

Material Behaviour

Thermal degradation and pyrolysis of mixtures based on poly(3-hydroxybutyrate-8%-3-hydroxyvalerate) and cellulose derivatives

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Abstract

Thermal degradation and pyrolysis behaviour of mixtures based on poly(3-hydroxybutyrate-co-8%-3-hydroxyvalerate) (P(HB-8%HV)) and cellulose derivatives has been studied. The effect of the formulation of mixtures in the thermal degradation of both co-components was evaluated. TG/DTG experiments and Py-GC-MS were used in this study. Solid–solid and gas–solid interactions between co-components were analyzed by using a simple mixture rule. Mixtures with microcrystalline cellulose (MC) resulted in an enhancement of thermal stability of both co-components due to strong hydrogen type interactions in the solid state and between gases evolved from polymer decomposition and solid MC. Crotonic acid seemed to induce a higher order in cellulose, causing disruption of some hydrogen bonds within it and promoting the formation of more stable cellulose structure. On the other hand, sisal fiber showed an unfavourable effect on polymer thermal stability. Acetic acid produced from hemicellulose thermal decomposition seemed to act as acid promoter for the random scission of ester linkages in P(HB-8%HV). © 2005 Elsevier Ltd. All rights reserved.

Keywords: Thermal degradation; Poly(3-hydroxybutyrate-co-3-hydroxyvalerate); Cellulose; Thermogravimetric analysis; Pyrolysis-GC-MS

1. Introduction

Poly(hydroxyalcanotes) (PHAs), such as poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) P(HB-co-HV), are bio-based polyesters produced from renewable resources by a variety of bacteria as intracellular storage material [1,2]. They are considered to be very promising materials for use as environmentally benign plastics to be applied in the packaging, agriculture and medical field due to their genuine biodegradability, slow hydrolysis rate and low water vapour permeability [3].

PHB is somewhat brittle and consequently limited in its commercial scope, due to the fact that it shows a narrow processing window as it exhibits melt instability due to thermal degradation at temperatures just above the melting point (170–200 °C) [1,4,5]. Nevertheless, copolymers with varying molar ratio of 3-hydroxyvalerate (HV), P(HB-co-HV), result in more ductile and processable materials, which make them suitable for many commercial applications [6,7]. The major drawback of using PHAs in large-scale applications is their rather high cost, compared to that of the commodity plastics [8,9].

One strategy to overcome some of the above mentioned problems is by adding natural fibres in order to obtain biocomposites with similar properties to those of the traditional synthetic fiber-reinforced composites, with the advantage of being completely biodegradable.

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Biocomposites based on PHAs and different cellulose derivatives, such as cellulose fibers [8–10], wood fiber [11], steam exploded straw [12] and flax fiber [13], are reported in the literature. PHAs-based biocomposites are usually processed by extrusion or injection moulding at temperatures just above their melting point. The main reactions involved during biocomposite processing are chain scission of the polymer matrix, with the concomitant decrease in the molecular weight, and cellulose fiber degradation due to hydrolytic reactions promoted by PHA decomposition products. Gatelhom and Mathiasson [8,9] reported a synergistic effect of processing cellulose fibers with PHB. The reduction in cellulose-fiber size was related to the molecular weight decrease of PHB during compounding. The crotonic acid formed as a result of the thermal degradation of PHB [14–16,18] during the homogenising step may act as acid catalyst for producing in situ hydrolysis of the cellulose components, which yields a dramatic reduction in the fiber aspect ratio. The addition of hydrogen bonding additives improves the fiber-matrix interaction and enhances thermal stability of the resulting biocomposite [13]. As a consequence, the development of commercial applications for PHAs-based biocomposites requires the understanding of the thermal degradation behaviour of such mixtures in order to optimise the processing conditions and their final properties.

Thermal degradation of the pure components of these biocomposites, polymer matrix and cellulose derivatives, has been extensively studied [3,4,14–25]. Mechanisms proposed in the literature suggest that PHB thermal degradation occurs almost exclusively by random chain scission (*cis*-elimination) [3–15]. The major pyrolysis product of PHB is crotonic acid produced by the *cis*-elimination reaction [3,4,16]. Significant quantities of PHB oligomers and small quantities of isocrotonic acid were also detected on heating the polymer above 300 °C. Secondary products, such as propylene, CO₂, acetaldehyde, etc., were also formed by further decomposition of the initial products. Aoyagi et al. [14] analysed PHB thermal degradation under isothermal conditions. An inverse relationship between the number-average degree of polymerization (P_n) with time was found, which is associated with a completely-random chain scission. In addition, Gas-Chromatography coupled to Mass Spectrometry (GC/MS) analysis performed on volatiles evolved from PHB at 280 °C gave mainly oligomers of crotonic acid, which can be related with scission of the ester groups. Similar results were reported for PHB and its copolymer with 30% molar ratio of HV, but some slight differences in the products of the thermal decomposition were found, as it was determined by Infrared spectroscopy and GC/MS analysis [15]. Differential Scanning Calorimetry (DSC) was also used to analyse PHB thermal degradation in the presence of two plasticizers [17]. Authors concluded that degradation of PHB is marginal below 170 °C, even in the presence of glycerol (protodegradant additive), and proposed that PHB thermal degradation proceeds by the random scission of polymer chains.

On the other hand, the thermal degradation mechanism of P(HB-*co*-HV) copolymers has been reported to be analogous to that for PHB, with a similar degradation kinetics [18].

The study of thermal degradation and pyrolysis of cellulose and their derivatives has been the object of recent research [19–22]. Cellulose fibers are mainly constituted by hemicellulose, cellulose and lignin. Several studies have indicated the existence of slight interactions between the main components of natural fibers during pyrolysis, and consequently that the degradation process is not a simple sum of the individual ones [22]. Hemicellulose is less stable than cellulose and gives rise to more non-combustible gases, mainly acetic acid [21]. Cellulose thermal degradation is reported to proceed through two competing reactions [19–21], i.e. dehydration and depolymerization. The first reaction progresses forming char, CO₂, CO, H₂O and other volatiles (i.e. aldehydes) with the intra-ring scission of the glucose unit in the cellulose chain. The second reaction is initiated by depolymerization at high temperatures producing CO₂, CO, liquid products and char. Several studies have been devoted to the study of the thermal decomposition of mixtures of polymers and lignocellulosic materials [19,20,23–25]. Jakab et al. [19,20] analysed the effect of the presence of cellulose derivatives on thermal decomposition of vinyl polymers. The presence of lignocellulosic materials slightly affects high density polyethylene (HDPE) decomposition, as the main degradation processes of cellulose derivatives have ended before HDPE begins to degrade. On the other hand, the effect of the presence of PP on the thermal decomposition of cellulose derivatives was negligible. When degradation of biomass and polystyrene (PS) mixtures was evaluated, the yield of monomer, dimer and trimer from PS decomposition was reduced, indicating that the radical chain reactions and intramolecular hydrogen transfer reactions were hindered by the presence of lignocellulose char [19]. In some cases, the polymeric matrix can influence the thermal degradation of cellulose materials. Matsuzawa et al. [24] 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 to promote the dehydration reaction rather than the depolymerization reaction in cellulose pyrolysis. Similar results for mixtures of different kind of paper and vinyl polymers were reported by Sorum et al. [25]. A similar approach can be introduced in the case of biocomposites. It is important to point out that thermal degradation of the co-components in a mixture may behave in a different way than in the case of pure components, mainly due to the presence of strong interactions in the solid or in the gaseous state [24–26]. The mutual influence of co-components in mixtures of biodegradable polymers, such as polycaprolactone (PCL), and cellulose derivatives was analysed by thermogravimetry [26]. PCL/microcrystalline cellulose mixtures were more stable than pure components, due to the presence of strong hydrogen interactions between

carbonyl groups from PCL and OH groups in cellulose. On the other hand, sisal fibers had an unfavourable effect on thermal stability of the mixtures.

Interactions between biodegradable polymers and biomass are not well-known. The main goal of the present paper is to analyse the effect of the presence of cellulose derivatives (CD), such as microcrystalline cellulose (MC) and sisal fiber (SF), on the thermal stability of poly(3-hydroxybutyrate-co-8%(3-hydroxyvalerate), P(HB-8%HV). Thermal analysis of pure components and binary mixtures (represented as P(HB-8%HV)/wt%CD) was performed by Thermogravimetric Analysis (TGA) under dynamic conditions. The calculation of apparent activation energies was based on the application of the isoconversional Friedman method [27]. Gaseous products evolved from pyrolysis experiments were identified by Gas Chromatography coupled to Mass Spectrometry (GC/MS).

2. Materials and methods

P(HB-8%HV) was supplied by Aldrich (Steinheim, Germany), and was used as received without further treatment. Microcrystalline cellulose (MC) was purchased from Merck (Darmstadt, Germany). Sisal fibre (SF) was provided by Brascorda (Brazil). Fibers were chopped before using in order to obtain a powder with an average length of about 2 μm , as was determined by Scanning Electronic Microscopy (SEM), and then dried under vacuum.

Mixtures with microcrystalline cellulose and sisal fiber, i.e. P(HB-8%HV)/MC and P(HB-8%HV)/SF, containing up to 35% in weight of cellulose derivative were prepared manually without any additive and at room temperature. All mixtures were stored to protect them from moisture and ambient humidity, at room temperature before testing.

Dynamic thermal degradation measurements were performed in a Mettler-Toledo 851e-TGA-SDTA thermal gravimetric analyser (Schwarzenbach, Switzerland). Temperature was raised from room temperature up to 500 °C using different heating rates, between 5 and 40 °C/min. All runs were carried out under nitrogen atmosphere (200 cm³/min) in order to prevent any thermo-oxidative reaction. Kinetic parameters were calculated from TG/DTG experimental data by using the isoconversional Friedman method [27] which was already successfully applied for the calculation of the kinetic behaviour of biomass based mixtures, such as asphaltene/sugarcane bagasse, and polycaprolactone/cellulose derivatives [26].

Pyrolysis (Py) measurements were performed by using a home-made reactor [28]. Approximately, 60 mg of sample were placed into a ceramic container which was introduced at 5 mm/min into a furnace at 300 °C. Pyrolysis temperature was fixed from the maximum degradation rate data obtained from TG/DTG experiments.

Evolved gases were collected in Tedlar bags supplied by Teknokroma (Barcelona, Spain) and were analysed by Gas

Chromatography by using 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 \times 0.25 mm I.D. and 0.2 μm film thickness). Measurements were carried out at 260 °C (isothermal program) with the injector temperature at 300 °C. Relevant peaks were identified by Mass Spectrometry (MS) (15–150 amu) by using electron impact (70 eV) as ionisation mode.

3. Results and discussion

TG/DTG curves obtained at 10 °C/min and under nitrogen atmosphere for the individual components of the mixtures are shown in Fig. 1. From similar curves at different heating rates, degradation temperatures and kinetic parameters, such as initial decomposition temperature (T_i), maximum degradation rate (T_{max}), final temperature (T_f), and average apparent activation energy (E_a) can be calculated. Degradation and kinetic parameters of both individual pure materials and mixtures are summarized in Table 1. Weight loss pattern of P(HB-8%HV) is a one-step process with a maximum degradation rate around 280 °C (Fig. 1) [29]. The shape of weight loss curves do not change with variations in heating rate, but T_{max} values shift toward higher temperatures, as was reported elsewhere for the same materials [15]. Microcrystalline cellulose also shows a single step-degradation process with a T_{max} at about 347 °C at 10 °C/min. On the other hand, sisal fiber thermal decomposition seems to be a gradual process with no clear steps in the TG curve. However, two overlapped peaks can be observed in DTG curves: the first at 299 °C corresponds to hemicellulose and the second and main peak, is associated with cellulose degradation (359 °C) [22,26]. The lignin peak is completely overlapped by the other two because it shows a wide range of degradation temperatures

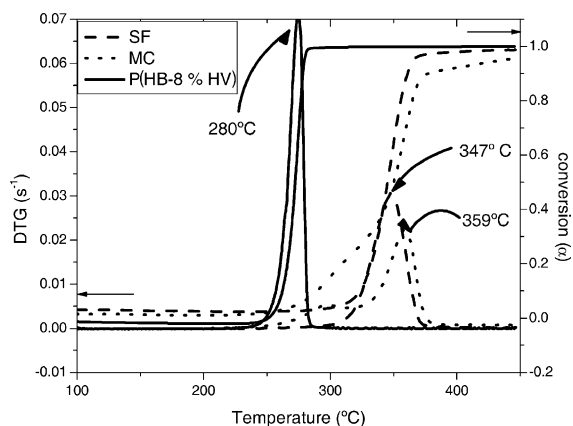


Fig. 1. TG/DTG curve of the pure components obtained at 10 °C/min and under nitrogen atmosphere: (—) P(HB-8%HV), (---) SF, (····) MC.

Table 1
Thermal and kinetic parameters of pure components and mixtures based on P(HB-8%HV) and 35 wt% of cellulose derivatives

Material	Decomposition stage	T_i (°C) ^a	T_{max} (°C) ^b	T_f (°C) ^c	E_a^d (kJ/mol)
P(HB-8%HV)	1	253	280	294	111
MC	1	300	347	377	187
SF	1	254	299	322	166
	2	322	359	389	119
P(HB-8%HV)/ 35 wt%MC	1	243	284	303	114
	2	310	360	383	220
P(HB-8%HV)/ 35 wt%SF	1	238	275	295	116
	2	308	359	388	250

^a Taken from the onset of the decomposition process.

^b Maximum of the DTG curve.

^c Taken from the TG curve as the point of return to constant weight.

^d Average apparent activation energy determined from the slope of Friedman isoconversional plots.

(up to 800 °C). These results are in accordance with those reported in the literature for different lignocellulosic materials [13,22,25].

Apparent activation energies (E_a) for the pure components were determined from TG/DTG data obtained at different heating rates in the range of 5–40 °C/min under nitrogen atmosphere by applying the isoconversional Friedman method [27]. Fig. 2 represents the isoconversional plots for P(HB-8%HV) and E_a values obtained from the slopes are summarized in Table 1. The average apparent activation energy determined for conversion degrees (α) varying from 0.1 to 0.9 was 111 ± 8 kJ/mol. Considerable variations among the reported E_a values may be found when analysing the literature: 74 kJ/mol for PHB determined by Osawa's method [14]; 300 and 370 kJ/mol for PHB and

P(HB-30%HV) respectively, determined by the Coats and Redfern method [15]; 311 kJ/mol for P(HB-11%HV) [30]. The wide spread in E_a values may be attributed to differences in the origin of the polymers, the molecular weight, the molar-ratio content in the copolymers and the different approaches used to calculate E_a .

Reaction order (n) was also calculated from the intercepts in Fig. 2, resulting in an average value of 0.95, which is in the range of those reported in the literature for the same materials [15]. As can be concluded from the analysis of the slopes in Fig. 2, E_a values do not change significantly with conversion, thus P(HB-8%HV) seems to proceed through the cleavage of linkages with similar energy bonds. Mechanisms proposed in the literature suggest that PHB thermal degradation occurs almost exclusively by random chain scission (*cis*-elimination), crotonic acid being the major pyrolysis product [4,5,14,15]. Thermal degradation mechanism of P(HB-co-HV) copolymers has been reported to be analogous to that for PHB, with a similar activation energy and degradation kinetics [18].

Kinetic parameters of microcrystalline cellulose and sisal fiber were determined from isoconversional Friedman plots in our previous work [26], and average values are also reported in Table 1. For MC, E_a was 187 kJ/mol and was in the range of values reported in the literature for different kinds of Avicel [23]. In the case of SF, two regions were clearly identified: the first process ($\alpha < 0.3$) corresponding to the hemicellulose degradation had an E_a of 165.5 kJ/mol, while for the second ($\alpha > 0.4$), corresponding to the cellulose degradation, an average E_a of 119 kJ/mol, was found. These values were in agreement with those found in the literature for lignocellulosic materials [22,23]. As can be concluded from the analysis of Table 1, cellulose derivatives are more thermally stable than P(HB-8%HV), thus some kind of changes in thermal stability of the polymer should be expected when mixed.

In order to check possible interactions between components, the effect on thermal degradation of the addition of MC and SF (35 wt%) to P(HB-8%HV) was analysed and thermograms obtained are shown in Fig. 3(a) and (b). In both mixtures, co-components show a different behaviour from that of the pure materials. In the case of P(HB-8%HV)/35 wt%MC (solid line in Fig. 3(a)), both co-components increase their thermal stability, as can be concluded from the shift of T_{max} toward higher values (Table 1). On the other hand, presence of sisal fiber decreases the thermal stability of P(HB-8%HV) (solid line in Fig. 3(b)), meanwhile SF does not suffer major changes in T_{max} values. Indeed, sisal fibers have an unfavourable effect on the thermal stability of P(HB-8%HV).

Although thermal degradation of P(HB-8%HV) is almost completed before the beginning of that corresponding to MC or SF, the decomposition curves of both co-components in the mixture are partially overlapped, as can be seen in Fig. 3. Therefore, some type of solid–solid and/or gas–solid interactions between co-components must be

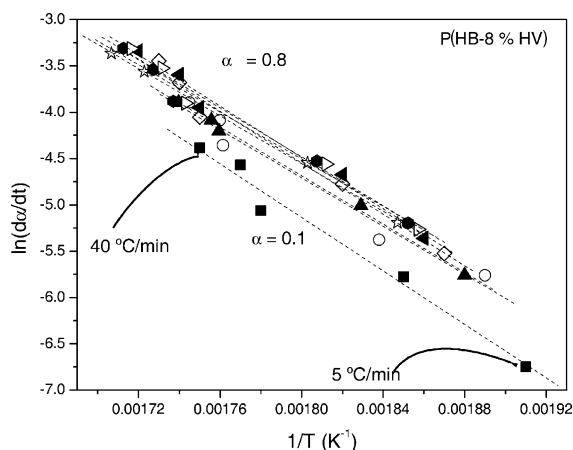


Fig. 2. Isoconversional Friedman plots ($0.1 < \alpha < 0.9$) of P(HB-8%HV).

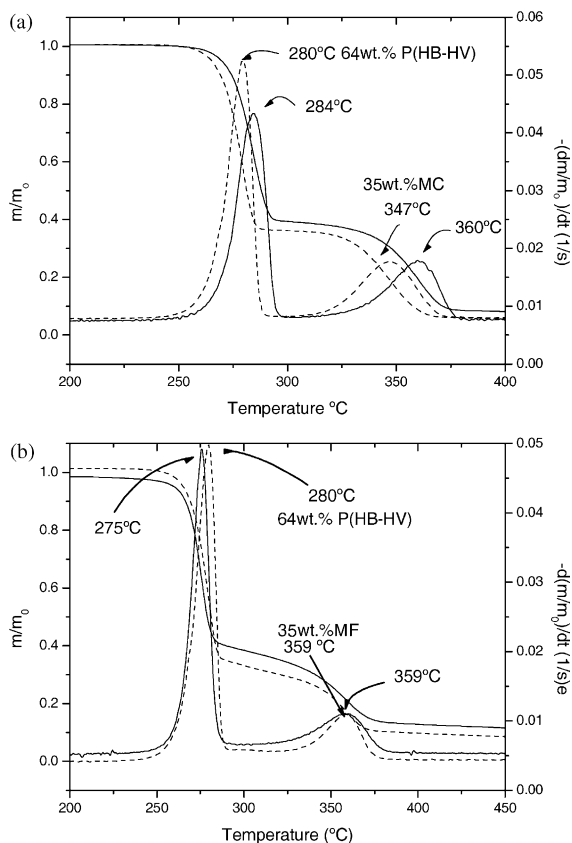


Fig. 3. Experimental (—) and calculated by Eq. (1) (---) TG/DTG curves for mixtures of P(HB-8%HV) with 35 wt% of cellulose derivatives. (a) P(HB-8%HV)/35 wt%MC, (b) P(HB-8%HV)/35 wt%SF.

considered. These interactions could affect, in a 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 [24,25].

$$(m/m_0)_{\text{sum of individual components}} = \sum_j Y_i (m/m_0)_i \quad (1)$$

where Y_i 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 weight 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 (Fig. 1), were used. Calculated TG/DTG curves of P(HB-8%HV)/35 wt%MC and P(HB-8%HV)/35 wt%SF, are shown in Fig. 3(a) and (b) (dashed lines). Some discrepancies between experimental and calculated

curves are observed: the mixtures with MC, both co-components increase their thermal stability, meanwhile SF increases the reactivity of P(HB-8%HV), as can be concluded from the shift in T_{max} values. Therefore, it is necessary to evaluate the effect of chemical interactions in the mixture.

For mixtures with MC, strong solid–solid interactions may be present between the P(HB-8%HV) carbonyl groups and hydroxyl groups from MC. These interactions delay the random scission of ester linkages in P(HB-8%HV). As degradation proceeds, the effect of solid interactions decreases, but gases evolved from P(HB-8%HV) (mainly crotonic acid [14–16,18]), may interact with MC (solid). It is difficult to explain the increment in MC thermal stability because acidic products, in particular HCl, are reported as catalysts of cellulose degradation [24,25]. Crotonic acid is not as strong as HCl, thus its effect on cellulose degradation may be different. George et al. [31] explained that the increment in thermal stability of cellulose may be a consequence of the effect of substances which induce a more ordered structure between cellulose chains, such as hydrogen bonding additives. In our case, strong hydrogen-type interactions may be present between carbonyl group of crotonic acid and OH-groups from cellulose. These hydrogen interactions may induce a higher order in cellulose, similar to mercerisation with acid or alkali, and cause disruption of some hydrogen bonds within cellulose and promote the formation of more stable cellulose structures. Thus, the degradation process should need higher energies to proceed.

Apparent activation energies for each step in P(HB-8%HV)/35 wt%MC decomposition were determined by the isoconversional Friedman method (Fig. 4). Two different regions corresponding to the degradation process of each compound in the mixture, with a transition area for $0.4 < \alpha < 0.6$, are observed. Average E_a calculated with this

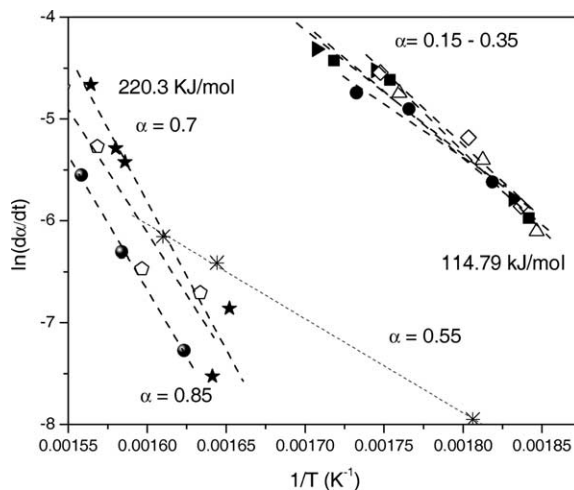


Fig. 4. Isoconversional Friedman plots for P(HB-8%HV)/35 wt%MC.

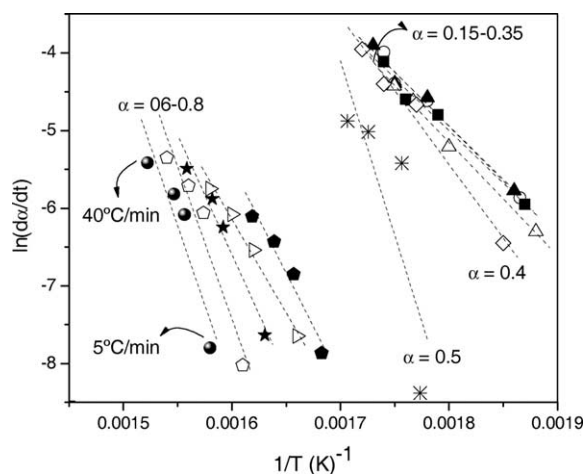


Fig. 5. Isoconversional Friedman plots for P(HB-8%HV)/35 wt%SF.

method are 114 kJ/mol for the first region ($\alpha < 0.4$) and 220.3 kJ/mol for the second one ($\alpha > 0.6$). When comparing these results with those of the pure materials (Table 1), it is easy to note that the presence of MC does not significantly change the apparent activation energy of thermal decomposition of P(HB-8%HV) (within the error of the method), but the E_a value for MC in the blend was higher than for the pure material. Thus, P(HB-8%HV) stabilizes MC in the mixture, as was concluded from the analysis of thermal properties and the mixture rule. Therefore, the overall effect of the addition of MC to P(HB-8%HV) is the stabilization of the mixture with higher degradation parameters.

Sisal fibers have an unfavourable effect on P(HB-8%HV) thermal degradation. Calculated curves for a mixture with 35 wt% of sisal fiber are presented in Fig. 3(b) (dashed line). It is observed that sisal fiber

does not significantly change its thermal stability while P(HB-8%HV) shifts its T_{max} to lower temperatures than the pure component. As it was mentioned above, sisal fibers are mainly composed by cellulose and hemicellulose, which is the less stable component of fibers and degrades almost completely within the degradation window of P(HB-8%HV). Thus, some type of interaction between both co-components or their degradation products may be assumed. The main constituents of hemicellulose are galactoglucomannan (70% mannan), which makes up approximately 60% of the total hemicellulose 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 hemicellulose [21]. The formation of acetic acid as a decomposition product of hemicellulose may be the main factor for consideration in the changes of P(HB-8%HV) degradation. Since P(HB-8%HV) decomposition proceeds by random scission of ester linkages, acetic acid may promote the reaction. As a result, fibers destabilize the polymer and lower energies should be required to get the complete degradation of mixtures. This result is in contrast with the predicted activation energies (Fig. 5). For the first zone ($0.1 < \alpha < 0.25$), the predicted E_a value was 116 kJ/mol and was attributed to polymer decomposition; for $\alpha > 0.55$, E_a was 250 kJ/mol, and it was related to sisal fiber degradation. Discrepancies may be attributed to the fact that the isoconversional method does not take into account the actual kinetic expression of the studied reaction. In addition, as it was stated before in this paper, sisal fiber thermal degradation must be visualized as a multi-step process, due to the complex nature of lignocellulosic materials. Apparent activation energy for the sisal fiber in the mixture was calculated assuming a single-step process, thus error in the E_a value may be enlarged.

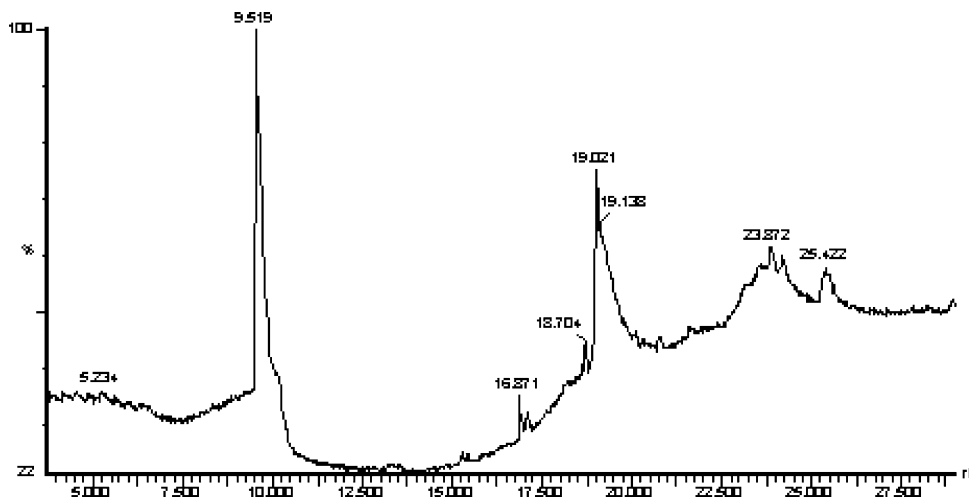


Fig. 6. Gas chromatogram of P(HB-8%HV) after pyrolysis at 300 °C.

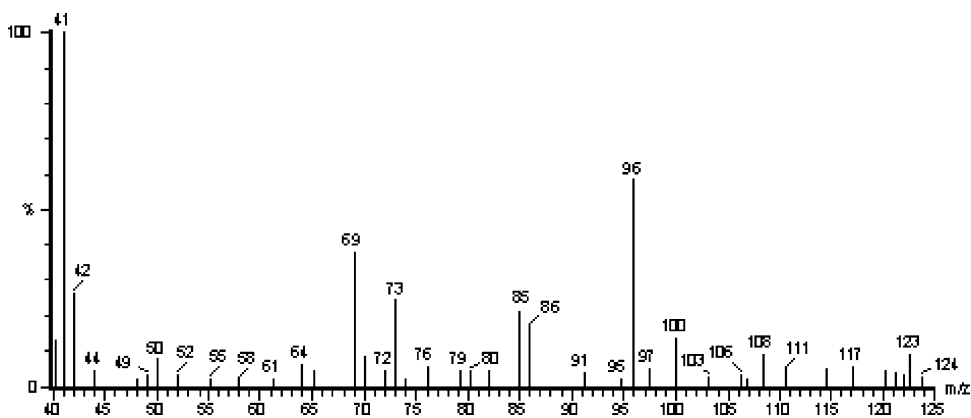


Fig. 7. Mass spectrum of P(HB-8%HV) pyrolysis products at 300 °C for the maximum peak in the chromatogram.

3.1. Evolution of volatile compounds

Py-GC/MS is an adequate technique for identification of gases evolved from polymers and biocomposites during their thermal degradation. GC-MS analysis was carried out in order to determine the gaseous products evolved from P(HB-8%HV) and its mixtures as well as their influence in the co-pyrolysis process. Gas chromatogram obtained after pyrolysis at 300 °C of P(HB-8%HV) is shown in Fig. 6.

Mass spectrum for the most intense peak of the P(HB-8%HV) chromatogram is shown in Fig. 7. The main peaks are those characteristic of crotonic acid and some derivatives ($m/z=41$, 69, 73 and 85). The intense peak at $m/z=96$ may correspond to one of the compounds produced during the fragmentation of this polyester, with formation of crotonic acid. Other relevant peaks correspond to propene ($m/z=42$), 2-butenic acid ($m/z=86$) and 2-pentenoic acid ($m/z=100$). These peaks are indicative of ruptures in the molecular structure of P(HB-8%HV) and are in agreement with results reported by Li et al. [15]. Nevertheless, some of these peaks (in particular those at higher m/z) show a lower intensity than those of crotonic acid. Moreover, other peaks

observed by those authors, such as propenyl-2-butenate ($m/z=126$), were not observed in our GC/MS measurements. The reason of these differences in results may be the large variation in pyrolysis temperatures, i.e. 590 °C in previous studies [15], while we used much lower temperatures (300 °C). That higher pyrolysis temperature would lead to a greater rupture of organic molecules and consequently to the differences in mass spectra.

In the case of P(HB-8%HV)/35 wt%MC mixtures, mass spectra are very similar to those of P(HB-8%HV), as shown in Fig. 8. As in the case of P(HB-8%HV) pyrolysis, the only Lewis-acid formed during the pyrolysis of P(HB-8%HV)/35 wt%MC mixtures is crotonic acid, which was supposed to contribute to the stability of cellulose structures, as was previously indicated [31]. This observation is in agreement with the results obtained by TG/DTG measurements.

Mass spectrum for the highest peak of the pyrolysis of P(HB-8%HV)/35 wt%SF mixtures is shown in Fig. 9. In this case, a small peak at $m/z=60$ corresponding to acetic acid is observed, which indicates that a low but significant amount of this acid is formed during pyrolysis of sisal fibers-reinforced P(HB-8%HV). Acetic acid proceeds

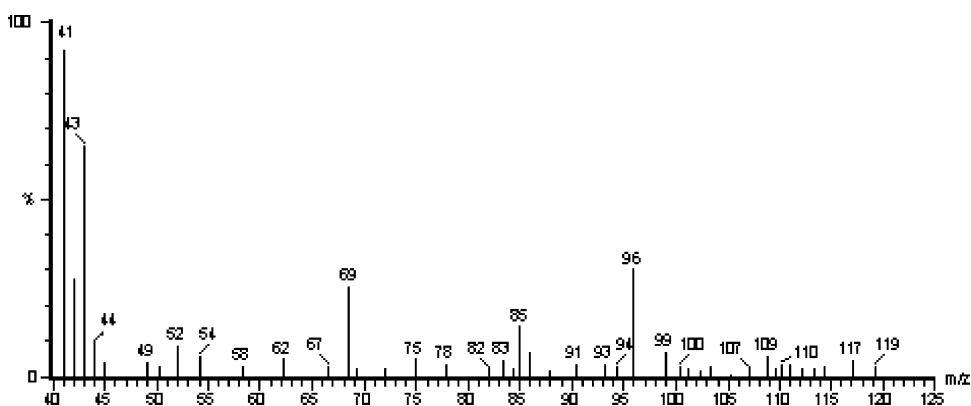


Fig. 8. Mass spectrum of P(HB-8%HV)/35 wt%MC mixture pyrolysis products at 300 °C for the maximum peak in the chromatogram.

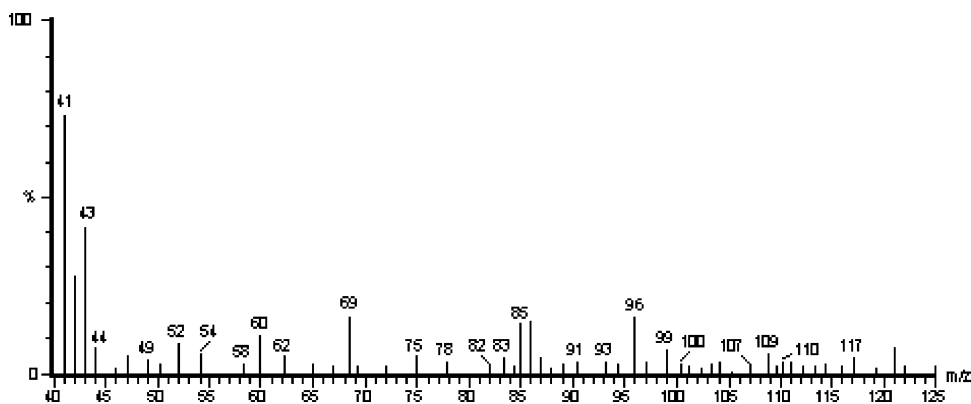


Fig. 9. Mass spectrum of P(HB-8%HV)/35 wt%SF mixture pyrolysis products at 300 °C for the maximum peak in the chromatogram.

mainly from hemicellulose decomposition, that is the component of SF which overlaps with P(HB-8%HV) decomposition [21]. Even though the amount is small, acetic acid shows a strong enough acid character to initiate thermal degradation of P(HB-8%HV) earlier and therefore, to reduce the thermal stability of the polymer.

4. Conclusions

Interactions between P(HB-8%HV) and cellulosic materials are an important factor in the thermal degradation and pyrolysis behaviour of this kind of binary mixtures. The increase or decrease of thermal stability of mixtures based on P(HB-8%HV) is a consequence of the mutual influence of one component on each other. Interactions between co-components were evidenced by calculating TG/DTG curves, considering the individual components. In mixtures with MC, gases evolved from P(HB-8%HV) decomposition seemed to act as stabilizers of MC. The same effect was observed for the fraction of cellulose in the mixtures based on SF. However, P(HB-8%HV) was slightly less stable in the presence of sisal fiber than without it. This behaviour was associated with the effect of acetic acid (evolved from hemicellulose decomposition), which seemed to promote the random scission of ester linkages in P(HB-8%HV).

It is important to point out that the results reported herein have very important practical implications. Processing a composite material based on PHAs and sisal fiber (and probably other lignocellulosic fibers) will require lower temperatures (in the absence of any additive) than those actually used for processing PHAs, to avoid polymer thermal degradation. On the other hand, mixing PHAs with lignocellulosic materials may be economically favourable for recycling because of the low energy required to produce complete pyrolysis.

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