Thermal and thermo-mechanical degradation of poly(3-hydroxybutyrate)-based multiphase systems

Elodie Hablot, Perrine Bordes, Eric Pollet, Luc Avérous*
LIPHT-ECPM, UMR 7165, Université Louis Pasteur, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France

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Abstract

The influence of fermentation residues and quaternary ammonium salts on the thermal and thermo-mechanical degradation of a biodegradable bacterial poly(3-hydroxybutyrate), PHB, was studied. The results obtained from DSC, SEC and TG analyses performed on blends reveal that ammonium cations greatly enhance the degradation leading to a dramatic decrease in PHB molecular weight. These results are confirmed by the thermo-mechanical study. Besides, we show that the presence of fermentation residues does not affect significantly the PHB thermal stability in comparison to the ammonium cations. A kinetic analysis based on the Coats and Redfern model was applied to the non-isothermal TGA data. This method completed by NMR characterizations led us to determine the most probable mechanism for PHB degradation in the presence of the ammonium salts. The results demonstrate that ammonium surfactants commonly found in commercial nanoclays (for nanocomposites’ production) effectively have a catalytic effect on the PHB degradation.
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Keywords: Polyhydroxybutyrate; Thermal degradation; Ammonium surfactants; Biopolymer; Renewable resources

1. Introduction

Polyhydroxyalkanoates (PHAs) represent an interesting alternative to synthetic polymers due to many advantages. Not only are they biodegradable and biocompatible, but they can also be produced from renewable resources. Poly(3-hydroxybutyrate) (PHB), the most common PHA, was first discovered in 1926 by Lemoigne [1,2], but PHAs were really exploited since 1980s and particularly in the last decade considering the decreasing reserves of fossil fuel and the increasing public concern for environmental protection.

PHB accumulation by various bacterial strains [3–5] from different biomass substrates [5,6] has been widely described in the literature as well as the recovery process [6,7]. The extraction and purification processes are the decisive production steps since fermentation residues (metal, crude biomass, etc.) could remain and then alter the PHAs’ properties [8,9]. PHB is already produced on the industrial scale but this material shows some drawbacks compared to conventional polymers, such as high stiffness and brittleness. Besides, PHB shows poor thermal stability at temperature above the melting point [9–17].

To improve the PHAs’ properties, nano-biocomposites [18,19] (nanocomposites based on biodegradable matrices) seem to be a good answer since they have raised great interest in recent years, thanks to the enhancement of material properties. Some studies were dedicated to nano-biocomposites based on PHB or PHBV with montmorillonite (MMT) [20–24]. Most use the environmentally unfriendly route of solvent intercalation [20,22–24], due to the particular temperature sensitivity of these biopolymers that restricts the use of melt processing. Many studies dedicated to thermal [10–12,14–17,25] and thermo-mechanical [26,27] degradation of neat PHB and PHBV have revealed that the degradation occurs rapidly near the melting point according to mainly a random chain scission process (Scheme 1). They have also shown that melt processing parameters must be optimized to limit this phenomenon resulting in a really narrow processing window. Some authors have shown that fermentation residues [8,9] or plasticizers [28,29] have an
influence on the PHAs’ degradation. Recently, Maiti et al. [30] have reported that, in the case of PHB-based nano-biocomposites reinforced by MMT, the presence of aluminium Lewis acid sites in the silicate layers enhances the thermal degradation of PHB by catalysing the hydrolysis of ester linkages. Xie et al. [31] have studied the thermal degradation of montmorillonite organo-modified (OMMT) by quaternary ammonium surfactants. This recent work has pointed out the complex degradation reactions that could exist in organically modified MMT and consequently, in polymer–(O)MMT nanocomposite systems.

This paper aims at investigating the influence of both the addition of ammonium salts (used in common commercial OMMT) and the presence of organic fermentation residues on the PHB thermal and thermo-mechanical degradation. Differential scanning calorimetry (DSC) analyses and size exclusion chromatography (SEC) measurements were performed to compare the melting temperatures and the weight average molecular weights of the different systems. Eventually, a kinetic analytical model [32] was applied to non-isothermal thermogravimetric (TG) measurements. This method completed by nuclear magnetic resonance (NMR) characterizations led us to identify the possible mechanism for PHB degradation in the presence of ammonium salts.

2. Experimental section

2.1. Materials

Poly(3-hydroxybutyrate) (PHB), produced by bacterial fermentation, was kindly supplied by Biocycle PHB Industrial S/A, Brazil. The PHB production plant is entirely integrated into the sugar mill to obtain an environmentally sound plastic resin [33]: the Ralstonia eutropha bacterial strains growing and the fermentation steps are made from cane sugar, and the recovery process uses exclusively natural solvents, by-products of ethanolic fermentation. The weight average molecular weight ($M_w$) and the polydispersity index (PDI) have been determined by size exclusion chromatography (SEC) ($M_w = 650,000$ and PDI = 2). Melt flow index (MFI) and density are 12 g/10 min and 1.22 g/cm$^3$, respectively.

The quaternary ammonium salts — di(hydrogenated tallow)dimethylammonium chloride (S-Alk), (vegetable oil)benzyldimethylammonium chloride (S-Bz) and oleyl-bis(2-hydroxyethyl)methylammonium chloride (S-EtOH) in isopropyl alcohol — from Akzo Nobel were kindly supplied by Brenntag Specialities (see Table 1). Tetramethyldiamonium chloride (TMA) (reagent grade, 97%) was supplied by Sigma–Aldrich and pentadecane (puriss p.a. $\geq 99.8\%$) by Fluka. Triethylamine 99% pure purchased from Acros Organics was distilled from CaH$_2$.

2.2. Polymer purification

Purification of PHB was performed by Soxhlet extraction with diethyl ether (SDS Carlo Erba) for 24 h. The purified PHB (PHBp) was then recovered and dried at 80 °C under vacuum. The liquid phase was collected and the extracted fermentation residues (Rsd) were recovered after solvent evaporation. The initial amount of fermentation residues in the raw PHB is ca. 2 wt%, as determined by gravimetry.

These residues were identified by thin-layer chromatography (TLC). The solvent elution system used was hexane—diethyl ether—formic acid (80:20:2 by volume). The separation revealed that the residues are a mixture of lipids like free fatty acids, mono-, di- and triacylglycerols, phospholipids, cholesterol and cholesterol esters. The total amount of nitrogen in the extracted residues was also determined. The titration leads to about 0.5% of nitrogen in the extract that corresponds to less than 50 ppm in the raw PHB.

2.3. Sample preparation

To remove isopropyl alcohol and water from the commercial ammonium solutions, S-Alk and S-Bz were dispersed

<p>| Table 1 |</p>
<table>
<thead>
<tr>
<th>Structure of the ammonium cations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ammonium cations</strong></td>
</tr>
<tr>
<td>S-Alk</td>
</tr>
<tr>
<td>S-Bz</td>
</tr>
<tr>
<td>S-EtOH</td>
</tr>
<tr>
<td>TMA</td>
</tr>
</tbody>
</table>
into diethyl ether, filtered and dried under vacuum in order to obtain white powders. Then, they were added and intimately mixed to the dried PHBp. Regarding the fermentation residues (Rsd) and the S-EtOH surfactant, the pasty nature of these compounds makes homogeneous mixing with the PHBp powder difficult. Thus, they were dispersed into diethyl ether and mixed to the purified PHB. Then, once the solvent was evaporated, the mixture was dried under vacuum. A ternary blend was prepared by adding the S-Alk powder to the binary mixture PHBp + Rsd.

For the thermo-mechanical degradation study, the samples were prepared in an internal mixer Haake Rheocord 9000 at 170 °C. Because of the technical difficulties of obtaining large amounts of purified PHB, this study was performed on samples prepared with the “as-received” raw PHB, i.e., PHB containing 2 wt% of fermentation residues. Different rotation speeds and processing times were tested, ranging from 50 to 150 rpm and from 3 to 15 min, respectively. The torque and the melt temperature were recorded during the processing. The mechanical energy was calculated using Eq. (1) where \( N \) is the rotation speed (rad s\(^{-1}\)), \( M \) the sample mass (kg) introduced in the mixing chamber and \( S \) is the area defined by the torque vs. time curve.

\[
E_m (kJ/kg) = \left( \frac{N}{M} \right) \times S \tag{1}
\]

Additives’ contents in the PHB-based samples are 10 wt% for the residues and 3 wt% for the ammonium cations, respectively. Such high amounts were chosen to have more pronounced degradation and thus to observe and identify more easily the occurring phenomena.

To determine the degradation mechanism, further experiments were performed on polymer additives’ (97:3) blends. The raw PHB was directly mixed with pentadecane, tetramethylammonium (PHB + TMA) and distilled triethylamine (PHB + TEA), and each blend was processed at 170 °C and 50 rpm for 15 min. Another PHB + S-Bz sample containing 30 wt% of surfactant was also prepared. Eventually, S-Bz was degraded by annealing at 170 °C for 15 min.

2.4. Characterizations

Thermal degradation was studied by differential scanning calorimetry (DSC 2910 TA Instruments) under airflow. To determine the influence of the additives (fermentation residues or surfactants) on the neat polymer, the samples (5–10 mg placed in an aluminum pan) were heated up to 500 °C at different heating rates, ranging from 5 to 20 °C/min.

Size exclusion chromatography (SEC) measurements were performed using a Shimadzu apparatus equipped with an RID-10A refractive index detector and an SPD-M10A UV detector. The columns used were PLGel Mixed-C and PLGel 100 Å. The calibration was performed with PS standards from 580 to 1,650,000 g/mol. Chloroform (puriss p.a., Riedel-de Haën) was the mobile phase and the analyses were carried out at 40 °C with a solvent flow rate of 1 ml/min. The SEC measurements were performed on the samples recovered at the end of the DSC analyses and after given processing times in the internal mixer.

The \(^1\)H and \(^13\)C nuclear magnetic resonance (NMR) analyses were carried out on a Bruker Ultrashield\textsuperscript{TM} 300 MHz spectrometer. The spectra were recorded at room temperature using sample solutions in CDCl\(_3\) (20 mg/ml).

3. Coats and Redfern model

In this part we give the theoretical basis of the Coats and Redfern method applied to the experimental TGA data. This model assumes that the rate of conversion can be expressed by Eq. (2), where \( \alpha \) represents the fractional extent of conversion (i.e., weight loss), \( \frac{d\alpha}{dt} \) is the rate of conversion, \( f(\alpha) \) is a temperature-independent function of conversion that depends on the degradation mechanism and \( k(T) \) is a temperature-dependent function [34].

\[
\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{2}
\]

According to Arrhenius equation, the expression of \( k(T) \) is given by Eq. (3), where \( A \) is the pre-exponential factor independent of temperature, \( E_a \) the activation energy, \( R \) the gas constant and \( T \) the absolute temperature. By combining Eqs. (2) and (3), we obtain Eq. (4).

\[
k(T) = A \exp \left(-\frac{E_a}{RT}\right) \tag{3}
\]

\[
\frac{d\alpha}{dt} = A \exp \left(-\frac{E_a}{RT}\right)f(\alpha) \tag{4}
\]

For non-isothermal measurements at constant heating rate \( \beta = \frac{dT}{dt} \), we obtain Eq. (5).

\[
\beta \frac{d\alpha}{dT} = A \exp \left(-\frac{E_a}{RT}\right)f(\alpha) \tag{5}
\]

By multiple integration and combination of these equations, the Coats and Redfern method [32] is expressed by Eq. (6), where \( g(\alpha) \) is a function depending on the type of degradation mechanism and is related to \( f(\alpha) \) by Eq. (7). By plotting \( \ln[g(\alpha)/T^\beta] \) as a function of \( 1/T \), the slope of the obtained straight line is directly proportional to \( E_a \).
\[
\ln \left( \frac{g(\alpha)}{T^2} \right) = \ln \left( \frac{A R \beta}{\beta} \right) - \frac{E_a}{RT}
\]

\[
g(\alpha) = \frac{1}{\alpha} \int [f(\alpha)]^{-1} \, d\alpha
\]

4. Results and discussion

4.1. Effect of annealing on PHB characteristics

The key step of the DSC thermal treatment consists in annealing the samples for 10 min at 200 °C to promote chain scission reactions. The influence of the different additives on the PHB thermal degradation has been studied by monitoring the change of both the polymer melting temperature and its weight average molecular weight after this thermal treatment. Table 2 summarizes the melting temperatures \( T_m \) and weight average molecular weights \( M_w \) of the polymer-additive samples compared to the annealed purified polymer (PHBp) as a reference.

DSC analyses show that the melting temperature of purified PHB with fermentation residues (PHBp + Rsd) displays only a slight \( T_m \) decrease (3 °C). But PHBp with S-Alk, S-Bz or S-EtOH present considerable \( T_m \) decreases of 25, 41 and 28 °C, respectively. These significant \( T_m \) decreases are likely due to lower PHB weight average molecular weight as a direct consequence of the chain scission reactions occurring. This is confirmed by the SEC analyses performed on the samples after the thermal treatment. Table 2 shows a dramatic decrease in \( M_w \) for PHB added with surfactants, compared to neat PHBp.

Indeed, PHBp + S-Alk, PHBp + S-Bz or PHBp + S-EtOH samples show \( M_w \) divided by 18, 52 and 25, respectively. These results demonstrate that the polymer degradation is strongly enhanced in the presence of surfactants. In contrast, it seems that the fermentation residues only have a small influence on the PHB thermal degradation, at least in the experimental conditions of this study. Besides, through these different results, one can conclude that S-Bz seems to be more degrading than S-Alk and S-EtOH.

4.2. Thermogravimetric analyses on PHB-based systems

To better understand the thermal degradation of PHB-based systems, their related reaction mechanisms and kinetic parameters, a specific study was performed on the mass loss data obtained from dynamic thermogravimetric analyses. Fig. 1 shows the weight loss curves (TG) for all the systems obtained at a heating rate of 10 °C/min. It can be seen that the fermentation residues have only little influence, whereas the surfactants favour the PHB degradation since the corresponding TG curves are shifted towards lower temperatures. This is in agreement with the previous results obtained from DSC and SEC analyses.

Looking attentively to the TG curves, one can see that there is a main degradation step corresponding to the PHB degradation but also secondary degradations occurring before and/or after the principal one. When superposing the TG curves of neat PHBp, the surfactant and the corresponding blend (see Fig. 2 for a representative example), we can rationally attribute these secondary mechanisms to the degradation of the additive itself. Indeed, the ammonium surfactants degrade on a wide range of temperatures (150–460 °C) compared to neat PHBp.

After these observations about the influence of additives on the PHB degradation, the dependence, if any, between the degradation mechanisms of both the polymer and the additive has to be analysed.

According to Torre et al. [35], if the degradations of each compound of a blend are independent, the weight loss obtained by TGA is given by Eq. (8), where \( W \) is the residual weight fraction of the blend. \( W_a \) and \( W_{PHBp} \) are the residual weight fractions of the additive and the purified PHB,
respectively, and $x_a$ and $x_{PHBp}$ are the original weight fractions of the additive and the purified PHB in the blend, respectively.

$$W = W_a x_a + W_{PHBp} x_{PHBp}$$  \hspace{1cm} (8)$$

Thus, starting from the experimental TGA of PHBp and each additive, one can build up the calculated TG curve for all respective blends. For the PHB–surfactant systems, the calculated and the experimental curves (not shown here) are not superposed. For the PHBp + S-Alk sample, the experimental curve is shifted of 20 °C towards lower temperatures, compared to the calculated curve. For PHBp + S-Bz and PHBp + S-EtOH, the same observation has been noticed and experimental curves are slightly shifted towards lower temperatures. Moreover, we can observe that both experimental and calculated curves do not present exactly the same shape. Thus, we can conclude that, in such a blend, the degradation of purified PHB and the degradation of surfactants are inter-dependent. This phenomenon highlights that surfactants play a key role in the PHB thermal degradation.

Concerning the effect of the fermentation residues on the PHB degradation, we can assume that these impurities have a limited influence on the main degradation step since the experimental and calculated TG curves (not shown here) are almost superposed with a quite similar shape. This is in perfect agreement with the previous results based on $T_m$ and $M_w$ determinations.

An additional experiment was done on a ternary mixture of purified PHB with S-Alk and fermentation residues (PHBp + S-Alk + Rsd) to determine whether the additives have a synergistic effect on the polymer degradation. In this case, the experimental curve is shifted of 10 °C towards lower temperatures compared to the calculated one determined from the experimental thermograms of the binary mixture (PHBp + S-Alk) and the fermentation residues. Thus, the surfactants seem to act in synergy with the fermentation residues to degrade PHB but the corresponding mechanism is still unexplained.

### Table 3

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Code</th>
<th>$g(\alpha)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exponential law</td>
<td>–</td>
<td>$-\ln(\alpha)$</td>
</tr>
<tr>
<td>Avrami–Erofeev law</td>
<td>$A_1$</td>
<td>$[-\ln(1-\alpha)]^{2/3}$</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>$[-\ln(1-\alpha)]^{1/2}$</td>
</tr>
<tr>
<td></td>
<td>$A_3$</td>
<td>$[-\ln(1-\alpha)]^{1/3}$</td>
</tr>
<tr>
<td></td>
<td>$A_4$</td>
<td>$[-\ln(1-\alpha)]^{1/4}$</td>
</tr>
<tr>
<td>Prout–Tompkins law</td>
<td>$B_1$</td>
<td>$\ln[\alpha/(1-\alpha)]$</td>
</tr>
<tr>
<td>Chemical reaction of $n$th order</td>
<td>$F_1$</td>
<td>$-\ln(1-\alpha)$</td>
</tr>
<tr>
<td></td>
<td>$F_2$</td>
<td>$\ln(1-\alpha)$</td>
</tr>
<tr>
<td></td>
<td>$F_3$</td>
<td>$\ln[(1-\alpha)^2]$</td>
</tr>
<tr>
<td>Phase boundary controlled reaction</td>
<td>$R_2$</td>
<td>$[1 - (1 - \alpha)^{1/2}]$</td>
</tr>
<tr>
<td>(contracting area)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase boundary controlled reaction</td>
<td>$R_3$</td>
<td>$[1 - (1 - \alpha)^{1/3}]$</td>
</tr>
<tr>
<td>(contracting volume)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Three-dimensional diffusion spherical symmetry (Jander equation)</td>
<td>$D_3$</td>
<td>$[1 - (1 - \alpha)^{1/3}]^2$</td>
</tr>
</tbody>
</table>

### 4.3. Analytical treatment of TGA data by Coats and Redfern method

To obtain additional information about the degradation mechanism, the activation energy has been calculated with the Coats and Redfern method for each system. These values are obtained by plotting $\ln[g(\alpha)/T^2]$ as a function of $1/T$. Table 3 presents 12 different probable forms of $g(\alpha)$ among the most commonly used functions of solid-state processes [36–38]. Typically, for each TG curve, all the $g(\alpha)$ functions were tested and the one which presents the best linearity ($r^2$ closest to 1) is considered as the most probable reaction mechanism for the thermal degradation. The analysis has been performed from TG data obtained at the lowest heating rate (5 °C/min), to better observe the degradation phenomenon and thus to have a better discrimination between the possible mechanisms.

Table 4 shows the main results obtained with the Coats and Redfern method by plotting $\ln[g(\alpha)/T^2]$ vs. $1/T$ for each system. For each system, the most suitable reaction mechanism and its related values for the activation energy $E_a$ and the pre-exponential factor $A$ are presented. Regarding these results, several points can be discussed. First, the activation energy of PHBp and PHBp + Rsd, i.e., 395 and 327 kJ/mol, respectively, is close and relatively high compared to other systems. Moreover, it appears that the thermal degradation of these two samples follows the same mechanism, namely a first-order reaction (F1 type). This statement is in agreement with previously published results [16] and it can also be concluded that residues have just a little influence on PHB thermal degradation. Surfactants have a stronger influence on the thermal degradation of PHBp. This is confirmed by the activation energy values obtained for these systems which are greatly inferior to the PHBp activation energy (see Table 4). Even if these calculated values of activation energy can hardly be regarded as having a real chemical significance, they allow us to compare the thermal stability of the different systems.

Finally, from the most probable reaction mechanisms which are determined for these systems, one can conclude that the studied surfactants favour and enhance the PHBp thermal degradation through a phase boundary controlled process (R type).

### 4.4. Thermo-mechanical degradation

By analogy and to simulate the preparation of nano-bio-composites, the thermo-mechanical degradation was also studied to analyse the PHB degradation during processing. The
torque and the temperature have been monitored during the experiment. Samples have been taken from the mixer during the experiment at 3, 5 and 10 min to determine the weight average molecular weight ($M_w$) by SEC.

On one hand, the torque, the temperature and the weight average molecular weight curves follow the expected trends. On the other hand, we can notice some strong differences between PHB and PHB with additives (Fig. 3 and Table 5). First, in the case of the PHB sample, the maximum torque value is higher and is reached earlier. Secondly, the torque decreases more rapidly for the PHB–surfactant samples compared to neat PHB or PHB + Rsd. At 50 rpm, the torque reaches a constant value (a plateau) at ca. 700 s, in the case of PHB and PHB + Rsd samples, whereas a zero-torque is recorded at around 590, 280 and 230 s, for PHB + S-EtOH, PHB + S-Alk and PHB + S-Bz, respectively. This zero-torque is probably a direct consequence of the PHB degradation. Indeed, Table 6 shows that the samples collected after 5 min of processing already show a significant $M_w$ decrease for PHB + S-Alk and PHB + S-Bz.

All these observations show that in the presence of surfactant, the melt is less viscous due to an enhanced degradation. This phenomenon is particularly favoured with S-Bz and S-Alk. On the contrary, the fermentation residues do not affect significantly the viscosity, and then, the degradation. All these observations are in total agreement with the previous results.

A zero-torque value is observed in the early stage of processing in the case of PHB–surfactant systems. This unusual phenomenon could be explained by lower $T_m$ for these blends and by a possible lubricant behaviour of the surfactants.

Same trends have been also observed at 100 and 150 rpm (not reported here). Nevertheless, it can be concluded that the rotation speed plays a significant role in the thermo-mechanical degradation of PHB since the higher the rotation speed, the earlier and greater the degradation.

To emphasize these results, the mechanical energies ($E_m$) provided to the different systems for 5 and 15 min of processing have been determined and are presented in Table 7. The mechanical energy, which is connected to the viscosity, is greatly superior for PHB and PHB + Rsd than for PHB with surfactants. These results confirm the conclusions drawn before indicating that PHB with surfactants, particularly S-Alk and S-Bz, presents a really lower viscosity compared to PHB and PHB + Rsd, due to the great ability of these surfactants to enhance the PHB degradation.

Further experiments were performed to find out the functional group of the surfactant which could be responsible for the polymer degradation. Two entities were considered, namely the ammonium function and the long alkyl chain. First, PHB was processed in the presence of long alkyl chains (pentadecane). The results (not reported here) show that, under the experimental conditions, this chemical entity has no influence on PHB thermal stability. Thus, PHB was mixed with tetramethylammonium chloride (TMA) to determine whether the quaternary ammonium cation could favour or not the polymer degradation. This system was processed in the internal mixer (170 °C, 50 rpm, 15 min) and the PHB weight average molecular weight after 5 min was determined by SEC. Like the other polymer–surfactant systems, the $M_w$ of PHB in the presence of TMA ($M_w = 117,000$) has considerably decreased compared to the PHB sample ($M_w = 412,000$ at 5 min, see Table 6). This observation attests that the quaternary ammonium cation chemical entity has a significant effect on the polymer degradation.

According to Xie et al. [31], the well-known Hofmann elimination could take place at these temperatures (around

<table>
<thead>
<tr>
<th>System</th>
<th>Maximal torque (N m)</th>
<th>$t_{\text{max}}$ (s)</th>
<th>$t_{\text{plateau}}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB</td>
<td>24</td>
<td>114</td>
<td>700</td>
</tr>
<tr>
<td>PHB + S-Alk</td>
<td>6</td>
<td>126</td>
<td>280</td>
</tr>
<tr>
<td>PHB + S-Bz</td>
<td>7</td>
<td>138</td>
<td>230</td>
</tr>
<tr>
<td>PHB + S-EtOH</td>
<td>7</td>
<td>126</td>
<td>590</td>
</tr>
<tr>
<td>PHB + Rsd</td>
<td>16</td>
<td>102</td>
<td>700</td>
</tr>
<tr>
<td>PHB + TMA</td>
<td>15</td>
<td>90</td>
<td>500</td>
</tr>
<tr>
<td>PHB + TEA</td>
<td>16</td>
<td>65</td>
<td>200</td>
</tr>
</tbody>
</table>

Table 6

<table>
<thead>
<tr>
<th>$t$ (s)</th>
<th>$M_w \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB</td>
<td>180 625 527</td>
</tr>
<tr>
<td>PHB + S-Alk</td>
<td>286</td>
</tr>
<tr>
<td>PHB + S-Bz</td>
<td>680</td>
</tr>
<tr>
<td>PHB + S-EtOH</td>
<td>753</td>
</tr>
<tr>
<td>PHB + Rsd</td>
<td>300 412 106</td>
</tr>
<tr>
<td>PHB + S-Alk</td>
<td>39</td>
</tr>
<tr>
<td>PHB + S-Bz</td>
<td>263</td>
</tr>
<tr>
<td>PHB + S-EtOH</td>
<td>605</td>
</tr>
<tr>
<td>PHB + Rsd</td>
<td>600 337 21</td>
</tr>
<tr>
<td>PHB + S-Alk</td>
<td>15</td>
</tr>
<tr>
<td>PHB + S-Bz</td>
<td>210</td>
</tr>
<tr>
<td>PHB + S-EtOH</td>
<td>313</td>
</tr>
</tbody>
</table>

Table 7

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{\text{ref}}$ (kJ/kg)</th>
<th>$E_{\text{m15}}$ (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB</td>
<td>400</td>
<td>640</td>
</tr>
<tr>
<td>PHB + Rsd</td>
<td>235</td>
<td>420</td>
</tr>
<tr>
<td>PHB + S-EtOH</td>
<td>70</td>
<td>130</td>
</tr>
<tr>
<td>PHB + S-Bz</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>PHB + S-Alk</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Fig. 3. Evolution of the torque at 170 °C and 50 rpm for 15 min for the different systems.
170 °C), turning the quaternary ammonium salt into an amine [31], creating alkenes and releasing a proton (see Scheme 2). This proton could then enhance the polymer chain scission by an acidic catalytic reaction [39]. Another possible reaction that could occur at these temperatures is the nucleophilic attack of the chloride (counter-ion of the S-Bz ammonium salt) on the quaternary ammonium yielding chloroalkanes and tertiary amine [31] (see Scheme 3). Furthermore, the amines resulting from either Hofmann elimination or from nucleophilic attack could then enhance the mechanism of random chain scission due to their nucleophilic character. The formed amines could also react according to an aminolysis, and aminoglycolysis in the particular case of PHB [170].

To verify these hypotheses regarding the role of the ammonium salts or their degradation products, further experiments were conducted. Triethylamine (TEA) was mixed with PHB and processed in the same conditions as mentioned before (170 °C, 50 rpm). The $M_w$ of the PHB + TEA blend processed for 5 min revealed a considerable decrease ($M_w = 54,400$) compared to the PHB and PHB + TMA samples, $M_w = 412,000$ and 117,000, respectively. Besides, the PHB + TEA torque curve is similar to the PHB + TMA one but shifted to shorter times (see Table 5). This experiment demonstrates that the enhanced PHB degradation is certainly caused by amines resulting from the in situ degradation of ammonium surfactants.

To emphasize the presence of amines as degradation products, the S-Bz surfactant was annealed at 170 °C for 15 min. The $^1$H NMR spectrum of the obtained material (see Fig. 4) revealed typical peaks of the initial product S-Bz (* indexes) as well as characteristic peaks of amines ($\delta_B = 2.2$ ppm and $\delta_C = 2.35$ ppm for the two methyl groups of the $N,N$-dimethylalkylamine and $N,N$-dimethylbenzylamine, respectively, $\delta_D = 3.45$ ppm for the methylene protons of the benzyl group), chloroalkanes ($\delta_D = 3.5$ ppm for the CH$_2$–Cl methylene protons and $\delta_A = 1.5$–2.0 ppm for the methylene protons in $\beta$ and $\gamma$ of the chloride) and benzyl chloride ($\delta_E = 4.59$ ppm for the methylene protons). No peaks that could be attributed to alkenes were detected. Thus, we can conclude that S-Bz degrades rather by nucleophilic attack of the chloride on the quaternary ammonium ($R_4N^+$) than by Hofmann elimination. Nevertheless, this last mechanism cannot be totally excluded. Indeed, its degradation products (e.g. octadecene, b.p. ~ 180 °C) could evaporate during processing and the S-Bz TG curve indicates a 3 wt% of weight loss at 170 °C that proves some matter have vaporized at this temperature. Eventually, the $^{13}$C NMR spectrum (not shown here) revealed small peaks at 112–113 ppm, typically attributed to alkene carbons.

With the aim to determine the role of the surfactant on the PHB degradation mechanism, a blend with a very high S-Bz content was prepared. The degradation products of PHB + S-Bz (70:30) were studied by $^1$H and $^{13}$C NMR (not shown here). The $^1$H NMR spectrum of PHB + S-Bz (70:30) shows peaks of each compound of the blend but also additional peaks resulting from the degradation products. These additional peaks can easily be attributed to the typical chain end crotonyl groups ($\delta = 1.84$–1.87 ppm and 2.1–2.5 ppm for the $trans$ and $cis$ methyl protons, respectively, $\delta = 5.76$–5.82 ppm and $\delta = 6.9$–7.0 ppm for the olefinic protons) resulting from the PHB random chain scission (see Scheme 1). We note that the $trans$ configuration is favoured ($trans/cis$ ratio equals to 13) as described in the literature [9,12]. Furthermore, the $^{13}$C NMR spectrum does not show any specific peak of amide. Thus, we can conclude that the surfactant acts, through the formation of amines, as a catalyst of the PHB random chain scission and that aminolysis can be neglected.

As a result, we can reasonably assume that the difference of influence on PHB degradation observed between S-EtOH, S-Alk and S-Bz can be explained by their ability to turn into amine. Nevertheless, the reactions can vary depending on the ammonium substituent groups and thus additional experiments are needed to determine precisely their role on the ammonium thermal stability, the type of amines formed and their activity towards PHB degradation.

**5. Conclusions**

The first part of this work is based on the analysis of the thermal degradation of purified PHB and blends containing...
fermentation residues (Rsd) or quaternary ammonium surfactants (S-Alk, S-Bz or S-EtOH). DSC analyses associated with SEC and TGA measurements showed that the fermentation residues have low influence on the PHB degradation. On the contrary, the addition of ammonium surfactants greatly boosts the PHB degradation. To quantify the thermal degradation, the activation energy and the degradation reaction mechanism of each system have been determined from TGA results using the Coats and Redfern model.

Several conclusions have been drawn: (i) the degradation mechanisms of both the purified PHB and the surfactant in the blend are inter-dependent, whereas the fermentation residues have almost no influence on the polymer main degradation step, (ii) both unpurified and purified PHB (i.e., with and without fermentation residues) degrade according to a first-order reaction, whereas PHBp with surfactant likely degrades following a phase boundary controlled mechanism, (iii) S-Alk and S-Bz appear to be the most degrading surfactants compared to S-EtOH.

The thermo-mechanical study has led to the same conclusions regarding the influence of surfactants and fermentation residues on the polymer degradation. Nevertheless, these results have also shown that processing conditions have a great influence on the PHB thermal stability since the higher the mixer rotation speed, the faster and greater the degradation.

Besides, TG analysis on a ternary mixture has shown that a synergistic effect between surfactants and fermentation residues occurs and favours the polymer degradation. A possible mechanism of degradation has been proposed based on NMR characterizations. The R₂N⁺ surfactant turns into an amine through either nucleophilic attack of the ammonium counter-ion or Hofmann elimination. Then, the released acidic proton and/or the nucleophilic amine formed act as catalysts of the PHB random chain scission. Thus, the differences in surfactants’ activity towards PHB degradation are directly linked to the variations in ammonium thermal stability stemming from the different substituent groups.

These conclusions are remarkable because they demonstrate why it is presently difficult to obtain PHB/OMMT nano-biocomposites by a melt intercalation process. Indeed, it has been demonstrated that quaternary ammonium surfactants used as montmorillonite organo-modifiers for nano-biocomposites purposes increase the PHB thermal sensitivity so that their presence during melt processing of such materials is thus not favourable. On the contrary, fermentation residues have quite no influence on the PHB thermal degradation and thus do not hinder the use of the melt processing way.

Using the same approaches, this study could easily be extended to other thermally sensitive biodegradable polymers (e.g. polyhydroxybutyrate-co-hydroxyvalerate, polysaccharides, polylactide…) for which the elaboration of nano-biocomposites based on organo-modified montmorillonites is also of great interest.

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