

Pyrolysis of glass-hardened polyamides used in the automotive industry

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Thermogravimetry and on-line flash pyrolysis–gas chromatography–mass spectrometry were used for studying thermal decomposition processes in filled polyamides deriving from used cars. The thermal decomposition of each polymer begins at about 350 °C and proceeds with a weight loss of 100% for the non-glass fibres, under nitrogen atmosphere. The analysis of the pyrolyzate compounds shows that from polyamide 66, the most abundant product volatile at degradation temperatures is cyclopentanone, while from polyamide 6 there is a considerable yield of ϵ -caprolactam.

1. Introduction

Considerable research over a number of years has been devoted to the development of pyrolysis processes for tertiary recycling of plastics [1–4]. This particular technique seems to be very important especially for composite polymeric materials deriving from used cars due to the expensive process necessary to separate the materials and to recycle them. Tertiary recycling involves breaking the polymer structure down into simple molecules, which can then be used as chemical feedstocks.

The advantage of pyrolysis over combustion is a high reduction in the volume of product gases which leads to considerable savings in the gas conditioning. In order to evaluate the possibility of adopting the recycling of glass-hardened polyamides from used cars in a commercial scale, we have carried out thermogravimetric and Curie-point Py–GCMS. Curie-point Py–GCMS is a technique of flash pyrolysis followed by gas chromatography–mass spectrometry analysis. It involves some advantages in comparison with slow pyrolysis; first of all it allows a reproducible and fast analysis and eliminates the possibility of secondary reactions [11]. The technique is based on the property of the ferromagnetic material to be magnetized when it is placed in an induction coil and the coil energized. When the current polarity is changed the magnetic poles (N and S) are reversed. If the current polarity is changed rapidly, hysteresis heating occurs in the ferrous material due to the friction of the changing dipoles. Self-heating will cause the ferrous material to very rapidly reach a temperature at which it will lose

its magnetism (Curie-point) and then maintain that temperature for as long as the power supply is maintained.

2. Materials

The materials studied (1–6) were supplied by Fiat Auto (Turin, Italy) and find applications primarily in the moulding of under-hood components subjected to high temperatures (radiator fans, cooling device) or in touch with fuel (fuel tube, filler lid panel) or exposed to different conditions (rear-view mirror, handles) or subjected to weight (brake and accelerator pedals).

All the materials analysed contain a nylon matrix. Some of them are reinforced with glass-fibres and mineral dust, some others are modified polymer in order to obtain elastomers. Both methods are used to get blends with improved physical, mechanical and chemical properties (i.e. they show higher tensile strength, resistance to chemical agents, thermal stability etc.).

The materials were reduced to powder by a mixer, IKA-Universalmuhle M20. Each sample was identified with the following codes:

- | | | | | |
|----|-------|------|---------|-------------------------------------|
| 1. | PA 66 | GF30 | SNIAMID | SSD300
(glass fibre 30%) |
| 2. | PA 66 | | SNIAMID | AP/SSD |
| 3. | PA 66 | | SNIAMID | SSD/ET
(elastomer) |
| 4. | PA 6 | M-30 | SNIAMID | ASN 27/300 EP
(mineral dust 30%) |

5. PA 6 SNIAMID 40 BMC E/2 (elastomer)
 6. PA 6 SNIAMID ASN 27/ET (elastomer)

PA 66 is the code for nylon 66 (poly-hexamethylene adipamide) and PA 6 is the code for nylon 6 (polycaprolactam).

3. Experimental procedure

3.1. Analytical methods

Thermal degradations were performed in a Mettler TA 3000 thermogravimetric analyser, coupled with a Mettler TC 10A processor. The temperature calibration of thermobalance was made according to the procedure indicated in the user's operating instructions [12], based on the change of the magnetic properties of three metal samples (alumel, nickel and Trafoperm) at their Curie points. For calibrations we used the Curie points of 149.3, 357.0 and 745.6 °C for the three metals, respectively, as suggested by the supplier.

Degradation experiments were conducted in dynamic heating conditions, using alumina crucibles under a pure nitrogen flow (10 ml min⁻¹). The weight losses of the samples as a function of time or of temperature were measured and stored in the data list of the appropriate built-in program of the TC 10A processor. The degradation experiments were carried out by heating the samples from 35 °C up to 950 °C at the chosen heating rates.

The DTA (differential thermal analysis) spectra were produced by a thermobalance Linseis L 81 under nitrogen atmosphere (5% H₂) and under a programmed increase in temperature (20–800 °C). Conventionally, endothermic peaks are plotted in a downward direction and exothermic peaks in an upward direction.

The Curie-point Py-GCMS was carried out by using a Horizon Instrument's Curie-point pyrolyser fitted to a Hewlett Packard 5890 GC interfaced to a VG ZAB-2F mass spectrometer.

The GC separation was carried out on a 30 m long, 0.32 mm i.d. capillary column with a programmed temperature range from 40 to 250 °C.

The VGZAB-2F was in the EI mode, ionization energy 70 eV, scanning into a digital PDP 11/250 datasystem.

The samples were analysed by using iron wires (Curie point 770 °C). The samples were suspended in acetone and then coated as evenly as possible on the iron wires, the wires cut to length, one end folded over and placed in glass sample tubes (*F* = 2.3 mm). The tubes were then placed in the sample probe and inserted into the pyrolysis interface, which was then gas purged. The time to reach the pyrolysis temperature is less than 0.4s while the pyrolysis time itself can be selected over a 0.5–5 s range in accurate 0.5 s steps.

4. Results and discussion

The analysis of the thermogravimetric spectra (Fig. 1) shows that all the samples have a very similar behav-

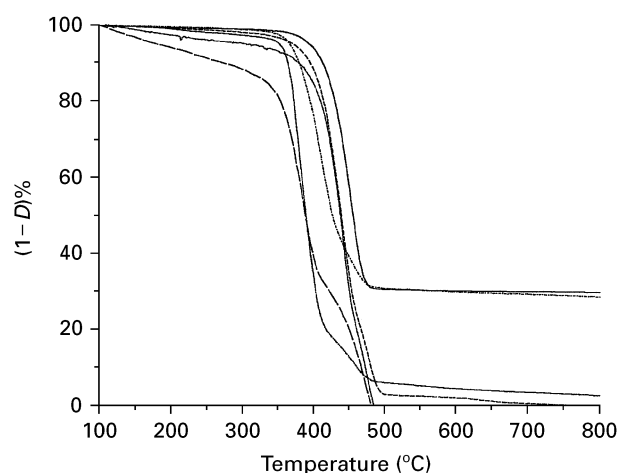


Figure 1 TG curves under N₂ flow at the heating rate of 10 °C min⁻¹. Each sample corresponds to a different line (1. ---; 2. -.-.-; 3. —; 4. —; 5. ·····; 6. - - - -).

TABLE I Thermal characterization of polymers 1-6

Polymer	T _m ^a	Weight loss (%) ^b	Residual (%) ^c	T _{100%} ^d
1	414	70	30	—
2	378	97.6	2.4	—
3	387	100	—	482
4	454	70	30	—
5	443	100	—	485
6	421	100	—	756

^a Temperature at maximum rate of weight loss (°C).

^b Weight loss in dynamic conditions under N₂ (%).

^c Residual % determined at 800 °C.

^d Temperature at 100% weight loss (°C).

our during the thermal degradation up to 300–350 °C and only at higher temperatures the loss of weight depends on the sample. For example, at 450 °C sample 1 lost 70% of the initial weight while sample 2 lost 100% (Table I). This is probably due to the fact that sample 1 is a glass-hardened polyamide, with the presence of glass residuum into the crucible. The thermal stabilities of the polyamides investigated, indicated by the maxima in their differential thermogravimetric curves (temperature of maximum decomposition rate) are reported in Table I. The glass-fibre-reinforced polyamides show, as expected, higher temperatures than the non-composite ones because of their higher thermal stability.

The DTA spectra (Figs. 2, 3) show an exothermic peak at about 200 °C and an endothermic one which starts at the same temperature of the weight lost. The exothermic peak in the first step is typical of cross-linking reactions while the endothermic one is due to the chain breaking with the probable formation of monomer or volatile molecules.

All the samples yielded characteristic GC profiles with a variety of components which could be identified by library matching of the mass spectra.

Figures 4 and 5 show some examples of the total positive ion current (TIC) traces from pyrolysis

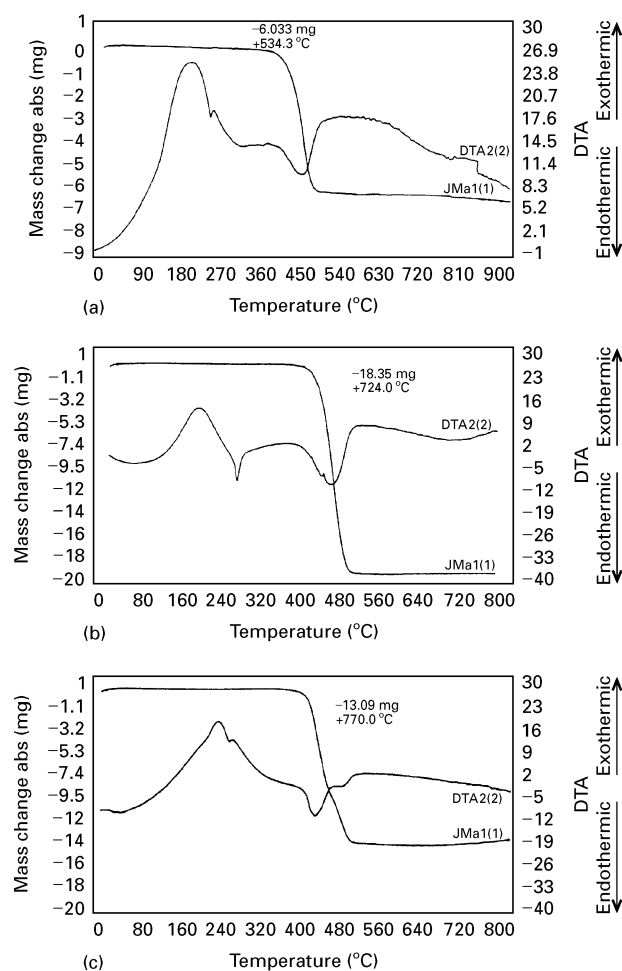


Figure 2 TG/DTA spectra in nitrogen atmosphere of PA 66 samples ((a) 1, (b) 2, (c) 3).

respectively of PA 66 (sample 2) and PA 6 (sample 4). The pattern of the TIC trace characterizes the type of polymer present while the mass spectra of the resolved components enables identifications of the polymer constituents.

The chromatogram of sample 2 (polymer PA 66) shown in Fig. 4a exhibits three peaks with high intensity corresponding to scans 8, 23 and 137. The retention time is easily valued from the scanning rate: 1 scan/5s. The mass spectra of each peak are reported in Fig. 4b while the library compounds are collected in Table II.

The compounds corresponding to peak 8 represent the most volatile portion of the pyrolysis breakdown products, while the more significant peaks correspond to cyclopentanone (scan 23, MW = 84) and to 1,6-hexandiamine (scan 137, MW = 116). Similar spectra were obtained by the analysis of the other PA 66 samples (1 and 3), in particular we have noticed that the molecular ion peak (m/z 84) characteristic of the cyclopentanone appears in all the PA 66 spectra. The evidence is that one of the major pyrolysis products from Nylon 66 is cyclopentanone [10]. This might be derived directly from the polyamide by a hydrogen transfer process leading to cyclopentanone and to compounds with amine and isocyanate

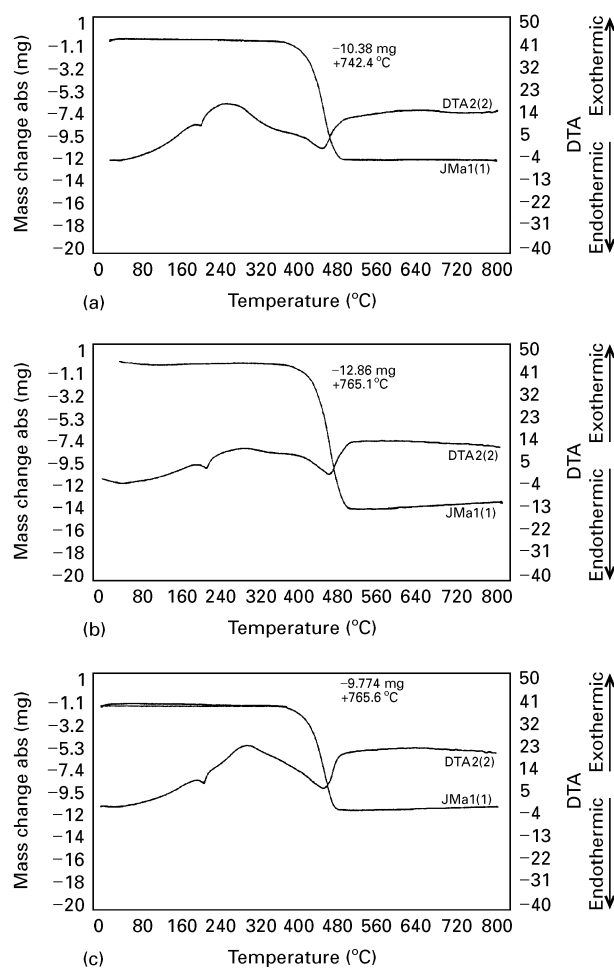
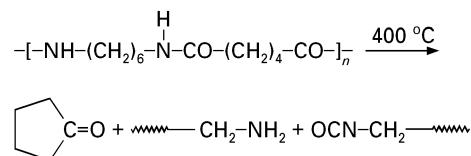


Figure 3 TG/DTA spectra in nitrogen atmosphere of PA 6 samples ((a) 4, (b) 5, (c) 6).

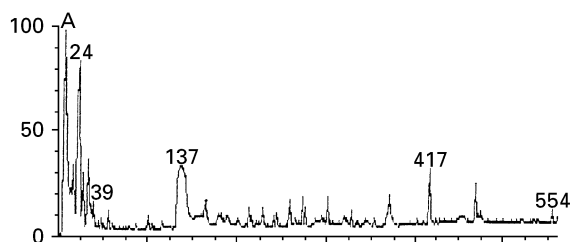
end-groups as secondary thermal fragments



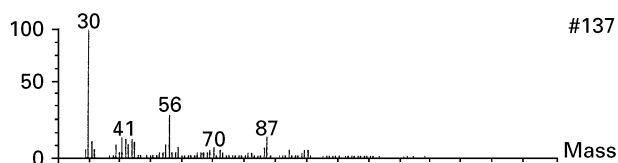
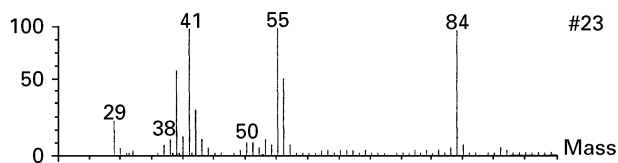
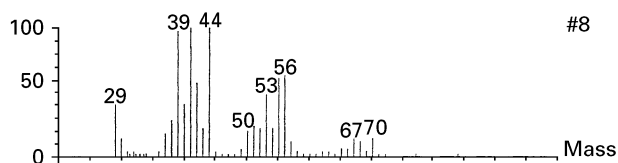
The comparison of each GC-MS spectrum of PA66 samples does not exhibit considerable differences between the pyrolytic products yielded and this suggests that the presence of glass or other kind of fillers does not influence the pyrolytic degradation of these materials.

The chromatograms concerned with PA6 samples (Fig. 5) exhibit the same trace: there are two intense peaks corresponding to scans 7 and 244. The first is due to more volatile products such as cyclohexane and 1-hexene while the second (the more intense one) corresponds to ϵ -caprolactam (MW = 113) which is the monomer generating Nylon 6.

In conclusion, this work shows that the presence of fillers does not influence the thermal degradation of hardened polyamides; in fact the pyrolysis products seem to be as similar as those for unfilled ones [10]. Such information could be very important when it is necessary to recycle a mixture of filled and unfilled polyamides because of their expensive separation.



(a)



(b)

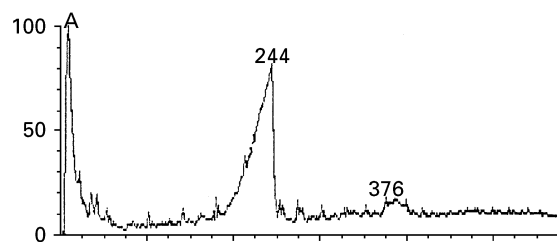
Figure 4 (a) Gas-chromatogram of sample 2 after pyrolysis at 770°C. (b) Mass spectra corresponding to scans 8, 24 and 137 of the pyrogram in (a).

TABLE II Pyrolysis products identified by comparison with library spectra

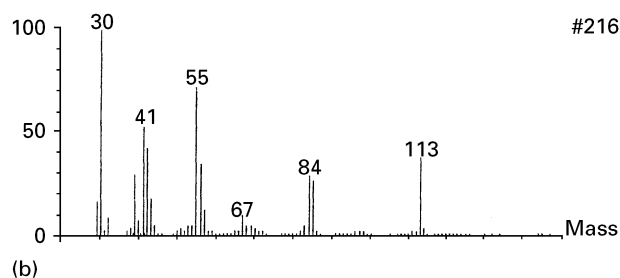
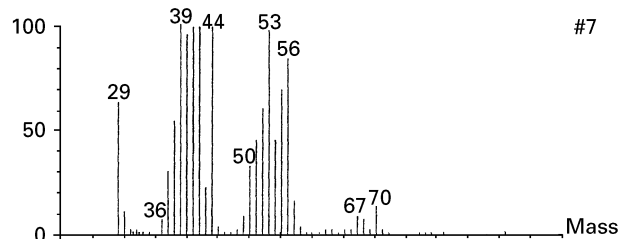
Number of scans	Library identification	Main peaks
Sample 2-PA 66		
6	2-methyl-1-propene	39,40,41,42,56
8	1-hexene	39,41,42,43,55,56,67
10-16	amyne end-group	30
20-24	cyclopentanone	39,41,55,84,56
137	1,6-hexanediene	30,56,70,87
Sample 4-PA 6		
21	1-hexene	39,41,55,56,84
244	caprolactam	30,41,42,55,84,113

Moreover, the production of monomers, by pyrolysing the polymer, offers the possibility of recycling the materials with both economical and environmental advantages.

Further developments of our work will aim to find the best methods for monomer collecting and energy recovering from pyrolysis of plastics.



(a)



(b)

Figure 5 (a) Gas-chromatogram of sample 4 after pyrolysis at 770°C. (b) Mass spectra corresponding to scans 21 and 244 of the pyrogram in (a).

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