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# Analytical Assessment of the Thermal Decomposition of Cotton-Modacryl Knitted Fabrics

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## Abstract

*Fabric flammability is affected by various factors such as the fibre composition, fabric construction, FR (flame retardant) finish, oxygen concentration and environmental conditions (moisture content, heat). Inherently FR fabrics are synthetics which have been changed at the molecular level to make the fabrics thermally stable and able to pass FR tests. The thermal properties of knitted fabrics produced from cotton, modacryl and their blends were investigated in this paper. The design of FR knitted fabrics and an optimal blend ratio were evaluated by different thermoanalytical methods: the flame behaviour and thermal stability with the limited oxygen index (LOI), thermal gravimetric analysis (TGA), coupled thermal gravimetry – Fourier transform infrared technique (TG-FTIR) and microscale combustion calorimetry (MCC). Surface characterisation of the knitted fabrics designed was evaluated by the streaming potential method. Knitted fabric in the blend ratio C50:M50 proved to possess the most favourable FR characteristics, additionally confirmed by optimal hydrophilic properties evaluated through zeta potential measurement.*

**Key words:** knitted fabric, modacryl/cotton blend, thermal decomposition, flame retardancy, zeta potential.

Among all textile fibres, cotton is one of the most commonly used in many applications (clothes, bedding, furniture, wall-hangings, etc.). However, it is also one of the most flammable materials. In order to obtain self-extinguishing performance, its LOI must be enhanced to the minimal range from 26 to 28. It should be taken into consideration that all textile materials used in public places must be flame retardant, according to the law. Modacryl is a synthetic copolymer similar to acrylic but with self-extinguish properties and is difficult to ignite. Modacrylic's FR properties are durable and comparable to those of wool. Modacryl is soft, warm, and resilient without a crease tendency. Additionally knitted fabrics are lightweight, flexible and commonly used for fire-fighters' underwear, socks and gloves because of their excellent mechanical and comfort properties [1].

Novel FR textile products should fulfill basic and specific requirements including a negligible and no adverse effect on the textile physical properties. These requirements are the following: retaining the textile aesthetics and physiological properties; being produced by a simple process with conventional equipment and cheap chemicals; and being durable to repeated launderings, tumble dryings, and dry cleaning [2-11].

Despite the focus on the flame retardant property of fire-protective clothing, com-

fort of wear still remains a stringent requirement. A direct measurement of the comfort of wear is not possible, and thus it is commonly assessed by applying test panels. The results of these test panels pertain a qualitative nature. However, it is approved that the comfort of wear correlates with the hydrophilicity of fibres and yarn employed for textile fabrics [12]. The hydrophilicity of material surfaces is obtained by measurement of the water contact angle. While contact angle measurement is straightforward for solid material with a planar surface, the analysis of fibres or even fabrics is made complicated by the shape of fibres and the porous structure of fabrics. The indirect approach for calculation of the contact angle when making use of the capillary forces of knitted fabrics and measuring the water uptake according to Wilhelmly [13] are accepted but subject to significant measurement error. On the other hand, an empirical correlation between the water contact angle and zeta potential at the solid-water interface was reported for polymer systems [14, 15]. The zeta potential of a randomly arranged plug of knitted fabrics is determined by measurement of the streaming potential [16]. This electrokinetic effect arises from the driving force of a pressure difference between both ends of the fabric sample plug, which introduces the advantage of being independent of the fabric structure, with excellent reproducibility being obtained by simply monitoring the hydrodynamic permeability of the fabric plug. The zeta potential is related to the surface charge

## ■ Introduction

Most textile materials are flammable, therefore the application of flame retardants (FR) in finishing becomes necessary in order to ensure a protection level and human safety under many different circumstances. The FR properties of textiles are influenced by material reactive groups, composition, structure, finish, active surface and hydrophilicity, while FR parameters depend on measuring conditions such as oxygen concentration, humidity, heat, air flow etc.

**Table 1.** Characteristics of knitted fabrics produced from cotton, modacryl and their blends.

| No | Label   | Knitted fabric composition | Yarn fineness, tex | Q (surface area), g/m <sup>2</sup> | D (density of course/wale), cm <sup>-1</sup> |
|----|---------|----------------------------|--------------------|------------------------------------|----------------------------------------------|
| 1  | C100    | 100% cotton                | 25                 | 155.00                             | 15/21                                        |
| 2  | C40:M60 | 40% cotton/60% modacryl    | 25                 | 148.57                             | 14/22                                        |
| 3  | C50:M50 | 50% cotton/50% modacryl    | 20                 | 107.24                             | 14/22                                        |
| 4  | M100    | 100% modacryl              | 20                 | 180.00                             | 10/26                                        |

**Table 2.** LOI of cotton, modacryl and their blends.

| Knitted fabric | LOI, % |      |         |         |
|----------------|--------|------|---------|---------|
|                | C100   | M100 | C50:M50 | C40:M60 |
| Course         | 18     | 28   | 32      | 27      |
| Wale           | 18     | 28   | 32      | 27      |

**Table 3.** Calorimetric evaluation of FR behavior of knitted fabrics produced from cotton (C100), modacryl (M100) and their blends (C50:M50; C40:M60). **Note:**  $\eta_c$ : heat release capacity;  $Q_{max}$ : maximum specific heat release rate;  $h_c$ : specific heat release;  $hc, gas$ : specific heat of flammable gases;  $T_{max}$ : temperature at maximum specific heat release rate.

| Parameters                  | Composition |       |         |         |
|-----------------------------|-------------|-------|---------|---------|
|                             | C100        | M100  | C50:M50 | C40:M60 |
| $\eta_c, J(g \cdot K)^{-1}$ | 254.0       | 49.7  | 68.3    | 43.0    |
| $Q_{max}, Wg^{-1}$          | 256.6       | 23.7  | 51.1    | 43.7    |
| $h_c, kJg^{-1}$             | 11.5        | 4.5   | 3.7     | 5.6     |
| $hc, gas, kJg^{-1}$         | 12.27       | 7.61  | 6.76    | 11.61   |
| $T_{1,max}, ^\circ C$       | 358.7       | 255.3 | 259.5   | 262.7   |
| $T_{2,max}, ^\circ C$       |             | 404.4 | 406.4   | 329.1   |
| Residue, %                  | 5.9         | 41.5  | 41.1    | 30.9    |

and informs about the state, quality and properties of macroscopic surfaces within a polar medium. Information about the active solid/liquid interface (i.e. fibre/process liquid) and the macroscopic material's reactivity becomes accessible; the adsorption ability of a material surface can be predicted from the nature of its electrokinetic character [17].

Recently different techniques for textile fabric characterization with some focus on the zeta potential have been reviewed [18, 19]. Most textile materials are negatively charged in neutral aqueous solutions due to specific reactive groups or the preferential adsorption of ions from the bulk solution [20].

Blending natural and synthetic textile fibres should therefore have an impact on the surface charge and hydrophilic/hydrophobic balance [21, 22]. The aim of this research was to study the FR properties of cotton, modacryl and blended knitwear by thermoanalytical and electrokinetic methods, in order to optimise proportions of fibres applied within their blends.

## Material and methods

Characteristics of knitted fabrics composed of cotton, modacryl and their blends selected for analytical assessment of the thermal decomposition and zeta potential determination are shown in *Table 1*.

Different methods were used for characterisation of the optimal proportion of cotton/modacryl blends in order to achieve high effectiveness of FR protection. The limiting oxygen index (LOI) technique provided a quantitative measure for determination of reduced flammability for knitted fabric. It was used for assessing the ease of ignition, which is very important for textile materials. LOI values of the samples were determined according to ASTM D2863 – 10 and presented the maximum percentage of oxygen [O<sub>2</sub>] in an oxygen-nitrogen gas mixture [O<sub>2</sub>] + [N<sub>2</sub>] that will sustain burning a standard sample for a certain time. The LOI values were calculated according to *Equation (1)* [23].

$$LOI [\%] = \frac{[O_2]}{[O_2] + [N_2]} \cdot 100 \quad (1)$$

A microscale combustion calorimeter (MCC) was applied for thermal characterisation of the knitted fabrics' FR behavior. Measurement was performed using an MCC-2 micro-scale combustion calorimeter (Govmark, USA) according to ASTM D7309-2007. The sample thus prepared, approximately with a mass of 5 mg, was heated to a specified temperature using a linear heating rate of 1 °C/s in a stream of nitrogen with a flow rate of 80 cm<sup>3</sup>/min. The thermal degradation products were mixed with a 20 cm<sup>3</sup>/min stream of oxygen. Each sample was run in three replicates and the data presented here are averages of the three measurements.

Thermogravimetric analysis (TGA) was carried out using a Pyris 1 TGA (Perkin Elmer, USA). The sample weight was adjusted to 5-6 mg and the experiment was conducted in air atmosphere. All samples for TGA were analyzed in a temperature range from 30 °C to 850 °C in a continuous air or nitrogen flow. The temperature was increased at a rate of 30 °C/min.

The TGA was connected to a Fourier transform infrared spectrometer (FT-IR) with a TG-IR interface. Evolution profiles of different compounds were tracked by FTIR. The combination of TGA with FTIR allowed analysis of the nature of the gaseous product formed in the TGA and its online monitoring. Nitrogen, which does not exhibit IR-absorption, was used as the purge gas and air as the reaction gas, thus the end-products of the decomposition were pyrolyzed rather than oxidative degraded products. FT-IR spectra were acquired throughout the run at a temporal resolution of 4 seconds and spectral resolution of 4 cm<sup>-1</sup>. A Thermal Analysis Gas Station (TAGS) equipped with a detector was used for the FT-IR analysis. The transfer line, high-temperature flow cell, and TG interface were kept at 280°C for the duration of the run to prevent sample condensation. The evolved gases were transferred through the FT-IR flow cell by a peristaltic pump at a flow rate of 60 cm<sup>3</sup>/min.

The zeta potential was determined by measurement of the streaming potential (SurPASS, Anton Paar, Austria). The streaming potential is generated by the flow of an aqueous solution across a permeable plug of knitted fabric that is driven by the pressure difference applied between both ends of the fabric plug. The change of the streaming

potential with differential pressure, i.e., the streaming potential coefficient  $dU_{str}/d\Delta p$ , is then related to the zeta potential according to [22].

$$\zeta = \frac{dU_{str}}{d\Delta p} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \kappa_B \quad (2)$$

with  $\eta$ ,  $\varepsilon \times \varepsilon_0$  and  $\kappa_B$  being the dynamic viscosity, dielectric constant and electrical conductivity of the aqueous solution. For each measurement, 300 mg of the fabric sample were mounted in a glass tube (14 mm inner diameter) and compressed by the proprietary mechanism of the measuring cell. The packing density, and thus the hydrodynamic permeability, of the fabric sample were controlled by measurement of the pressure difference and corresponding volume flow rate of the aqueous solution. The zeta potential was determined in the presence of an aqueous 0.001 mol/l KCl solution at different pH. The electrolyte pH was adjusted with 0.1 mol/l HCl and 0.1 mol/l NaOH, respectively. The reproducibility of the zeta potential was evaluated by the subsequent measurement of three individual samples for each knitted fabric.

## Results and discussion

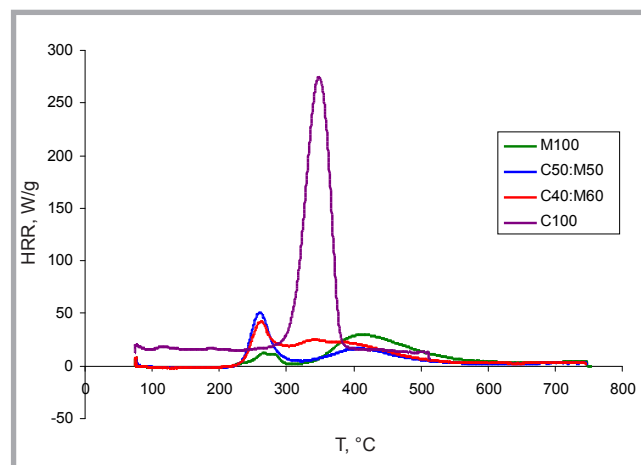
Results of Limited Oxygen Index (LOI), a convenient parameter for measuring the minimum oxygen concentration necessary for combustion, are presented in *Table 2*.

Knitted fabric with a blend ratio of C50:M50 proved to possess better FR characteristics (LOI 32%) compared to the sample with higher modacryl content C40:M60 (LOI 27%) or even the pure modacryl fabric (LOI 28%). An increase in the modacryl component in the blend resulted with an LOI decrease.

A microscale combustion calorimeter (MCC) was applied for characterisation and a more detailed explanation of the FR behaviour of cotton, modacryl and their blends, the most relevant parameters of which are presented in *Table 3*.

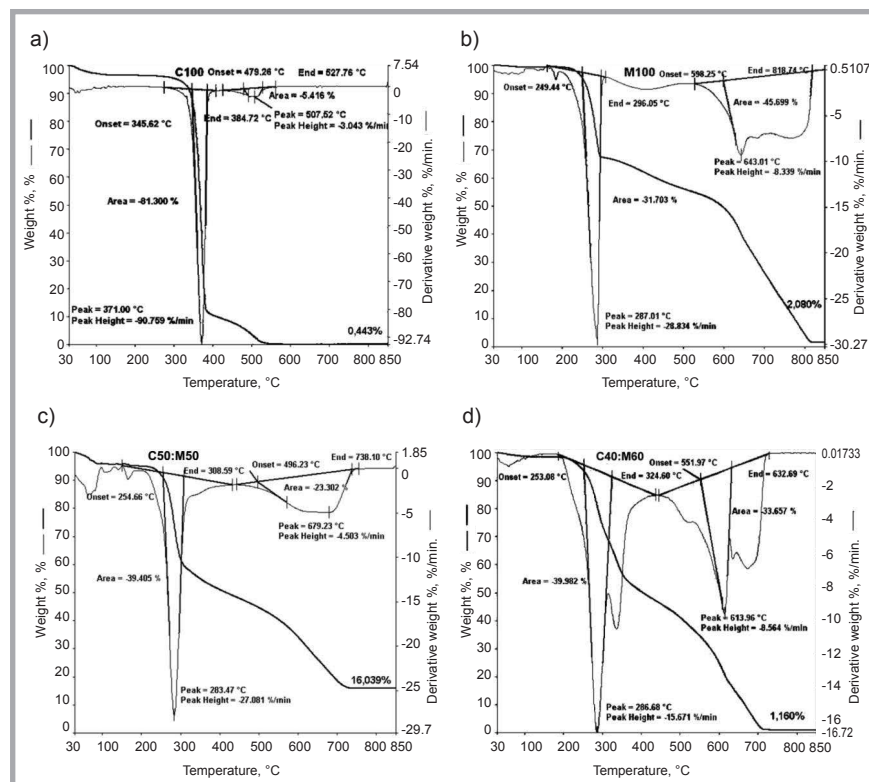
Pure modacryl knitted fabric (M 100) shows the greatest heat released rate  $23.7 \text{ Wg}^{-1}$  at a temperature of  $404 \text{ }^\circ\text{C}$ . For blends C50:M50 and C40:M60, larger heat released rates of  $51.1$  and  $43.7 \text{ W/g}$  were observed at lower temperatures of  $259.5$  and  $262.7 \text{ }^\circ\text{C}$ . At these temperatures, where  $Q_{max}$  is achieved, samples undergo pyrolytic decomposition and

**Figure 1.** Curves of knitted sample heat release rate (HRR) vs temperature.

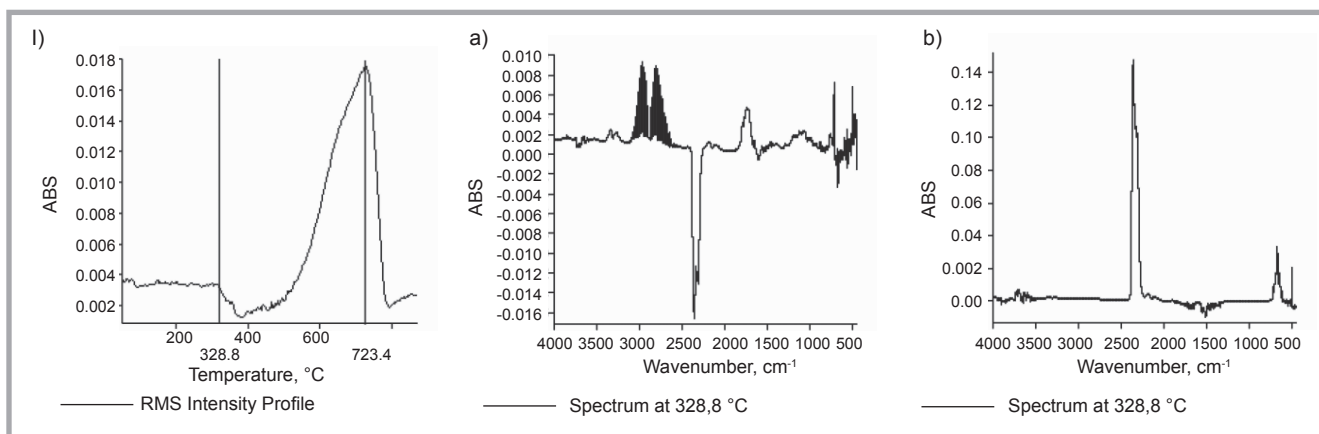


the combustion of gaseous products occurs, while at temperatures of  $406.4$  and  $329.1 \text{ }^\circ\text{C}$  a smaller heat released rate is recorded,  $16$  and  $23.8 \text{ Wg}^{-1}$  respectively, indicating greater thermal stability with respect to knitted fabric of pure cotton and modacryl (*Figure 1*). The modacryl component in a blend with cotton limits the spread of fire by replacing oxygen around the flame with other gases that do not burn. For the synergistic effect of a modacryl and cotton blend, which is important for achieving high resistance to flame, it is necessary to determine the best ratio of individual components [24]. From the results shown in *Table 3*, we

can conclude that sample C50:M50 has the lowest specific heat release, and the specific heat of flammable gases was also the lowest compared to other samples measured. The low value of maximum specific heat released at a temperature of around  $400 \text{ }^\circ\text{C}$  and the high percentage of residues indicate the achievement of extremely high thermal stability of sample C50:M50. The high values obtained of LOI for sample C50:M50 (LOI 32%) can be confirmed by the results obtained in the analysis of the MCC. The effect of the modacryl component on the thermal stability of the cotton/modacryl blends was investigated with TGA.



**Figure 2.** TG and DTG curves of knitted fabrics: a) C100, b) M100, c) C50:M50, d) C40:M60. The char residue is given as % of the initial sample weight.



**Figure 3.** TG-IR analysis of cotton/modacryl blend (C50:M50) during thermooxidative decomposition: l) Intensity profile FTIR spectra of gas evolved: a) FTIR spectra of gas evolved at 328.8 °C, b) FTIR spectra of gas evolved at 723.4 °C.

From the first derivation of the mass change curve it is possible to determine the temperature at which the degradation rate is the highest, thus defined as the degradation point. **Figure 2** shows the TG and DTG (the first derivative of the TG curve) curves of knitted cotton, modacryl and blends thereof in air atmosphere. The cotton sample (C100) undergoes a major weight loss in the temperature range of 345–385 °C due to thermal decomposition of the organic compound. A minor degradation step occurred in the second temperature range of 480–530 °C due to oxidation of the residue formed during thermal decomposition, as presented in **Figure 2.a**. The char residue of C100 was 0.443%. The modacryl knitted fabrics (M100) had different trends of thermal degradation, which were not as rapid as in the case of pure cotton, as shown in **Figure 2.b**. The shape of DTG curves indicated a two step degradation, the first in the temperature range of 249–296 °C and the second in the range of 598–818 °C, shown in **Figure 2.a**. The two step degradation of M100 polymer is explained by the formation of acrylic and modacrylic (halogen containing) components in a ratio of approx. 60:40 wt%. Halogens contained in modacryl act on the principle of radical reaction, while the acrylic component works on the principle of char formation [25].

It can be noticed that cotton/modacryl blends, **Figures 2.c** and **2.d**, had more char residues than pure cotton. Comparison of the knitted blends' DTG curves indicated two step degradation processes. The first step in the thermal decomposition of blend fabrics in both ratios was recorded at a lower temperature than the

first step in the decomposition of pure cotton fabric with significant sample weight loss at % min<sup>-1</sup> (e.g. 91%/min for C100, 29%/min for M100, and 27%/min for C50:M50, 16% C40:M60).

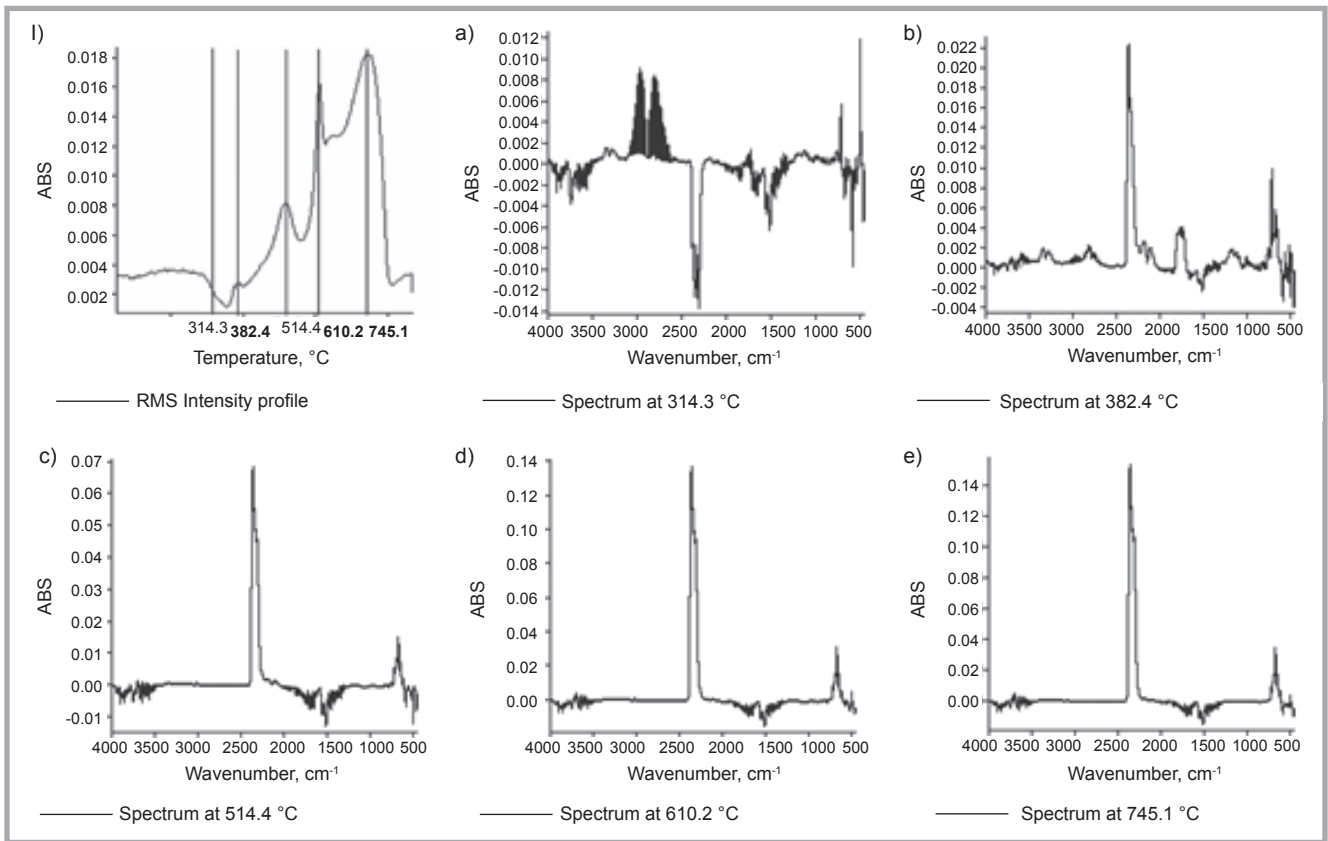
**Figures 2.a-2.d** clearly show the impact of the modacryl component in a blend with cotton on FR durability. The slope of the TG curve of C50:M50 is different compared to the other TG curves. Significant differences between cotton knitted fabrics and their blends were noticed in the initial decomposition temperature and final char residue. These parameters can be directly related to the FR properties of knitted fabrics. The initial decomposition of cotton (C100) starts at 345 °C and of modacryl (M100) at 249 °C while C50:M50 blends decompose at 255 °C and C40:M60 at 253 °C. The hydrophobic nature of modacryl caused earlier decomposition of modacryl-containing fabrics, since the moisture regain of modacryl fibres is within the range 3.0–3.5%. The char yield of samples analysed at 850 °C indicated a much higher value of 16.039% for the blend of modacryl with cotton (C50:M50 samples) compared to the pure cotton (0.443%) and modacryl (2.080%). Results of the knitted fabric samples: cotton, modacryl and their different ratio blends were subjected to TGA/FT-IR analysis, as shown in **Figures 3-4**.

It was previously determined [26] that specific volatilised products formed during the thermal degradation of cotton were identified as CO<sub>2</sub> (characteristic peaks at 2359 and 2322 cm<sup>-1</sup>), volatilised water (characteristic peaks at 1550 and 1566 cm<sup>-1</sup>), aldehyde (characteristic peaks at 2951 and 1184 cm<sup>-1</sup>) and car-

bonyl compounds (characteristic peak at 1500 cm<sup>-1</sup>). The peak registered at 1050 cm<sup>-1</sup> indicates the formation of levoglucosan, confirming a complete degradation of cellulose.

In the case of the C50:M50 blend, the first high intensity of evolved gases was observed at a temperature of 328.8 °C (**Figure 3.a**). In this area, toxic gases HCN (3200–3300 cm<sup>-1</sup>) and HCl (2600–3100 cm<sup>-1</sup>) were recorded for the first time, but it is important to stress that the amount of these gases was low (**Figure 3**). Further intensity of evolved gases was recorded at a temperature of 723.4 °C (**Figure 3.b**). Gases identified were CO<sub>2</sub> (characteristic peaks at 2359 and 2322 cm<sup>-1</sup>) and carbonyls (peaks at 2179 and 2110 cm<sup>-1</sup>). DTG curves, presented previously in **Figure 2.c**, determined the temperature of maximum evolved gases which corresponded with the temperature of second degree decomposition. Gases detected at relatively low temperatures indicate an initial decomposition of modacrylic within the blend (**Figures 3.a, 3.b**). The TG curve of C50:M50 (**Figure 2.c**) confirms the influence of non-combustible gases developed during the initial modacryl decomposition upon decreased decomposition of the cellulose component.

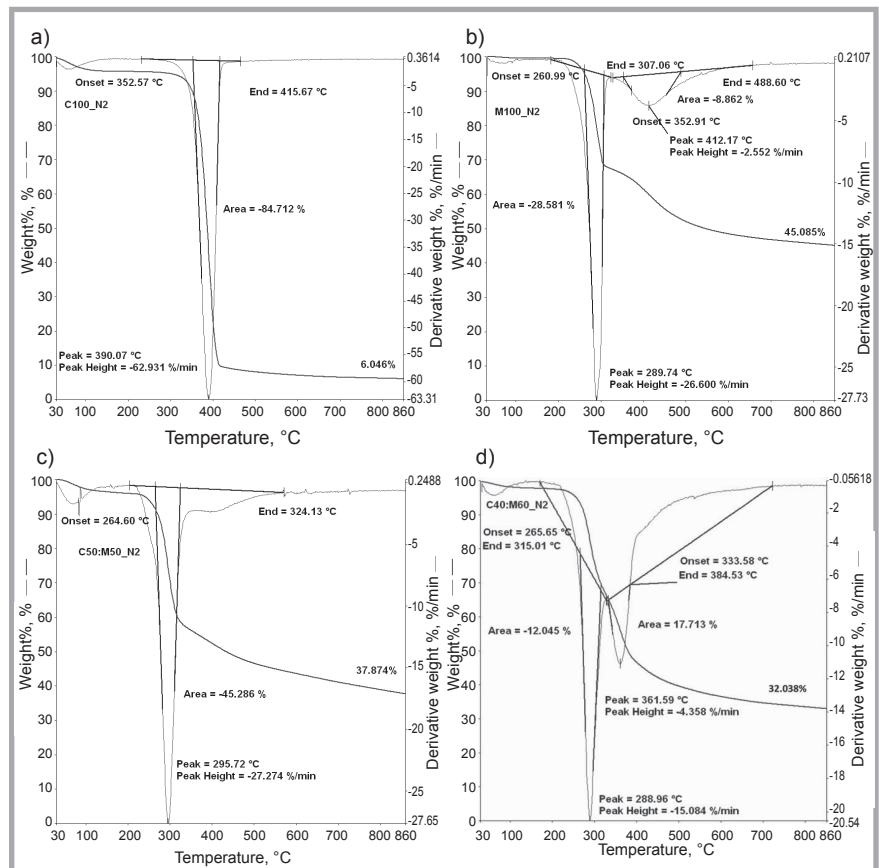
TG-IR analysis of the modacryl:cotton blend (C40:M60) during thermooxidative decomposition is shown in **Figure 4**. The initial step of thermal decomposition of the blend resulted with similar peaks as in the case of the cotton sample (**Figure 2.a**), but thermal degradation of the blend had started at lower temperature (253.08 °C) as compared to cotton (350 °C). This behaviour is typical for



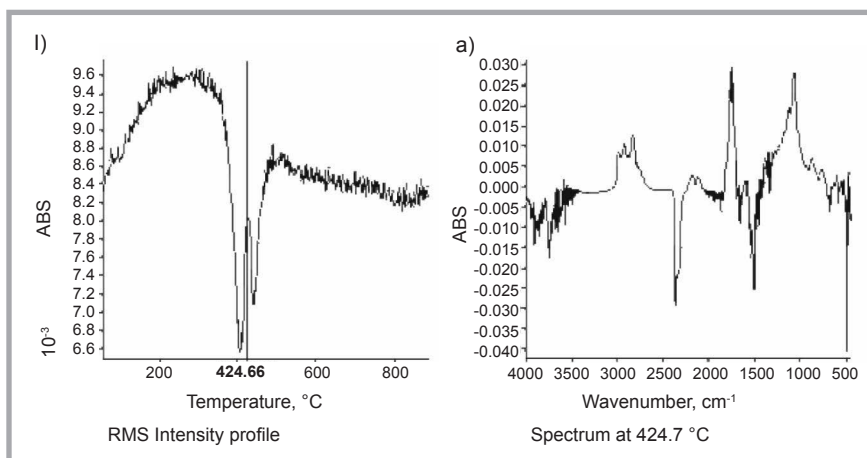
**Figure 4.** TG-IR analysis of modacryl/cotton blend (C40:M60) during thermooxidative decomposition: l) Intensity profile FTIR spectra of gas evolved, a) FTIR spectra of gas evolved at 314.3 °C, b) FTIR spectra of gas evolved at 382.4 °C, c) FTIR spectra of gas evolved at 514.4 °C, d) FTIR spectra of gas evolved at 610.2 °C, e) FTIR spectra of gas evolved at 745.1 °C.

FR materials. Further heating caused five absorption maxima of evolved gases at a temperature of 314.3 °C (Figure 4.a), 382.4 °C, (Figure 4.b), 514.4 °C (Figure 4.c), 610.2 (Figure 4.d) and 745.1 °C (Figure 4.e). The gaseous products of HCN and HCl were recorded at temperature 314 °C, that is within an area in which there had been maximum degradation of sample C40:M60, seen in Figure 2.a. In addition, the occurrence of toxic HCN gas is visible at 382° C but in a lower intensity (Figure 2.b). Peaks CO<sub>2</sub> (characteristic peaks at 2359 and 2322 cm<sup>-1</sup>) and CO (peaks at 2179 and 2110 cm<sup>-1</sup>) (Figures 4.c, 4.d and 4.e) were identified at high temperature [27]. The highest amount of the gas recorded was observed at a temperature of 745 °C, where the sample was completely decomposed, as proven by the TG and DTG curves, shown in Figure 2.e.

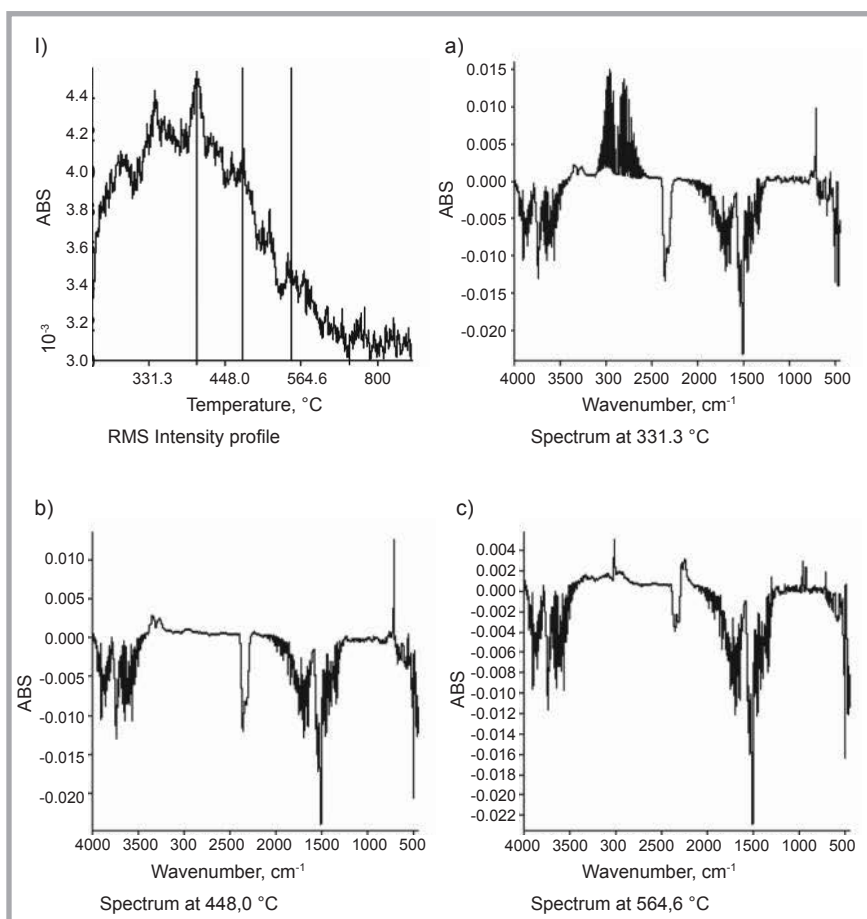
In order to better investigate the impact on modacryl when reducing the flammability of cotton, thermogravimetric analysis of the samples was carried out in nitrogen. Figure 5 shows the TG and DTG curves of knitted fabrics after non-linear pyrolytic degradation in nitrogen atmosphere.



**Figure 5.** TG and DTG curves of knitted fabrics measured in nitrogen atmosphere: a) C100, b) M100, c) C50:M50, d) C40:M60.



**Figure 6.** TG-IR analysis of cotton during pyrolytic decomposition in nitrogen atmosphere: l) Intensity profile FTIR spectra of gas evolved, a) FTIR spectra of gas evolved at 424.7 °C.



**Figure 7.** TG-IR analysis of modacryl (M100) during decomposition in nitrogen atmosphere: l) Intensity profile FTIR spectra of gas evolved, a) FTIR spectra of gas evolved at 331.3 °C, b) FTIR spectra of gas evolved at 448.0 °C, c) FTIR spectra of gas evolved 564.6 °C.

The char residue is given as % of the initial sample weight. Thermograms of all samples in nitrogen atmosphere reveal complementarity with the HRR value obtained by MCC analysis, meaning that the temperatures of the thermal decomposition of DTG curves is similar to that

at the maximum specific heat release rate ( $T_{max}$ ), presented in **Table 3**. The value of specific heat of flammable gases (hc), presented within **Table 3** is expected due to the combustion in nitrogen atmosphere. The lowest value of hc (6.76 kJ/g) was measured for sample C50:M50, where-

as the highest value (12.27 kJ/g) measured was for the cotton (C100) sample. An increase in the modacryl component within the blend does not have a significant influence on the hc value, supporting our data that the optimal blend ratio is C50:M50. The blend proposed possesses better thermal stability performance compared to the M100 sample. Additionally the composition of gaseous products during thermodynamic degradation in nitrogen atmosphere is an important value. Combustion products are the main cause of deaths in fire accidents.

**Figures 6-9** presents TG-IR spectral curves of all samples measured in nitrogen flow. The adsorption intensities of gas products, presented in **Figure 6.I**, and gasses developed at this temperature (**Figure 6.a**) revealed that the decomposition of cotton occurred at 424 °C, due to pyrolytic gasses composed of ethan (3000  $cm^{-1}$ ), CO, hydrocarbons and levoglucosan. The pyrolytic degradation of M100, **Figure 7**, revealed a much lower absorption maximum in comparison with the cotton sample, supporting the fact of the better thermal stability of modacryl. **Figures 7.a, 7.b** and **7.c** present degradation gasses at 331.3 °C, 448.0 °C and 564.6 °C, giving evidence of the presence of HCN (3200-3300  $cm^{-1}$ ) and HCl (2600-3100  $cm^{-1}$ ). Both gasses are extremely poisonous, and even very low temperatures can cause severe damage to human health.

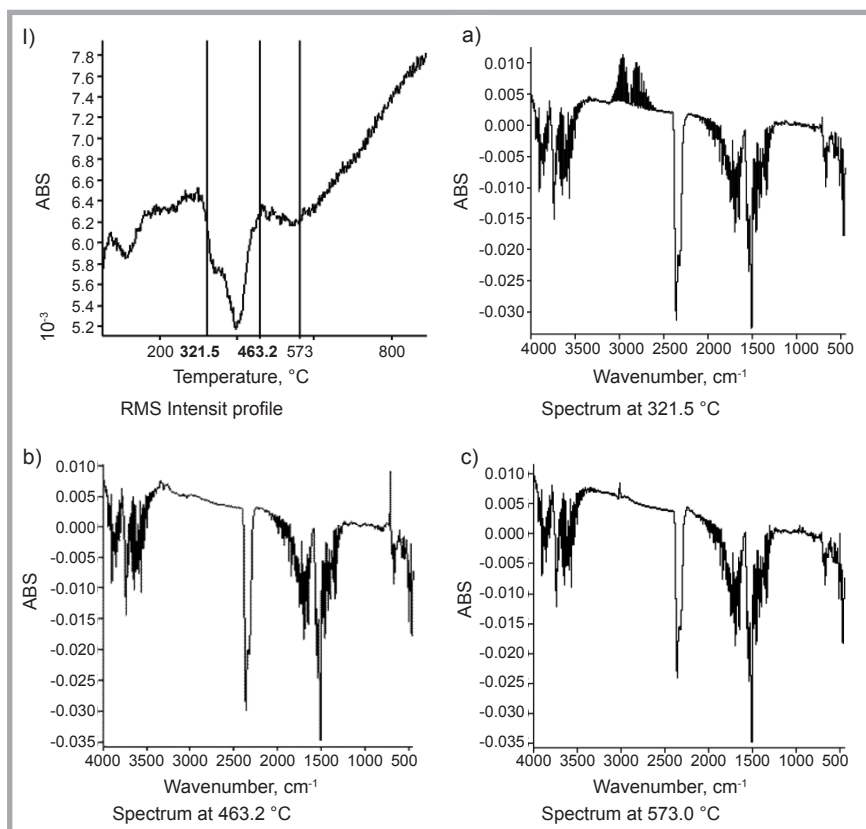
Comparison of TG-IR results of both modacryl/cotton blends (**Figure 8** and **9**) revealed much better results in the case of the C50:M50 blend. The highest intensity of thermal degradation in nitrogen flow was measured for sample C40:M60 at 463.22 °C, owing to HCN and CO gasses. This intensity shows a slight increase in the value, in comparison to the modacryl sample (**Figure 7**). Pyrolytic degradation of the C50:M50 sample, shows that the gaseous products developed give strong evidence of a lower gas quantity in comparison with both 100% cotton and C40:M60. The key issue is the low amount of poisonous HCN and HCl gasses in the case of the C50:M50 mixture, which is the major advantage of this particular blend ratio, as seen in **Figures 9.a, 9.b** and **9.c** [27-29].

**Figure 10.a** shows the pH dependence of the zeta potential for cotton-modacryl knitted fabrics with different bulk composition. Such titration curves contain in-

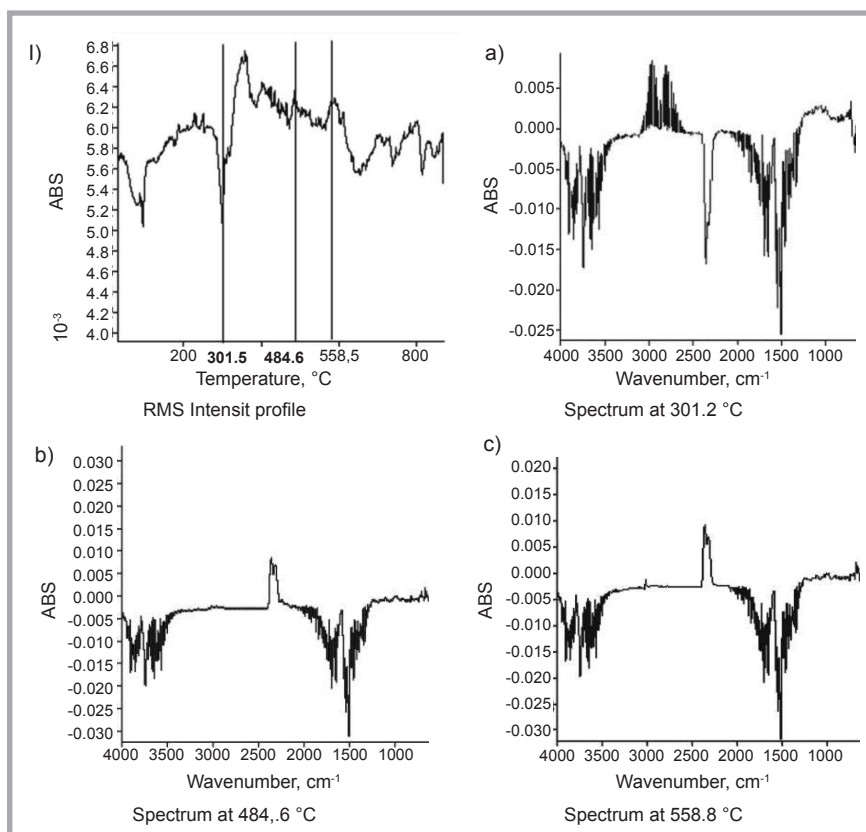
formation about the charge (represented by the sign of the zeta potential) that is generated at the fabric-water interface in contact with an aqueous solution. They provide further information about the surface chemistry indicated by the isoelectric point (IEP, i.e., the pH of the aqueous solution at which the zeta potential vanishes). A detailed analysis of the titration curve also informs about possible swelling effects which are expected for hydrophilic fibres with an open structure, such as cotton [30].

The pH dependences of the zeta potential in **Figure 10** clearly distinguish between knitted fabrics made of pure cotton (C100) and pure modacryl (M100). Interestingly the IEPs for both materials are found at pH 2.5. While an IEP in the acidic range is common for bleached cotton due to the presence of carboxylic acid groups [31], the deviation of the IEP from pH 4, which is expected for a pristine polymer surface [32], to lower pH also confirms the presence of such acidic functional groups in the modacryl fabric. However, the difference in the negative zeta potential between modacryl and cotton fabrics at a pH above the IEP is most striking. The main reason for the more negative zeta potential for modacryl as compared to cotton is the different mechanism of charge formation at the fibre-water interface for the material surfaces. In the presence of a significant surface concentration of functional groups, a surface charge is introduced by the dissociation of acidic and basic groups like hydroxyl and carboxylic acid groups of cotton. If surface functionality is reduced or even absent, the interfacial charge is dominated by the accumulation of water ions, hydroxide (OH<sup>-</sup>) and hydronium (H<sub>3</sub>O<sup>+</sup>) [33]. If functional groups are missing, the surface behaves hydrophobically and its water repellence drives the replacement of interfacial water molecules observed by charged ions (assuming that impurities such as surfactants are not present in the aqueous solution). On the other hand, surface functional groups render the material surface hydrophilic, and (neutral) water molecules strongly determine the composition of the charged solid-water interface. In addition, hydrophilic surfaces such as cotton tend to swell in water, which reduces the (negative) zeta potential further due to the shift of the shear plane at the solid-water interface [34].

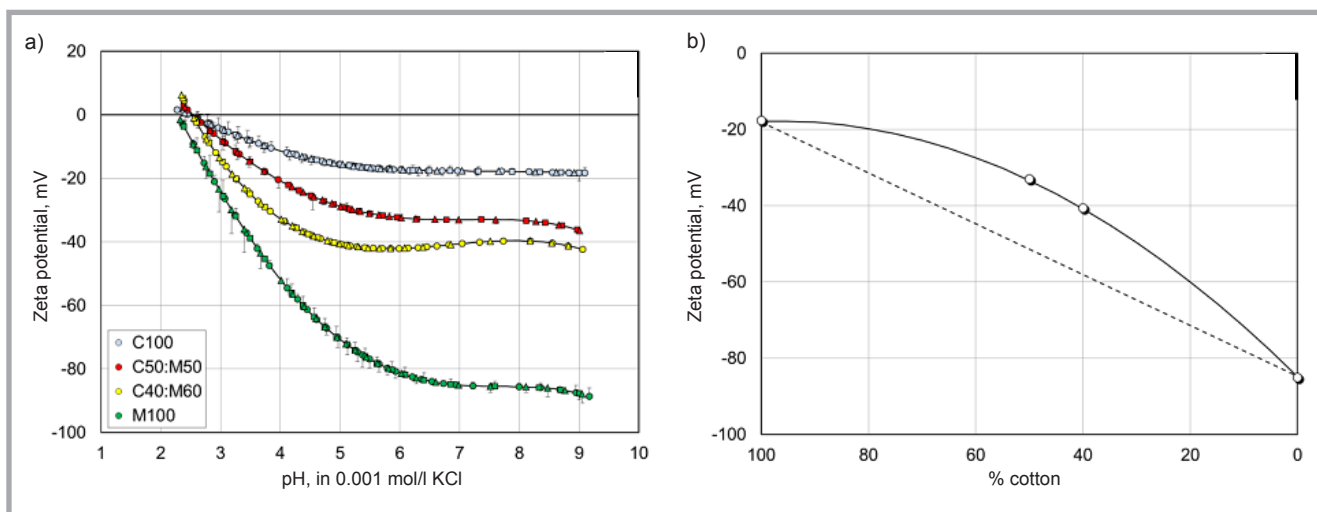
The blended knitted fabrics made by a combination of cotton and modacryl



**Figure 8.** TG-IR analysis of modacryl/cotton blend (C40:M60) during decomposition in nitrogen atmosphere: 1) Intensity profile FTIR spectra of gas evolved, a) FTIR spectra of gas evolved at 321.5 °C, b) FTIR spectra of gas evolved at 463.2 °C, c) FTIR spectra of gas evolved 573.0 °C.



**Figure 9.** TG-IR analysis of modacryl/cotton blend (C50:M50) during decomposition in nitrogen atmosphere: 1) Intensity profile FTIR spectra of gas evolved, a) FTIR spectra of gas evolved at 301.2 °C, b) FTIR spectra of gas evolved at 484.6 °C, c) FTIR spectra of gas evolved 558.8 °C.



**Figure 10.** a) Zeta potential of knitted fabrics with different compositions produced from cotton and modacryl yarn. The error bars indicate the deviation between the zeta potential at individual pH and the average zeta potential obtained for a series of measurements of three fabric plugs (○ sample 1, □ sample 2, △ sample 3), b) Dependence of the zeta potential at pH 7 on the fabric composition.

exhibit a zeta potential in between those of C100 and M100. The negative zeta potential decreases in the series M100 > C40:M60 > M50:C50 > C100. An obvious trend of a decrease in the negative zeta potential with an increasing content of cotton is thus observed. For a combination of different materials inside the measuring cell, streaming potential measurement gives the average zeta potential with a contribution of each material surface. For preparation of the knitted fabrics, cotton and modacryl were blended according to the weight of the individual yarns. When plotting, e.g., the zeta potential at pH 7 against the weight composition of the blended knitted fabrics (**Figure 10.b**), we observe, however, a deviation between the zeta potential observed and expected when assuming an equal contribution [35]. The negative zeta potential data of the blended fabrics are shifted to less negative values, i.e., in favour of the cotton fabric. The significantly higher surface area of cotton as compared to modacryl thus introduces a dominating effect of cotton on the zeta potential of the blended fabrics.

As a consequence of the zeta potential analysis, we observe that blended fabric C50:M50 shows a similar zeta potential as compared to the purely cotton fabric despite the equal (weight) contributions of cotton and modacryl yarns. We conclude that the hydrophilicity of fabric C50:M50 is significant, thus satisfying the requirement for the comfort of wear.

## Conclusions

Untreated cotton knitted fabric, characterized by a low LOI (18%) and high heat release rate ( $256.0 \text{ Wg}^{-1}$ ), is a hazardous and inconvenient material for FR protection. The residue after its combustion is approx. 1%. Modacryl knitted fabric is well known FR material with an LOI value of 28%. Its heat release rate is lower than in the case of cotton material, but still quite high ( $23.7 \text{ Wg}^{-1}$ ). Residue is 41.5%, contributing to the fact that modacryl based materials will be less damaged after thermal combustion. The LOI of a blended knitted fabric in ratio C40:M60 is determined as 27%. The cotton component in a blend with modacryl reduced the LOI by 1% in comparison to modacryl knitted fabric. The blend ratio of C50:M50 proved to possess the most favourable FR characteristics (LOI 32%). This ratio proved to be the best since a synergistic effect occurred between the components, contributing to high flame resistance. TG curves confirmed the assumption of improved FR properties of cotton modacryl blends compared to pure cotton. It can be noticed that cotton/modacryl blends have more char residues than pure cotton. The shape of DTG curves of the knitted blends showed a two step degradation process. The first step of thermal decomposition of cotton/modacryl blends was recorded at a lower temperature in comparison to cotton fabric.

TGA/FT-IR analysis of cotton, modacryl and their blends identified HCN,

HCl,  $\text{CO}_2$  and CO as characteristic toxic products. Their intensity was quantified very precisely during the thermooxidative decomposition. The volatilised products, HCN and HCl, observed during the degradation of the C40:M60 blend in an air or nitrogen stream were recorded at lower temperatures, while  $\text{CO}_2$  and CO were recorded at higher temperatures. In the case of the modacryl/cotton C50:M50 blend, the intensity of toxic evolved gases was observed at lower temperatures (at  $328.8 \text{ }^\circ\text{C}$  for the sample analysed in air or at  $301.2 \text{ }^\circ\text{C}$  for the sample analysed in the nitrogen stream). Through the further process of thermal decomposition, the intensity of gas evolved decreases, which is of great importance for FR materials. The results of the optimal ratio of modacryl and cotton in the blend presented lower values of harmful gases during thermooxidative decomposition (0.14) compared to both the cotton (0.30) and modacryl (0.40) fabrics.

Analytical assessment revealed the most favorable FR properties of modacryl/cotton blend at a ratio of C50:M50. This ratio has a smaller second HRR peak ( $16 \text{ Wg}^{-1}$ ) at  $406 \text{ }^\circ\text{C}$  than sample M100 ( $23.8 \text{ Wg}^{-1}$ ) at  $329 \text{ }^\circ\text{C}$ , indicating the high thermal stability of sample C50:M50, caused by the synergistic action of components due to the lowest amount of combustible gases. MCC values of hc ( $3.7 \text{ kJg}^{-1}$ ) and hc gas ( $6.76 \text{ kJg}^{-1}$ ) are the lowest in comparison with all samples applied. This particular blend has a sufficient LOI value (32%), specific for the group of self-extinguishing materials.



The TG curve is characterised by slower 2 step thermal degradation, where the char yield is 16.039% at a temperature of 850 °C.

Titration curves of the zeta potential proved asignificant impact of the modacryl component in the blend with cotton, specified through more negative surface charge in the whole pH. The advantage of the modacryl and cotton blend (C50:M50) was confirmed by optimal hydrophilic properties evaluated with zeta potential measurements.



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