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Flammability and Thermal Degradation Behaviour of Wool/Polyamide 6.6 Blends

Yün/Poliamid 6.6 Karışımlarının Yanma ve Isıl Bozunma Davranışları

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FLAMMABILITY AND THERMAL DEGRADATION BEHAVIOUR OF WOOL/POLYAMIDE 6.6 BLENDS

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ABSTRACT: Wool (WO) is often blended with polyamide 6.6(PA) at certain ratios in order to obtain fabrics with superior comfort and mechanical features. This type of wool rich upholstery fabrics are commonly preferred in aircraft seats. Flammability is an important characteristic of aircraft materials in terms of safety and regulatory purposes and it is highly dependent on the composition of blends. Since WO/PA blended fabrics cannot meet the flammability requirements, they are used in aircraft after flame retardant finishing. Needs for innovative new flame retardant chemicals for wool and wool blended fabrics are continuing. This study aims to present a comprehensive investigation and understanding of the fire and thermal degradation behaviour of 100% WO and wool rich blends (88.6% WO/11.4% PA and 78.5% WO/21.5% PA). The data obtained in this work can be used to identify the effect of polyamide 6.6 on the flammability of the wool and to develop new flame retardant chemicals for WO/PA blended fabrics. According to the results, the peak of heat release rate of 100% WO increased about 25% when blended with 21.5% PA as measured by the cone calorimeter and decreased about 12% as measured by the micro-scale combustion calorimeter. This is because the decomposition steps of the two materials are different. Regardless of the equipment used for measurements, the total heat release during combustion increased with the increasing PA ratios in blends. The thermal analyses were performed to study various stages occurred during thermo-oxidative decomposition of wool and its blends. The thermal degradation of PA could be observed as a separate stage during decomposition. On the other hand, the kinetics of thermal decomposition, even during the early stages of decomposition was modified for the blended fabrics. The results will contribute to the understanding of the effect of polyamide ratio on the flammability of the wool.

Keywords: wool, polyamide 6.6, thermal analysis, micro-scale combustion calorimeter, cone calorimeter

YÜN/POLİAMİD 6.6 KARIŞIMLARININ YANMA VE ISIL BOZUNMA DAVRANIŞLARI

ÖZET: Yün (WO), konfor ve mekanik özelliklerin iyileştirilmesi için, genellikle poliamid 6.6(PA) ile belirli oranlarda karıştırılarak kullanılmaktadır. Bu tip yünlü döşemelik kumaşlar sağladıkları yüksek konfor nedeniyle özellikle uçak koltuklarında tercih edilmektedir. Ancak yanma dayanımı uçak malzemelerinde mutlaka olması gereken bir özelliktir ve yasal kurallarla düzenlenmiştir. Malzemenin yanma davranışı bileşime önemli oranda bağlıdır. Yün/poliamid karışımlı kumaşlar bu gereksinimleri karşılayamadıklarından güç tutuşur apre işlemlerinden sonra uçaklarda kullanılırlar. Günümüzde yün ve yün karışımlı kumaşlara etkin güç tutuşur özellik kazandıran yenilikçi aprelere ihtiyaç bulunmaktadır. Bu çalışmada %100 WO ve WO/PA karışımlı kumaşların (%88,6 WO/ %11,4 PA ve %78,5 WO/%21,5 PA) yanma ve termal bozunma davranışlarının farklı teknikler kullanılarak incelenmesi ve açıklanması amaçlanmıştır. Buradan elde edilen veriler uygun WO ve WO/PA karışımlarının belirlenmesi ve bu kumaşlar için yeni güç tutuşur kimyasallar geliştirilmesi için kullanılabilecektir. Elde edilen sonuçlara göre %100 yün için konik kalorimetreyle ölçülen maksimum ısı salım hızı, %21,5 PA içeren kumaşa göre, %25 daha düşük çıkarken mikro ölçekli yakma kalorimetresinde %12 oranında daha fazla çıkmıştır. Bu durum iki malzemenin bozunma adımlarının farklı olmasından kaynaklanmaktadır. Test ekipmanından bağımsız olarak yanma sırasında açığa çıkan toplam ısının, karışımda artan PA oranına bağlı olarak arttığı tespit edilmiştir. Yün ve yünlü kumaşların termo-oksidatif bozunması sırasında meydana gelen çeşitli proseslerin belirlenmesi için termal analizler gerçekleştirilmiştir. Karışımların termal analizinde PA'nın bozunması ayrı bir adım olarak gözlenebilmiştir. Diğer taraftan, karışımların termal bozunma kinetiğinde, bozunmanın ilk aşamalarından itibaren yüne kıyasla meydana gelen farklılıklar, kinetik analizlerle ortaya konmuştur. Bu sonuçlar poliamidin yün ile karıştırılmasının yanma mekanizmasına etkisinin açıklanmasına katkı sağlayacak niteliktedir.

Anahtar Kelimeler: Yün, poliamid 6.6, termal analiz, mikro ölçekli yakma kalorimetresi, konik kalorimetre.

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1. INTRODUCTION

Wool (WO) and its blends have a variety of end-uses in aircraft cabins, e.g.; upholstery, floor coverings etc. [1]. Wool fibres exhibit relatively low flammability (LOI~25%) due to their distinctive chemical features such as; high moisture regain (15%), low content of hydrogen (6-7%), high content of elemental nitrogen (15-16%) and sulphur (3-4%) [2; 3]. On the other hand, the intrinsic flame retardancy of wool products is not sufficient to comply with the requirements established by aviation organizations (FAR/CS 25.853). For instance, very few wool fabrics can pass the vertical flame test according to FAR 25.853 [4]. In order to comply with the flammability requirements for aircraft interiors, wool textiles are often subjected to flame retardant (FR) treatments. A limited number of flame retardant chemistries have been developed up to date and are currently in use. These include; the exhaustion of negatively charged metal complexes (K_2ZrF_6, K_2TiF_6) onto wool in acidic media (Zirpro treatment)[4] and coating fabrics with intumescent systems such as melamine phosphate-dipentaerythritol [5]. Most of the existing technologies fail to comply with the up-to-date requirements in terms of safety and environmental susceptibility, therefore, there is a certain need for novel and effective FRs for wool [6]. Understanding the thermal degradation and fire behaviour of the fibre itself and in blends is a fundamental issue to be considered for the development of novel flame retardants that fulfil the latest demands such as high performance, low cost and low toxicity.

Polyamide 6.6 (PA) is often blended with wool in order to obtain aircraft seat fabrics with superior performance characteristics. PA fibres exhibit excellent abrasion resistance, mechanical strength, chemical resistance and lightweight features, however they are very flammable (LOI~21%) [3; 7]. Unlike wool which tends to char during burning, PA tends to melt and drip [3; 5]. Considering these characteristics of PA fibres, the fire behaviour of the blended fabrics would change with respect to to the PA ratio in blends. It is difficult to predict such change in fire behaviour of blends in terms of the additive behaviour of component fibres as they have different burning characteristics [8].

The flame spread and heat release rate are important parameters to evaluate the fire behaviour of materials [9].The cone calorimeter, which was developed back in the 80s at the National Institute of Standards and Technology (NIST) by Babrauskas, has been widely used for the measurement of heat release rate at the laboratory scale [10; 11]. Along with the heat release rate, cone calorimeter allows for the measurement of the parameters such as effective heat of combustion, mass loss rate, ignitibility, smoke, soot and toxic gases [12]. The bench-scale tests for measuring the heat release rate, have the disadvantage of requiring samples with certain dimensions and thickness which is sometimes difficult to achieve when working with textiles at laboratory-scale [13]. Micro-scale combustion calorimetry (MCC), on the other hand, is a useful technique to evaluate the inherent heat release properties using milligram-size samples. This technique has recently been used to investigate the heat release properties of cotton, polyamide, polyester, Kevlar, acrylic, nylon and silk fabrics [14]. The cone calorimeter and MCC were previously used to study the fire behaviour of wool [15; 16]. However, according the authors' knowledge, these techniques have not been used to study the fire behaviour of wool / polyamide 6.6 blends.

In the presence of oxygen, the thermal degradation of PA 6.6 reportedly takes place in two steps [17]. The first step, which starts at 380ºC is assigned to the decomposition of the polymer and the second step, which starts at 450ºC is assigned to the oxidation of char. Three major mass loss steps were investigated for the thermal degradation of wool in the presence of oxygen [18]. The first step that ends at before 130ºC is associated to the loss of absorbed water. The pyrolysis of wool takes place at the second step which starts a little above 200ºC. The oxidative destruction occurs at the third step which starts above 400ºC. When the blends are considered, it was previously mentioned that the reactions occur during the thermal degradation of one component is affected by the presence of the other component [8]. Obviously, the combination of polyamide and wool fibres would result in a different mechanism of thermal degradation.

Kinetic analysis of thermogravimetric data provides a quantitative expression for the mechanism of thermal degradation. As proposed earlier by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) committee, the methods of kinetic analysis are often classified as model-free (isoconversional) and model-fitting methods [19]. The model-free methods allow for the determination of Arrhenius parameters without any assumption based on the reaction model in a wide temperature range and thus the dependence of activation energy on the degree of conversion can be correlated [19; 20]. Such dependence provides evidence on multi-stage processes and certain mechanistic conclusions can be drawn [19].

The purpose of the present study is to present a comprehensive understanding of the flammability and fire behaviour of wool (WO)/polyamide 6.6 (PA) blended fabrics. WO/PA ratio was chosen considering those widely applied for commercial aircraft seating fabrics. Cone calorimeter and micro-scale combustion calorimeter were used in this work to determine important parameters of combustion and fire behaviour wool / polyamide blends. Simultaneous thermal analyses were used to investigate the effect of polyamide ratio on the thermo-oxidative decomposition behaviour of wool. Moreover, isoconversional method of Friedman and integral isoconversional method of Kissinger-Akahira-Sunose (KAS) were used to evaluate the activation energy of thermo-oxidative decomposition of WO/PA blends.

2. EXPERIMENTAL

2.1. Materials and Measurements

Wool (23 µ, 68 m) and polyamide (3.3 dtex, 85-90 mm, white, semi dull) fibres in top form were blended on gilling machine in three different ratios (100% WO, 88.6% WO/11.4% PA and 78.5% WO/21.5% PA). Nm 20/1 yarns were spun on ring spinning machine and doubled to produce Nm 20/2 yarns by ring doubling machine. The fibre blend ratio of the yarn samples was determined according to Method 2 described in TS1700 standard. The yarns were knitted in a single-jersey circular knitting machine (Faykom CKM-01S, Ipekcioglu, Turkey) and fabrics (~450 g/m^2) were produced. The fabrics were washed with 3% (owf) detergent (Enzym WO, Busan, Turkey) at a liquor ratio L/G=10/1 for 30 min. at 60ºC, subsequently rinsed for 20 min. at 40ºC in a jet dyeing machine (JFO, Mathis AG, Switzerland), then dried flat at room temperature before any analysis.

The flame spread of fabric samples (75mmx305mm) was measured in multi-purpose test cabinet (Govmark, USA) according to the 12 Second Vertical Bunsen Burner Test described in the Federal Aviation Administration (FAA) handbook. The *flame time*, which is the time that the specimen continues to flame after the removal of the burner and the *burn length*, which is the distance from the lower edge of the specimen to the farthest evidence of damage to the test specimen were recorded. The burn length was measured by applying a tearing force from the lower edge of the fabric with a weight of 200 g.

Important fire response parameters such as heat release rate (HRR) and smoke release rate (RSR) were measured by the cone calorimeter (Fire Testing Technology Ltd., UK) according to ASTM E 1354 under a heat flux of 35 kW·m^{-2}. The fabric samples (100 mm x 100 mm x 0.6 mm) were tested using a standard retainer frame along with a wire grid having rods of 2 mm diameter each placed within a distance of 20 mm, in order to prevent sample folding. MCC (Fire Testing Technology) was used to measure the heat release rate (HRR), peak of heat release rate (PHRR), temperature of peak heat release rate (T_{PHRR}) and total heat release (THR), heat release capacity (HRC) according to ASTM D 7309-13, Method A. 5 (±0.1) mg of sample was heated up to 750ºC at a heating rate of 1K/s under N_2 flow (80 cm^3/min) in the pyrolysis chamber. The evolved gases were combined with O_2 (20 cm^3/min) prior to entering the combustion chamber where a constant temperature of 900ºC is maintained. The residue at the end of the test was weighed and char yield (%) was calculated. All samples were tested in triplicates. [21]

Thermal analysis of yarns were carried out by STA equipment (STA Q6000, Perkin Elmer) at various heating rates (β= 5ºC/min, 7ºC/min, 10ºC/min, 15ºC/min) under air flow (50 ml/min) up to 700ºC. Approximately 5 mg of sample was used for the analysis. The real time spectra of the evolved gases were collected by an FTIR (Cary 600, Agilent Technologies) coupled to a thermal analyser (SDT Q600, TA Instruments) with a heated transfer line.

2.2. Kinetic Analysis

The solid state decomposition is expressed with the single step rate equation where, α is the conversion degree and $f(\alpha)$ is a specific function. The rate constant, k, depends on temperature and is not constant throughout the process [19].

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha) \qquad (1)$$

In terms of thermogravimetric analysis α,is expressed by Eq. (2) where m_0 is the initial weight, m_∞ is the final weight and m_t is the weight at time t (in milligrams) [22].

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \qquad (2)$$

The temperature dependency of the reaction rate constant, k, is explained by the Arrhenius equation where A (min^{-1}) is the frequency factor, E_a is the activation energy (J·mol^{-1}) and R is the universal gas constant (8.314 J·mol^{-1}·K^{-1}) [23]:

$$k(T) = Aexp\left(-\frac{E_a}{RT}\right) \qquad (3)$$

Eq. (1) and Eq. (3) are combined to give Eq. (4) which is the differential form of the rate law [23]:

$$\frac{d\alpha}{dt} = Aexp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (4)$$

Integrating Eq. (4) yields to Eq. (5) where $g(\alpha)$ is the integral form of the reaction model [23]:

$$g(\alpha)=\int_0^{\alpha}\frac{d\alpha}{f(\alpha)}=A\int_0^{t}exp\left(-\frac{E_a}{RT}\right)dt \tag{5}$$

Linear heating rate, β ($K\cdot min^{-1}$), is expressed by the Eq. (6) [23]:

$$\beta=\frac{dT}{dt} \tag{6}$$

For the constant heating rate, the integral with respect to time is replaced with the integral with respect to temperature to obtain [23]:

$$g(\alpha)=\frac{A}{\beta}\int_{T_0}^{T}exp\left(-\frac{E_a}{RT}\right)dT \tag{7}$$

Since the value of the integral $exp(-E_a/RT)$ between the limits 0 and T_0 is very small, it can be neglected, thus Eq. (8) is obtained [24]:

$$g(\alpha)=\frac{A}{\beta}\int_{0}^{T}exp\left(-\frac{E_a}{RT}\right)dT \tag{8}$$

Eq. (8) has no analytical solution therefore a number of approximations were proposed in the literature [24].

The Friedman method is a differential isoconversional method and is based on the following Eq.(9) which can be obtained by implying the isoconversional principle to Eq. (4)

$$ln\left(\frac{d\alpha}{dt}\right)_{\alpha}=ln\left[f(\alpha)A_{\alpha}\right]-\frac{E_a}{RT_{\alpha}} \tag{9}$$

Kissinger-Akahira-Sunose method is an integral isoconversional method and uses the logarithm of Eq. (8) and White-Murray approximation to obtain:

$$\ln\frac{\beta}{T^2}=\ln\left[\frac{AR}{g(\alpha)E_a}\right]-\frac{E_a}{RT} \tag{10}$$

The value of E_a can be obtained from the slope of $ln(\beta/T^2)$vs. $1/T$ plot [25].

The differential isoconversional methods are considered to be more accurate than the integral methods as they do not make use of any approximations. However, the numerical differantiation of the integral TGA data may also be a potential source of inaccuracy [23]. Therefore, the use of both integral and differential methods was considered for this study. The code generated in MATLAB software by the authors was used for the kinetic analysis of thermogravimetric data.

3. RESULTS AND DISCUSSIONS

3.1. Vertical Flammability

Vertical flame test was used to evaluate the potential fire risks associated to the spread of flame. The flame time was noted after the removal of the burner and the char length was measured after the test in order to evaluate the compliance with the requirements of FAR 25.853 (average flame time<15s and average burn length<203mm). The fabric compositions and results of the vertical flame tests are tabulated in Table 1. It is important to note that drip flame time was not reported as no drips were observed during the tests of 100% WO sample (R1), only 1-2 drips which were self-extinguished instantaneously were observed for the blend fabrics. For all the samples tested, during the test, the flames propagated longitudinally towards the upper edge of the sample consuming the entire sample length, thus, the sample integrity could not be maintained (Figure 1). The charring took place towards the sides of the sample holder along the sample length but obviously charring was not sufficient to prevent the spread of flames in the longitudinal direction and provide self-extingushing. The shortest after flame time was measured for R1. Compared to R1 the flame time of R2 was longer as flames propagated through the sides of the sample holder and sustained flaming occurred at both sides due to the inefficient charring. The flame time of R3 was barely shorter than R2. Such inconsistency could be ascribed to the localized fabric density variations [16]. Overall, the fabric samples (R1-R3) failed to meet the requirements of the Vertical Flame Test according to FAR 25.853.

3.2. Cone Calorimetry

The heat release rate (HRR) curves of the fabrics, obtained by the cone calorimeter are shown in Figure2a. All the fabric samples exhibited a sharp HRR peak with a relatively small shoulder at the beginning, which is characteristic to thin samples [26]. The total heat evolved (THE) which is obtained by the integration of HRR curve at the end of the test as well as peak rate of heat release (PHRR) and average mass loss rate (AV-MLR) data are tabulated in Table 2. PHRR and THE were reduced when the ratio of wool in the blend was increased. The MLR didn't significantly change with respect to composition of blends.

Table 1. Fabric compositions and vertical flammability

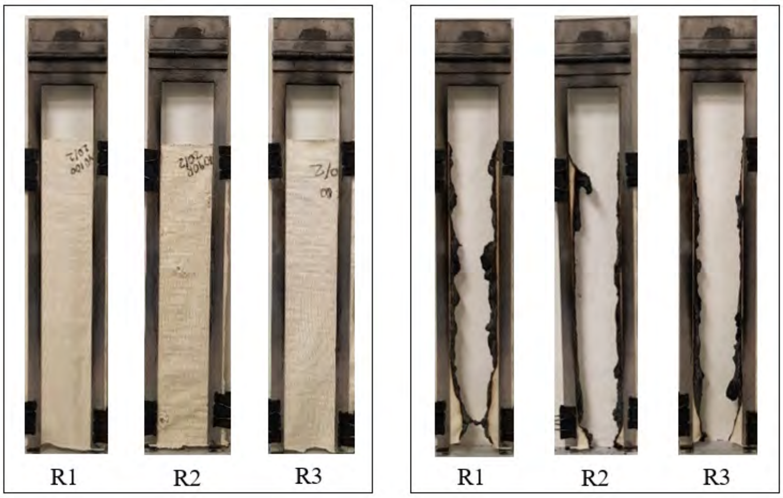
Fabric composition	Sample Code	Flame Time (s)	Burn Length (mm)	Fail/Pass?
100% WO	R1	39.5	-	Fail
88.6% WO / %11.4% PA 6.6	R2	87.0	-	Fail
78.5% WO / 21.5% PA 6.6	R3	84.2	-	Fail

(a) (b)

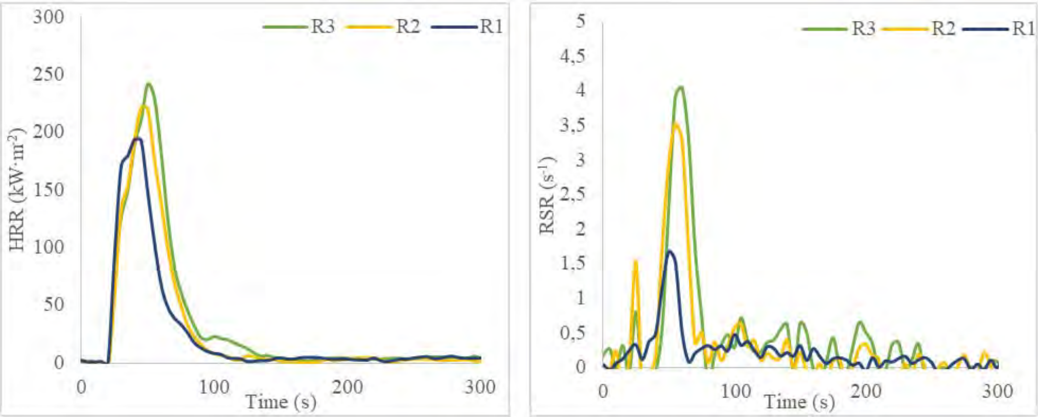
Figure 1. Photos of samples a) before b) after vertical flame tests

Table 2. Cone calorimeter test results

Sample Code	THE (MJ·$^{-2}$)	PHRR (kW·m^{-2})	AV-MLR (g·s^{-1})	PRSR (s^{-1})	TSR (m^2·m^{-2})	SmkFct (MW· m^{-2})
R1	7.5	193.7	0.012	1.68	68.6	13.3
R2	8.5	221.8	0.013	3.52	105.1	23.3
R3	10.1	242.0	0.013	4.05	133.5	32.3

The rate of smoke release (RSR) curves of fabrics obtained by the cone calorimeter are shown in Figure2b. RSR curves follow the trends similar to respective HRR curves. The peak rate of smoke release (PRSR) as well as total smoke release (TSR) data of fabrics are tabulated in. The total smoke release (TSR) is expressed as the smoke obscuration (1 obscura ~10 m human visibility) generated per unit area of the sample and is the cumulative smoke yield at the end of the test. TSR is an indicator of the smoke that is to be generated in a real fire. TSR tends to increase with the increasing polyamide content in the blend. Similarly, PRSR also increased when the PA 6.6 content in the blend was increased. Smoke factor (SmkFct) was proposed as a good indicator of smoke that would be generated by materials in real fire. Smoke factor is calculated as the product of PHRR and TSR, so it takes into account the fact that materials with low PHRR are less likely to burn completely in a fire and cause less smoke to be generated from the ignition of other materials [27; 28]. The calculated SmkFct values are also tabulated in Table 2. Higher SmkFct values were obtained as the content of polyamide in blend increased.

The photographs of fabrics after cone calorimeter tests are shown in Figure 3. Wool burns in an intumescent manner and produces a carbonaceous char which is mainly responsible for its flame retardancy [29]. The % mass losses in the fabrics were the range of 77.1-81.9%.



(a) (b)

Figure 2. HRR (a) and RSR (b) curves of the fabrics obtained by cone calorimeter

Figure 3. Photographs of cone calorimeter residues

3.3. Micro-scale Combustion Calorimetry

The HRR (W·g^{-1}) curves obtained by MCC tests are shown in Figure 4. The THR (kJ·g^{-1}), HRC (J·g^{-1}·K^{-1}), PHRR (W·g^{-1})˒ T$_{PHRR}$ (ºC) values of all tested fabrics as well as the residue (%) at the end of the test are tabulated in Table 3. A single HRR peak was observed at 335.4ºC for R1. A shoulder peak appeared starting from 435 ºC for R2. Compared to R1, the rate of heat release from R2 was higher between 360-520ºC. A secondary HRR peak occurred at 436 ºC in R3 (91.5 W·g-1), possibly due to the degradation of PA 6.6. As a result, THR of the fabrics were increased with the increasing polyamide ratio in blends. On the contrary HRC and PHRR values were decreased. The reduced PHRR (and HRC) of R1 at earlier temperature (335.4 ºC) can be attributed to the availability of more thermal decomposition products of wool at this temperature which could further go through oxidative combustion. In the blended samples (R2 and R3), the amount of wool was reduced therefore less amount of decomposition products were produced at the temperature of first peak of heat release rate. The dependency of peak heat release rate on the sample weight has also been previously reported in the literature [30].

In MCC the char yield decreased in the order R1>R2>R3 and was in the range of 14.9-20.4%. The higher char yields obtained in cone calorimeter compared to those obtained in MCC were attributed to the incomplete pyrolysis/decomposition of samples in cone calorimeter [16].

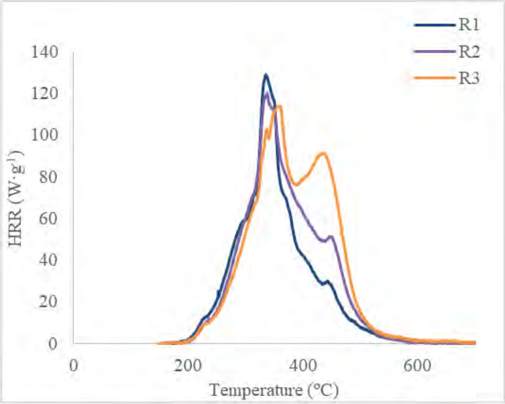


Figure 4. HRR curves of the samples obtained by MCC

3.4. Thermal Analysis

Three main mass loss stages were observed in the oxidative degradation of 100% wool (Figure 5). The first step, which ends before 130ºC is associated to the loss of absorbed water. The pyrolysis of wool takes place at the second step which starts just above 200ºC. The pyrolysis of wool was reported to be endothermic between 200-400 ºC [31]. The rate of mass loss increases until 274ºC and reaches 3.1 wt%/min at this temperature and then decreases. The oxidative destruction occurs at the third step which starts around 440ºC. It was previously mentioned that during the thermo-oxidative decomposition, the processes which occur between 450-600 ºC are highly exothermic[31]. For the blended yarns, another degradation stage was observed starting from 390ºC. This is slightly visible for R2 particularly at low heating rates. However, for R3, the value of mass loss rate reaches 2.1 wt%/min at 432ºC and between 390-465ºC, a weight loss of 13% occurs. This additional stage is assigned to the pyrolytic degradation of PA 6.6. The oxidation of the residue reportedly starts around 450ºC [17]. For the blended yarns, the oxidative destruction begins at higher temperatures for R2 and R3.

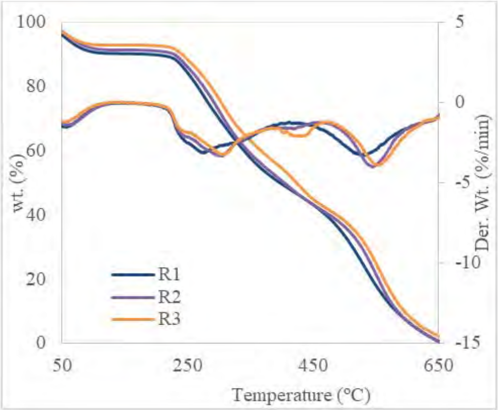


Figure 5. TG/DTG curves of the samples at a heating rate of 10ºC/min

DTG curve from thermal analysis and Gram-Schmidt curve from FTIR were superimposed and the time required for the transfer of evolved gases from the simultaneous thermal analyser to FTIR was calculated for each sample. Accordingly, FTIR results were deconvoluted from time units to temperature units. As shown in Figure 6, below 130ºC, the bands at 1508 cm-1 in FTIR spectra for R1 are associated to the loss of absorbed water in wool. For R1, as early as 238ºC CO_2 (2360 2320cm^{-1}), COS (2071/2048 cm^{-1}) CS_2 (1541/1523 cm^{-1}) and NH_3 (965/930 cm^{-1}) were evolved. In FTIR analysis of R3 (Figure 7), CO_2 did not appear until 260ºC. During the second decomposition step, the maximum rate of mass loss occurred at 274ºC and 304ºC for R1 and R3 respectively. For R1 at 274ºC, the formation of C_2H_3NO (methyl isocyanate) (2256 cm^{-1}) besides CO_2 (2358/ 2310 cm^{-1} accompanied by a smaller band at 669 cm-^{1}), COS (2072 cm^{-1}/2045 cm^{-1}) CS_2 (1541 cm^{-1}), NH_3 (965/ 930 cm^{-1}) were detected. The formation of the bands at 1768/1749 cm^{-1} accompanied by 2972/2936 cm^{-1} may be due to the formation of α-pyrrolidone and C_5H_8O (cyclopentanone) as the decomposition products of R1 and R3. More detailed analysis of organic gases may be required in this aspect. In the FTIR spectra of R3 at 432ºC, the major products detected were CO_2 (2358/ 2310 cm^{-1} accompanied by a smaller band at 669 cm^{-1}), C_2H_3NO (2252 cm^{-1}) and CO (2193/2115 cm^{-1}). The evolution of CO_2 and CO dominates higher temperature region where exothermic reactions take place for all samples.

Table 3. MCC test results

Sample Code	HRC ($J \cdot g^{-1}K^{-1}$)	PHRR ($W \cdot g^{1}$)	THR ($kJ \cdot g^{-1}$)	T_{PHRR} (ºC)	Residue %
R1	132	129.2	13.7	335.4	20.4
R2	122	120.3	15.7	337.8	17.7
R3	117	114.4	18.0	360.0	17.6

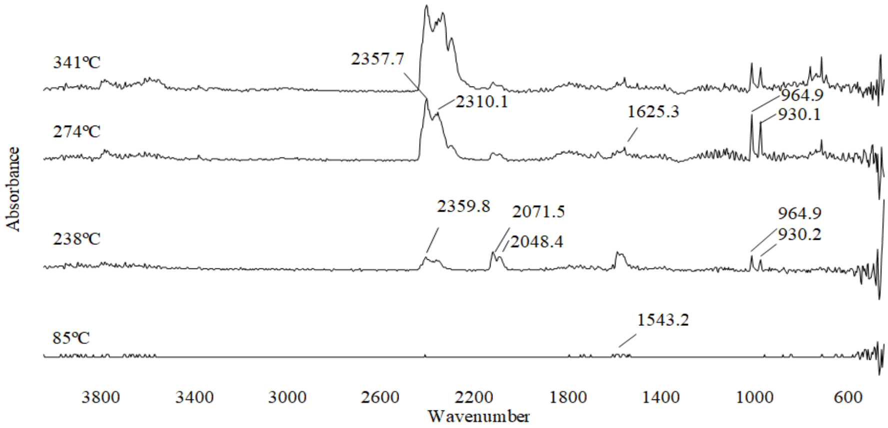


Figure 6. Gas phase FTIR spectra of R1 (β=10 ºC·min^{-1})

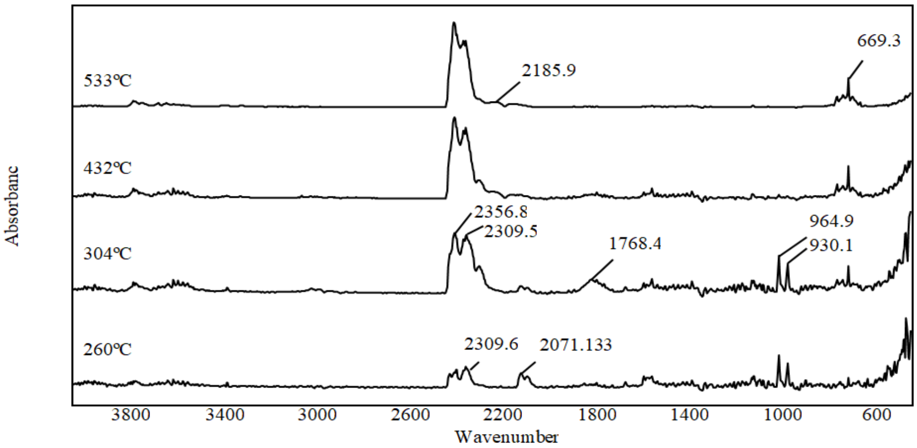


Figure 7. Gas phase FTIR spectra of R3 (β=10 ºC/min)

3.4. Evaluation of Activation Energy

The α vs T curves of samples (Figure 8) shifted towards higher temperature with the increase in heating rate whereas their shape remained consistent within any mass loss region. The activation energy of the samples obtained by Friedman and KAS methods are shown in Figure 9. The activation energies computed by Friedman method have shown a similar trend compared to those computed by KAS methods.

The activation energy of 100% wool (R1) rises within the conversion range 0.1≤α<0.3. The correlation coefficients (R^2) obtained by both Friedman and KAS methods were approximately 0.99 within this range. Therefore, it implies that both methods could be used to investigate the kinetics of this decomposition stage [32]. The values of activation energy computed by Friedman and KAS methods at α=0.3 were 468.6 and 446.4 kJ·mol^{-1} respectively. The activation energy then decreased possibly due to the decomposition of the thermally stable char. The variation in activation energy with respect to conversion can be associated to the multi-stage decomposition in which several mechanisms of decomposition may be present [33]. The activation energy of R2 and R3 have shown different tendencies with the increasing conversion. The activation energy of R2 reached to a maximum at α=0.3 whereas the maximum activation energy was observed at α=0.525 for R3.

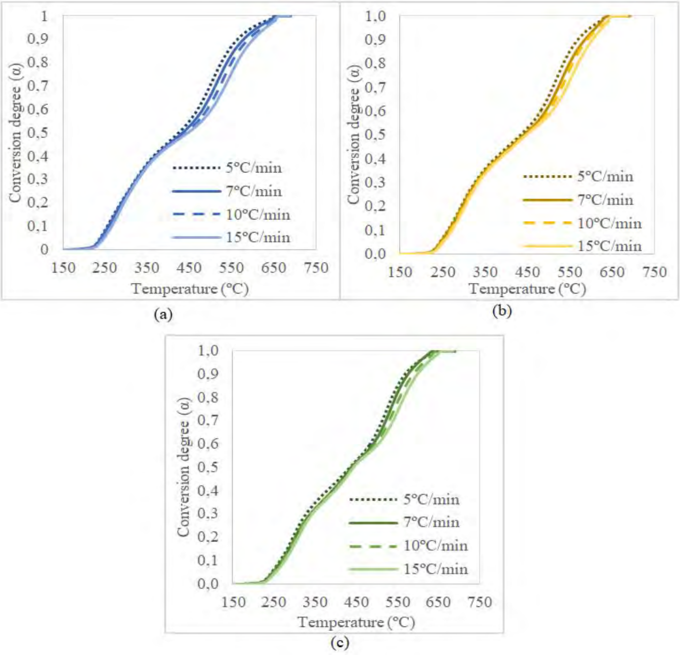


Figure 8. α vs T plots of a)R1, b)R2 and c)R3 at various heating rates

4. CONCLUSIONS

The fire risks and hazards of wool (WO) and wool/polyamide 6,6(PA) blended fabrics were evaluated by means of flame spread, heat release and smoke production. PA is a highly flammable material, therefore, the blends of PA showed poor performance in terms of vertical flame tests. In the cone calorimeter tests the PHRR increased with increasing PA content. A single peak of HRR was observed for 100% wool. When the PA ratio in blend was 21.5 wt.% (R3) two peaks of HRR appeared in MCC. The evolution of this second peak at 436ºC was attributed to the decomposition of PA. Similarly, a second weight loss rate peak was observed at 432ºC in DTG curve of R3. The E_a vs α profile of sample R1 was significantly different than R2 and R3. Therefore, it was concluded that the thermal decomposition behaviour of the wool-polyamide blended fabrics was significantly different than the 100% wool.

Understanding the flammability and thermo-oxidative decomposition behaviour of WO/PA blends will provide a basis for the development of efficient flame retardants for the blended fabrics.

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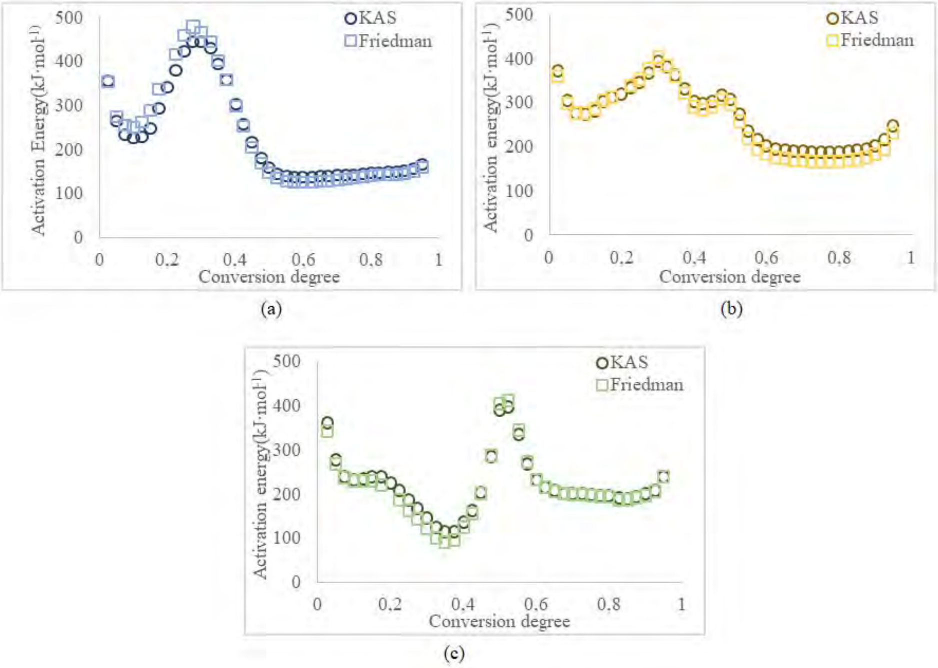

Figure 9. Ea vs α plots of a)R1, b)R2 and c)R3

REFERENCES

1. Horrocks, A. R., Anand, S. C. (Eds.). (2000). *Handbook of Technical Textiles: Technical Textile Applications* (Vol. 2). UK: Woodhead Publishing.

2. Cardamone, J. M. (2013). Flame resistant wool and wool blends. In F. S. Kilinc (Ed.), *Handbook of fire resistant textiles*. UK: Woodhead Publishing Ltd.

3. Horrocks, A. R., Alongi, J. (2013). Fundamental Aspects of Flame Retardancy. In J. Alongi, A. R. Horrocks, F. Carosio ,G. Malucelli (Eds.), *Update on Flame Retardant Textiles: State of the Art, Environmental Issues and Innovative Solutions* (pp. 19-52). Shropshire: Smithers Rapra Technology Ltd.

4. Benisek, L. (1984). *Zirpro Wool Textiles*. Fire and Materials, 8(4), 183-195.

5. Horrocks, A. R., Davies, P. J. (2000). *Char Formation in Flame-Retarded Wool Fibres. Part 1. Effect of Intumescent on Thermogravimetric Behaviour*. Fire and Materials, 24, 151-157.

6. Cheng, X.-W., Guan, J.-P., Chen, G., Yang, X.-H., Tang, R.-C. (2016). *Adsorption and Flame Retardant Properties of Bio-Based Phytic Acid on Wool Fabric*. Polymers, 8(4), 122.

7. Deopura, B. L., Padaki, N. V. (2014). Synthetic Textile Fibres: Polyamide, Polyester and Aramid Fibres. In R. Sinclair (Ed.), *Textiles and Fashion Materials, Design and Technology* (pp. 98-114). UK: Woodhead Publishing.

8. Fukatsu, K. (1990). *Kinetic and Thermogravimetric Analysis of Thermal Degradation of Polychlal Fiber/Cotton Blend*. Journal of Fire Sciences, 8, 194-206.

9. Pereira, C. M. C., Martins, M. S. S. (2014). Chapter 17 - Flame Retardancy of Fiber-Reinforced Polymer Composites Based on Nanoclays and Carbon Nanotubes. In C. D. Papaspyrides ,P. Kiliaris (Eds.), *Polymer Green Flame Retardants* (pp. 551-595). Amsterdam: Elsevier.

10. Janssens, M., Parker, W. J. (2013). Oxygen Consumption Calorimetry. In V. Babrauskas ,S. J. Grayson (Eds.), *Heat Release in Fires* (pp. 31-60). London: Interscience Communications Ltd.

11. Babrauskas, V. (2016). Heat Release Rates. In M. J. Hurley (Ed.), *SFPE Handbook of Fire Protection Engineering* (5 ed., pp. 799-904). New York, NY: Springer-Verlag.

12. Babrauskas, V. (2016). The Cone Calorimeter. In M. J. Hurley (Ed.), *SFPE Handbook of Fire Protection Engineering* (5 ed., pp. 952-980). New York, NY: Springer-Verlag.

13. Yang, C. Q., He, Q., Lyon, R. E., Hu, Y. (2010). *Investigation of the flammability of different textile fabrics using micro-scale combustion calorimetry*. Polymer Degradation and Stability, 95(2), 108-115.

14. Yang, C. Q., He, Q. (2012). *Textile heat release properties measured by microscale combustion calorimetry: experimental repeatability*. Fire and Materials, 36(2), 127-137.

15. Price, D., Liu, Y., Hull, T. R., Milnes, G. J., Kandola, B. K., Horrocks, A. R. (2000). *Burning behaviour of fabric/polyurethane foam combinations in the cone calorimeter*. Polymer International, 49, 1153-1157.

16. Galaska, M., Sqrow, L., Wolf, J., Morgan, A. (2019). *Flammability Characteristics of Animal Fibers: Single Breed Wools, Alpaca/Wool, and Llama/Wool Blends*. Fibers, 7(1), 3

17. ,Apaydin, K., Laachachi, A., Ball, V., Jimenez, M., Bourbigot, S., Toniazzo, V., Ruch, D. (2014). *Intumescent coating of (polyallylamine-polyphosphates) deposited on polyamide fabrics via layer-by-layer technique*. Polymer Degradation and Stability, 106, 158-164.

18. Popescu, C., Vasile, M., Oprea, C., Segal, E. (1992). *A thermogravimetric study of flame-proofed wool*. Thermochimica Acta, 205, 205-211.

19. Vyazovkin, S. (2000). *Computational aspects of kinetic analysis. Part C. The ICTAC Kinetics Project- the light at the end of the tunnel?* Thermochimica Acta, 355, 155-163.

20. Budrugeac, P. (2001). *The evaluation of the non-isothermal kinetic parameters of the thermal and thermo-oxidative degradation of polymers and polymeric materials: its use and abuse*. Polymer Degradation and Stability, 71, 185-187.

21. Vlaev, L., Nedelchev, N., Gyurova, K., Zagorcheva, M. (2008). *A comparative study of non-isothermal kinetics of decomposition of calcium oxalate monohydrate*. Journal of Analytical and Applied Pyrolysis, 81(2), 253-262.

22. Khawam, A., Flanagan, D. R. (2006). *Solid-State Kinetic Models: Basics and Mathematical Fundamentals*. J. Phys. Chem. B, 110, 17315-17328.

23. Vyazovkin, S., Burnham, A. K., Criado, J. M., Pérez-Maqueda, L. A., Popescu, C., Sbirrazzuoli, N. (2011). *ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data*. Thermochimica Acta, 520(1-2), 1-19.

24. Órfão, J. J. M. (2007). *Review and evaluation of the approximations to the temperature integral*. AIChE Journal, 53(11), 2905-2915.

25. Balart, R., Garcia-Sanoguera, D., Quiles-Carrillo, L., Montanes, N., Torres-Giner, S. (2019). *Kinetic Analysis of the Thermal Degradation of Recycled Acrylonitrile-Butadiene-Styrene by non-Isothermal Thermogravimetry*. Polymers, 11(2), 281.

26. Schartel, B., Hull, T. R. (2007). *Development of fire-retarded materials—Interpretation of cone calorimeter data*. Fire and Materials, 31(5), 327-354.

27. Hirschler, M. M. (1992). *Smoke and Heat Release and Ignitability as Measures of Fire Hazard from Burning of Carpet Tiles*. Fire Safety Journal, 18, 305-324.

28. Hirschler, M. M. (1991). *The Measurement of Smoke in Rate of Heat Release Equipment in a Manner Related to Fire Hazard*. Fire Safety Journal, 17, 239-258.

29. Bhattacharyya, D., Subasinghe, A., Kim, N. K. (2015). Natural fibers: Their composites and flammability characterizations. In K. Friedrich ,U. Breuer (Eds.), *Multifunctionality of Polymer Composites Challenges and New Solutions* (pp. 102-143). Oxford, UK: Elsevier.

30. Zhuge, J., Chen, X., Ks, A., Manica, D. P. (2016). *Microscale combustion calorimeter-application and limitation*. Fire and Materials, 40(8), 987-998.

31. Popescu, C., Segal, E., Iditoiu, C. (1995). *A kinetic model for the thermal decomposition of wool*. Termochimica Acta, 256, 419-427.

32. Lian, D., Ren, J., Han, W., Ge, C., Lu, J. (2019). *Kinetics and evolved gas analysis of the thermo-oxidative decomposition for neat PPS fiber and nano Ti–SiO2 modified PPS fiber*. Journal of Molecular Structure, 1196, 734-746.

33. Albano, C., Trujillo, J., Caballero, A., Brito, O. (2001). *Application of different kinetic models for determining thermal stability of PA 66/HDPE blends*. Polymer Bulletin, 45, 531–538.