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BINARY MIXTURES BASED ON POLYCAPROLACTONE AND CELLULOSE DERIVATIVES
Thermal degradation and pyrolysis

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Pyrolytic process has a promising potential for the environmentally friendly upgrading of lignocellulosic and plastic waste. Thermogravimetry and pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) were used to get information about the reactive decomposition of PCL in binary mixtures with microcrystalline cellulose (MC) or sisal fibres (SF). Preliminary thermogravimetric investigation showed that biomass is thermally degraded at lower temperatures than PCL and this process has a predominant influence on the thermal behaviour of the mixtures. Discrepancies between the experimental and predicted TG/DTG profiles were considered as a measurement of the extent of interactions occurring on co-pyrolysis. It was found that reactivity of PCL was slightly increased in PCL-SF binary mixtures. Evolution of acidic products from cellulose and hemicelluloses decomposition may promote PCL degradation in binary mixtures with SF. It seems that the co-pyrolysis process could have potential for the environmentally friendly transformation of biocomposites.

Keywords: *cellulose derivatives, mass spectrometry, polycaprolactone, pyrolysis, thermal analysis*

Introduction

Eco-friendly biocomposites derived from bio-fibres and biodegradable polymers are novel materials which can contribute to reduce the widespread dependence on fossil sources [1]. The abundant supply, low cost, high modulus and high aspect ratio of bio-fibres, combined with biodegradable polymers, conducts to environmentally benign composite materials with similar properties to the already known synthetic fibre-reinforced–polymers [1, 2].

Polycaprolactone (PCL) is one of the most versatile and commercially available biodegradable polymers, since it combines properties similar to those of low density polyethylene with biodegradability, compostability and compatibility with different forms of waste disposal [3]. However, the high cost of PCL has restricted its use only to specific applications. In order to reduce its cost, polycaprolactone was successfully blended with natural polymers including chitosan [4], and starch [5–8]. This last resulted in commercial materials with a variety of processing grades able for large-scale applications [8]. PCL was also used in traditional formulations such as glass-fibre composites, because it has low melting and crystallization temperatures, which make them suitable for a better control of the composite processing conditions by using conventional methods, such as extrusion/calendering [9]. On the other hand, quite recently, PCL-based nanocomposites were developed with enhanced mechanical, thermal and barrier properties [10, 11].

In spite of the well demonstrated versatility of PCL, little information is available about PCL-based biocomposites [12]. In general, there are some factors limiting the use of biodegradable polymers and bio-fibres in engineering fields, being the sensitivity to the temperature of compounding processes (injection moulding or extrusion) one of the most important drawbacks of biocomposites [13, 14]. Consequently, knowledge of the thermal behaviour of mixtures based on cellulose materials and polymers is of great importance from the processing point of view. In this sense, many reports in literature were devoted to the analysis of the effect of co-pyrolysis of cellulose derivatives and synthetic polymer mixtures [15–19]. The thermal decomposition of vinyl polymers in the presence of wood flour, lignin, cellulose and charcoal was recently studied by Jakab *et al.* [15, 16]. In mixtures based on wood and polypropylene (PP), the main devolatilization stage of wood occurred at lower temperatures than that of polymer, enabling that char formed from wood to influence the degradation process of PP. The charcoal derived from biomass had two effects: it shifted the beginning of the degradation to

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lower temperatures and reduced the maximum degradation temperature [15]. In the case of polystyrene (PS) decomposition, yields of monomer, dimer and trimer were reduced in the presence of cellulose derivatives indicating that the radical chain reactions were hindered by the presence of lignocellulosic char. However, biomass materials show a small effect on polyethylene (PE) degradation process [16]. Matsuzawa *et al.* [17] reported that poly(vinyl chloride) (PVC) and poly(vinylidene chloride) (PVdC) may affect the cellulose thermal degradation. HCl evolution in the dehydrochlorination reaction of vinyl chlorides seems to act as acid-catalyst favouring dehydration over depolymerization in cellulose pyrolysis. Sorum *et al.* [18] carried out the study of mixtures of newspaper and vinyl polymers from municipal solid wastes. Significant interactions between PVC and cellulose fractions were observed at low temperatures, where dehydrochlorination of PVC increased the reactivity of paper. In summary, depending on the nature of the polymer, a mutual interaction of the two degradation processes may be expected.

Thermal degradation of PCL has been investigated, but the mechanism is still under debate [19–22]. Persenaire *et al.* [19, 20] claimed that thermal degradation of PCL proceeds by a two-stage mechanism occurring at different temperatures. At temperatures lower than 300°C, pyrolysis produces random ester chain scission via *cis*-elimination, being 5-hexenoic acid and olefins the main degradation products. At higher temperatures, PCL depolymerizes via an unzipping mechanism which requires the presence of hydroxyl end groups and leads to the formation of ε-caprolactone. Aoyagi *et al.* [21], based on isothermal kinetic studies, proposed that PCL thermal degradation follows a one-step unzipping depolymerization mechanism from the polymer-chain ends, with only ε-caprolactone detected by Py-GC/MS. Sivalingam *et al.* [22] analyzed PCL thermal degradation by thermogravimetry in dynamic and isothermal conditions. Under non-isothermal conditions their results suggested that the governing mechanism changes during degradation and this fact was explained by two parallel mechanisms: random chain and specific chain-end scission. Apparent activation energy changed from low to high temperatures during degradation, which was an indication of changes in the mechanism during non-isothermal heating. On the other hand, under isothermal conditions, degradation proceeded only by unzipping. This last result was confirmed by mass spectrometry of the evolved gases: the main molecular fragments were ε-caprolactone (m/z=114) and CO_2 (m/z=44).

Therefore, whatever the mechanism proposed, PCL thermal degradation leads to the evolution of acid products, mainly 5-hexenoic acid, which may influence cellulose thermal degradation. Interactions in the solid and/or gaseous state between degradation products and the constituents of the mixture may change (either delay or accelerate) the thermal behaviour of the individual components. In a previous work, the effect of the presence of cellulose derivatives on PCL thermal stability was analyzed by thermogravimetric analysis [23]. A mutual stabilizing effect of both co-components in mixtures based on microcrystalline cellulose (MC) and PCL was found. This behaviour was attributed to some kind of solid–solid and gas–solid interactions. On the other hand, sisal fibre (SF) showed an unfavourable effect on the thermal stability of PCL.

The objective of the present work is to analyze the co-pyrolysis of microcrystalline cellulose (MC), sisal fibre (SF) and polycaprolactone (PCL) under inert atmosphere by thermogravimetry (TG) and pyrolysis coupled to gas chromatography and mass spectrometry (Py/GC-MS).

Experimental

Polycaprolactone (PCL, molar mass 80 kDa) was supplied by Sigma-Aldrich (Steinheim, Germany). MC was purchased from Merck (Darmstadt, Germany). SF was kindly supplied by Brascorda (Brazil). PCL was manually blended with MC and SF in 2:1 mass proportion. Mixtures were prepared at room temperature in order to avoid any degradation reaction induced by processing operations.

Dynamic degradation measurements were carried out by using a Mettler-Toledo 851e-TGA-SDTA system (Schwarzenbach, Switzerland) coupled to STAR-E software. These tests were performed in order to determine the maximum degradation rate ($T_{\max}$) of pure components and mixtures. $T_{\max}$ values were used as the input temperatures for Py-GC/MS experiments. Experiments were run from 30 to 600°C at different heating rates (5–30°C min^{-1}) and under nitrogen atmosphere (20 mL min^{-1}). Samples were placed in alumina crucibles (5–10 mg) without further treatment.

Py-GC/MS measurements were performed by using an off-line method based on the use of a home-made reactor [24]. Samples (approximately 60 mg) were introduced into the furnace at the selected temperature. Evolved gases were collected in a Tedlar bag supplied by Teknokroma (Barcelona, Spain) and were immediately transferred to a HP-5890 GC/MS (Palo Alto, CA, USA) with an injection port able to receive gas samples and equipped with a DB-5 capillary column (50 m×0.25 mm I.D. and 0.2 μm film thickness). Relevant peaks were identified by MS (15–125 amu) by using electron impact (70 eV) as ionization mode.

Results and discussion

Thermal degradation of all components was studied by TG/DTG in order to establish pyrolysis temperatures near degradation. Figure 1 shows the derivatives of the mass loss curves of each component obtained at 10°C min^{-1}. PCL and MC degrade in a single-step process, with maximum degradation temperatures centered at 412 and 347°C, respectively. On the other hand, SF shows a multi-step decomposition process due to its composite nature. SF is mainly composed by hemicelluloses (12%, $T_{\max}$=300°C), cellulose (66–72%, $T_{\max}$=358°C) and lignin (10–14%, $T_{\max}$ in the range 250–800°C). From the maximum degradation temperatures obtained by TG/DTG experiments, pyrolysis temperatures were established at 410°C for PCL and the binary mixtures, and 300°C for cellulose derivatives.

Since PCL degradation peak slightly superimposes with both, MC and SF, some interactions between decomposition products could be possible. These interactions may affect, in positive or negative way, the thermal behaviour of the components of the actual mixture. An easy way to evaluate the presence of interactions is by predicting the TG/DTG curves as the sum of individual components as follows [17, 18].

$$(m/m_0)_{\text{sum of individual components}} = \sum\nolimits_j Yi(m/m_0)_i \qquad (1)$$

where Yi is the mass fraction of component i, $(m/m_0)_i$ is the normalized mass loss for component i derived from TG experiments for the individual components, j denotes the number of components in the actual mixture. Derivatives for the sum of individual components are obtained in the same way as mass loss. If there are no interactions between co-components, experimental degradation curves should be reproduced by Eq. (1). For predicting purposes, experimental mass loss data of pure components obtained at 10°C min^{-1} (Fig. 1), were used. Calculated (dashed lines) and experimental (solid lines) TG/DTG curves of PCL-MC and PCL-SF, are shown in Figs 2a and b. Some discrepancies between experimental and calculated curves are observed: in the mixtures with MC, both co-components increase their thermal stability, meanwhile SF decreases thermal stability of PCL, as can be concluded from the shift in $T_{\max}$ values. In PCL-MC mixtures, since MC degradation occurs at lower temperature than PCL, two main interactions can be assumed: in the solid state, hydrogen type interactions may be present between the PCL carbonyl groups and hydroxyl groups from MC. These interactions delay the MC dehydration reaction, which takes place at lower temperatures than depolymerization. As degradation proceeds, the effect of the above mentioned interactions decreases, but char and gases evolved from cellulose degradation may interact with solid PCL. Particularly, char issued from MC degradation may act as thermal stabilizer for PCL. These results are in agreement with the apparent activation energy values calculated for each component of the mixture and previously reported [23].

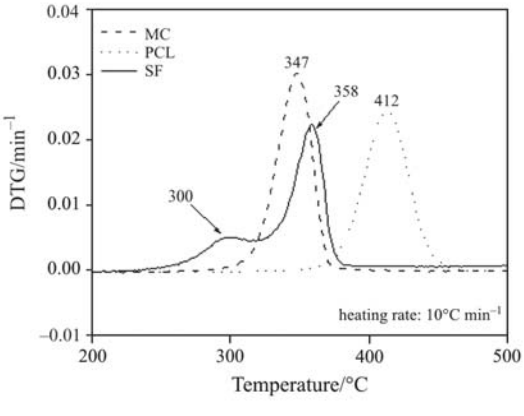

Fig. 1 Derivative curve of all components used in the formulation of mixtures

On the other hand, mixtures of PCL with SF were also analyzed (Fig. 2b). Solid state interactions, similar to those assumed for the PCL-MC mixture, may be responsible of the increment in SF thermal stability: $T_{\max}$ for the cellulose fraction shifts from 357°C (predicted curve in Fig. 2b) to 364°C in the actual mixture. However, SF shows a slight unfavourable effect on PCL thermal stability since $T_{\max}$ shifts from 412 (dashed line) to 409°C (solid line). As it was mentioned above, sisal fibres are mainly composed by cellulose and

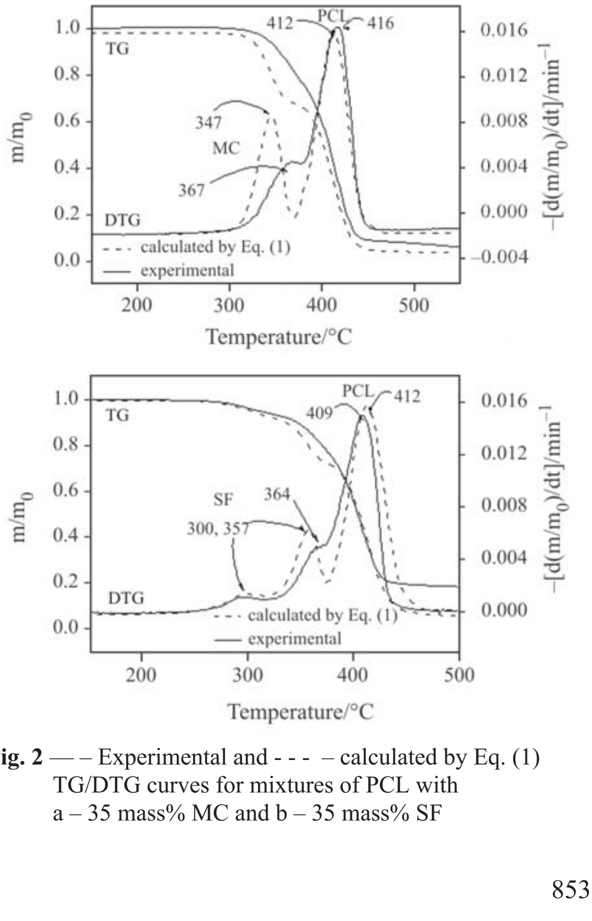

Fig. 2 —— – Experimental and - - - – calculated by Eq. (1) TG/DTG curves for mixtures of PCL with a – 35 mass% MC and b – 35 mass% SF

hemicelluloses, which degrade almost completely before PCL degradation begins. Thus, the degradation products generated may interact with PCL. The main constituents of hemicelluloses are galacto–glucomannan (70% mannan), which makes up approximately 60% of the total hemicelluloses content, and arabino-4-0-methylglucuronoxylan (65% xylan), which constitutes the remaining 40%. Most hemicelluloses do not yield significant amounts of levoglucosan, but most of the acetic acid liberated from wood pyrolysis is attributed to the deacetylation of hemicelluloses [25]. The formation of acetic acid as a decomposition product of hemicelluloses may be the main factor in the slight decrease of PCL thermal stability. If PCL decomposition proceeds by random scission of ester linkages, acetic acid may promote the reaction. As a result, fibres destabilize the polymer and lower energies should be required to get the complete degradation of mixtures.

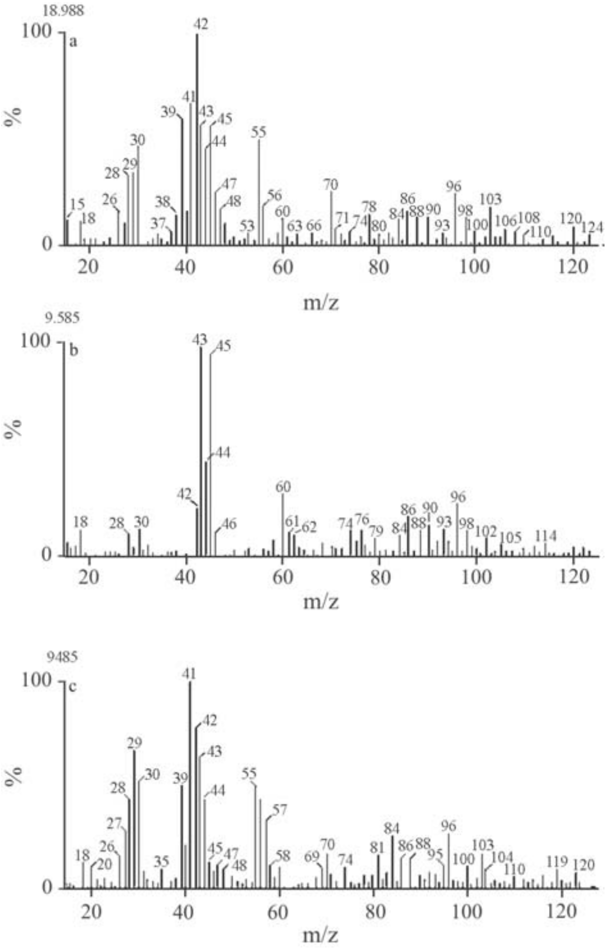

Fig. 3 Mass spectra of pyrolysis products at a – 410 and b, c – 300°C for the maximum peak in the chromatogram for each individual component: a – PCL, b – MC and c – SF

In order to analyze gases evolved from the degradation of the individual components and their possible influence in the co-pyrolysis of the binary mixtures, Py-GC/MS analysis of pure materials was carried out. The mass spectrum for the highest peak in PCL gas chromatogram at retention time (*rt*) of 18.988 min is shown in Fig. 3a. Molecular ions of H_2O (*m*/*z*=18), CO (*m*/*z*=28), acetaldehyde derivatives (*m*/*z*=41–43) can be easily assigned. In addition, molecular fragments associated to the decomposition of 5-hexenoic acid (*m*/*z*=114) were found at *m*/*z*=96 (ketenic fragment: 114–H_2O); *m*/*z*=70 (decarboxylated derivative: 114–CO_2) and *m*/*z*=55, (rupture of the ε-caprolactone ring), which agree with those reported in [19]. In our previous study performed by TG/DTG we reported that PCL decomposes throughout a one-step degradation process with a constant apparent activation energy (E_a) 203 kJ mol^{-1}, which indicates that degradation mechanism remains unchanged within a wide conversion range ($0.1<\alpha<0.9$) [23]. These results suggest a single-step degradation mechanism and are in agreement with those reported by Aoyagi *et al.* [21]. However, the two-step mechanism proposed by Persenaire *et al.* [19] can not be excluded due to two factors: firstly, high resolution TG (as indicated by authors) based on the application of a continuously variable heating rate in response to changes in the sample decomposition rate was used in their experiments [19], thus results may be different from other authors. Nevertheless, gases evolved were ionised by the same technique and energy (electron impact and 70 eV) than in our experiments, so no influence can be attributed to these parameters. Secondly, authors claimed that 5-hexenoic acid (the main product of the first step of degradation) was produced at temperatures lower than 300°C. In our experiments, temperature was 410°C during the whole process, thus, if 5-hexenoic acid molecules were formed, they would degrade immediately at that temperature. However, fragments related to the monomer were found. As a consequence, the pyrolysis joined to TG/DTG results allows us to propose a one-step thermal degradation mechanism for PCL at temperatures higher than 410°C. On the other hand, no evidence of the two parallel model reported by Sivalingam *et al.* [22] was found, because apparent activation energy was invariant within a large conversion range.

Pyrolysis of cellulose is reported to follow a two-stage mechanism; dehydration and depolymerization [17, 26, 27]. The first mechanism is an intra-ring scission and produces H_2O (*m*/*z*=18), CO (*m*/*z*=28), CO_2 (*m*/*z*=44) and aldehyde derivatives (*m*/*z*=29), and acetaldehyde derivatives (*m*/*z*=43), meanwhile the second (at higher temperatures) is the transglycosilation and levoglucosan formation initiated by depolymerization, which produces CO, CO_2, tar, oils and char [25]. Figure 3b shows the mass spectrum obtained for the highest GC peak of MC (*rt*=9.585 min). As expected from the pyrolysis temperature used (300°C), the main gaseous products agreed with those obtained during dehydration process, including acetic acid (m/z=60). Acidic products may influence pyrolysis in mixtures with polyesters which degrade at higher temperatures than MC, such as PCL.

Figure 3c shows the pyrogram for SF at 300°C. Keeping in mind that SF is a complex material, the main peaks in the mass spectrum of the most intense GC peak (rt=9.485 min) should be associated with cellulose and hemicelluloses decomposition. The main peaks observed were CO (m/z=28), aldehyde derivatives (m/z=27–29) and acetaldehyde derivatives (m/z=39–43). Some significant peaks are also observed at m/z=55, 70, 96 and 103 corresponding to ruptures in the cellulose structure, which is the most common in cellulose fibres. The peak at m/z=60 corresponds to acetic acid mainly formed from hemicelluloses degradation [25, 26]. In particular, small peaks at m/z=84 and 104 can correspond to aromatic structures formed during the sisal decomposition and rearrangement of hydrocarbon structures [26].

Binary mixtures were pyrolyzed at 410°C in order to investigate the effect of gases evolved from cellulose and cellulose fibres on PCL decomposition. For all the mixtures analyzed (PCL-MC and PCL-SF), two main chromatographic peaks were observed with retention times around 9.4 and 19 min corresponding to cellulose (and cellulose derivatives) and PCL degradation respectively.

Difference mass spectra between PCL-MC mixtures and pure components are shown in Figs 4a and b. Mass spectrum of MC in the mixture (Fig. 4a) shows peaks at m/z=41, 55, 70 and 103, which were absent in the pure MC pyrogram (Fig. 3b). Particularly, peak at m/z=41 which is associated to acetaldehyde derivatives clearly increases while that at m/z=60 (attributed to acetic acid) decreases. Variations in the proportion and nature of the generated products strongly depend on pyrolysis conditions. In particular, the influence of pyrolysis temperature on the chemical composition of the cellulose pyrolysate was reported [27]. Acidic compounds issued from PCL decomposition may favour other mechanisms different to the formation of levoglucosan, which is one of the main paths during pyrolysis of cellulose above 400°C [27]. Consequently, MC pyrolysis is modified by the presence of PCL.

Figure 4b shows the effect of the addition of MC to PCL. Some interactions between gas products evolved in MC pyrolysis and PCL should be considered as responsible of the observed differences. Peaks at m/z=55, 70 and 96 decrease, meanwhile an increment in m/z=45 and 86 is observed. The presence of a peak at m/z=86, which corresponds to the loss of CO from ε-caprolactone (114–CO) is caused by acidic components formed during the MC pyrolysis (m/z=45, major fragment of acetic acid). Acidic compounds promote polyester depolymerization, thus a destabilizing effect should be expected. However, the slight increment in thermal stability of PCL in a mixture with MC observed during TG experiments may be attributed to a synergetic effect. In fact, acidic products evolved from MC degradation may promote the random scission of ester linkages of PCL, but also an increase in the char formation during cellulose decomposition which in turn, may act as thermal stabilizer of PCL.

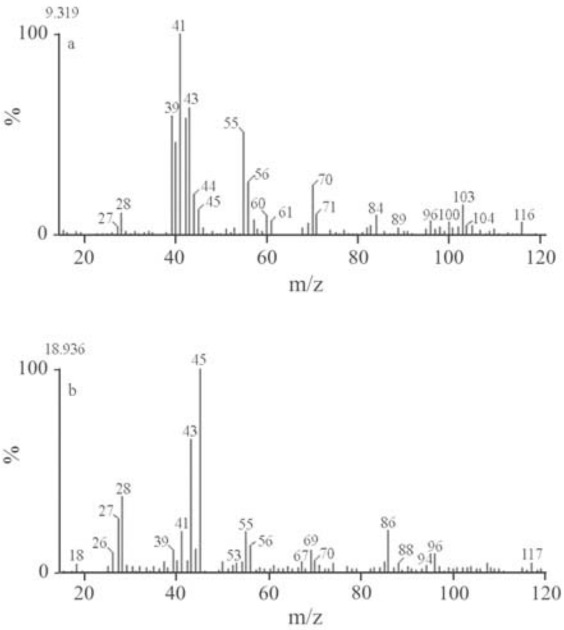

Fig. 4 Difference mass spectra of pyrolysis products of the mixtures and each pure component in the PCL/MC mixture; a – MC peak (rt=9.319 min), b – PCL peak (rt=18.936 min)

A similar study was carried out for PCL-SF mixtures. Figure 5 shows the difference spectrum for PCL in the mixture. The most significant difference is the increase in intensity of the peak corresponding to acetic acid (m/z=60). This effect is more pronounced than in the case of PCL-MC because both, cellulose and hemicelluloses from fibres, contribute to the produc-

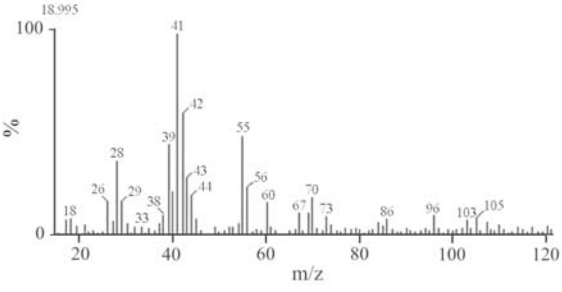

Fig. 5 Difference mass spectrum of pyrolysis products of the PCL/SF mixture (rt=18.995 min)

tion of acetic acid during pyrolysis. Consequently, the formation of PCL degradation products, as those forming structures at *m*/*z*=55 and 70, is significant, and acidic catalysis of PCL depolymerization by random scission prevails over the stabilizing effect of char generated during SF decomposition. This last promotes PCL decomposition in binary mixtures with SF. Therefore, a partial destabilization of PCL by SF is observed, in agreement with TG results.

Conclusions

The effect of the formulation of mixtures based on PCL and cellulose derivatives on the thermal degradation of both co-components was evaluated. TG/DTG experiments of the binary mixtures of PCL and MC or SF gave different results from those obtained for pure components. MC and PCL increased their mutual stability meanwhile SF showed an opposite effect on PCL. These results allowed us to assume interactions between PCL and cellulose derivatives (solid–solid, solid–gas or gas–solid), which were later confirmed by Py-GC/MS experiments. The increment in thermal stability of PCL in mixtures with MC was related to the stabilizing effect of char formed during pyrolysis, which prevail over the effect of acidic gases evolved from MC pyrolysis. Thus, solid–gas are the main kind of interactions to be considered in PCL–MC binary mixtures. Contrary, the presence of SF increased reactivity of PCL, which was mainly attributed to the catalytic effect of acetic acid issued from cellulose and hemicelluloses decomposition. Consequently, co-pyrolysis in binary mixtures of PCL and cellulose fibres should be considered as an economically favourable alternative for the pyrolysis treatment of solid wastes because lower energy will be required. It seems that the co-pyrolysis process could have potential for the environmentally friendly transformation of lignocellulose fibres-reinforced biodegradable polyesters.

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