Characterization of Fibers Obtained from Shredded Tires

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ABSTRACT: The importance of recovering waste materials generated by industrialised societies is mainly due to the environmental impact they have, and one of the principal problem areas is tires. In recent years, an enormous amount of tires have been recycled. Metals contained in them have been recovered and the tire particles have been used in diverse applications. A third material that appears in the recovery process is the fibers, which act as reinforcement. Before addressing the possible reuse of these fibers, it is necessary to characterise and identify them. The diverse techniques of thermal analysis allow these fibers to be identified through melt point analysis, the results of which show the presence of polyamide 6 and 6.6. Moreover, the combination of pyrolysis-gas chromatography/mass spectrometry corroborates the identification made with the techniques previously mentioned and also indicates the presence of certain additives used in the manufacture of tires, such as resorcinol and benzothiazole. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2136–2142, 2009

Key words: fibers; polyamide; thermal properties; pyrolisis

INTRODUCTION

In recent years, the reuse 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 heating 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 fibers is also obtained, fibers incorporated in the tires for reinforcement. The aim of this work is to identify and characterise the fibers obtained from the tire shredding process, so that they may be used again in other areas such as reinforcement for ceramic materials.[1]

The characterisation and identification of these materials were done using diverse analytical techniques, such as thermogravimetry analysis (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 fibers–mainly additives.

EXPERIMENTAL

Materials

Two types of fiber were used: virgin fibers 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 fibers derived from the tire shredding process were supplied by Industrias del Neumatico, S.A., Aspe (Alicante)–Spain. The tire arrives at the recovery plant, where, after a first crushing process, the tires are crushed to sizes of about 100 mm, then reduced to sizes of about 20 mm by crushing, and finally reduced to small sizes (7–0.2 mm) by milling. The number of stages of crushing and milling depends

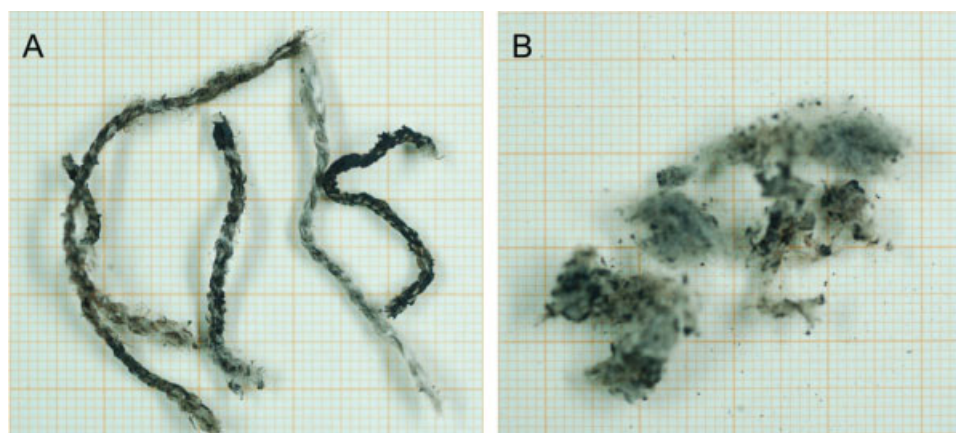*Correspondence to:* F. Parres (fraparga@dimm.upv.es).

Figure 1 Images of different types of fiber and microfiber after the shredding process. (A) Fiber and (B)– microfiber. [Color figure can be viewed in the online issue which is available at www.interscience.wiley.com]

on the wished grain size. We use only crushing in the case of big sizes (100–20 mm). To obtain grain sizes between 7 and 0.2 mm, we combine crushing and milling. Steel fibers are separated by using electromagnets. The separation of the textile fibers always takes place by aspiration on the sieve that the wished grain size defines and in the processes that combine crushed and milling. The stages of crushing are usually two, one reducing the whole tire to 100 mm pieces, the second reducing this size to a 20 mm size. The milling stages oscillate between one and three based on the wished gain size (7–0.2 mm). Crushing and milling takes place at room temperature, and cryogenic process are not used.

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 350°C at 10°C min^{-1}). The tests were performed in a nitrogen environment (flow rate 50 mL min^{-1}).

TGA

The weight loss of fibers 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 30–800°C at a heating rate of 10°C min^{-1}.

Py-GC/MS analyses

All samples were pyrolyzed 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) with a 0.25 mm thickness and a 0.25 mm stationary phase was programmed as follows: (1) The initial temperature was 40°C and was maintained for 5 min. (2) The temperature was then increased from 40°C to 240°C at a rate of 4°C 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 pyrolyzed at 500°C for 5 s.
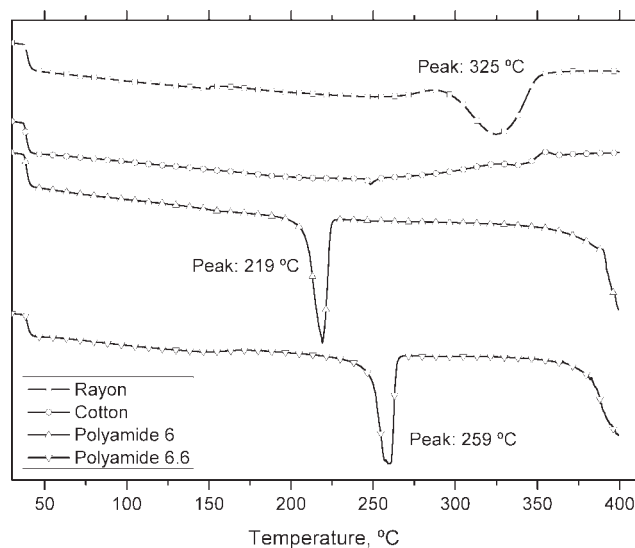

Figure 2 Calorimetric curve of the reference fibers [rayon, cotton, polyamide 6, and polyamide 6.6.

TABLE I
Melt Point of the Reference fibers

Reference Fiber	Melt point, °C
Rayón	325
Polyamide 6	219
Polyamide 6.6	259

RESULTS AND DISCUSSION

Morphological study

The fibers obtained from the recovery process come from the tire's internal reinforcements incorporated to improve the characteristics of the tire. Over time, many diverse fibers 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 fibers used are of synthetic origin.[4–7]

The shredding process affects the final morphology of the fibers. After this process, two main types of fiber can be identified: fiber and microfiber. In the first case, the fibers maintain their original form (cord) and their length is variable
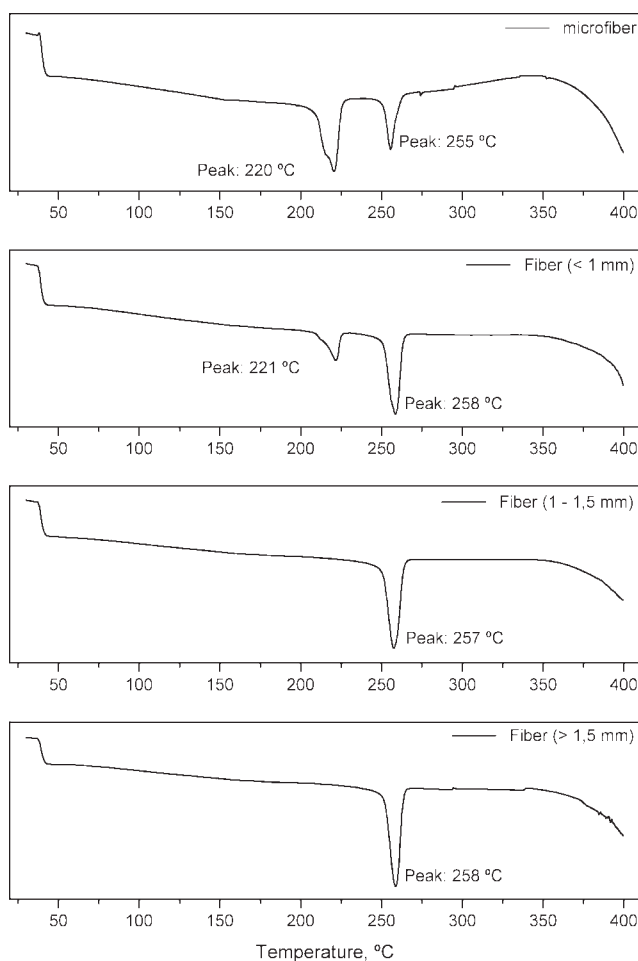

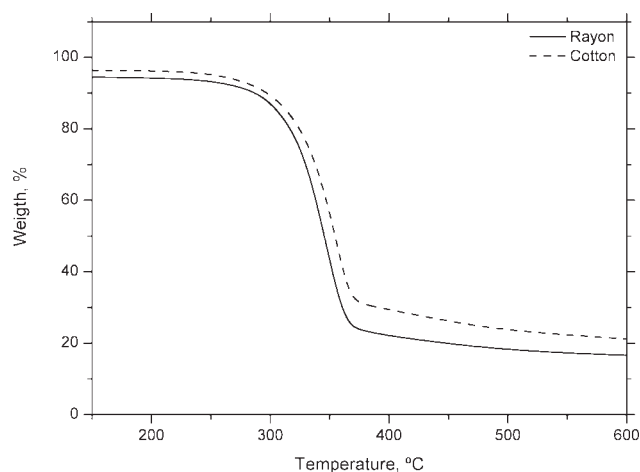**Figure 3** Calorimetric curve of the different tire fibers.

Figure 4 TGA corresponding to the thermal degradation of cotton and rayon.

(>1.5 mm, 1.5–1 mm, <1 mm), whereas the microfibers are a consequence of the different stages in the shredding process, which cause the original fibers to break up or unravel (Fig. 1).

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 localizing the different thermal transitions shown by polymers. This technique has also been used to find the initiation of degradation in fibers 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 fiber: polyamide 6, polyamide
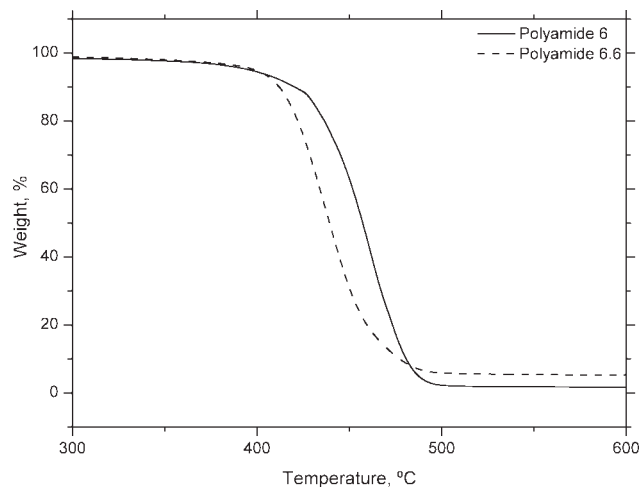

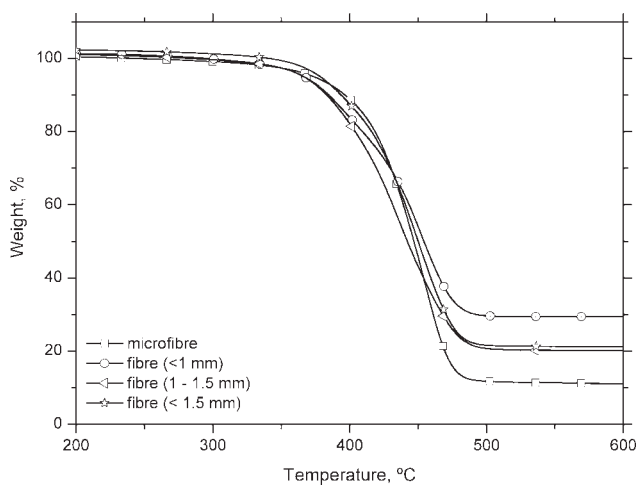**Figure 5** TGA corresponding to the thermal degradation of polyamide 6 and 6.6.

Figure 6 TGA corresponding to the thermal degradation of tire fiber and microfiber.

6.6, cotton, and rayon. These four types will be used as references.

The calorimetric curves show differences between the reference fibers; 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 despite their structural similarities. The
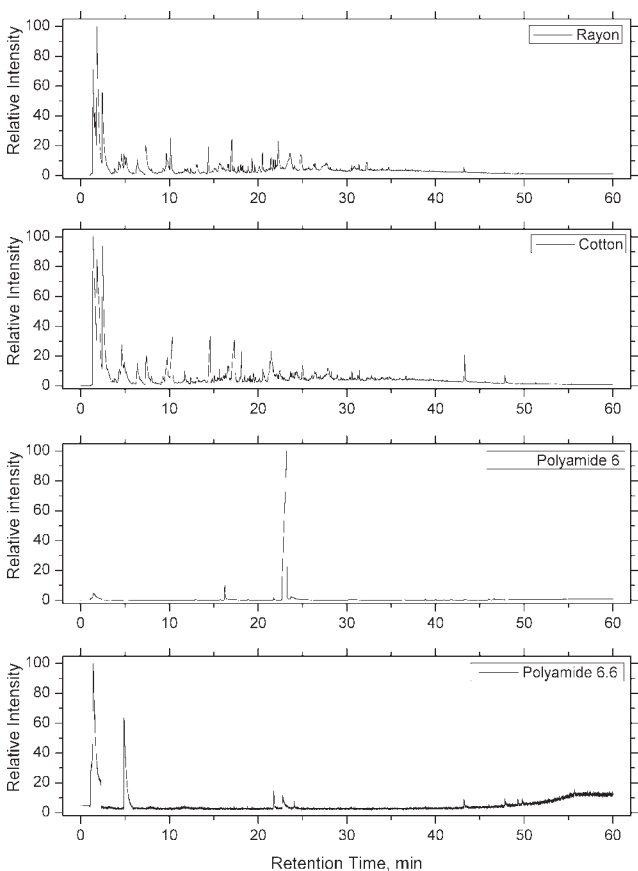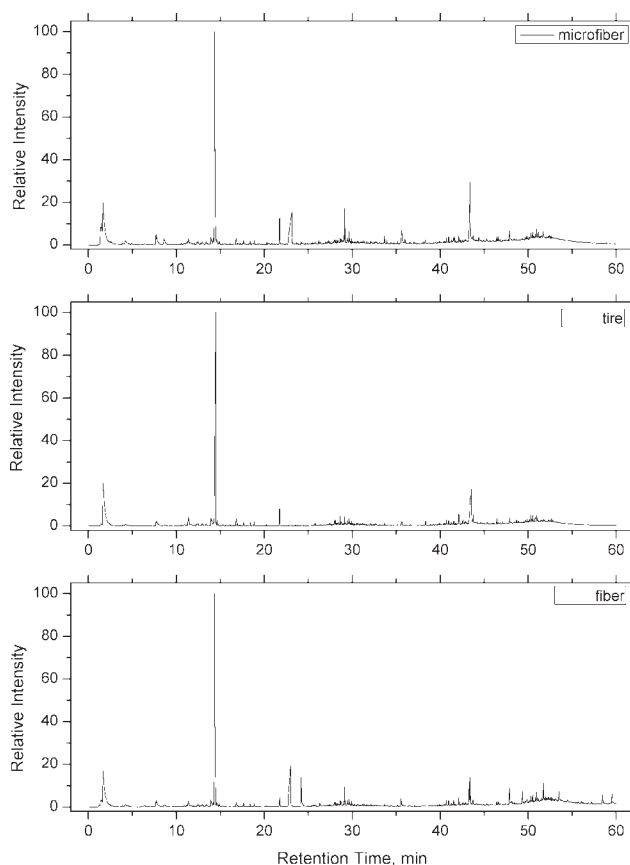

Figure 8 Py-GC/MS spectum of fibers and tire.

study of rayon shows an endothermic peak that begins at about 260°C and reaches its minimum at approximately 325°C, due to the decomposition of the cellulose in laevoglucose, whereas cotton shows no significant thermal transition.[9,10] On the other hand, polyamides 6 and 6.6 show endothermic peaks corresponding to the melt point of spherulites at about 220 and 260°C, respectively (Fig. 2).[11]

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

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

The calorimetric curves show significant differences; the longest fibers, with values above 1 mm, show a single endothermic peak at around 260°C. The shorter fibers and the microfibers show two peaks of differing intensity. The first of these, of lesser intensity, begins at 220°C, and the second, of greater intensity, at 260°C. These results show that the fibers 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

Figure 7 Py-GC/MS analysis of reference fibers.

TABLE II
Compounds Derived from the Degradation of Tires

Compound	Retention time (min)
Toluene	4.19
p-Xylene	7.71
Styrene	8.60
D-Limonene	11.34
Benzene, 1-methyl–4-(1-methylethyl)-	14.18
Benzene, methyl(1-methylethenyl)	16.78
1,3,8-p-Menthatriene	17.64
2,4,6-Octatriene,3,4-dimethyl-	18.38
Benzene, 2-ethenyl–1,3,5-trimethyl-	20.21
Quinoline,2,4-dimethyl-	29.01
Benzothiazole, 2-(methylthio)	33.67
Benzene, 1,1′-(1,3-propanediyl)bis-	35.17
2(3H)-Benzothiazolone	35.64
Pyrene	46.41
Heptadecanenitrile	46.57
Octadecanoic acid	47.85

fibers together during the tire manufacturing process (Fig. 3).

Despite the presence of small particles of tire adhered to the surface of fibers, calorimetry shows no thermal transition resulting from this.

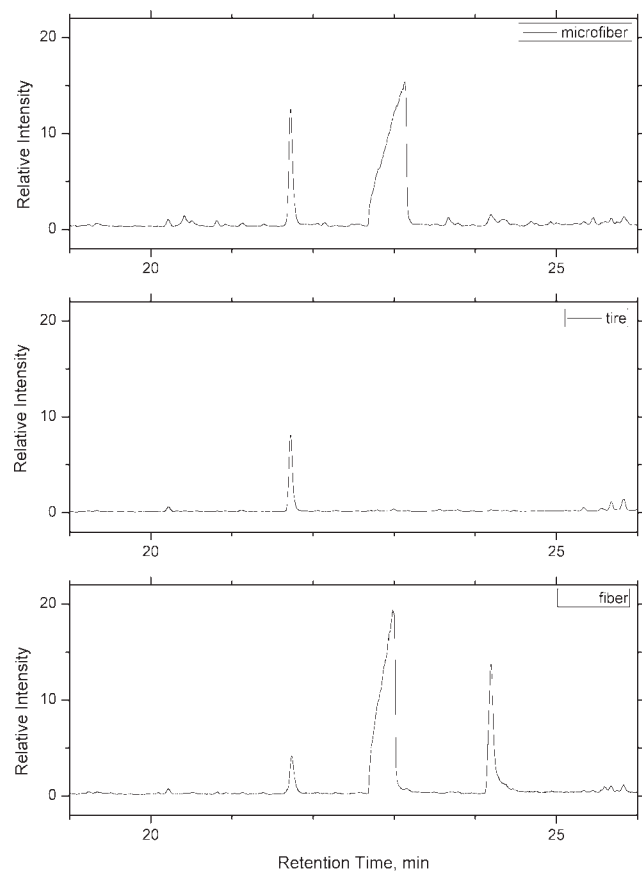Another of the analytical techniques widely used to characterise polymers is thermogravimetry. This technique indicates the start and end temperatures of degradation and so is extremely useful in the characterisation of recovered materials.

As in the previous section, the use of reference fibers allows us to study the difference between fibers being studied and reference control fibers. The results obtained through thermogravimetry are fairly diverse; the degradation process begins much earlier in fibers of cellulose character (rayon, cotton), around 316.6°C and 322.3°C, respectively. Conversely, the final part of the degradation process occurs more slowly, a gradual loss of mass being observed up to about 600°C, at which temperature the process finishes completely (Fig. 4).

On the other hand, polyamides 6 and 6.6 show a much higher degradation start and finish temperature than the cotton and rayon fibers as well as presenting less residual waste material than fibers of cellulose character (Fig. 5).

The study of fibers 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 fibers under analysis (Fig. 6).

PY-GC/MS analyses of virgin fiber and tire fiber

Although with the use of thermal analysis techniques it is possible to identify the fibers 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 fibers. Previously, and following the same analysis technique, different textile fibers have been analysed, including cotton, rayon, polyamide 6 and 6.6, and these will be used as references to make correct identification.

The chromatograms of the different reference fibers indicate clear differences between them. We find two fibers with few peaks (polyamide 6 and 6.6) whereas pyrolysis of cotton and rayon shows more than 40 peaks. Other authors have already observed this behavior in analyses of cotton and rayon[9] (Fig. 7).

The fibers obtained in the recovery process can be classified in two groups, short fibers and microfibers. The first of these have the characteristic of maintaining their original shape (cord) and show a variable length, whereas the microfibers 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 fibers.
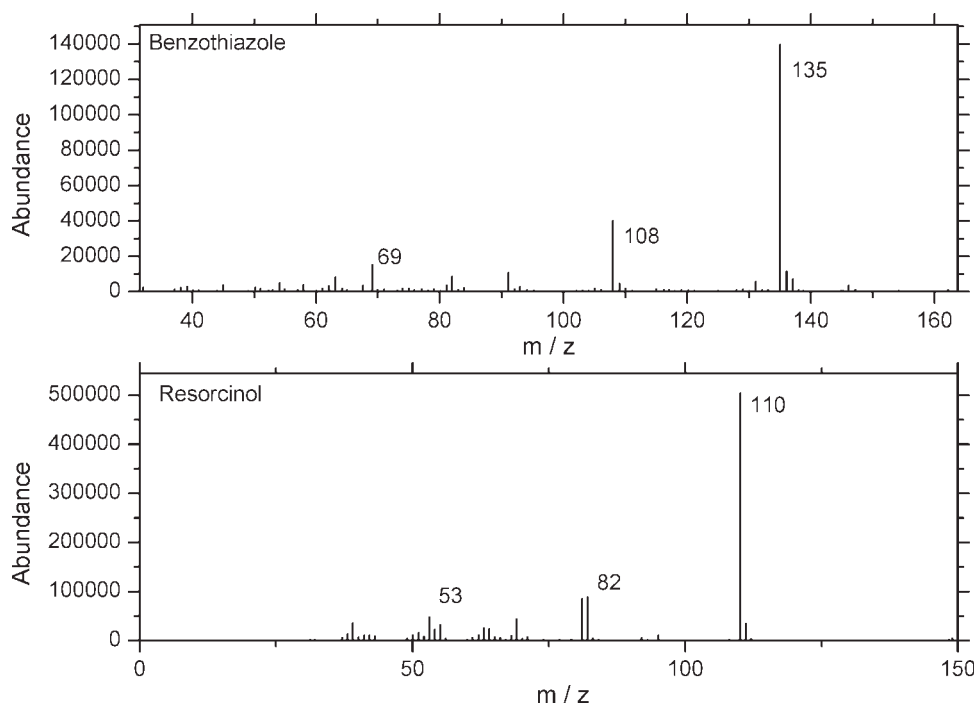

Figure 9 Detail of pyrogram of fibers and tire (retention time, 19–26 min).

Figure 10 Mass spectrum of benzothiazole and resorcinol.

Figure 8 shows the pyrolysis-GC/MS chromatograms of tire, fiber, and microfiber, 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.[12,13]

We can also observe more than 10 peaks of lesser intensity, where different compounds derived from the thermal decomposition of the tire appear (Table II).

Initially, only one difference was observed between the fibers 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) (Fig. 9), and this compound was observed in the analysis of the reference fibers corresponding to polyamide 6.

We can also see other peaks which correspond to the vulcanisation activators (Benzothiazole, 21.73 min)[14] or additives used to improve fiber 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 fibers, given that it is also used to counteract UV radiation or as a flame retardant.[15] The identification of these compounds was made using the database available (Fig. 10).
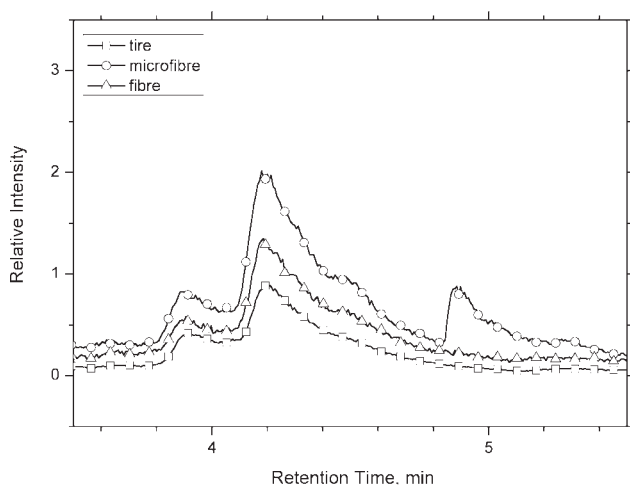

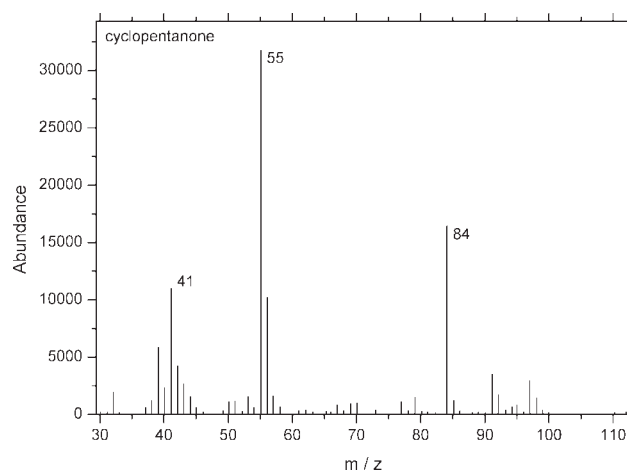**Figure 11** Detail of pyrogram of fibers and microfibers (retention time, 3.5–5.5 min).

Figure 12 Mass spectrum of cyclopentanone (retention time, 4.88 min).

The calorimetric curves of the fibers of lesser length also show the presence of polyamide 6.6, and in this case, the Py - GC/MS corroborates the results obtained. The chromatogram indicates the presence of a peak corresponding to the thermal degradation of polyamide 6.6 (cyclopentanone, retention time, 4.88 min)[16] (Figs. 11 and 12).

CONCLUSIONS

Thermal analysis techniques allow us to identify fibers 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 fibers. Thermogravimetry provides complimentary information on the degradation process of the fibers, and in this case, the presence of of tire particles adhered to the fiber 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 fibers with the tire (resorcinol); as well as the presence of small particles of tire.

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