Identification of tires fibres and additives using Py – GC/MS

Parres F., Crespo J.E., Nadal-Gisbert A.
Department of Mechanical and Materials Engineering, Polytechnic University of Valencia, Plaza Ferrandiz y Carbonell, 2; 03801; Alcoy - Alicante (Spain)

Introduction.

In recent years, the re-use of waste materials has become extremely important for two main reasons: economic and environmental. With the first of these, the recovery of material often means a reduction in manufacturing costs of certain products which enables them to compete with virgin products. However, it is the second reason, the environmental impact factor, which is assuming greater importance nowadays. Over the last decade many governments have imposed diverse legislation to deal with this problem. In the case of thermoplastics, recovery processes are generally not very complicated and the simple use of temperature allows new products with similar characteristics to be obtained. On the other hand the recovery of other materials such as tires is more complicated as new tires cannot be manufactured by recycling old ones. One of the solutions adopted has been the use of recycled tires in other applications such as acoustic insulation, flooring for children's parks and other products obtained from shredded tires. In the tire recovery process a diverse range of fibres is also obtained, fibres incorporated in the tires for reinforcement. The aim of this work is to identify and characterise the fibres obtained from the tire shredding process so that they may be used again in other areas such as to obtain activated carbons.[1].

The characterisation and identification of these materials were done using diverse analytical techniques, such as thermogravimetry (TGA) and differencial scanning calorimetry (DSC). These techniques have been used by other authors for the analysis of diverse polymers [2,3]. As well as these techniques, pyrolysis - gas chromatography / mass spectrometry (Py - GC / MS) allowed us to identify other products which may be present in the fibres - mainly additives.

Experimental.

Materials.

Two types of fibre were used: virgin fibres from different sources (the Polyamide 6 and Polyamide 6.6 were supplied by Industrias Quimicas Textiles, S.A., Andoain (Guipuzcoa) - Spain; the rayon was supplied by Sniace, S.A., Torrelavega (Cantabria) - Spain; the cotton was supplied by Mediterraneo Algodon, S.A., Dos Hermanas (Sevilla) - Spain; and fibres derived from the tire shredding process, were supplied by Insaturbo(Grupo soledad)., Aspe (Alicante) - Spain.

DSC analyses.

Calorimetric analysis was carried out using DSC Metler-Toledo 821 equipment (Mettler-Toledo, Schwerzenbach, Switzerland). Samples of weight between 6 and 7 mg were used. A first heating (30 - 150°C at 10°C min^{-1}) was completed, followed by a cooling process (150 - 30°C at 10°C min^{-1}) to eliminate the thermal history, and was finished with a second heating (30°C at 400°C at 10°C min^{-1}). The tests were performed in a nitrogen environment (flow rate 50 mL min^{-1}).

TGA analyses.

The weight loss of fibres was measured in nitrogen atmosphere by thermogravimetry analysis (TGA) with Mettler-Toledo TGA/SDTA 851 equipment (Mettler-Toledo, Schwerzenbach, Switzerland). The TG curves were obtained in the temperature range of 30 to 800 ºC at a heating rate of 10ºC min^{-1}

Py - GC/MS analyses.

All samples were pyrolysed with the use of a pyrolysator (Pyroprobe® 1000 by CDS Analytical Inc.), interconnected with a GC/MS (6890 N Agilent Technologies) equipped with a 5973 N mass selective detector (MSD) (Agilent Technologies España S.L., Madrid - Spain). A 30 m long capillary column (HP-5 ms) 0.25 mm thickness, with a 0.25 mm stationary phase, which was programmed as follows: (1) The initial temperature was 40ºC and was maintained for 5 min. (2) The temperature was then increased from 40ºC to 240ºC at a rate of 4ºC min^{-1}, and was subsequently maintained at the highest temperature for 5 min. The gas used was helium with a 50:1 split ratio. The MSD was programmed to detect masses between 50 and 650 amu. Samples (around 0.7-0.9 mg) were pyrolised at 500ºC for 5 s.

Results and discussion.

Morphological study.

The fibres obtained from the recovery process come from the internal tires reinforcements incorporated to improve the characteristics of the tire. Over time many diverse fibres have been used as reinforcement, of natural origin (cotton or rayon) and synthetic origin (polyamide 6 or polyamide 6.6). Currently, the majority of the fibres used are of synthetic origin [4-7].

The shredding process affects the final morphology of the fibres. After this process, two main types of fibre can be identified: fibre and microfibre. In the first case the fibres maintain their original form (cord) and their length is variable (>1.5mm, 1.5 - 1mm, <1mm), while the microfibres are a consequence of the different stages in the shredding process which cause the original fibres to break up or unravel (Figure 1)

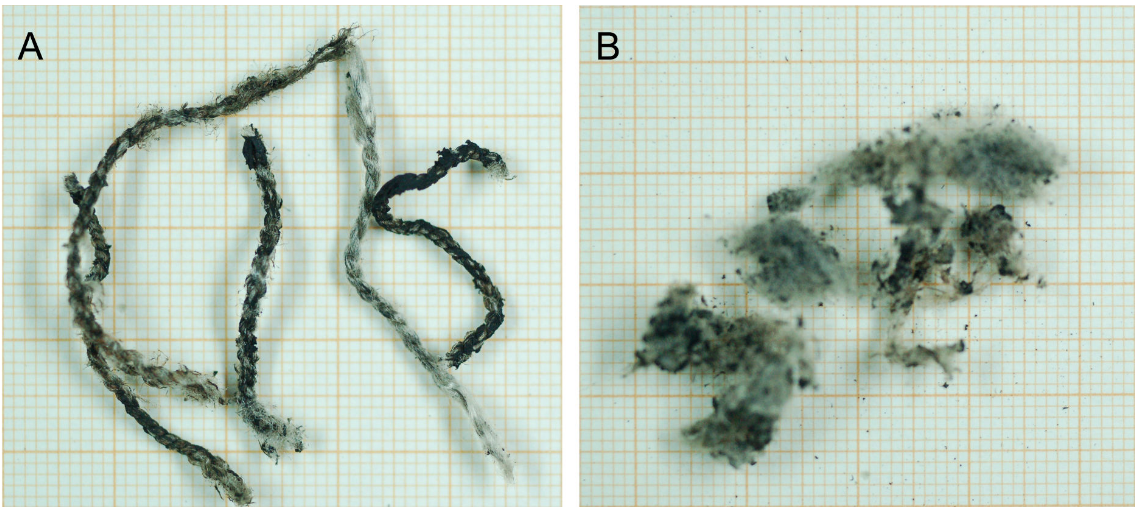

Figure 1. Images of different types of fibre and microfibre after the shredding process. A - fibre, B - microfibre

2.2. Thermal analysis, DSC and TGA results.

Differential scanning calorimetry (DSC) has been used by different authors for the identification of materials [8], especially when dealing with polymer materials. This identification is based on localising the different thermal transitions shown by polymers. This technique has also been used to find the initiation of degradation in fibres of natural origin [9].

The identification of polymers using this technique is much more straightforward if control references are used for comparison with the samples being analysed. In this work calorimetric studies were carried out on four types of fibre: polyamide 6, polyamide 6.6, cotton, and rayon. These four types will be used as references.

The calorimetric curves show differences between the reference fibres; all of which, except for cotton, show endothermic peaks at different temperatures. It is important to highlight the differences existing between cotton and rayon when exposed to high temperature in spite of their structural similarities. The study of rayon shows an endothermic peak that begins at about 260ºC and reaches its minimum at approximately 325ºC, due to the decomposition of the cellulose in laevoglucose, whereas cotton shows no significant thermal transition [10].On the other hand, polyamides 6 and 6.6 show endothermic peaks corresponding to the melt point of spherulites at about 220 and 260ºC respectively (Figure 2) [11].

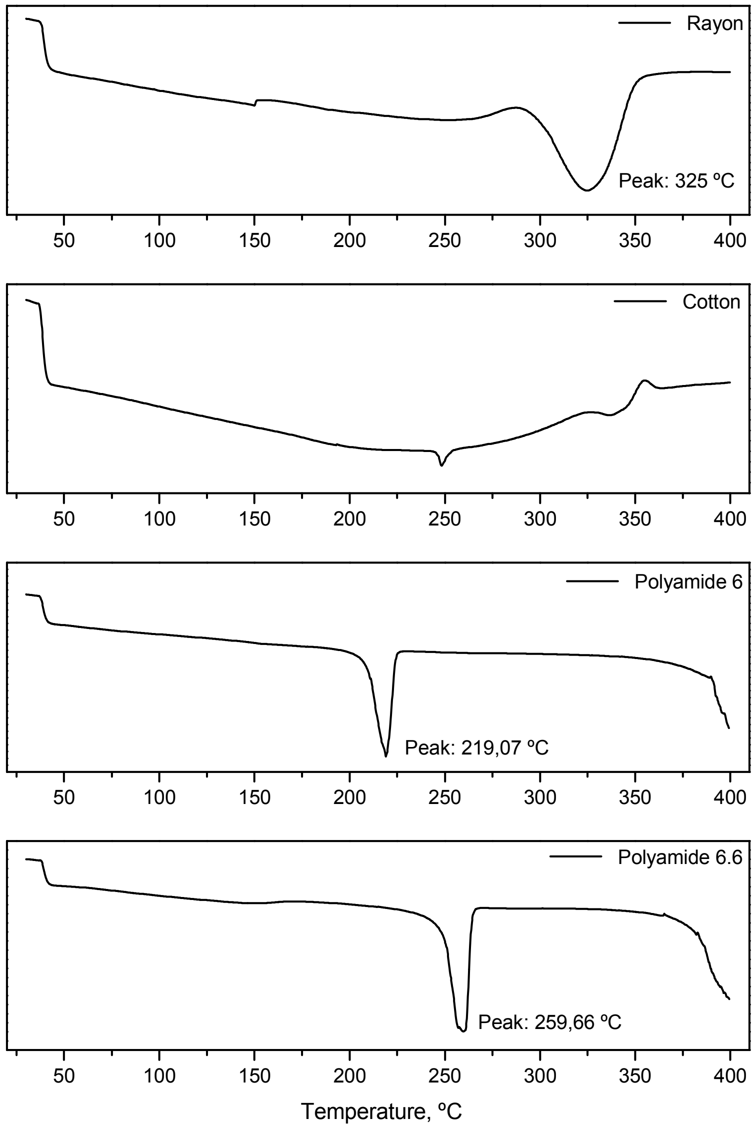

Figure 2. Calorimetric curve of the reference fibres (rayon, cotton, polyamide 6 and polyamide 6.6

The low point of the endothermic peak indicates the melt temperature and can be used to identify the fibres obtained from shredded tires. Table 1 shows the melt temperature values of the fibres used as references.

Table 1. Melting point of the reference fibres

Reference fibre	**Rayón**	**Polyamide 6**	**Polyamide 6.6**
Melting temperature, ºC	325	219,07	259,66

The fibres obtained from shredded tires show different morphologies in terms of their length and can be classified as fibres (>1.5mm, 1.5mm - 1mm, <1mm) and microfibres.

The calorimetric curves show significant differences; the longest fibres, with values above 1mm, show a single endothermic peak at around 260ºC. The shorter fibres and the micro fibres show two peaks of differing intensity. The first of these, of lesser intensity begins at 220ºC, and the second, of greater intensity, at 260ºC. These results show that the fibres used for reinforcement in tires are principally polyamide 6.6. The presence of polyamide 6 is due to the existence of filaments used to hold the fibres together during the tire manufacturing process (Figure 3).

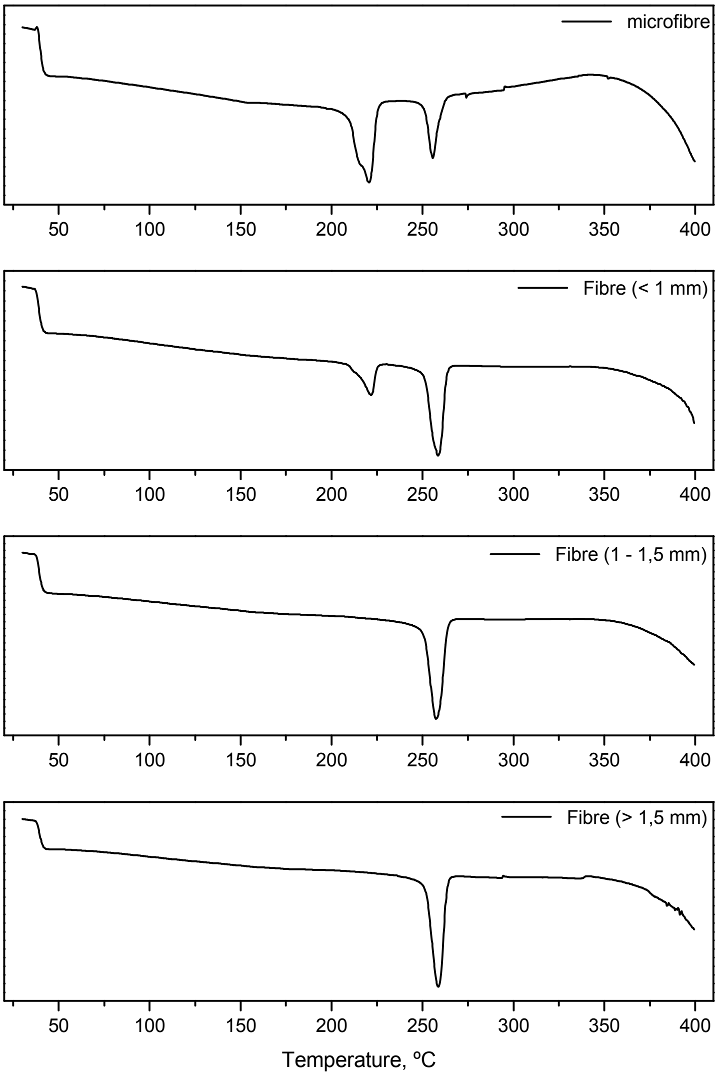

Figure 3. Calorimetric curve of the different tire fibres.

In spite of the presence of small particles of tire adhered to the surface of fibres, calorimetry shows no thermal transition resulting from this.
Another of the analytical techniques widely used to characterise polymers is thermogravimetry. This technique indicates the start and end temperatures of degradation and so is extremely useful in the characterisation of recovered materials.

As in the previous section, the use of reference fibres allows us to study the difference between fibres being studied and reference control fibres. The results obtained through thermogravimetry are fairly diverse; the degradation process begins much earlier in fibres of cellulose character (rayon, cotton), around 316.6ºC and 322.3ºC respectively. Conversely, the final part of the degradation process occurs more slowly, a gradual loss of mass being observed up to about 600ºC, at which temperature the process finishes completely. On the other hand, polyamides 6 and 6.6 show a much higher degradation start and finish temperature than the cotton and rayon fibres as well as presenting less residual waste material than fibres of cellulose character (Figure 4).

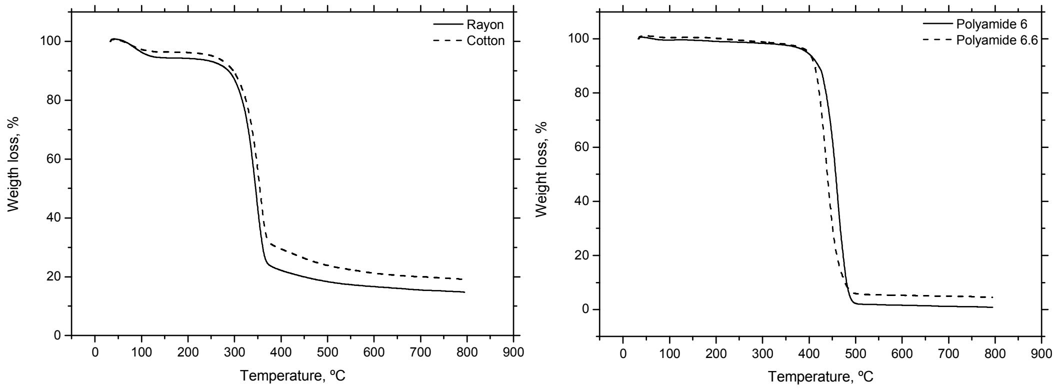

Figure 4. TG analyses corresponding to the thermal degradation of cotton, rayon, polyamide 6 and 6.6.

The study of fibres derived from the recovery process using thermogravimetry does not show significant differences in terms of degradation start and finish temperature; whereas the residual waste formed at the end of the degradation process oscillates between 10 and 30 % of the original weight. These differences are a consequence of a variation in the presence of tire particles adhered to the surface of the fibres under analysis (Figure 5).

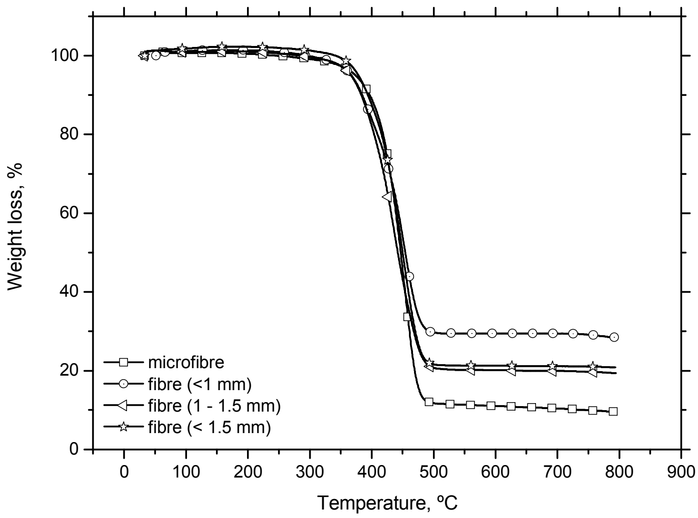

Figure 5. TG analyses corresponding to the thermal degradation of tire fibre and microfibre

2.3 PY - GC/MS analyses of virgin fibre and tire fibre

Although with the use of thermal analysis techniques it is possible to identify the fibres used as reinforcement in tire manufacture, the combination of pyrolysis - gas chromatography / mass spectrometry allows us to corroborate this identification as well as identify the presence of any additives used in the manufacture of these fibres.

Previously, and following the same analysis technique, different textile fibres have been analysed, including cotton, rayon, polyamide 6 and 6.6, and these will be used as references to make correct identification.

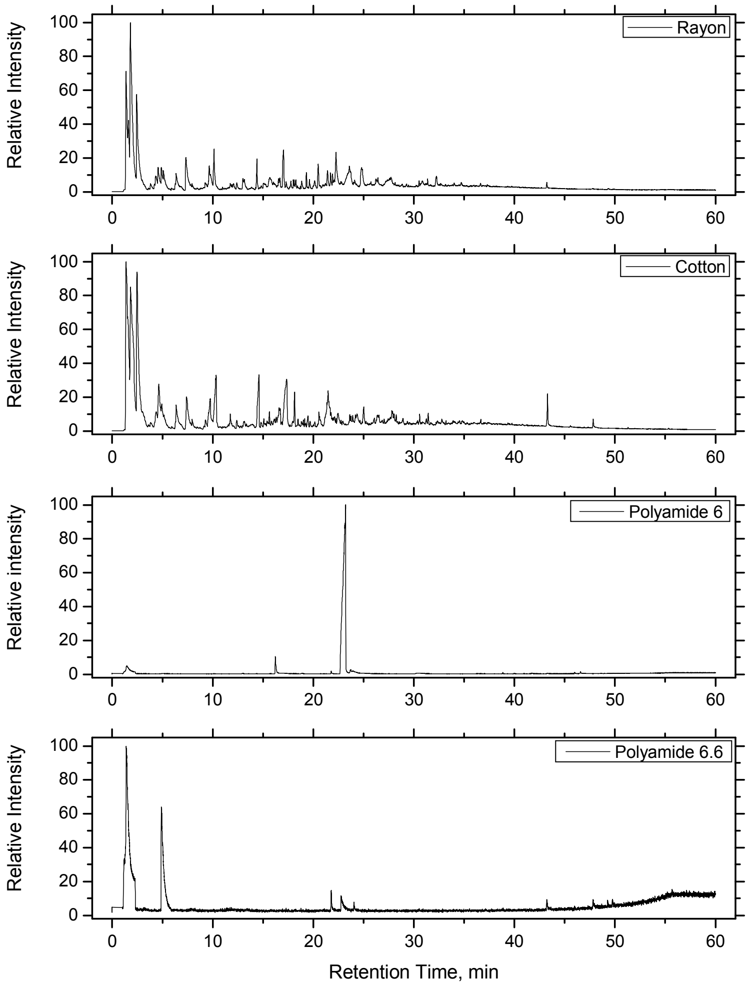

Figure 6. Py - GC/MS analysis of reference fibres

The chromatograms of the different reference fibres indicate clear differences between them. We find two fibres with few peaks (polyamide 6 and 6.6) while pyrolysis of cotton and rayon shows more than 40 peaks. Other authors have already observed this behaviour in analyses of cotton and rayon [9] (Figure 6). The fibres obtained in the recovery process can be classified in two groups, short fibres and microfibres. The first of these have the characteristic of maintaining their original shape (cord) and show a variable length, whereas the microfibres are much shorter and have completely lost their original shape. However, in both cases some tire particles can be observed adhered to the surface of the fibres.

Figure 7 shows the pyrolysis - GC/MS chromatograms of tire, fibre and microfibre and we can see that the relative peak intensities of the major pyrolysis products are similar. We found three major products: 1,3 - butadiene, 2 - methyl (1.68 min), limonene (14.48 min), and hexadecanoic acid (43.46 min); this last compound being a consequence of the thermal degradation of palmitic acid used as a lubricant [1,12].

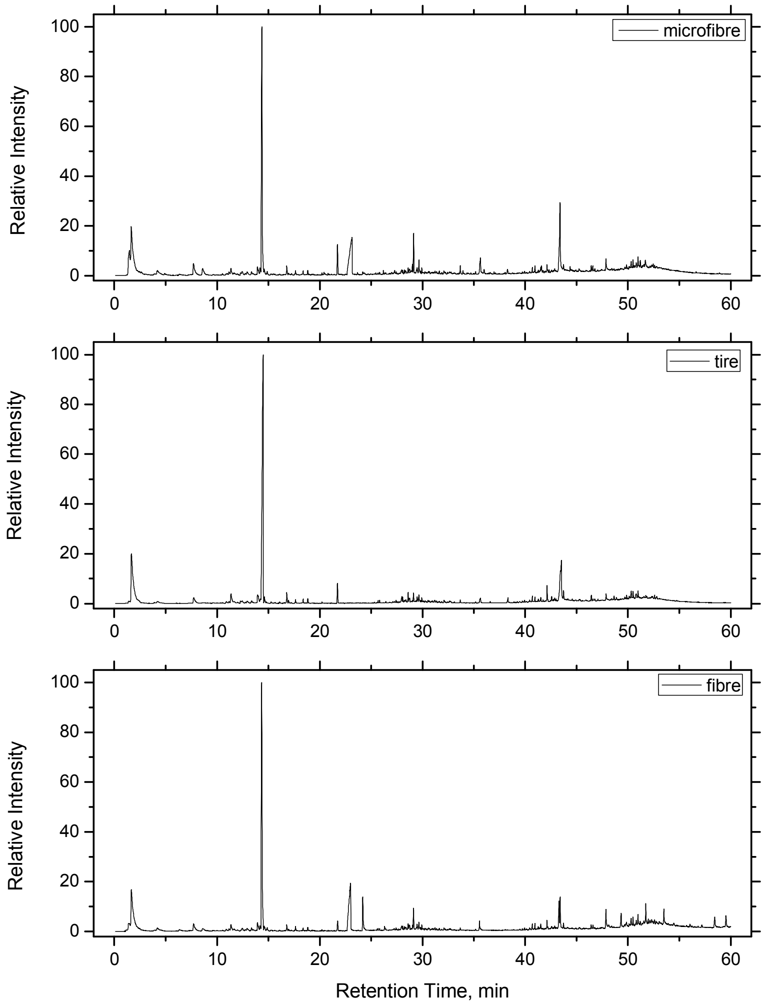

Figure 7. Py - GC/MS spectum of fibres and tire.

Initially, only one difference was observed between the fibres and the tire at a retention time of 19 - 26 min, where the mass spectrum shows that the peak corresponds with caprolactam (retention time 22.9 min), and this compound was observed in the analysis of the reference fibres corresponding to polyamide 6. We can also see other peaks which correspond to the vulcanisation activators (Benzothiazole, 21.73 min) [13] or additives used to improve fibre adhesion with the tire. (Resorcinol, 24.19 min). In this last case the presence of this compound may be of some importance in the recovery of the fibres, given that it is also used to counteract UV radiation or as a flame retardant [14]. The identification of these compounds was made using the data base available (Figure 8).

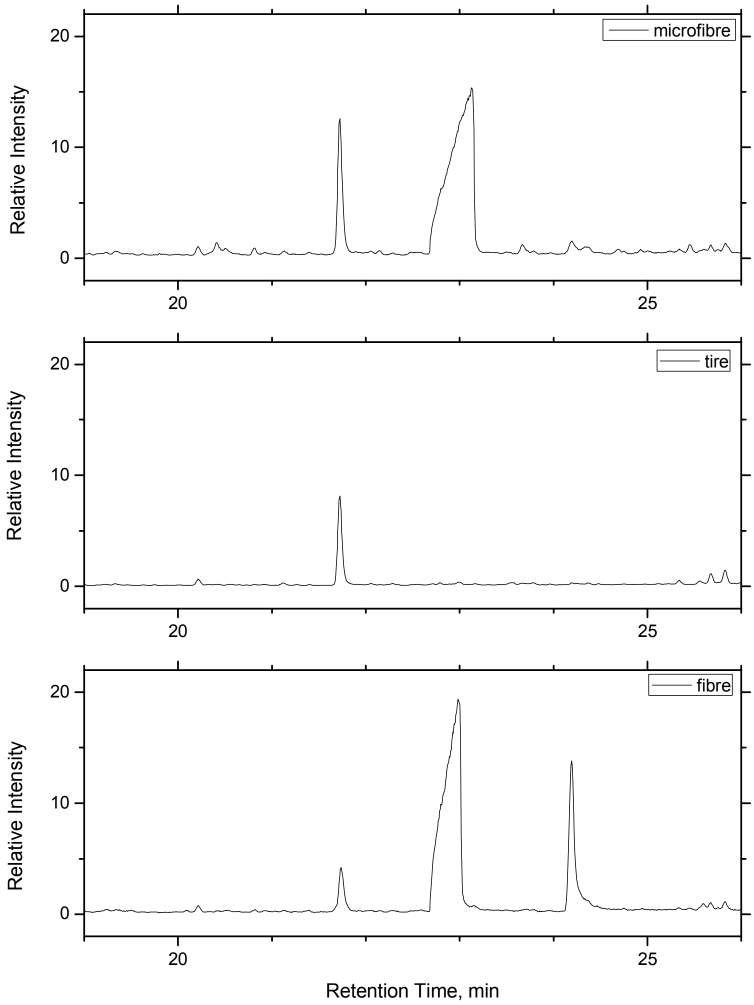

Figure 8. Detail of pyrogram of fibres and tire (retention time, 19 - 26 min).

Conclusions.

Thermal analysis techniques allow us to identify fibres recovered from the tire shredding process. The results of these analyses show the presence of polyamide 6 and polyamide 6.6; although the sensitivity of these techniques is not enough to give information on the presence of tire particles adhered to the surface of the fibres. Thermogravimetry provides complimentary information on the degradation process of the fibres and in this case the presence of tire particles adhered to the fibre surface causes a variation in the percentage of residual waste at the end of the thermal process.

Finally, the use of Py - GC/MS not only allows us to corroborate the results obtained from previous techniques but also to identify other compounds used in the tire's manufacture such as interlacing activators (Benzothiazole) or additives which improve the interaction of the fibres with the tire (Resorcinol); as well as the presence of small particles of tire.

The recovery of fibres from recycled tires is of great interest, in different areas; to obtain activated carbons, used as reinforcing elements in ceramics or polymers and for make recycled textiles for different purposes.

References.

1. M. López de Letona and A. Macías-García, *Applied Surface Science* **252**, 5984-5987. (2006)
2. H. P. Brack, D. Ruegg, H. Buhrer, M. Slaski, S. Alkan and G. G. Scherer, *Journal of Polymer Science Part B-Polymer Physics* **42**, 2612-2624 (2004)
3. D. Garcia, R. Balart, J. E. Crespo and J. Lopez, *Journal of Applied Polymer Science* **101**, 2464-2471 (2006)
4. R. S. Bhakuni, G. W. Rye and A. Piirma, *Rubber Age* **99**, 77-& (1967)
5. H. H. Gillman and R. Thoman, *Industrial and Engineering Chemistry* **40**, 1237-1242 (1948)
6. H. J. Philipp and C. M. Conrad, *Journal of Applied Physics* **16**, 32-40 (1945)
7. G. Raumann and J. L. Brownlee, *Journal of Macromolecular Science-Chemistry* **A 7**, 281-293 (1973)
8. A. Manivannan and M. S. Seehra, *Abstracts of Papers of the American Chemical Society* **214**, 20-FUEL (1997)
9. P. Zhu, S. Y. Sui, B. Wang, K. Sun and G. Sun, *Journal of Analytical and Applied Pyrolysis* **71**, 645-655 (2004)
10. S. Chen, Q. K. Zheng, G. D. Ye and G. H. Zheng, *Journal of Applied Polymer Science* **102**, 698-702 (2006)
11. P. A. Eriksson, A. C. Albertsson, K. Eriksson and J. A. E. Manson, *Journal of Thermal Analysis and Calorimetry* **53**, 19-26 (1998)
12. Y. Kawamura, A. Nakajima, M. Mutsuga, T. Yamada and T. Maitani, *Journal of the Food Hygienic Society of Japan* **42**, 316-321 (2001)
13. A. S. Aprem, K. Joseph, T. Mathew, V. Altstaedt and S. Thomas, *European Polymer Journal* **39**, 1451-1460 (2003)
14. D. A. Bright, S. Dashevsky, P. Moy and B. Williams, *Journal of Vinyl & Additive Technology* **3**, 170-174 (1997)
15. H. Soto-Valdez and J. W. Gramshaw, *Journal of Materials Science Letters* **19**, 823-825 (2000)