/PET blends as a crosslinker with novel FR chemical (Fire-off). Flame retardancy performance of CO/PET fabrics treated with Fire-off and Fire-off/DMDHEU were investigated and compared. In addition, wrinkle resistant test was performed for untreated and Fire-off/DMDHEU treated fabrics to investigate the effect of the treatment on wrinkle recovery performance of fabrics. Results showed that Fire-off/DMDHEU system is a more effective nitrogen provider than Fire-off alone to enhance the flame retarding performance of the treated CO/PET fabrics through phosphorus–nitrogen synergism, therefore the presence of DMDHEU in the flame retardant finishing system increases the flame resistance of the treated CO/PET fabric. In addition, DMDHEU does not significantly change the wrinkle recovery of fabrics when used with Fire-off.

1. Introduction

Reducing the flammability of textile fibers and fabrics has been one of the major challenges facing the scientific and industrial researchers. Flame resistance is a desirable property that can be imparted to fabrics by means of chemical finishing. Due to the fact that conventional organo halogen-based flame retardants are getting banned more and more [1-4], several halogen-free substitutes have been developed, for instance, polyphosphates, organic phosphates, or nitrogen compounds [5-6]. However, the reactive organophosphorus flame retarding system contains significant levels of formaldehyde, a known carcinogen. Precondensate/ammonia process (known as “Proban” technology) requires the use of an ammoniation chamber, which is not compatible with most of the finishing operations in the industry. Those finishing treatments may also cause excessive fabric strength loss and adverse effects on fabric handle properties [7]. In this context nitrogen and phosphorus containing chemicals are especially in importance, because of their P–N synergistic effect in flame retardant applications [8]. However, their low stability with regard to washing and mechanical abrasion is limiting their applicability [9-10]. Using crosslinkers in FR systems is an option to lead better bonding properties of FR agents on textile fibers. N-methylol reagents, such as DMDHEU (dimethylol dihydroxyethyleneurea) have long been used in the textile industry as the crosslinking agents for cotton to produce wrinkle-resistant cotton fabrics and garments [11]. Few studies have indicated that it was also suitable as a crosslinker for flame retardant agents on cotton fabrics [12-13].

In our previous study [14], a nonformaldehyde flame retarding system, PVP (PR)-P-DCDA was synthesized by polyvinyl alcohol, hydrophilic polyester resin, phosphoric acid, and dicyandiamide. 100% polyester, 100% cotton, and 50/50% cotton/polyester fabrics were treated with PVP (PR)-P-DCDA by impregnation method. Flammability characteristics, thermal decomposition, surface



morphology, and chemical structure of treated and untreated fabrics were investigated by vertical flammability test, limiting oxygen index, differential scanning calorimetry, thermogravimetric analysis, scanning electron microscopy, and Fourier-transform infrared, respectively. The results showed that PVP (PR)-P-DCDA are able to protect all three types of fabrics against their thermal degradation and favoring the formation of a stable char. The results suggested that the addition of FRs onto the cotton, polyester, and CO/PET might have reduced the flammability via PVP (PR)-P-DCDA dehydration into char. In addition to being an eco-friendly flame retardant system, a good char-forming flame retardant agent, PVP (PR)-P-DCDA has also superior ease of application for cotton, polyester, and cotton/polyester blends unlike commercially available “Proban” technology. At larger scale, Eksoy Chemical Company commercialized PVP (PR)-P-DCDA under the name Fire-off EBR.

In this study, a new FR finishing system based on Fire-off and DMDHEU were developed in order to improve durability for cotton part of the blend. CO/PET fabric samples (292 and 300 g/m²) were treated Fire-off and Fire-off/DMDHEU FR systems. Flammability characteristics, thermal stability and chemical structure of treated fabrics were investigated by LOI, Micro Cone Calorimeter, DSC and FTIR, respectively. The wrinkle resistance properties of untreated and Fire-off/DMDHEU treated fabrics were also evaluated.

2. Experimental Study

2.1. Materials

The experiments were carried out using scoured 35/65% CO/PET (300 g/m², twill) and 50/50% CO/PET blend fabrics (292 g/m², twill) supplied from Ata Textile in Turkey. Experimental fabrics selected for this study represent those used in apparel and home textiles. The hydroxy-functional FR agent with the commercial name of “Fire-off” (supplied by Eksoy Chemical-Turkey) and DMDHEU with the commercial name of Reaknitt TW (supplied by CHT Chemical in Turkey) were used.

2.2. Fabrics Finishing Procedure

The fabrics were first immersed in a finish solution containing 350 g/L Fire-off and DMDHEU (10%) (Including a catalyst) (in two solutions: pH:3 and pH:6), then passed through a laboratory padder with two dips and two nips, dried at 100°C for 3 min, and finally cured in an oven at 165°C for 10 min.

In order to compare FR results of Fire-off with Fire-off/DMDHEU systems, the fabrics were also treated with Fire-off only (pH:6) via pad-dry-cure process (350 g/L Fire-off, 100°C for 3 min drying and 180°C for 3 min curing).

2.3. Characterization techniques

The chemical structure of the untreated and treated fabrics was characterized by Fourier-transform infrared spectroscopy (FTIR) using Perkin Elmer spectrum One FTIR-ATR System.

The thermal behaviours of untreated and treated CO/PET fabric samples were investigated by differential scanning calorimeter (DSC). DSC thermograms for CO/PET samples were obtained using a Perkin- Elmer model differential scanning calorimeter, from 30°C to 275°C with a heating and cooling rate of 10°C/min. Samples of about 4-5 mg were sealed in aluminum pans. Nitrogen was used as the purge gas to provide an inert atmosphere and to prevent sample degradation. All DSC thermograms were analyzed using Pyris software for quantitative evaluation of melting, crystallization temperatures, and their associated heat capacities and enthalpies.

2.4. Fabric Performance Evaluation

Limiting oxygen index (LOI) test was carried out according to BS 4589-2 standard for flammability characteristics of fabrics. In addition, Micro Cone Calorimeter (MCC) was performed to investigate heat release properties of treated fabrics in accordance with ASTM D7309.

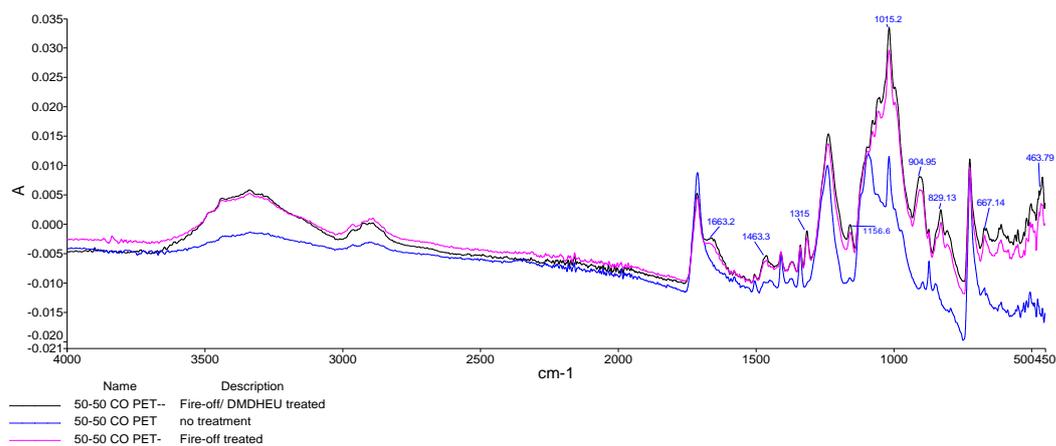
The conditioned wrinkle recovery angle (WRA) was measured according to ISO 2313 “Textile Fabrics: Determination of the recovery from recovery creasing of a horizontally folded specimen by measuring the angle of recovery” using SDL Atlas Recovery Tester.

3. Results and Discussion

3.1. FTIR analysis of untreated and treated fabrics

FTIR spectra of untreated and treated CO/PET fabrics are given in Figure 1.

50/50% CO/PET (292 g/m²)



35/65% CO/PET (300 g/m²)

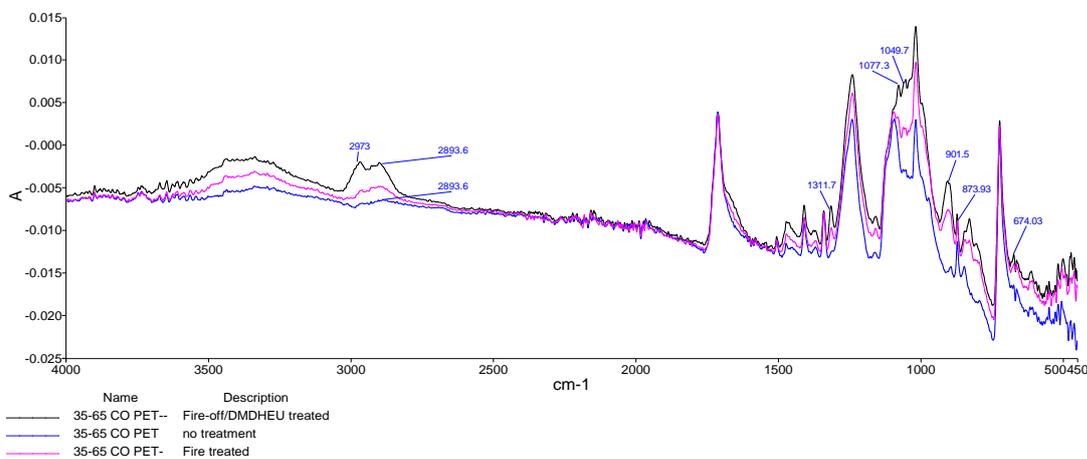


Figure 1. FTIR spectra of untreated and treated CO/PET fabrics (cm⁻¹: data is wavenumber, A: data is absorbance %).

As seen in Figure 1, FTIR spectra of Fire-off and Fire-off/DMDHEU treated fabrics are almost overlapped. However, FTIR spectrum of Fire-off/DMDHEU treated fabrics have sharper absorption peaks at 2973 (N), 901 cm⁻¹ (P) and extra peaks at 1077, 1049 cm⁻¹ (C–O–P), which indicate that Fire-off/DMDHEU treatment provides more phosphor and nitrogen than the Fire-off treatment into the fabric construction.

3.2. Differential scanning calorimeter results of treated and untreated fabrics

Table 1 shows the collected data of DSC.

Table 1. Collected data of DSC.

Fabric Type	Treatment	T _m (°C) / ΔH _m (J/g)	T _c (°C) / ΔH _c (J/g)
50/50 % CO/PET (292 g/m ²)	-	255.12/38.44	208.91/27.45
35/65 % CO/PET (300 g/m ²)	-	253.44/40.17	208.59/29.30
50/50 % CO/PET (292 g/m ²)	Fire-off	250.71/36.33	211.92/33.48
35/65 % CO/PET (300 g/m ²)	Fire-off	251.16/44.95	212.27/40.38
50/50 % CO/PET (292 g/m ²)	Fire-off / DMDHEU	248.63/37.45	209.08/33.69
35/65 % CO/PET (300 g/m ²)	Fire-off / DMDHEU	249.63/43.07	209.92/40.15

It is seen from the Table 1 that both Fire-off and Fire-off /DMDHEU treatments lead a decrease in melting temperatures, an increase in crystallinity temperatures. There are also an increase in enthalpy values with treatments during crystallinity. These results indicated that thermal stability of CO/PET fabrics has changed with Fire-off and Fire-off /DMDHEU treatments. It is also obvious that decrease in melting temperatures for Fire-off /DMDHEU treated samples are higher than the Fire-off treated ones.

3.3. Evaluation of the flame retardancy of treated fabrics

Table 2 shows LOI test results of untreated and treated cotton and CO/PET fabric samples, which were also associated with related add-ons (%).

Table 2. LOI values of untreated and treated CO/PET fabrics.

No	Fabric Types	Treatment	Add-on (%)	LOI (%)
1	50/50 % CO/PET (292 g/m ²)	-	-	18.8
2	35/65 % CO/PET (300 g/m ²)	-	-	18.6
3	50/50 % CO/PET (292 g/m ²)	Fire-off pH:6	19.3	27.0
4	35/65 % CO/PET (300 g/m ²)	Fire-off pH:6	17.2	26.0
5	50/50 % CO/PET (292 g/m ²)	Fire-off / DMDHEU pH: 3	16.5	26.7
6	35/65 % CO/PET (300 g/m ²)	Fire-off / DMDHEU pH: 3	15.2	26.2
7	50/50 % CO/PET (292 g/m ²)	Fire-off / DMDHEU pH: 6	23	27.2
8	35/65 % CO/PET (300 g/m ²)	Fire-off / DMDHEU pH: 6	23.8	27.2

It is seen from the Table 2, in general, LOI values of treated fabrics increase with the increase in add-ons. Fire-off treatment leads an increase in LOI values of CO/PET fabrics from 18.6 to 26-27, whereas Fire-off/DMDHEU system increase LOI values of CO/PET samples up to 27.2. Fire-off / DMDHEU treatment imparts flame retardancy to CO/PET fabrics at around 15 add-on values (at 15.2 add-on LOI: 26.2). However, add-on of Fire-off treatment for LOI of 26 should be at least 17.2 for the same CO/PET fabric. Thus, addition of DMDHEU in finishing bath has a positive effect on flame retardancy properties of fabrics. These results are in line with the FTIR and DSC results. In addition, pH of the finishing solution affects the ease of application of treatment.

Test results of MCC test are shown in Table 3. As seen from Table 3, there is a decrease in Heat Release Capacity (HRC), peak heat release rate (PHRR), time to peak heat release rate (T_{max}), total heat release rate (THR) and mass loss values for treated samples, which indicates that flammability and fire risk of fabrics decrease. Decrease in mass loss shows that FR treatments leads char formation. When compared Fire-off and Fire-off/DMDHEU treatments, it is seen that addition of DMDHEU in finishing bath leads more decrease in HRC, pHRR and mass loss of CO/PET fabrics, which indicate this FR

system imparts better flame retardancy on CO/PET blends. These results are also in line with LOI test results.

Table 3. MCC Test Results of untreated and treated fabrics.

Fabric Type	Treatment	HR Capacity (J/k K)	PHRR (W/g)	T max (°C)	THR (kJ/g)	Mass loss (%)
50/50% CO/PET-292 g/m ²	-	196.33	181.27	379.13	16.27	90.98
50/50% CO/PET-292 g/m ²	Fire-off	136	123.53	437.77	13.53	83.63
50/50% CO/PET-292 g/m ²	Fire-off /DMDHEU	141.67	129.9	438.63	13.87	81.94
35/65% CO/PET-300 g/m ²	-	224.33	206.77	452.2	17.1	90.32
35/65% CO/PET-300 g/m ²	Fire-off	185.33	170.9	440.27	14.83	84.27
35/65% CO/PET-300 g/m ²	Fire-off /DMDHEU	178	163.83	442.9	14.5	83.34

3.4. Evaluation of wrinkle recovery of untreated and treated fabrics

The results of WRA of CO/PET fabrics in warp (W) and filling (F) directions are shown in Table 4.

Table 4. Wrinkle recovery angles of CO/PET fabrics.

50/50% CO/PET (292 g/m²)

Untreated				Fire-off/ DMDHEU treated			
face to face		back to back		face to face		back to back	
W1: 75°	F1:120°	W1: 105°	F1:95°	W1: 70°	F1:118°	W1: 105°	F1:99°
W2: 70°	F2:120°	W2: 110°	F2:95°	W2: 70°	F2:120°	W2: 105°	F2:104°
W3: 80°	F3:125°	W3: 105°	F3:95°	W3: 62°	F3:118°	W3: 105°	F3:107°
W4: 78°	F4:127°	W4: 100°	F4:95°	W4: 62°	F4:117°	W4: 105°	F4:94°
W5: 78°	F5:125°	W5: 100°	F5:95°	W5: 60°	F5:127°	W5: 105°	F5:102°
avg: 76.2°	avg: 123.4°	avg: 104°	avg: 95°	avg: 64.8°	avg: 120°	avg: 105°	avg: 101.2°

35/65% CO/PET (300 g/m²)

Untreated				Fire-off/ DMDHEU treated			
face to face		back to back		face to face		back to back	
W1: 100°	F1:135°	W1: 128°	F1:132°	W1: 85°	F1:130°	W1: 113°	F1:105°
W2: 82°	F2:136°	W2: 125°	F2:110°	W2: 85°	F2:130°	W2: 113°	F2:100°
W3: 98°	F3:130°	W3: 120°	F3:110°	W3: 85°	F3:130°	W3: 111°	F3:108°
W4: 110°	F4:136°	W4: 109°	F4:130°	W4: 85°	F4:129°	W4: 111°	F4:117°
W5: 88°	F5:155°	W5: 113°	F5:115°	W5: 82°	F5:128°	W5: 115°	F5:110°
avg: 96°	avg: 134.4°	avg: 119°	avg: 119.4°	avg: 84.4°	avg: 129.4°	avg: 112.6°	avg: 108°

It is seen that, Fire-off/ DMDHEU treatment lead a slight increase in WRA values of CO/PET fabrics. However, this change could be negligible. Wrinkle resistance of fabrics are not deteriorated dramatically with FR/DMDHEU treatment.

4. Conclusion

In this research, both heat release and flammability properties of CO/PET fabrics, which can be used in apparel and home textiles treated with a novel flame-retardant agent,-“Fire-off”- and Fire-off/DMDHEU were investigated. Results showed that DMDHEU functions as nitrogen provider for the flame retardant

system, thus enhancing its flame retarding performance. Flammability test results also demonstrated that Fire-off/DMDHEU treated CO/PET blend fabrics generated less heat of combustion and obtained better flame retardancy than Fire-off treated ones, which can be also confirmed by the increase of LOI values at lower add-ons. Both Fire-off and Fire-off/DMDHEU treatments induced a significant decrease in PHRR and THR, and increase in char formation for CO/PET blend fabrics. Consequently, DMDHEU could be used for cellulosic blends with Fire-off in finishing formulation and Fire-off/DMDHEU treatment does not significantly deteriorate wrinkle recovery of fabrics.

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