



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

Received 18 May 2007; received in revised form 12 November 2007; accepted 19 November 2007

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.

© 2007 Published by Elsevier Ltd.

Q1 *Keywords:* Polyhydroxybutyrate; Thermal degradation; Ammonium surfactants

1. Introduction

Polyhydroxyalkanoates (PHAs) represent an interesting alternative to synthetic polymers due to many advantages. Not only they are 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.

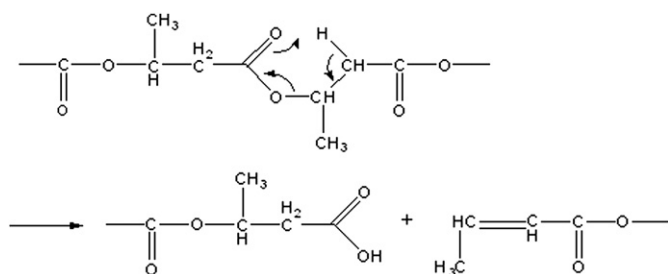
PHB accumulation by various bacterial strains [3–5] from different biomass substrates [5,6] has been widely described in the literature as has the recovery process [6,7]. The extraction and purification processes are the decisive production steps since fermentation residues (metal, crude biomass, etc.) 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

* Corresponding author. Tel.: +33 3 90 242 707; fax: +33 3 90 242 716.

E-mail address: averousl@ecpm.u-strasbg.fr (L. Avérous).



Scheme 1. PHB random chain scission.

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/cm³, respectively.

The quaternary ammonium salts – di(hydrogenated tallow)dimethylammonium chloride (S-Alk), (vegetable oil)benzylidimethylammonium 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). Tetramethylammonium 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 CaH₂.

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

Table 1
Structure of the ammonium cations

Ammonium cations	Structure
S-Alk	
S-Bz	
S-EtOH	
TMA	

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 difficulty 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.

$$E_m (\text{kJ/kg}) = \left(\frac{N}{M}\right) \times S \quad (1)$$

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 aluminium pan) were heated up to 200 °C at 10 °C/min. Then, the temperature was maintained for 10 min to get rid of thermal history and to promote the degradation. Finally, samples were cooled to room temperature at 10 °C/min and heated again to 220 °C at 10 °C/min. The PHB melting temperature was determined on the second heating scan.

Thermogravimetric analyses (TGA) were conducted under nitrogen flow using a Hi-Res TGA 2950 apparatus from TA Instruments. The samples (10–20 mg placed in an aluminium 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 ^1H and ^{13}C nuclear magnetic resonance (NMR) analyses were carried out on a Bruker Ultrashield™ 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 isothermal rate of conversion can be expressed by Eq. (2), where α represents the fractional extent of conversion (i.e., weight loss), $d\alpha/dt$ is the isothermal 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].

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

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).

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right)f(\alpha) \quad (4)$$

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

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

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 $\ln[g(\alpha)/T^2]$ as a function of $1/T$, the slope of the obtained straight line is directly proportional to E_a .

Table 2
Influence of additives on the PHB melting temperature (T_m) and weight average molecular weight (M_w) after annealing the sample for 10 min at 200 °C

System	T_m (°C)	M_w
PHBp	174	63,200
PHBp + S-Alk	149	3500
PHBp + S-Bz	133	1200
PHBp + S-EtOH	146	2500
PHBp + Rsd	171	51,700

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left(\frac{AR}{\beta E} \right) - \frac{E_a}{RT} \quad (6)$$

$$g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha \quad (7)$$

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.

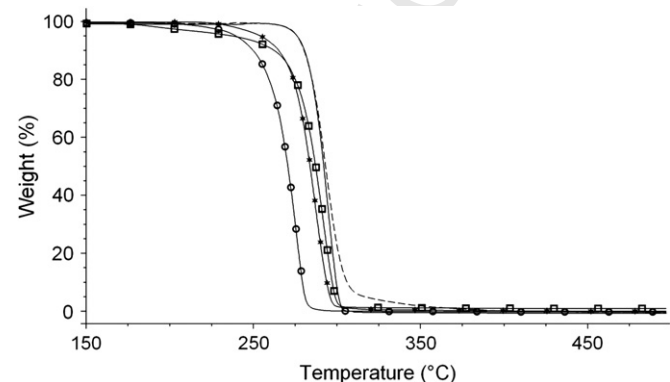


Fig. 1. TG curves at 10 °C/min for PHBp (—), PHBp + Rsd (---), PHBp + S-Alk (○), PHBp + S-Bz (□) and PHBp + S-EtOH (*).

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,

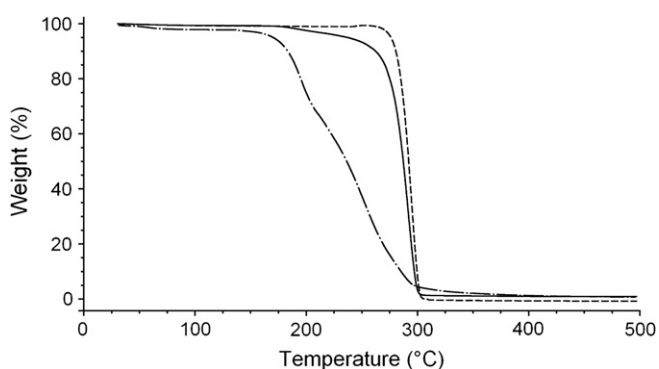


Fig. 2. Superposition of PHBp (---), PHBp + S-Bz (—) and S-Bz (— · —) TG curves recorded at 10 °C/min.