

Biodegradability of Thermally Aged PHB, PHB-V, and PCL in Soil Compostage

Derval dos Santos Rosa,^{1,2} Maria Regina Calil,¹ Cristina das Graças Fassina Guedes,¹ and Túlio César Rodrigues¹

The biodegradability of poly- β -hydroxybutyrate (PHB), poly- β -hydroxybutyrate-co-valerate (PHB-V) and poly- ϵ -caprolactone (PCL) were examined following thermal aging in an oven for 192, 425 and 600 h. Different temperatures, 100, 120 and 140°C for PHB and PHB-V and 30, 40 and 50°C for PCL were used to assess the influence of this parameter on biodegradation. The biodegradability tests were done in soil compostage at pH 11.0 and involved measuring the residual mass of polymer. Thermal analysis of the polymers was done using a differential scanning calorimeter (DSC). The melting temperature and crystallinity were also determined. Thermal ageing increased the biodegradability only for PHB at 120 and 140°C, and there was no correlation between crystallinity and the biodegradation of the polymers.

KEY WORDS: Thermal ageing; biodegradable polymers; soil compostage; polyester.

INTRODUCTION

Synthetic materials such as plastics have numerous applications in packaging, automobile manufacturing, food production, pharmaceuticals, and other areas. Approximately 2% of all plastics eventually reach the environment to contribute to an already acute environmental problem [1]. This situation is aggravated by the fact that polymeric materials are dumped in landfills along with domestic waste [2], thereby hampering the circulation of liquids and gases and delaying the stabilisation of organic matter.

Despite public policies for reducing the amount of solid residues in various countries, there is still a need for new ways to minimise this environmental

problem. Among the alternatives proposed is the recycling of polymeric products, controlled pyrolysis and the substitution of conventional polymers for biodegradable ones [2–4]. Conventional polymers have a low microbial decomposition rate and may have a lifetime of hundreds of years when buried in a typical solid waste site [5]. On the other hand, biodegradable polymers are polymers whose degradation results from the action of microorganisms such as bacteria, algae and/or fungi [6].

Among biodegradable polymers, the best known is poly- β -hydroxybutyrate (PHB), which is produced on a large scale through bacterial fermentation [7]. PHB can also be synthesised chemically by polymerisation through opening of the β -butyrolactone chain in the presence of catalysts such as aluminium or zinc [5].

Another biodegradable polymer, poly- β -hydroxybutyrate-co-valerate (PHB-V), is a copolymer of hydroxybutyrate and random hydroxyvalerate segments. Bacteria produce both PHB-V and PHB. Variations in the concentration of valerate in the copolymer may lead to degradation times that range

¹ Laboratório de Polímeros Biodegradáveis e Soluções Ambientais, Programa de Pós-Graduação *Stricto Sensu* em Engenharia e Ciência dos Materiais (PPG-ECM), Universidade São Francisco, Rua Alexandre Rodrigues Barbosa, No. 45, Centro, 13251-900, Itatiba, SP, Brazil.

² To whom all correspondence should be addressed. E-mail: derval.rosa@saofrancisco.edu.br

from a few weeks to many years. This copolymer is the first polyalcanoate to be explored commercially, and is used in hygiene products, agriculture, packing, and medical applications [8].

A third biodegradable polymer, poly- ϵ -caprolactone (PCL), has also been studied as a substrate for biodegradation and as a matrix for the controlled release of drugs [9,10]. PCL is generally prepared from the ring-opening polymerisation of ϵ -caprolactone [11].

The applications of a polymer are directly related to the mechanical characteristics and morphology of the material. Degradation caused by cleavage and thermal degradation during processing can alter the morphology and mechanical characteristics of the material [6]. By comparing the physical properties of a polymer before and after processing, one can make inferences about the compound's applications and even obtain data on its subsequent biodegradation [7]. Some of the mechanical properties and biodegradability of PHB, PHB-V, PCL and their blends with starch were investigated by Rosa et al. [12].

The thermal stability of PHB and PHB-V copolymers has received limited attention, with Grassie et al. [13–15] and Kunioka et al. [16,17] describing mechanistic studies in a series of papers. Degradation through mechanically-induced thermal processes occurs during the melting of polymers at high temperatures in an oxygen-deficient atmosphere and accounts for chemical changes in the polymer structure. Such degradation modifies the mechanical properties and weathering resistance of the final material [18–20].

In this study, we examined the effect of thermal ageing on the degradation of PHB, PHB-V and PCL in soil compostage.

EXPERIMENTAL

Materials

PHB was supplied by Copersucar (Cooperativa de Produtores de Cana, Açúcar e Alcool do Estado de São Paulo, Brazil) and had a weight average molecular weight (M_w) of 250,000 with 0.2% nitrogen and 0.66% ash (both w/w). PHB was supplied in powder form.

PHB-V was also supplied by Copersucar and had a weight average molecular weight (M_w) of 150,000 with 0.09% nitrogen and 0.27% ash (both w/w). PHB-V was supplied in powder form.

PCL was provided by Union Chemical Carbide Ltd. (P-767) (Cubatão, SP, Brazil). The melting index was 1.9 ± 0.3 g/10 min (ASTM-D-1238) [21], with a density of $1,140 \text{ kg/m}^3$ and a weight average molecular weight (M_w) of 80,000. PCL was supplied in pellet form.

Film Preparation

The films were prepared by the molding compression method, using mold temperatures of 205°C for PHB and PHB-V and 95°C for PCL. The original material was placed in the molds and kept under appropriate conditions for 3 min. The molds were then transferred to a hydraulic press and pressed at 5 MPa for 2 min. After removal from the press, the molds were cooled to room temperature. For each polymer, circular films of 37 mm in diameter and 1 mm thick were obtained.

Thermal Ageing

The films were weighed, placed on aluminium supports and hung in an oven for thermal ageing. The ageing temperatures were established based on the melting temperature of the polymers. Three temperatures were chosen, as follows: 100, 120 and 140°C for PHB and PHB-V, and 30, 40 and 50°C for PCL. The periods of incubation in the oven were 192, 425 and 600 h. The films were weighed again after thermal ageing.

Soil Compostage

The soil compostage consisted of 23% loamy silt, 23% organic matter (cow manure), 23% sand and 31% distilled water (w/w). Calcium hydroxide was added to provide a pH of 11.0.

Measurement of Biodegradability

After thermal ageing, the films of PHB, PHB-V and PCL were weighed and buried, in triplicate, in soil compostage of pH 11.0. Control samples, which had not been thermally aged, were also buried in the compostage. Biodegradation was monitored every 30 days for approximately 10 months by measuring residual mass. For this, the buried samples were recovered, washed with distilled water and dried at room temperature before being weighed and then

buried again in their respective trays. The residual mass was calculated as the ratio between the final and the initial weights.

Thermal Analysis

Thermal analysis was done using a DSC 204 TASC 414/3A differential scanning calorimeter (Netzsch-Gerätebau GmbH, Bavaria, Germany) under an atmosphere of nitrogen, at a heating rate of 10°C min⁻¹. Two heating cycles were used for each film. The PHB and PHB-V films were initially heated to 190°C at a heating rate of 10°C min⁻¹, to eliminate the thermal history of the sample, and then cooled to room temperature before being immediately reheated to 190°C. For PCL, the temperatures used were 80 and 100°C, respectively. The second scan was done at the same heating rate. All DSC experiments were done in duplicate and the thermograms shown refer to the second heating.

RESULTS AND DISCUSSION

Figures 1–9 show the residual mass during the biodegradation of thermally aged and control samples of PHB, PHB-V and PCL buried in soil compostage of pH 11.0. This pH soil was used because in previous studies with three different pH's (7.0, 9.0 and 11.0) the pH 11.0 showed better condition to biodegradation for these polymers [22]. Figures 1–3 show the results for PHB aged in an oven at 100, 120 and 140°C, respectively, and Figs. 4–6 show the results for PHB-V under the same conditions as for PHB. Figures 7–9 show the residual mass for PCL after thermal ageing at 30, 40 and 50°C, respectively.

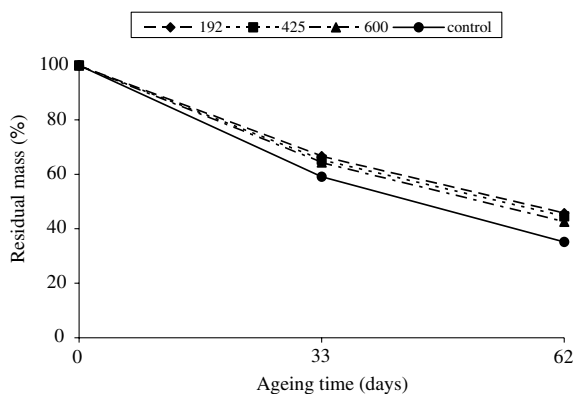


Fig. 1. Biodegradation in soil compostage of PHB exposed to 100°C for 192, 425 and 600 h.

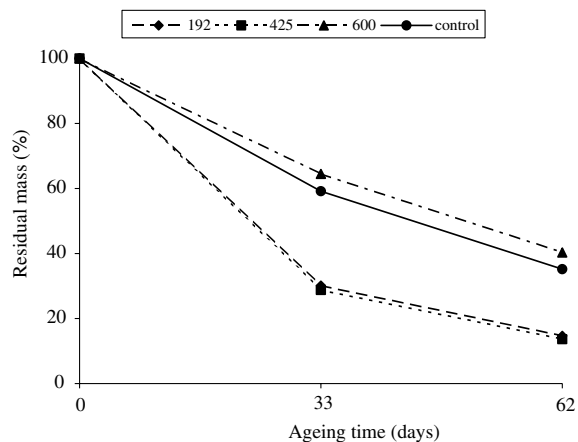


Fig. 2. Biodegradation in soil compostage of PHB exposed to 120°C for 192, 425 and 600 h.

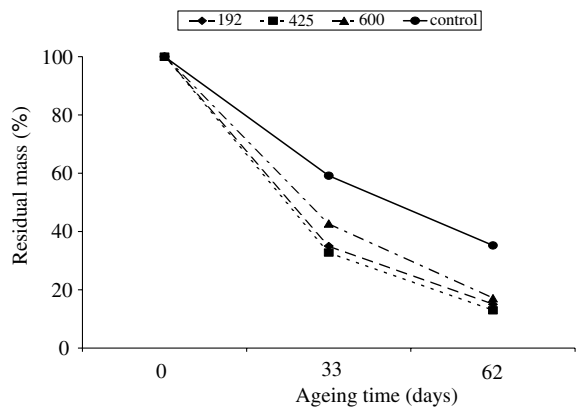


Fig. 3. Biodegradation in soil compostage of PHB exposed to 140°C for 192, 425 and 600 h.

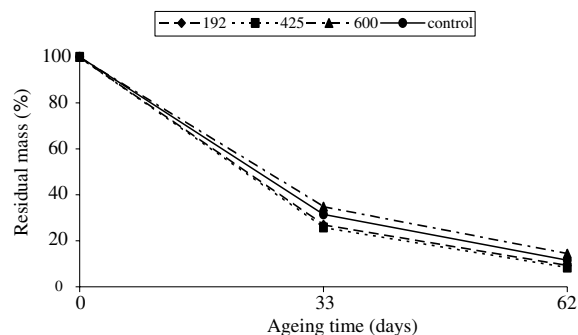


Fig. 4. Biodegradation in soil compostage of PHB-V exposed to 100°C for 192, 425 and 600 h.

The control samples of PHB-V showed the greatest biodegradation and those of PCL, the least, when buried in soil compostage. The higher

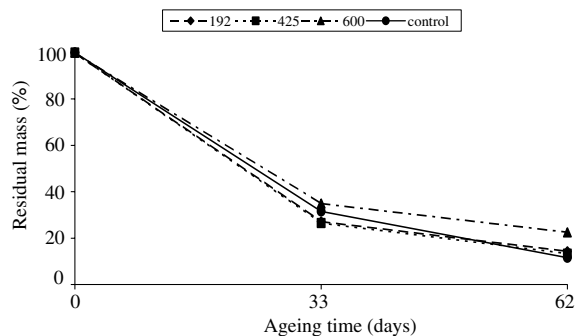


Fig. 5. Biodegradation in soil compostage of PHB-V exposed to 120°C for 192, 425 and 600 h.

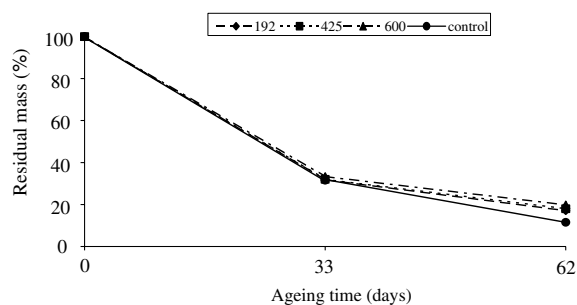


Fig. 6. Biodegradation in soil compostage of PHB-V exposed to 140°C for 192, 425 and 600 h.

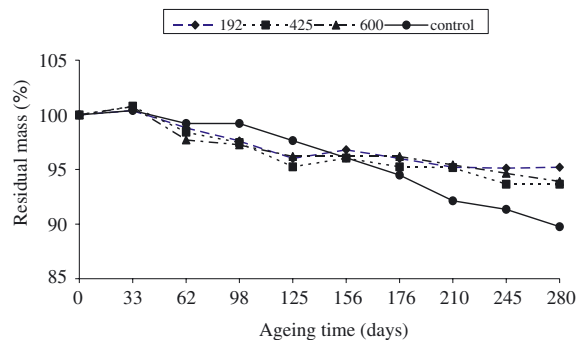


Fig. 7. Biodegradation in soil compostage of PCL exposed to 30°C for 192, 425 and 600 h.

biodegradation of PHB-V probably reflected the presence of a larger proportion of tertiary carbons in this polymer, making it more biodegradable than PHB and PCL. There are no ramifications in the linear structure of the PCL ester (Fig. 10a), whereas in PHB (Fig. 10b) there are a small number of ramifications involving CH_3 groups and PHB-V contains RH_2CH_3 groups (Fig. 10c).

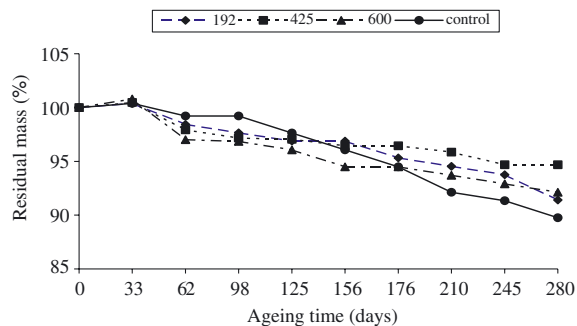


Fig. 8. Biodegradation in soil compostage of PCL exposed to 40°C for 192, 425 and 600 h.

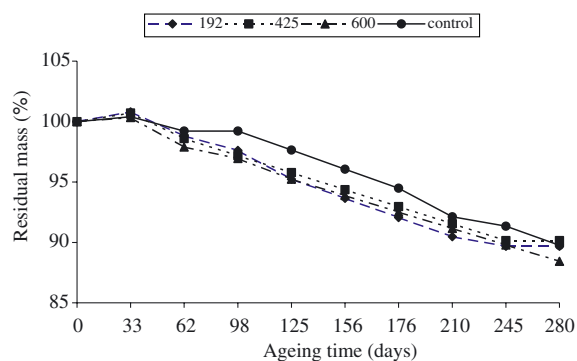


Fig. 9. Biodegradation in soil compostage of PCL exposed to 50°C for 192, 425 and 600 h.

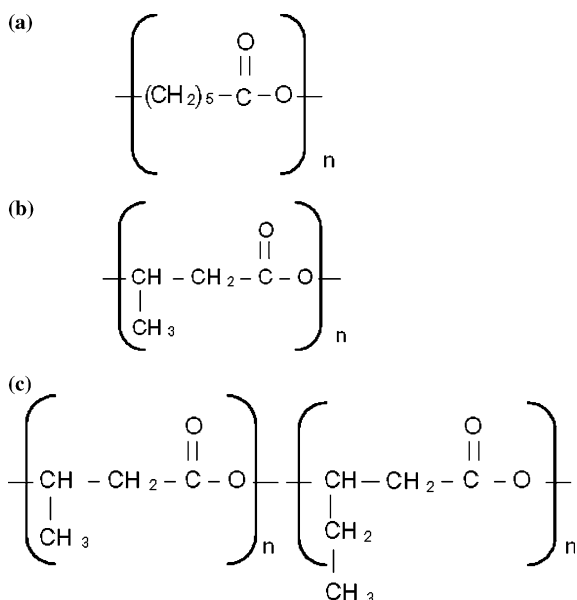


Fig. 10. Chemical structure of: (a) poly- ϵ -caprolactone (PCL), (b) poly- β -hydroxybutyrate (PHB) and (c) poly- β -hydroxybutyrate-co-valerate (PHB-V).

After 62 days, the residual mass of the control samples of PHB-V was 11.5% (Figs. 4–6), while that of PHB was 35.2% (Figs. 1–3). In contrast, the residual mass for control samples of PCL after 280 days was 89.8% (Figs. 7–9), indicating a much lower degradation in soil compostage than for the other polymers studied.

The thermal ageing of PHB at 140°C (Fig. 3) had a marked effect on degradation, with 25–35% more degradation than in the control samples after 33 days; the difference after 62 days was 18–23%. At 120°C (Fig. 2), the thermal effect on sample ageing for 192 and 425 h was significant, with a residual mass of 15%. Ageing to 100°C (Fig. 1) was probably not enough to cause thermal oxidation since because there was no reduction in the residual mass compared to the control samples.

In contrast, PHB-V showed no increase in biodegradation after ageing at different temperatures. The lack of variation in biodegradability between control and thermally aged samples reflects the fact that PHB-V is a polymer that already shows a high level of biodegradation since the hydrolysis of the ester bond is more favoured because of its chemical structure (Fig. 10c).

PCL was more resistant to biodegradation than PHB and PHB-V. For all ageing temperatures studied in soil compostage, there was a slight increase in residual mass relative to the initial weight of the sample after 33 days, probably because of water absorption from the soil compostage. After 62 days, however, there was a loss of mass which was greatest in samples aged thermally for 600 h at all ageing temperatures (Figs. 7–9). This difference relative to

Table I. Average Values for the Melting Temperature, Melting Enthalpy and Crystallinity of PCL, PHB, and PHB-V before and after Thermal Ageing for 600 h

| Sample | Melting temperature (°C) | Melting enthalpy (J/g) | Crystallinity (%) |
|----------------------|--------------------------|------------------------|-------------------|
| PCL film | 56.6 | 47.4 | 58.1 |
| PCL (50°C, 600 h) | 58.8 | 53.3 | 65.3 |
| PHB film | 166.9 | 64.5 | 44.2 |
| PHB (140°C, 600 h) | 135.0 | 85.0 | 58.2 |
| PHB-V film | 166.2 | 64.9 | 44.5 |
| PHB-V (140°C, 600 h) | 148.6 | 60.4 | 41.1 |

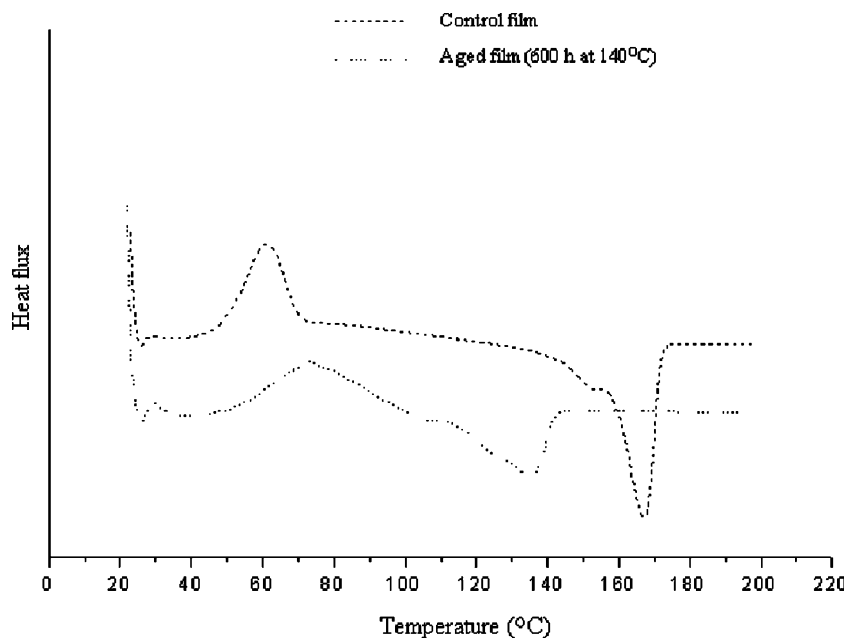


Fig. 11. DSC curves for control and aged PHB film.

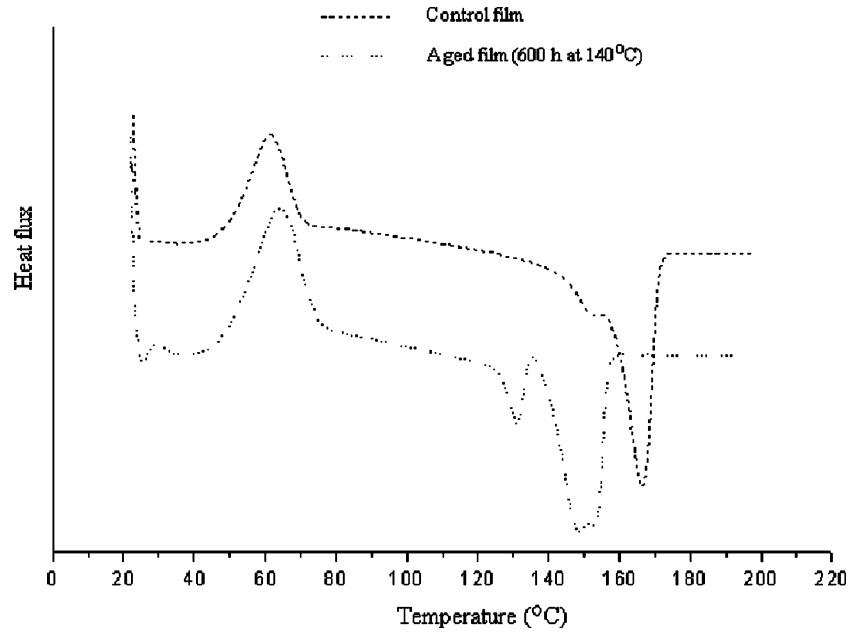


Fig. 12. DSC curves for control and aged PHB-V film.

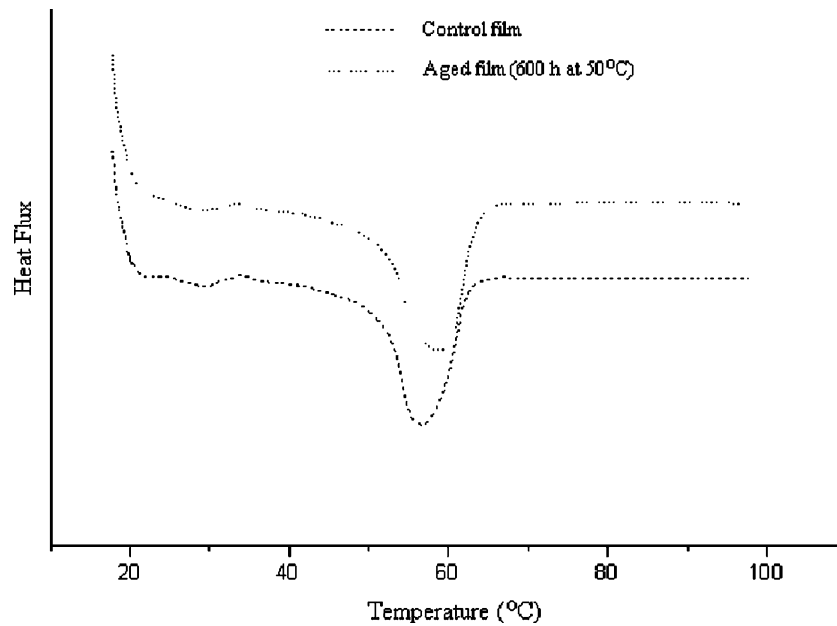


Fig. 13. DSC curves for control and aged PCL film.

the other times generally disappeared, after 156 days in soil compostage for samples aged at 30 and 40°C. The greatest effect of thermal ageing was seen at 50°C. Lower temperatures were probably unable to

cause more than small modifications in the structure of these molecules [23].

The DSC curves for PHB, PHB-V and PCL are shown on even in Figs. 11–13, respectively, and

Table I summarizes the melting temperatures, the melting heat and the crystallinity of the polymers.

The DSC curve for PHB-V (Fig. 12) had a short shoulder at low temperature, which possibly reflected the lower quantity of low molecular weight polymer. The biodegradation test showed that PHB-V degraded before the other polymers, probably because the fragments generated from thermal ageing were more easily hydrolysed.

Although greater crystallinity for aged samples was expected to lead to lower biodegradation under the conditions used here, there was no correlation between biodegradation and crystallinity since the control samples of PHB-V and heated samples of PHB and PCL showed high crystallinity and high biodegradation (Table I and Figs. 3, 6 and 9). In this case, thermal ageing could have initiated degradation in the polymers and, consequently, caused higher easily in the chain organisation, thereby accounting for the increase in crystallinity. This degradation of PHB and PHB-V could have lead to a reduction in molecular weight, as suggested by the lower peak at the melting temperatures shown in Figs. 11 and 12.

No thermal effect was observed for PHB-V, probably because the high content of tertiary carbons (Fig. 10c) facilitated hydrolysis of the ester groups and these in turn produced RCOOH groups that also accelerated ester hydrolysis through autocatalysis, as shown in Equation 1. In the case of aliphatic polyesters, the cleavage of ester bonds was autocatalysed by carboxyl groups present at the start or generated after the first stage of degradation [24]. Such cission can generate fragments that are easily degraded.



CONCLUSION

Of the polymers studied, PHB-V was the most biodegradable and PCL the least, when buried in soil compostage at pH 11.0. The exposure times used in this work were not sufficient to cause the degradation of PHB-V, whereas the duration of exposure and the temperature of thermal ageing had a significant effect on PHB and PCL.

The only significant effect of thermal ageing was seen with PHB at 140°C. For PCL at 30°C, there was initially an increase in the percentage of residual mass, whereas thermal ageing had no effect on the biodegradation of PHB-V. There was no correlation between crystallinity and the biodegradation of the polymers.

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