



About the end life of novel aliphatic and aliphatic-aromatic (co)polyesters after UV-weathering: Structure/degradability relationships

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ABSTRACT

A novel class of aliphatic polyesters, and their derived copolyesters, have been developed. Beside their specific mechanical and thermal properties, the durability, in terms of biodegradability and photodurability, has been investigated. In particular, the polymers were submitted to natural and accelerated photo-ageing and an original methodology based on melt rheology has been applied to determine molecular changes upon UV weathering. Both scission and recombination reactions, which strongly compete as a function of the exposure time, were found to cause a strong evolution of the molecular structure. The results indicate that chemical structure and stereochemistry of the novel materials define the predominant process and the overall behaviour of the samples upon UV exposure. Moreover, the changes of the molecular structure, induced by UV irradiation, could have a significant role into the further biodegradability of the polymers. Therefore, while the relationships between structure and durability enable to design materials with desired well-adapted performances according to their final destination, the biodegradable character upon lifetime use is considered as really questionable and needs further studies.

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1. Introduction

Nowadays, the urgency for substituting the traditional petrochemical polymers, which are not sustainable and biodegradable, with consequent widespread problems of waste and pollution, makes research for alternative polymers an absolute priority and a real challenge for society. Aliphatic polyesters are excellent candidates to have a significant role in the next generation of plastics: some of them are biobased (e.g. poly(lactic acid), PLA), biodegradable and biocompatible (e.g. poly(hydroxyalkanoates), PHAs), even if they often fail in terms of mechanical performance with respect to the aromatic polyesters (e.g., poly(ethylene terephthalate), PET or poly(butylene terephthalate), PBT. For this reason, notable efforts of both industrial and academic research aim to develop novel synthetic polyesters and copolyesters with improved properties and functionalities for specific applications.

In some previous works, the authors synthesized novel aliphatic polyesters and studied the effects of the chain length and

cyclohexyl groups on the macromolecular rigidity, crystallizability and thermal behaviour [1,2]. The preparation of copolyesters, including copolymers containing terephthalate units, allows one to modulate the final properties and performances [3,4]. From these studies it results that the molecular structure can be carefully chosen to reach a compromise between good thermal and mechanical properties, and biodegradability.

For a polymer also the durability is a property of great importance. Indeed, during service life, the material can be submitted to photodegradation, due to an outdoor use, as well as biodegradation and hydrolytic degradation. However, whereas the biodegradable character of polyesters has been intensively investigated using various methods and procedures [5–7], the photodurability has not been so widely analysed. Only few studies on the photodegradation of biodegradable copolyesters (PLA, poly-ε-caprolactone (PCL) and poly(butylene adipate) (PBA) and copolymers) have been already published [8–13]. For example, very recently some authors paid attention on the impact of UV irradiation which accelerates enzymatic degradation of PLA [8,9]. On the contrary, crosslinking of poly(butylene adipate)-co-(butylene terephthalate) (PBAT) mulch films exposed under field conditions is claimed to affect biodegradability [10]. In this context, the concept of durability of a

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material assumes a wide meaning, as it includes both biodegradability and photodegradability and the close correlations between them.

Thus, we decide to focus on the investigation of the photodegradation of new (co)polyesters in order to elucidate their durability regarding to their molecular structure and stereochemistry. It could be said that the mechanical properties of the studied copolymers are found to be similar to those of Ecoflex® (unpublished data). Therefore, a possible application is the flexible packaging. The related polymer, poly(butylene 1,4-cyclohexanedicarboxylate), PBCHD, is more rigid. Then, a possible application is the rigid trays, always in packaging. The complex relationships existing between biodegradability and photodurability, i.e. how the UV-weathering can influence the biodegradability, will be also considered. Indeed, attention is paid on the molecular structure evolution upon photodegradation as a key factor affecting the biodegradability of the polymeric films. We started by a preliminary study reported in Ref. [14] which is a general description of UV behaviour of such systems in the context of a comparison with the UV behaviour of standards and commercially available (bio)polymers, like PLA and Ecoflex®. In this paper, we performed a depth study of UV ageing of a novel class of aliphatic polyesters and derived copolyesters that we synthesized, including natural weathering.

Concerning the methodological approach, it is widely reported that photoageing is an oxidative process involving chain scission and recombination. The two mechanisms compete and one of them is usually predominant and characterizes the overall behaviour of the polymer under weathering. In the literature, the mass average molecular weight changes upon photodegradation were monitored by gel permeation chromatography (GPC) and tensile testing [8,11,12]. However, GPC can solely characterize the soluble fraction. Among tensile properties the elongation at break is very sensitive towards the change in molecular characteristics, but mechanical tests do not give information about mechanisms. Crosslinking causes the films to become more brittle, but, chain scissions produce a reduction of the tensile strength and percent elongation too.

It is well-known that linear viscoelastic properties in dynamic experiment directly reflect changes in molecular parameters and are especially sensitive to both chain scissions and three-dimensional network formation [15,16]. Therefore, we developed an original approach by melt rheology based on dynamic oscillatory measurements as a powerful tool (easy, accurate and very sensitive method) to put in evidence the molecular parameters changes of material through ageing. It provides a precise diagnosis about the degradation way with the aim of deeply studying the specific behaviour during photoageing of the selected aliphatic and aliphatic-aromatic (co)polyesters, depending on their chemical structure and their stereochemistry. On the other hand, thermal analysis was performed in an extensive way to take into account the morphological evolutions. The final goal is to establish a relationship between macromolecular structure and durability.

2. Experimental methods

2.1. Materials

Polyesters and copolyesters, whose chemical formulas are reported in Scheme 1, were obtained by a two-stage polycondensation, using titanium tetrabutoxide (TBT) as catalyst. All the samples and their molecular characteristics are described in Table 1.

The poly(butylene 1,12-dodecanoate) was synthesized by starting from 1,4-butanediol (BD) and 1,12-dodecanedioic acid (DA), as described in Ref. [17]. The sample was named 4-12, where 4

and 12 represent the number of carbon atoms in diol and diacid, respectively.

The poly(butylene 1,4-cyclohexanedicarboxylate) samples are named PBCHD_{xx}, where xx indicates the content of the *trans* isomer of the cycloaliphatic unit. PBCHD₉₁ was prepared from BD and 1,4-cyclohexanedicarboxylic acid (CHDA), containing 99 mol-% of *trans* isomer [3], whereas the other PBCHD specimens were obtained from BD and dimethyl-1,4-cyclohexane dicarboxylate (DMCD) [2]. In this latter case the different percentages of *trans* isomer in C₆ rings were obtained by starting with a convenient mechanical mixture of the two commercial DMCD monomers, with 22 and 100 mol-% of *trans* isomer, respectively.

The aliphatic, random copolymer was obtained from BD, 1,12-dodecanedioic acid (DA), and 1,4-cyclohexanedicarboxylic acid (CHDA), containing 99 mol-% of *trans* isomer [3]. The copolymer can be seen as formed by units of 4-12 and units of PBCHD; it is named (4-12)/PBCHD-30/70, where 30/70 indicates the feed molar ratio of DA/CHDA. The final *trans* content of the PBCHD units is equal to 92 mol-%.

Analogously, the aliphatic-aromatic, random copolymer was prepared starting from BD, DA, and terephthalic acid (TA) [4]. The copolymer is formed by units of 4-12 and PBT and is named (4-12)/PBT-30/70 where 30/70 indicates the feed molar ratio of DA/TA.

The samples were dissolved in chloroform and then precipitated in methanol for the purification. The (4-12)/PBT-30/70 sample was dissolved in a mixture of chloroform and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (90/10-vol.-%).

The ¹H NMR spectra were recorded on samples dissolved in CDCl₃. For the (4-12)/PBT-30/70 sample a mixture of CDCl₃/CF₃COOD (95/5-vol.-%) was used as solvent. The ¹H NMR spectra were used to confirm the structures, to determine the copolyester compositions, and to calculate the content of *trans* isomer of cycloaliphatic groups in PBCHD units. Molecular weights (expressed in equivalent polystyrene) were determined by gel permeation chromatography (GPC), using a Hewlett Packard Series 1100 liquid chromatography instrument equipped with a PL gel 51 Mixed-C column. Chloroform was used as eluent and a calibration plot was constructed with polystyrene standards. For GPC analysis the (4-12)/PBT-30/70 sample was dissolved in a mixture of CHCl₃/HFIP (98/2-vol.-%).

The photodegradability study was performed on films (about 100 μm) prepared by compression moulding between two Teflon sheets about 10 °C above the melting temperature, previously determined by DSC measurement.

2.2. Accelerated photo-ageing procedure

Samples were exposed to UV irradiation at 60 °C in dry air in an accelerated photo-ageing device (based on SEPAP 14-24 device and described elsewhere [18,19]). This polychromatic set up was equipped by a «medium pressure» mercury source filtered by borosilicate envelope (Mazda type MA 400) supplying radiation of wavelengths longer than 300 nm. This source is located along the focal axis of a cylinder with elliptical base. Sample films, fixed on aluminium holders, turned around the other focal axis. The inside of the chamber is made of highly reflecting aluminium. Temperature of samples was controlled by a thermocouple connected with a temperature regulator device which controls a fan. All experiments were carried out at 60 °C. Films were analysed after various exposure times.

2.3. Natural weathering

Natural weathering was performed at Clermont-Ferrand (Central town in France, latitude 45_450 N and longitude 3_100 E,

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