Effect of polyamide ratio on the flammability of wool/PA blended aircraft seat fabrics

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Abstract Wool and polyamide blended fabrics are widely preferred for aircraft seats**.** Due to the requirements of the flammability regulations of airline authorities, aircraft fabrics have to pass vertical flammability and smoke density tests. In this work, polyamide/wool blended yarns produced in five different ratios. Yarn samples were knitted on a circular knitting machine. Fabric samples were dyed in overflow dyeing machine. Following the washing of the fabric samples, well known low smoke Zirpro flame retardant treatment based on a zirconium salts were applied. The effect of polyamide content on the flammability properties, the thermal behavior and heat release properties of the wool/polyamide blended knitted fabric samples were investigated. For this aim, cone calorimetry, thermogravimetric analyses, smoke density and vertical burn tests were performed. Results showed that polyamide content decreased the flame retardancy of the wool fabrics.

***Keywords*—aircraft seat, flame retardant, polyamide, thermal behavior, wool**

I. INTRODUCTION

TEXTILES used in aircraft interiors including carpeting, curtains and seat coverings must meet flammability regulations throughout the world. Wool is known as the most flame retardant fiber among natural fibers because of its protein structure and chemical composition. Wool contains high level of moisture, nitrogen and Sulphur. The high Sulphur (3-4 wt%) and nitrogen content (15-16 wt%) present in both chain and side groups provide low flammability to wool fiber. Wool also contains about 15wt% moisture under standard atmospheric conditions (20 °C and 65% RH) [1]. The natural flame resistant properties of the wool (LOI value is approx.. 25%) are associated with these properties [2].

Polyamide (PA) fibers offer high strength and abrasion resistance to wool fabrics. On the other end, small percentage of PA fibers may improve the processing performance and durability of the final products. PA is also preferred for the blending with wool when the fabric is to be dyed because PA can be dyed with wool in the same bath. Therefore, aircraft seat fabrics are generally produced by blending with wool and PA fibers. On the other aliphatic polyamide fibers such as nylon 6 and 6.6 are less flame retardant than wool. Their LOI values are about 21.

Many flammability treatments for wool and wool blends did not satisfy the requirements of the flammability regulations of airline authorities. Therefore, a new flame retardant treatment process (Zirpro) were developed by the former International Wool Secretariat, based on the reaction of zirconium and titanium salts with wool [3]. Durable flame retardant finishing of wool fabrics based on Zirpro process is dominated by finishing agents includes the potassium hexafluorozirconate (K_2ZrF_6). Zirpro treatments are mainly based on the exhaustion of negative charged zirconium or titanium salts, under acid conditions, onto positively charged wool. Finishing agent should be applied under acidic (pH≤3) conditions. It was claimed that the application of only about 3% flame retardant to the fiber causes a negligible effect on properties such as handle. Zirpro application generally increases the smoke generation. Therefore generally, zirconium acetate solution is also applied to the fabrics after zirconium or titanium salt application for low smoke emission [4].

In this work, the effect of polyamide content on the flammability properties and the thermal behavior of the wool-PA blended knitted fabric samples were investigated. For this aim, cone calorimetry, thermogravimetric analyses, smoke density and vertical burn tests were used.

II. METHODS AND PROCEDURES

Potassium hexafluorozirconate (Aflammit ZR) and Zirconium acetate solution (Aflammit ZAL) are obtained from THOR Specialities Ltd. Company. Citric acid (monohydrate) and formic acid were supplied from Merck, Germany. Polyamide 6.6 (3.3 dtex, 85-90 mm) and wool fibers (23 micron, 68 mm) in top form were blended on gilling machine in five different blend ratio (100%wool, %95-5 wool-PA, 90-10% wool-PA, 85-15%wool-PA and 80-20% wool-PA). Nm 36/2 yarns were produced on ring spinning and doubling/twisting machines. Yarn samples were knitted on a circular knitting machine (Ipekcioglu, Turkey).

Fabric samples were dyed in overflow dyeing machine (Mathis AG, Switzerland). Following the washing of the fabric samples, low smoke Zirpro treatment was applied with 3% Aflammit ZR and 10% Aflammit ZAL for 45 min at 70ºC (liquor ratio was 1:20) in the same machine. Citric acid and formic acid were added to the solutions in order to maintain a pH 2 to 2.5 during the exhaustion process and decrease the smoke production. The treated samples were rinsed with deionized water and dried at room temperature.

Flame retardant flexible polyurethane foams, which are suitable for aircraft seating (100x100x30 mm^3), were covered by the fabric samples according to ASTM E1474-14 test standard. Fabric/foam combinations were tested by cone calorimetry test device (Fire Testing Technology, UK) under 35 kW/m^2 heat flux. Samples were tested without a retainer frame. Time to ignition (TTI), peak heat release rate (HRR), total heat release (THR), smoke production rate (SPR), specific extinction area (SEA), mass loss rate (MLR) and maximum average rate of heat emission (MARHE) values were measured and compared. Thermal analyses were carried out by SDT Q600 (TA Instruments, USA) at heating rates 10ºC/min under N_2. Vertical flammability tests were performed by FAA multi-purpose small scale flammability test chamber (Govmark, FAA MP-1-X, USA) according to FAR Part 25 App. F Part 1(ii). Burn length, after flame time and drippings flame time after exposing to bottom of the fabric sample (305x75 mm) for 12 s were calculated. According to FAA, the average burn length must not exceed 203 mm (8 in), and the average after flame time must not exceed 15 s. Smoke density tests were performed according to the FAR 25.853 (d), (App. F to part 25, part V). Specific optical smoke density value (D_s) which is a dimensionless measure of the amount of smoke produced per unit area when a material is exposed to both flaming and radiant heat sources was measured. The maximum value of D_s that occurs during the first 4min of the test, ^4D_m should be less than 200.

All samples were conditioned at 20 °C, 50% RH for at least 24 hours before testing.

III. RESULTS AND DISCUSSION

Fabric weight test results before and after FR treatment are shown in Table I. According to test results fabric weight of the samples increased about 40% percent after dyeing and flame retardant treatment.

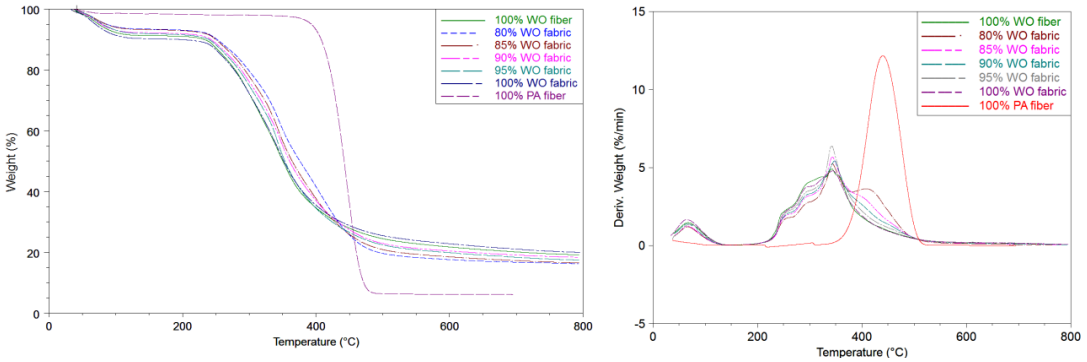
TABLE I.
FABRIC WEIGHT TEST RESULTS OF THE SAMPLES.

	Wool (%)	Fabric weight (g/m^2)	
		Before application	After application
1	100	227.5	336.5
2	95	236.6	330.9
3	90	243.6	334.8
4	85	255.1	344.9
5	80	249.3	348.1

Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the wool, polyamide fibers and dyed fabric samples before flame retardant finishing are shown in Fig. 1. The TGA data are listed in Table II where $T_{10\%}$ and $T_{50\%}$ are defined as the temperatures corresponding to weight loss of 10% and 50%.

Fig. 1 (a) shows that the thermal degradation of the untreated fabric samples includes two mass loss steps. In first step changes of the samples occur in its physical properties and weight loss were observed from 40 to 125 °C which was attributed to the desorption of water physically adsorbed by wool fibers. The second step is the main pyrolysis step occurred from 200 to 550 °C which was attributed a number of pyrolysis reactions take place in wool and polyamide fibers. The hydrogen-bond peptide helical structure ruptures and the ordered part of the wool protein undergo a solid-to-liquid phase change at 230 to 240 °C; also, the destruction of cystine disulphide bonds occurs and a number of volatiles including hydrogen sulfide and sulphur dioxide are released between 250 and 295 °C. Char forming reactions with dehydration and loss of other volatiles occur above 250 °C [5, 6]. The DTG curve of the polyamide fiber showed peak at 441 °C corresponding to thermal decomposition of polyamide. Major weight loss of the polyamide fibers are observed in the 360-500 °C region. Polyamide fibers lost about 94% of its weight at 600 °C.

Thermogravimetric test results indicated that the decomposition of wool and polyamide interact in the 350-500 °C region. $T_{10\%}$ and $T_{50\%}$ values are increased while the polyamide content increased because of the very low water content of the polyamide fibers and loss of H_2O, NH_3 and loss of H_2S, SO_2 and other small molecular weight volatiles from wool in 200-300 °C region [6]. Whereas the polyamide content increase, char residues of the samples decreased at 600 °C and 700 °C because of the thermal degradation of polyamide before 500 °C and enhanced char formation of wool above 450 °C. As the polyamide ratio increased in the fabric content, a second peak appeared prominently in the DTG curves at 410 °C.



(a) (b)

Fig. 1. TG (a) and DTG (b) curves of the wool, polyamide fibers and untreated samples.

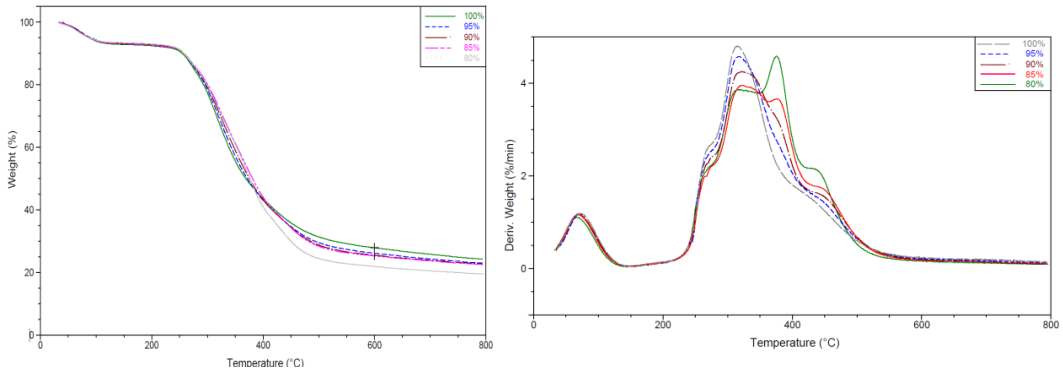
TABLE II.
TGA DATA OF THE WOOL, POLYAMIDE AND UNTREATED SAMPLES UNDER NITROGEN

Sample Code	$T_{10\%}$(°C)	$T_{50\%}$(°C)	Char Residues at 600 °C	Char Residues at 700 °C	pDTG (°C)
1	197.7	351.7	22.8	21.1	345.3
2	239.4	353.3	20.9	19.4	345.0
3	242.7	360.3	20.5	19.1	347.9
4	249.9	364.3	18.5	17.3	343.5
5	251.9	375.8	17.6	16.8	343.6
WO fiber	233.2	350.3	21.8	20.1	342.4
PA fiber	408.7	442.1	6.2	6.1	440.9

The thermogravimetric (TG) curves and derivative thermogravimetric (DTG) curves of the treated fabric samples are shown in Fig. 2. The TGA data are listed in Table III. Similar reaction peaks were observed when compared with the untreated fabrics. $T_{10\%}$ and $T_{50\%}$ temperatures of the treated fabrics are slightly higher than untreated fabrics.

DTG curves showed that second step happen below the thermal degradation of untreated fabric samples. It means that flame retardant treatment reacts on condensed phase [7], catalyzes the thermal decomposition of wool and accelerates the formation of volatiles from the samples. Second peak were also observed at treated fabrics about 380 °C.

When the samples compared, samples having higher polyamide fiber ratio exhibit lower weight loss at low temperatures and higher weight loss at high temperatures. This shows that the addition of polyamide changes the decomposition behavior of wool and decrease the thermal stability of the fabric. Char residues of the samples decrease while the polyamide content increase. On the other hand, amount of residue of the all samples were increased about 5% at 600 and 700 °C. It showed that the flame retardant finishing contribute the formation of more thermally stable carbonaceous char.



(a) (b)

Fig. 2. TG (a) and DTG (b) curves of the treated samples.

TABLE III.
TGA DATA OF THE TREATED SAMPLES.

Sample Code	$T_{10\%}$(°C)	$T_{50\%}$(°C)	Char Residues at 600 °C	Char Residues at 700 °C	pDTG (°C)
1	255.0	368.8	27.9	25.8	314.8
2	257.8	371.7	26.1	24.3	316.8
3	257.8	372.3	26.0	23.9	321.7
4	257.9	380.9	25.3	23.7	380.9
5	266.3	387.9	22.9	21.6	382.4

Cone calorimetry test results of the untreated and treated fabric samples are shown in Table IV. As reported by Price et.al [8] flexible polyurethane foams are easily ignited during the cone calorimeter test, even if they were treated by flame retardant. Therefore, very low TTI values were obtained.

HRR graphs of the samples are given in Figure 3. The peak heat release rate (HRR) of the treated samples decreased when compared with untreated samples under the same conditions. Flame retardancy of the fabrics decreased when the polyamide content increased. The lowest value was obtained by 100% WO fabrics. Specific extinction area values and SPR values were increased slightly after treatment (except 100% WO fabrics). It shows that samples continued to release additional smoke due to smoldering. MLR values of the 100%, 95% and 90% WO samples decreased whereas others remained the same. It is well known that wool fabric forms carbonaceous char while thermoplastic polyamide is melt during burning. These results showed that char was cracked and flaming increased. As a result, HRR and THR (MJ/m^2) values of samples having higher polyamide content higher than the other samples. MARHE values of the treated fabrics reduced when compared with untreated samples.

TABLE IV.
CONE CALORIMETRY TEST RESULTS OF THE UNTREATED AND TREATED SAMPLES.

Sample Code	TTI (s)		HRR (peak) (kW/m²)		THR(0-300s) (MJ/m²)		SPR(av) (m²/kg)		SEA (300s) (m²/kg)		MLR(300s) (g/s)		MARHE (kW/m²)	
	BT*	AT*	BT*	AT*	BT*	AT*	BT*	AT*	BT*	AT*	BT*	AT*	BT*	AT*
1	12	13	320.65	174.94	14.44	11.20	0.0021	0.0014	188.73	172.18	0.0222	0.0206	158.13	100.20
2	11	13	347.79	238.84	13.93	11.13	0.0039	0.0027	136.94	261.68	0.0212	0.0200	158.81	119.14
3	12	14	349.49	243.89	15.21	14.76	0.0030	0.0032	237.14	277.14	0.0232	0.0213	166.96	133.28
4	10	13	343.22	264.00	14.71	14.02	0.0034	0.0043	290.15	308.60	0.0216	0.0216	170.19	145.07
5	14	14	340.36	303.91	16.30	13.69	0.0011	0.0028	166.99	258.34	0.0231	0.0231	179.23	153.99

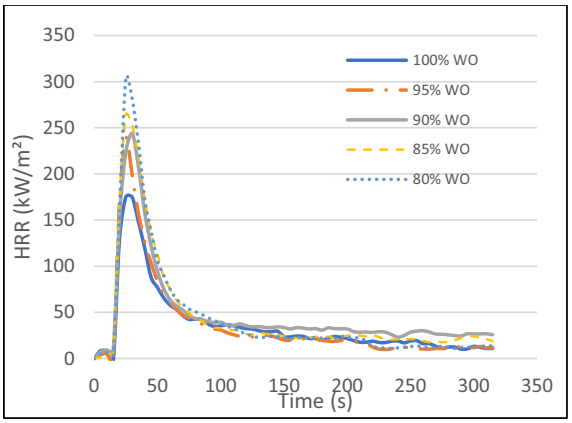


Fig. 3. HRR graphs of the treated fabric samples.

Ds values of the treated samples after smoke density test are given in Figure 4. As pointed out maximum $^{4}D_{m}$ value of the sample should be less than 200. Measured $^{4}D_{m}$ values of all treated samples were ranged between 31 to 59.

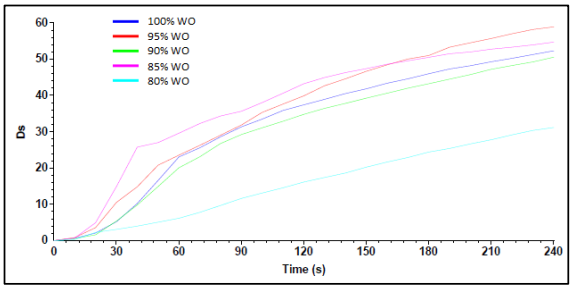


Fig. 4. Smoke density (Ds) test results of the samples.

Images of the samples after vertical flammability test are shown in Fig. 5. After flame time and burn length results are given in Table V. It is observed that an increase in polyamide content leads to an increase in after flame time and burn length. The results showed that the flame retardant application increased the flame retardancy of the samples. It can be concluded that %85 WO and %80 WO samples completely burnt and cannot pass the test. Therefore, more flame retardant is required because polyamide fibers are thermoplastic and less resistance to flame.

TABLE V.
VERTICAL FLAMMABILITY TEST RESULTS OF THE SAMPLES.

Sample Code	Flame Time (sec)	Burn length (mm)	Drip Flame Time (sec)	Pass/Fail
1	5.2	116	0	Pass
2	6.9	143	0	Pass
3	9.2	154	0	Pass
4	33.0	ND	0	Fail
5	39.9	ND	0	Fail

Fig. 5. Vertical flammability test results of the samples

IV. Conclusion

In this work wool/polyamide blended yarns were produced in five different ratios. Yarns were knitted, dyed and flame retarded by the Zirpro process. Thermogravimetric analysis showed that flame retardant chemical act in a condensed phase. Char residue of the samples containing polyamide fibers decreased. Zirpro process reduced the peak heat release rate of the wool and wool/polyamide blended fabrics. Cone calorimetry test results showed that fabrics having higher wool content form a stable char layer over the foam. All flammability tests confirmed that polyamide decreased the flame retardancy of the wool fabrics. Smoke density test results showed that the applied Zirpro process reduced the smoke production rate significantly.

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