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**Mechanical and Thermal Behaviors of First Choice, Second Choice and Recycled P-Aramid Fibers**

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**ABSTRACT**

*The paper reports cutting, abrasion, fire and thermal behavior of different para-aramide fibers. Different qualities of p-aramid fibers were evaluated: first choice fibers (Kevlar®), second choice fibers and recycled fibers. Despite of a very different cost, some properties (cutting and thermal behavior) remain very close and do not depend on the quality of the fibers. In the other hand, the different processes, to produce those fibers, make some difference in terms of behavior, which can cause damage, especially for protective clothing.*

***Keywords.*** *Aramid, recycled-aramid, protective clothing, cutting, abrasion, flame retardant.*

## I- Introduction.

The market of protective clothing is growing in many fields such as flame and heat-resistant clothes, cut-resistant-gloves, bullet-resistant vest... Textile used in individual protection has brought lightness, flexibility and durability, and is an ideal compromise between comfort and protection. In addition to protection, comfort is one of the most important features for such garments because without basic comfort, people dare to take off the clothing and so, risk is increased.

High performance fibers have been developed to provide properties such as high operating temperature, heat resistance, flame retardancy chemical resistance and tensile strength (1) (2). P-aramide fibers are the first high performance fibers launched on the market. They were discovered in the 1970s,

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by researchers at DuPont. They reported that the processing of extended chain all para-aromatic polyamides from liquid crystalline solutions produced ultrahigh strength, ultrahigh modulus fibers (3), (4)(5). The greatly increased order and the long relaxation times in the liquid crystalline state compared in conventional systems led to fibers with highly oriented domains of polymer molecules. The most common lyotropic aramid fiber is poly(p-phenylene terephtalamide) (PPTA) (see chemical structure on Figure 1) which is marketed as Kevlar by DuPont or as Twaron by Teijin (formerly developed by Akzo).

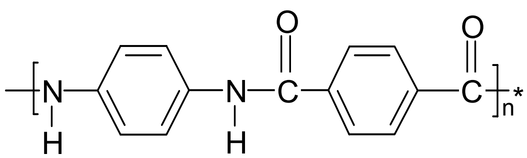

**Figure 1: Chemical structure of PPTA fibers**

The conventional market for PPTA is body armour, cables and composites for sports and space applications (3). The continuous operating temperature of PPTA is up to 190°C. PPTA degrades in air above 400°C and does not melt below this temperature. During ignition, PPTA does not melt but glows. It is observed no after burning after removal of flame. PPTA yields char above 450°C. The limiting oxygen index (LOI measured according to NF G 07-128) for PPTA fabrics lies between 28 and 30 vol.%. PPTA fibers are widely used in technical applications, especially in protective clothing, but because of their higher cost compared to natural fibers and traditional synthetic fibers (Nylon, polyester…) manufacturers are looking for cost's reduction (6). For this purpose, the processes of textile transformation can be improved and optimized; blends have been already investigated in many fields in this aim : Cotton, polyester and wool fibers in a triblended fabrics for FR (Flame Retardant) applications, Wool/HMPE (High modulus polyethylene) for cutting applications (8), Wool/PPTA for thermal applications (9).



An other way to decrease prices is also to use less expensive fibers. In this last case, several alternatives are conceivable, namely, the substitution of pure p-aramid fibers by second choice p-aramide fibers or recycled p-aramide fibers. The cost of 2$^{nd}$ choice PPTA fibers are 20%-30% lower than virgin p-aramide fibers whereas recycled PPTA fibers are between 2 and 3 times lower than virgin p-aramide ones. The economic advantages are then numerous.

The advantages of using second choice p-aramide fibers or recycled fibers are obvious because they permit to cut down cost of the final product. The impact on the properties of the fabric has never been reported in the literature and then it is not well known. The main goal of this study is to examine the mechanical, fire and thermal properties of a first-class para-aramide: Kevlar®, versus second choice para-aramide, or "without trademark", and recycled para-aramide.

Mechanical properties of the fabrics are first investigated in terms of abrasion and cutting resistance. Using a cutting apparatus the transverse performances of the fibers (for cutting protection applications) are evaluated. Second, the reaction to fire of the fabrics is also considered using the cone calorimeter as fire model. Third, the heat resistance of the fabrics is studied in isothermal conditions to evaluate their behavior operating at high temperature. Finally, the advantages and disadvantages of those fibers are discussed.

## II- Experimental.

### Samples

The yarns of Poly-p-phenylenediamine-terephtalamide (PPTA) fibers, used for this study, have the following characteristics:

- Kevlar® type 29 supplied by the company DuPont De Nemours

(USA) in spun yarn (1/28 Nm - 36 Tex).

- *2nd choice PPTA fibers, presenting length defaults and/or coating defaults, in comparison with 1st choice PPTA fibers. Spun yarn (1/14 Nm - 72 Tex).*

- Recycling PPTA fibers. The principle of recycling is as follows : Wastes of PPTA fibers are recovered in various companies. They undergo a very hard carding operation in order to recover relatively short fibers which are then spun to obtain a regenerated yarn. Spun yarn (1/14 Nm - 72 Tex).

PPTA spun yarns are then assembled as knitted fabrics. They were knitted on an automatic rectilinear machine gauge 7 – Shima Seiki SES 122 FF. The texture used is a double woven rib (Figure 2). Surface weight, thickness and number of knitted yarns are given in Table 1.

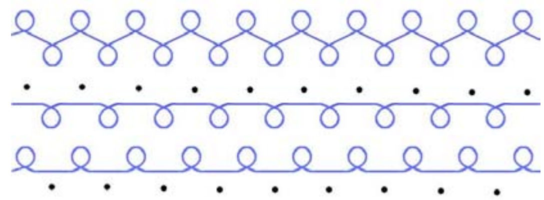

**Figure 2: Double woven rib knitted with blend of spun yarns**

| Type of fiber | Surface weight (g/m²) | Thickness (mm) | Number of knitted yarns |
|---|---|---|---|
| Kevlar® double woven rib | 1030 | 3,25 | 8 |
| Second choice PPTA double woven rib | 1040 | 3,31 | 4 |
| Regenerated PPTA double woven rib | 1080 | 3,41 | 4 |

**Table 1: characteristics of PPTA knitted structures**

**Cutting evaluation**

Cutting evaluation of our fabrics was determined by using the European standard EN 388 for gloves. This standard gives a cutting index "I" allowing comparing samples each other. The knitted fabrics were tested using the "Couptest". This apparatus is a circular blade cutting a textile structure (Figure 3). The circular blade makes a sinusoidal back and forth movement and the load on it is 5N. The apparatus count each tenth of cycle. The blade has a 45 mm diameter and a 0.3 mm thickness. The linear speed is about 10 cm/s. In order that the wear of the blade does not disturb measurements, a reference cotton fabric (pilot fabric) is tested between each sample and the results are then compared with it. The sample is cut when the blade touch the holder. An electric contact stops the blade movement and the counter.

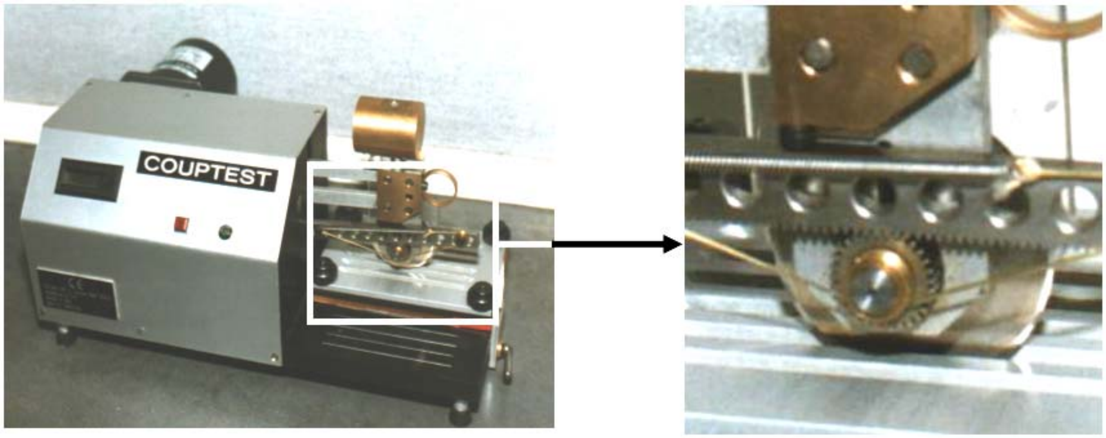


**Figure 3: pictures of the cutting apparatus "Couptest"**

The pilot fabric has the following characteristics:

- Yarns count: 161 Tex.
- Number of warp yarns: 18 yarns/cm.
- Number of weft yarns: 11 yarns/cm.
- Surface weight: 540 g/m².
- Thickness: 1.2 mm.

Each sample is tested 10 times in two different sequences of 5 tests.

The cutting index is calculating as follows:

"$C_n$" is the number of tenth of cycles necessary to cut the n[th] pilot sample and "$T_n$" the number of tenth of cycles necessary to cut the n[th] testing sample. We define "$i_n$" : the cutting index of the n[th] sample (see Table 2).

$$i_n = \frac{(\bar{C}_n + T_n)}{\bar{C}_n} \quad \text{with}$$

$$\bar{C}_n = \frac{(C_n + C_{n+1})}{2}$$

$I_1$ and $I_2$ are the cutting index of the 2 sequences of 5 tests previously made. They are determined as follows:

$$I_1 = \frac{1}{5}\sum_{n=1}^{5} i_n \quad \text{and}$$

$$I_2 = \frac{1}{5}\sum_{n=6}^{10} i_n$$

The final cutting index "I" is the minimum value of $I_1$ and $I_2$.

$$I = \mathrm{Min}\,(I_1, I_2)$$



| Sequence n | Pilot fabric « $C_n$» | Sample « $T_n$» | Pilot fabric « $C_{n+1}$» | Indice I |
|---|---|---|---|---|
| 1 | $C_1$ | $T_1$ | $C_2$ | $i_1$ |
| 2 | $C_2$ | $T_2$ | $C_3$ | $i_2$ |
| 3 | $C_3$ | $T_3$ | $C_4$ | $i_3$ |
| 4 | $C_4$ | $T_4$ | $C_5$ | $i_4$ |
| 5 | $C_5$ | $T_5$ | $C_6$ | $i_5$ |

**Table 2: the first 5 cutting index of the EN 388 Standard**

## Abrasion tests

Protective clothing against abrasive constraints is mainly provided by para-aramid articles. That's why the abrasion test is revealing for the mechanical behaviors of the tested materials.
The resistance to abrasion is evaluated by a Martindale abrasion tester type 325 with six independent heads of work according to the AFNOR standard NF EN 388-1994. Abrasive paper was Oakley 117 (100 grit) which is very aggressive and is required for testing technical knitted fabrics.

## Cone calorimetry by oxygen consumption

Samples were exposed to a Stanton Redcroft Cone Calorimeter at external heat flux of 75 kW/m². This flux corresponds to flashover conditions (10)(11). This high flux has been used because of the high fire performance of our fabrics: at a lower heat flux, the samples do not burn. The samples are put between two cut steel sheets. The surface exposed to the external heat flux is 9 x 9 cm². Our method does not correspond to any standard. One obtained conventional data (Rate of Heat Release (RHR), Volume of Smoke Production (VSP) (12), ...) using software developed in our laboratory. The experiments are repeated 3 times. When measured at 75 kW/m², RHR and VSP values are reproducible to within ±10%. The cone data reported in this work are the average of three replicated experiments.



## Thermal analysis

TGA measurements were performed using a Netzsch STA 449C Jupiter under air flow (50 mL/min) from 20°C to 1200°C. Samples (about 5 mg) were placed in open Pt crucibles. The calibration in temperature was made using standards (biphenyl, $KClO_4$, $K_2CrO_4$, $BaCO_3$, benzoic acid).

## III Results and Discussion

## Cutting resistance

The three PPTA fibers (1$^{st}$ choice – Kevlar® - and 2$^{nd}$ choice and recycled) have been assembled in spun yarn and knitted as a double-faced fabric as shown on Figure 2. The three fabrics have almost the same surface weight and so, the results are quite comparable.

Figure 4 shows the cutting behaviors of the three knitted fabrics. The cutting index falls between 18 and 20 for each sample which represents a very high potential. The "cutting index" standard ranks sample using 5 levels (1 to 5). The boundary between classes 4 and 5 is valued for a cutting index of 20. Only Kevlar® is ranked in the 5$^{th}$ class. Nevertheless, the two other para-aramide are very close of this class, especially if we consider that the precision of this measurement is about 2 (absolute value of the cutting index).

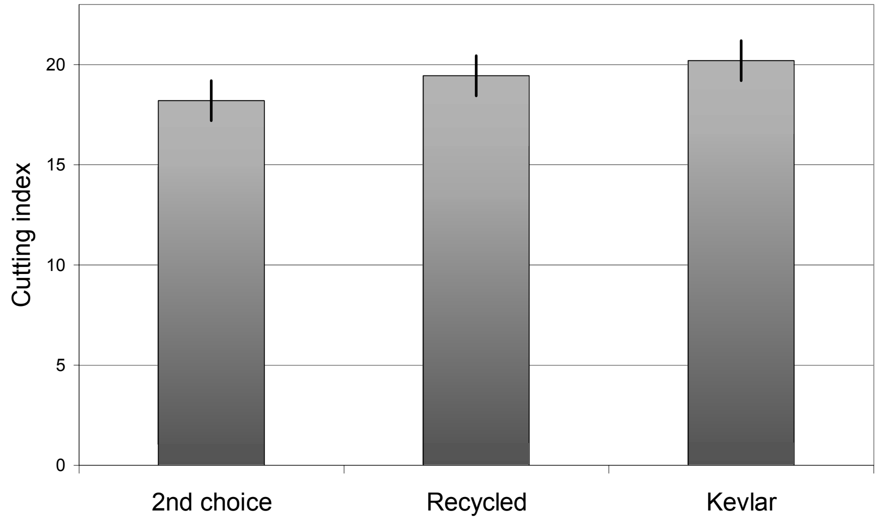


**Figure 4: cutting performances of the three PPTA fibers**

Cutting resistance is mainly due to the transverse characteristics of fibers. Thus it makes sense that the recycled p-aramid fibers exhibit good cutting performance since the physico-chemical characteristics of fibers are not (or slightly) modified during the regeneration. The percentage of foreign fibers (wool, cotton…) is not sufficient to reveal a significant fall of mechanical resistance in the case of transverse performance. In the other hand, it is worth to notice that the regeneration process of yarns creates fibrils which are favorable to the cutting resistance of the knitted fabrics. Indeed in a previous work (13), we have shown that the mobility of fibers and yarn improve the cutting resistance of knitted fabrics. In this case, the fibrils can move with the blade and dissipate a part of the cutting energy in friction. The regeneration process is therefore an advantage for the cutting resistance, by changing the surface of the fabric and by increasing the fibrillation.

**Abrasion resistance**

There are two methods for evaluating the abrasion resistance. The first one is to follow the weight loss versus the number of cycles and the second one is the determination of the number of cycles when a hole appears in the fabric. We have made a combination of the two methods : we have followed the weight loss to the apparition of a hole in function of the number of cycles

Figure 5 shows that the abrasion behavior of the three fabrics (recycled PPTA, 2nd choice PPTA and Kevlar® fabrics) are very different. The weight loss of recycled PPTA is 40% after 1000 cycles. This one of 2$^{nd}$ choice PPTA falls as 45% after 2000 cycles. The best behavior is obtained by Kevlar® which exhibits a weight loss of 30% after 2500 cycles. If we compare the three fabrics after 1000 cycles, the recycled PPTA has several holes associated to a weight loss value of 40%, while second choice PPTA and Kevlar® have weight losses of 12% and 10% respectively. The holes appear after 1000, 2000 and 2500 cycles for recycled PPTA, 2nd choice PPTA and Kevlar® respectively. It can be seen that regenerated p-aramide fibers exhibit poor abrasion resistance compared to the two other fabrics. It resists twice less than Kevlar® and should not be used when high abrasion performance is required.

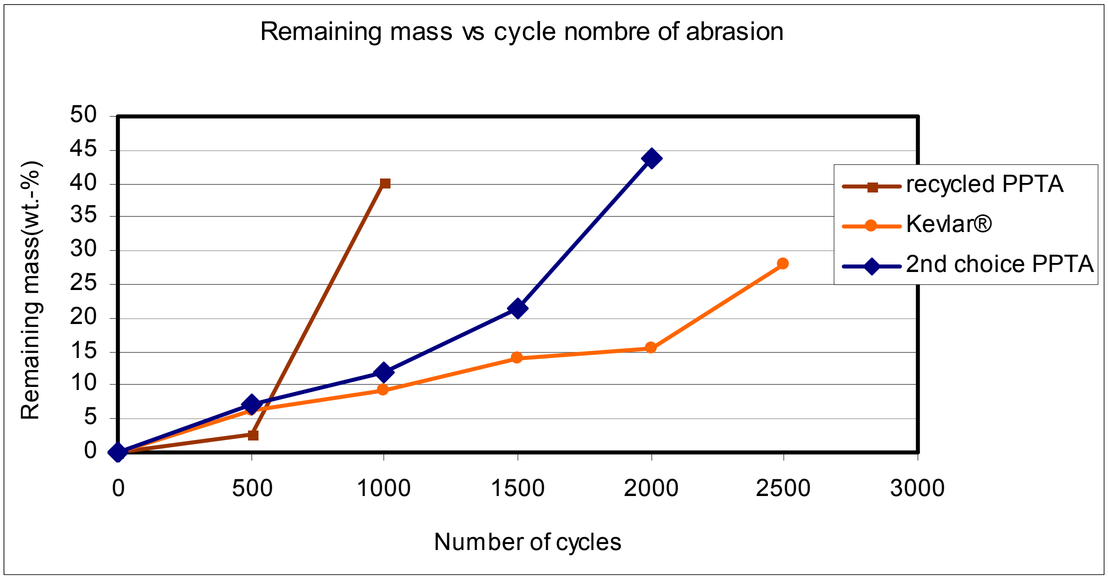


**Figure 5: Abrasion performances of the three PPTA fibers**

As stated in the previous section, the poor abrasion resistance of the recycled fibers can be attributed to the high fibrillation at the surface of the fabric due to the presence of foreign fibers. The yarns contain lots of small fibers perpendicular to the main yarn direction. It can be proposed that the wrapping fibers gradually break due to the abrasive forces facilitating the removal of loose fibers from the yarn structure. The fibrils and asperities, due to the regeneration process, increase the contact with the abrasive paper, and then decrease the abrasion performance of knitted fabrics.

## Flame resistance

Fire hazard is associated with a variety of properties of a material in a particular scenario. It is determined by a combination of factors including the material ignitability, the rate at which heat is released from it when it burns, the total amount of heat that is released, the flame spread, the smoke production and the toxicity of the smoke. It has now been established that the property which most critically defines a fire is the heat release, because two conditions are necessary for propagating a fire from the ignited material to another one and/or to the surroundings. First, sufficient energy, as heat, needs to be released to cause secondary ignition. Secondly, the heat release needs to be occurred sufficiently fast so that the heat is not quenched in the "cold" air. By using heat release equipment, as the cone calorimeter, the different parameters discussed above can be measured in the same instrument, in a manner generally relevant to real fires.



Figure 6 show the reaction to fire of Kevlar in the conditions of the cone calorimeter at an external heat flux of 75 kW/m². Kevlar fabric has a time to ignition of 25s, a peak of heat release (peak of RHR) of 225 kW/m² and burns from 25s to 140s. At this last time a plateau is reached (RHR is constant equaling 50 kW/m²) where the samples glows. After the glowing phase a residue is obtained. It is only constituted by some carbonaceous particles, is crumbly and has no mechanical properties.

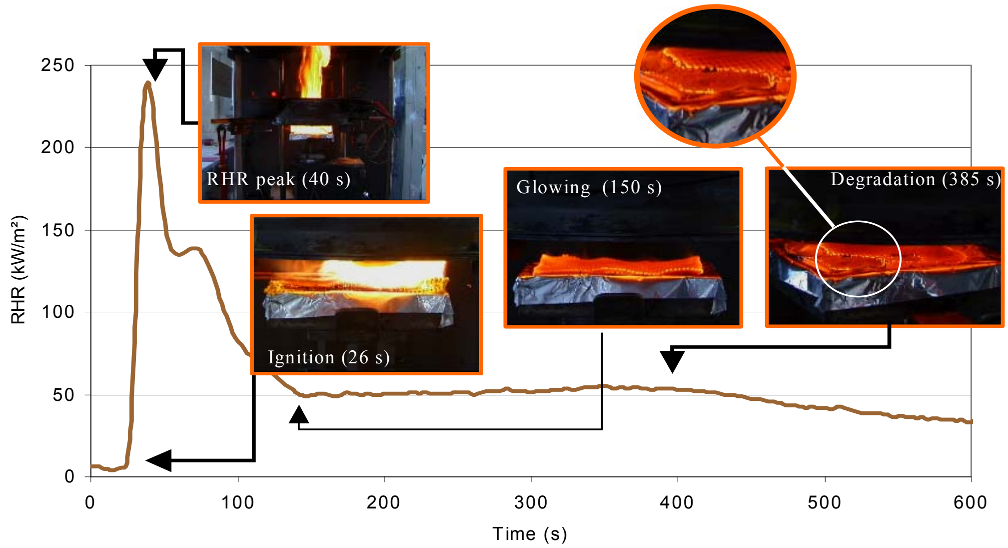


**Figure 6: Rate of Heat Release (RHR) curve of Kevlar at 75 kW/m²**

As it can be seen on Figure 7, the three RHR (Rate of Heat Release) curves have the same shapes. RHR peaks fall between 225 and 240 kW/m². However the time to ignition of recycled PPTA fabric ($t_{ig}$ = 10s) is much shorter than the ones of Kevlar and 2nd choice fabrics. The RHR curves of these last fabrics are then shifted at higher times but they reach a plateau in the same time range as the recycled PPTA fabric (50s < t < 80s). The differences in RHR of the two plateaus, from 115 to140 kW/m², are not significant.

The difference of the ignition times comes from the regeneration process. Indeed when the recycle apparatus receives waste of p-aramide yarns, those yarns contain impurities, like wasted fibers (cotton, wool and unknown fibers). Figure 8 shows the presence of wasted fibers in a recycled PPTA knitted fabric. Because of their chemical nature, the wasted fibers ignite earlier. Moreover, the process of recycling is very aggressive for the fibers what it leads to a significant fibrillation of regenerated fibers creating the so called "wick effect". These two effects combined together dramatically shorten the time to ignition of the fabric.



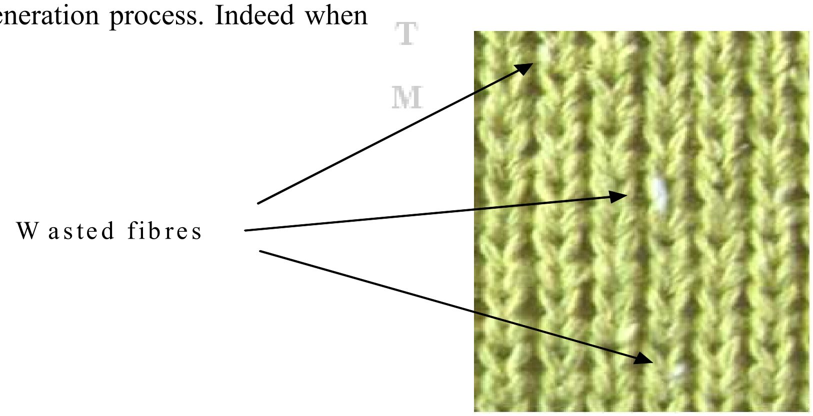


**Figure 7: RHR curves of the three PPTA fibers at 75 kW/m²**

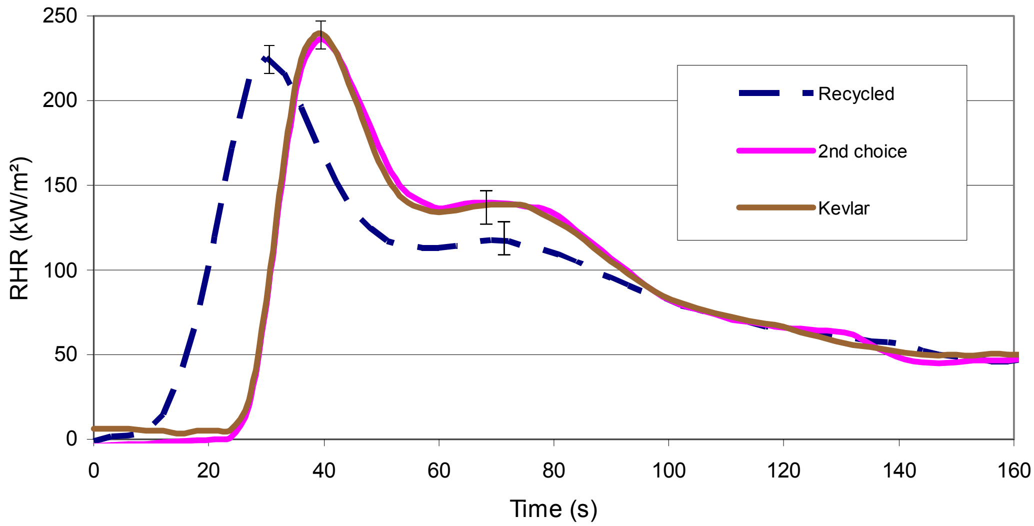


**Figure 8: Wasted fibers in a p-aramide recycled yarn in a knitted fabric**

Total heat evolved curves (THE) show an interesting result (Figure 9). The heat evolved presents the same shape for the three fibers. This means that the global contribution to fire is the same for the three fiber but the curve of recycled PPTA fibers start to increase at shorter times, due to the very short ignition time.

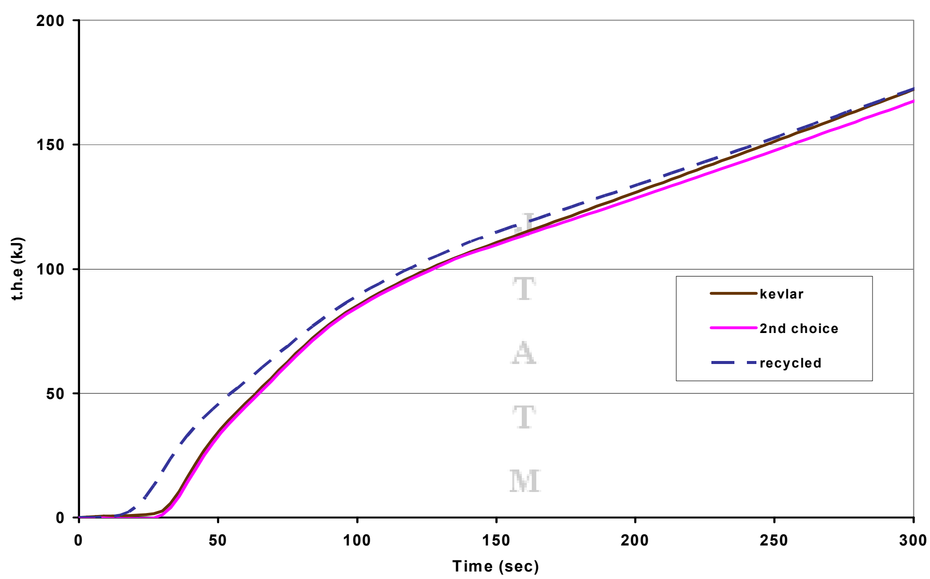


**Figure 9 :T.H.E. curves of the three PPTA fibers (external heat flux = 75 kW/m² )**

Smoke obscuration curves are shown on Figure 10. Virgin and second choice PPTA fibres evolve smoke with a peak at 0.0055 whereas the recycled PPTA fibers evolved smoke with a peak at 0,0048 m3/s. The differences between those values are not enough significant to conclude except for the time when it occurs (12 s for recycled PPTA fibers and 24 s for Virgin and second choice PPTA fibres). Those 12 seconds (between the apparitions of smoke) are very important in term of safety of people because the obscuration of a room or a corridor leads generally to a large panic effect. Indeed panic gives rise to more deaths than the fire itself (13).

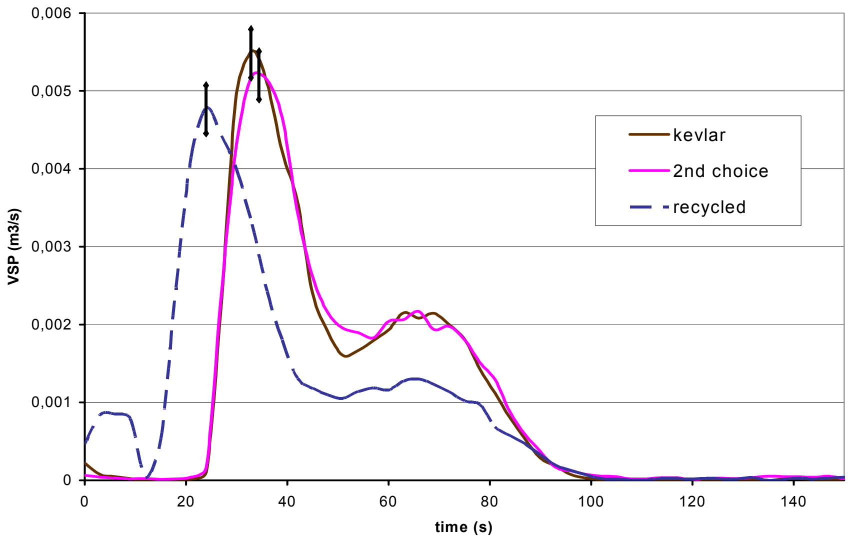


**Figure 10: VSP (Volume of smoke production) curves of the three PPTA fibers (external heat flux = 75 kW/m²)**

The tree fabrics exhibit good fire properties in the cone calorimeter conditions. The peaks of RHR are low which means that they do not spread out fire quickly. The main difference between the fabrics is the time to ignition which is dramatically shortened in the case of the recycled PPTA fabric.

## Heat resistance

In this section, thermogravimetric analysis (TGA) is used to simulate a thermal shock following by an isothermal temperature.
The protocol is a fast heating rate (50°C/min) simulating a thermal shock followed by an isothermal temperature of 300°C for one hour (operating temperature) and by the degradation of the fiber increasing temperature from 300 to 700°C at 10°C/min. Here only Kevlar and recycled PPTA fibers are considered (Figure 9). The thermal shock from room temperature to 300°C leads to 4% and 5% weight loss for Kevlar and recycled PPTA respectively. Slight additional weight loss (about 1%) is observed during the isothermal treatment of the two fibers at 300°C. Finally, Kevlar is degraded at higher temperature (T = 470°C) than recycled PPTA fibers (T = 400°C) but the two fibers exhibit no residue from 630°C.



After a thermal shock and an isothermal treatment, recycled PPTA fibers degrade at lower temperature than Kevlar®. However this difference is not large and the use of recycled fibers regard to Kevlar can be considered if only such thermal properties are required.

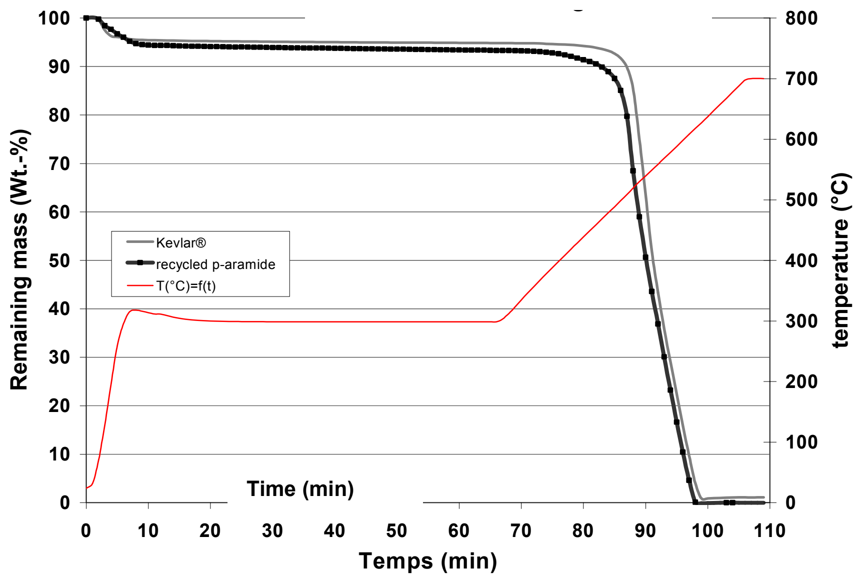


**Figure 11: Thermal treatment by TGA of recycled PPTA fibers and Kevlar**

## IV Conclusions.

This study has allowed to highlight the difference in terms of mechanical and thermal behavior of different p-aramide fibers (1st choice or pure Kevlar, 2nd choice and recycled fibers). Kevlar and 2nd choice PPTA provide similar performance. It means for 2nd choice PPTA fibers that the length defaults and/or coating defaults do not modify behavior of the examined properties (cutting, abrasion, fire and heat resistance). However other evaluations, such as dynamometric test, might show distinguishable different behavior. Recycled PPTA fibers exhibit excellent cutting resistance (almost as high as the pure Kevlar) and good fire properties (except for the time to ignition) associated with a low cost. However they have a very bad abrasion resistance due to their recycling process. This latter provides yarns with many fibrils at the surface and unknown fibers in it. This abundant fibrillation at the surface leads to shorten the time to ignition of the fabric.

Recycled PPTA fibers exhibit relatively good performance compared to pure Kevlar associated to low cost. However they look like pure Kevlar fibers and are hardly recognizable leading to the risk of counterfeit. Manufactured product with such fibers can become dangerous because of the not so high expected performance. A typical example could be protection gloves against cutting risk. The low abrasion resistance of the fabric can lead to a faster degradation and to the loss of the properties of gloves. Attention must be paid for choosing a type of PPTA fiber. If requirements are fabric without high abrasion resistance but exhibiting cutting performance with reasonable thermal and fire properties, recycled PPTA could be considered. On the contrary, if the abrasion resistance and/or the ignition of the product are major concerns, recycled PPTA must be avoided.



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