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# About Durability of Biodegradable Polymers: Structure/Degradability Relationships

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**Summary:** Up to now materials were chosen to satisfy specific property(ies) in relation with the required application. Nowadays, a specific attention has to be devoted to the durability of this property regarding to the lifetime duration. It is the reason why, we paid attention about degradability. Thus, a screening of bio- and photodegradability of various selected (co)polyesters has been achieved in order to get better insights about structure / durability relationships. We developed tools allowing the prediction of the behavior of materials upon ageing and the evolution of their properties, regarding to their initial chemical structures. Hence, we could be able to design (co)polyesters characterized by well-adapted physical, thermal and mechanical properties, but also, with high photostability and/or high biodegradability.

**Keywords:** biodegradable; copolymerization; degradation; polyesters; rheology

## Introduction

Nowadays, one of the major environmental problems consists in the plastics waste. Hence, bioplastics are a newly emerging field. Two main categories of innovative eco-friendly materials, based on two different concepts, are presently under development with the support of intensive worldwide research efforts. The first concept is based on the addition of specific prodegrading additives into the conventional material, e.g., polyethylene, which becomes consequently degradable by microorganisms. The second approach involves the synthesis of purely biodegradable materials from both renewable and petroleum resources.

Regarding to the latter way, in the field of polyesters some materials, alternative to the common PET and PBT, are commercially available, such as polylactic acid (PLA), poly(R)-3-hydroxybutyrate (PHB), Poly(butylene terephthalate-*co*-butylene adipate) (PBTA) (known with the trademark of Ecoflex®), Bionolle®, an aliphatic polyester derived from 1,4-butanediol and adipic acid and/or succinic acid. Given the great interest of the scientific community in developing novel biopolyesters, recently, we have proposed a novel class of synthetic random copolyesters, based on poly(alkylene dicarboxylate)s. These materials can be fully aliphatic or aliphatic-aromatic copolymers.[1,2] It is noteworthy to specify that properties and performances of these new copolyesters could be balanced by slight changes in chemical structure, as we have observed for the parent homopolymers.[3,4] Therefore, we are able to design material to final physical and thermomechanical performances according to their final destination.

Beside the specific mechanical and thermal properties and, of course, their biodegradable character, the durability of eco-friendly materials is a property of great

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importance. During service life, the material can be exposed to photodegradation due to outdoor use. Our study focuses on the whole durability of these different eco-friendly polymers, especially (co)polyesters, regarding to their chemical and morphological structures.

Firstly, our purpose is to evaluate the photodegradability. Attention was paid on the molecular structure evolution upon UV exposure measured by rheology in order to establish a relationship between structure/photodurability.

After that, a test of biodegradability has been perfected based on a respirometric method. Biodegradation experiments were carried out on fresh materials, *i.e.* before any use in order to predict the biodegradable character regarding to the chemical structure of the material.

Finally, a screening of bio- and photo-degradability has been achieved in order to get better insights about structure / durability relationships.

## Experimental Part

### Materials

Two commercially available polymers are studied as references: Ecoflex® is an aliphatic-aromatic copolyester synthesized from petroleum purchased by BASF; PLA is an aliphatic material obtained from renewable source and supplied by Cargill Dow.

Polyesters and copolyesters were obtained by two-stage polycondensation starting from 1,4-butanediol (BD), 1,12-dodecanedioic acid (DA), 1,4-cyclohexanedicarboxylic acid (CHDA), and terephthalic acid (TA), as described in ref..[1–4] The paths of synthesis of copolyesters are reported in Scheme 1. The aliphatic copolymers can be seen as formed by units of the poly(butylene 1,12-dodecanedioate), named 4-12 (where 4 and 12 represent the number of carbon atoms in diol and diacid, respectively), and units of poly(butylene 1,4-ciclohexanedicarboxylate), named PBCHD. The copolymers are indicated with the name (4-12)/PBCHD-x/y, where x/y indicates the the feed molar ratio of DA/CHDA.

The aliphatic-aromatic copolymers can be seen as formed by units of the poly(butylene 1,12-dodecanedioate), (4-12), and units of PBT. The copolymers are indicated with the name (4-12)/PBT-a/b, where a/b indicates the feed molar ratio of DA/TA.

In this paper the focus have been made on the 4-12 and PBCHD homopolymers and the (4-12)/PBCHD-30/70 and (4-12)/PBT-30/70 copolymers.

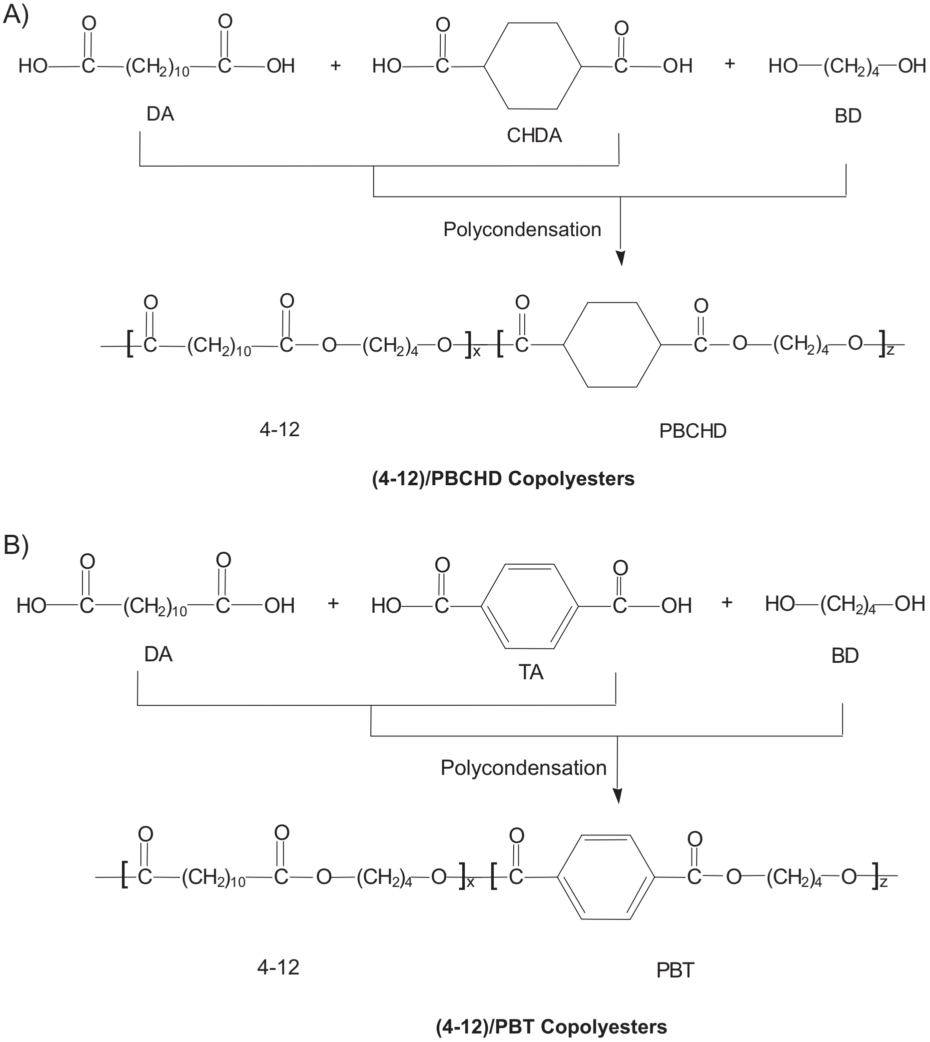
### Accelerated Photoageing Procedure

Samples were exposed to UV irradiation at 35 °C in an accelerated photo-ageing device (based on SEPAP 12-24 device from Atlas Corp.) and described elsewhere.[5–7] 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 reflectant aluminium. Temperature of samples is controlled by a thermocouple connected with a temperature regulator device which controls a fan. All experiments were carried out at 35 °C. Films were analysed after various exposure times.

### Biodegradation Tests

Before investigation, the samples were dissolved in chloroform and then precipitated from methanol for the purpose of purification. After being dried thoroughly under vacuum, the purified materials are white powders.

Among the different tests to evaluate the biodegradability,[8] the measurement of the biological breakdown in aerobic liquid medium is of main interest. The international standard of standardization (ISO: ‘‘International Standards Organization’’) ISO 14852 described the experimental



***Scheme 1.***
Chemical structure of synthesized copolyesters: (A) aliphatic copolymers, (B) aromatic copolymers.

conditions for the tests of biodegradability in aqueous medium.[9] They are rather easy to carry out and reproducible. The measurements are based on the evaluation of the $O_2$ consumption and the quantity of $CO_2$ released during the biological breakdown of the plastic specimen, as in the method of Sturm.[10] The material to be tested is placed in an aqueous mineral nutrient liquid medium inoculated by micro-organisms resulting from activated sludge, suspensions of active ground or compost.

An experimental device has been built based on this respirometric method, based on the measurement of pressure drop. Since $CO_2$ is trapped, the decrease of pressure inside the bioreactor is assigned to the $O_2$ consumption. In our experimental conditions, the colonization medium is a solution containing only inorganic species. This medium of growth was inoculated with a biological *inoculum* (sewage sludge taken *in situ* from a station of purification of the worn water). In this way, the only source of carbon available is from the tested polymeric film, whether soluble or not, which is submitted to biodegradation. The incubating test is performed at 30 °C under continuous shaking over 19 days and aeration ensures that there is sufficient oxygen in the bioreactor at all times. The percentage of biodegradation could be evaluated from the amount of $O_2$ consumed by the plastic sample compared to the total amount of $O_2$ which could be theoretically consumed (noted $ThO_2$). This parameter corresponding to the whole biodegradation of the sample is calculated by the following equation:

$$ThO_2 = (44/12)\ Q_r \cdot m \cdot X_c \quad \text{(in mol)} \tag{1}$$

Where $Q_r$ is the theoretical respirometric parameter considered as fixed to 0.7, $X_c$ is the average carbon in the material considered (%), and m is the mass of the studied sample in g. Hence, a mineralization level $T_{min}$ could be determined as the ratio of the measured $O_2$ consumed and the theoretical consumption value. The calculation is done according to the following equation:

$$T_{\min} = \frac{n}{ThO_2} \times 100 \qquad \text{(in \%)} \tag{2}$$

Where n is the number of consumed moles.

### Rheology

It is well-known that the evolution of the rheological material properties directly reflects changes in molecular parameters. The linear viscoelastic properties in dynamic experiments are sensitive both to the chain scission and to the three-dimensional network formation. Thus, melt rheology provides a convenient tool to view the particular behavior due to the competition of chain scissions and recombination reactions occurring through ageing.[11] Hence, molecular changes upon photooxidation were monitored by melt viscoelasticity experiments in oscillatory shear mode using a rotational controlled stress rheometer (StressTech /Rheologica) equipped with parallel plates geometry. Their diameter was 10mm and the gap between the plates was about 1 mm. In all cases, the values of the stress amplitude were checked to ensure that all measurements were conducted within the linear viscoelastic region. At different time during the photoageing, a frequency sweep extending from 0.01 to 30 Hz was performed. All experiments were carried out at temperature slightly above the melting temperature. The stability of oxidized samples at experimental temperature with respect to the measurement duration has obviously been verified.

## Results

### Photodegradation

It is well-known that chain scissions and/or recombinations occur through the photo- (as thermo-) oxidative process inducing changes in molecular parameters. Melt viscoelasticity provides a convenient tool to get deep information concerning the evolution of the molecular structure upon ageing.[7,11]

No single parameter can be used to characterize the stress-strain relationship in viscoelastic material. The *complex dynamic modulus* ($G^*$) is resolved into two components using complex notation:

$$G^* = \sigma/\varepsilon = G' + iG''$$

The real part of the complex modulus (G') describes stress-strain relationships that are in phase. G' is called the *storage modulus* (or *elastic modulus*). The imaginary component (G'') characterizes the out-of-phase component and is named the *loss modulus* (or *viscous modulus*).

Elsewhere, the *dynamic viscosity* ($\eta^*$) is related to the complex modulus by

$$\eta^* = \sigma/(d\varepsilon/dt) = G^*/(iw) = \eta' - i\,\eta''$$

with $\eta' = G''/\omega$ and $\eta'' = G'/\omega$. Then, the real component of the complex viscosity ($\eta'$) describes the viscous dissipation in the sample, while the imaginary component ($\eta''$) represents the stored elastic energy.

Furthermore, it is well-known that the zero shear viscosity η0 depends on the molecular weight and obeys to a power law [12]:

$$\eta_0 \propto M_w^{\alpha}$$

The zero shear viscosity η0 can be obtained from the complex viscosity $\eta^*(\omega)$ according to:

$$\eta_0 = |\eta*|\omega{-}{>}\ 0 = |\eta'|\omega{-}{>}\ 0$$

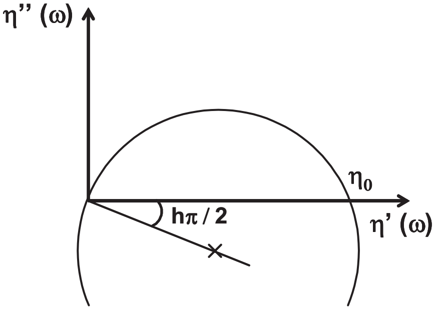
An empirical rheological model used to fit dynamic data is the Cole-Cole distribution expressed by [13–15]:

$$\eta*(\omega) = \eta_0/[1 + (\mathrm{i}\ \omega\lambda_0)1\text{-h}]$$

Where $\lambda_0$ is the average relaxation time and h the parameter of the relaxation-time distribution.

In the complex plane this model predicts the variation of the viscosity components (η'' versus η') to be an arc of circle. From this representation it is easy to determine the parameters of the distribution: $\eta_0$ is obtained through the extrapolation of the arc of the circle on the real axis and the distribution parameter h through the measurement of the angle Φ= hΠ/2 between the real axis and the radius going from the origin of the axis to the center of the arc of the circle (see Scheme 2).

The Figure 1 displays the evolution of complex viscosity components through the photo-oxidation at 35 °C of the two standard materials. The viscosity components curves in Figure 1A (η' versus η'') exhibit a strong decay of zero shear viscosity $\eta_0$ through the first hours of UV exposure of a PLA film. Thus, mass-average molecular weight rapidly decreases from the very beginning of the photo-oxidative process pointing out that scission reactions prevail.



**Scheme 2.**
Cole-Cole plot.

On the contrary, the zero shear viscosity increases providing evidence of a molecular weight increase due to recombination reactions in case of Ecoflex®, see Figure 1B.

While chain scissions are predominant in case of PLA, we assume that chain recombinations prevail in case of this commercially available aliphatic-aromatic copolymer.

On the basis of these preliminary results, the set of synthesized copolyesters offers the possibility to check the relationship between chemical structure and the behavior upon photodegradation.

Similar results are obtained through the photo-oxidation of aliphatic-aromatic copolyester films (see 4-12/PBT in Table 1). The variation of viscosity components puts in evidence that chain recombination reactions proceed (η0 increases from the beginning of exposure). The gradual distortion of the Cole-Cole diagram suggests that gelation occurs through photo-oxidation. After 50 hours of UV exposure, Cole-Cole diagram looks like a straight line which is the characteristic feature of a fully crosslinked material.

In addition, dynamic viscoelastic properties underlines the decay in molecular weight upon UV exposure of fully aliphatic copolyesters, indicating a behavior quite similar to those of PLA. Hence, we claim that aliphatic structures rather undergo chain scissions, whereas aromatic units induce preferentially chain recombination reactions.

Cyclo-aliphatic copolyesters were submitted to photo-ageing under our accelerated conditions. The evolution of the molecular structure is rather unexpected and clearly exhibits a dual process. While chain scissions are predominant at the start of the UV exposure, an inversion is observed in the second stage of the photo-ageing of PBCHD polymer films. The

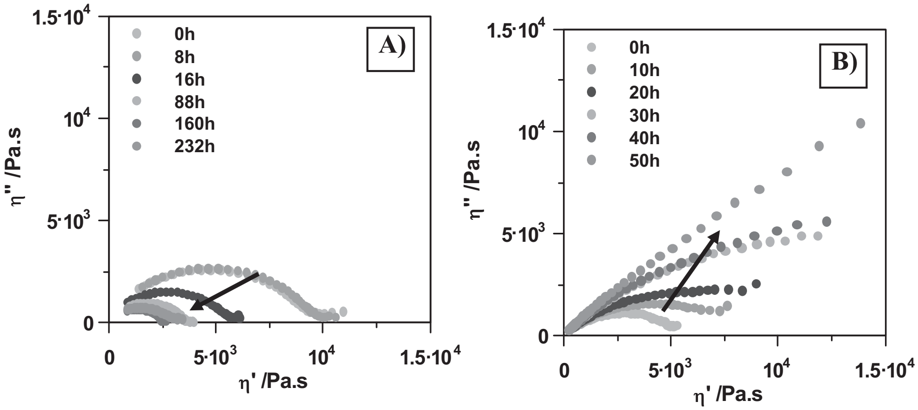


***Figure 1.***
Evolution of complex viscosity components through the photo-oxidation at 35 °C: (A) in case of PLA, (B) for Ecoflex®.

***Table 1.***
Molecular structure evolution upon accelerated photooxydation of (co)polyesters.

| Sample | Chemical structure | UV exposure 10 hours | UV exposure 25 hours | UV exposure 50 hours |
|---|---|---|---|---|
| 4-12 | aliphatic homopolymer | Chain scissions | Chain scissions | Chain scissions |
| PBCHD | cycloaliphatic homopolymer | Scissions / Recombinations concomitant | Recombinations | Crosslinking |
| 4-12/PBCHD-30/70 | aliphatic/cyclic copolymer | Scissions /Recombinations concomitant | Recombinations | Crosslinking |
| (4-12)/PBT-30/70 | aliphatic/aromatic copolymer | Recombinations | Recombinations | Crosslinking |
| Ecoflex® | | Recombinations | Recombinations | Crosslinking |

Table 1 summarizes data. Indeed, the variation of viscosity components describes firstly a decrease of $\eta_0$ which actually increases after about 50 hours of UV exposure. These materials illustrate the fact that scissions and recombinations strongly compete during the photo-oxidation of (co)polyesters. Therefore, chain scissions prevail in the first step of the photo-oxidative process of cycloaliphatic (co)polymers; then, recombinations become predominant in a second stage, involving possible crosslinking phenomenum.

To conclude, although both scission and recombination reactions compete during oxidative ageing, one of them is dominant, characterizing the overall behavior of oxidized polymer which strongly depends upon the chemical structure of the studied copolyester.

Hence, from our experimental results, the two considered commercially available polymers have quite different behaviors. In case of Ecoflex®, with aromatic units, recombination reactions prevail through the photo-ooxidative process leading to rapid crosslinking. On the other hand, aliphatic PLA undergoes chain scissions. These results are confirmed in the case of our synthetic copolyesters and a general feature could be drawn.

Finally, we assume that the molecular evolution is induced by the initial chemical structure of the polymers. Aliphatic structure promotes preferentially chain scis-

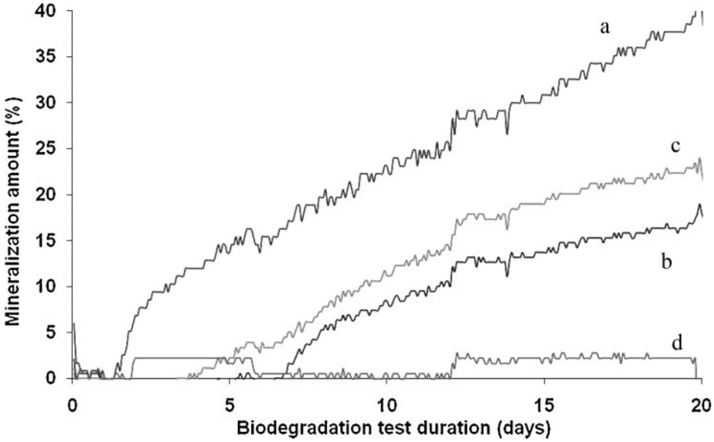


***Figure 2.***
Mineralization level as a function of the time for: (a) a standard biodegradable reference (cellulose), (b) a pure aliphatic copolyester 4-12, and its copolymers (c) an cycloaliphatic-aliphatic copolyester (4-12)/PBCHD-30/70 and (d) an aromatic-aliphatic copolyester (4-12)/PBT-30/70; according to ref. 2.

sions, while aromatic units in the polymer backbone are responsible of recombination reactions.

## Biodegradation

Biodegradation experiments were carried out on both aliphatic and aromatic copolyesters.

The Figure 2 shows the trends of the mineralization level versus time for a standard biodegradable material (cellulose powder), aliphatic homopolymer 4-12 and its copolymers 4-12/PBCHD-30/70 and (4-12)/PBT-30/70 samples. Indeed, these latter two samples show interesting thermal and mechanical properties with respect to those of the 4-12 homopolymer: good thermal stability, high melting temperatures (notably higher than the value of 74 °C of 4-12), and actual improvement of mechanical properties without significant decay in crystallinity level.

All the curves of biodegradation are characterized by an induction time, i.e. a time-lag during which no evolution of the signal is recorded. For the cellulose powder the induction time is about 1.5 days and the final mineralization level, after 19 days of testing, is 37%.

We observed that aliphatic 4-12 polymer is characterized by an induction time of 6 days, indicating that the biodegradation process requires a certain time to take place. After that, the mineralization level increases up to about 16% in 19 days. For this behavior, 4-12 is assumed as a biodegradable polymer, such as other poly(alkylene dicarboxylate)s described in literature.[16,17] This result is consistent with those obtained from commercially available PCL under our experimental conditions; the mineralization level was about 27% after 19 days.

On the contrary, the introduction of aromatic units in the polymer backbone strongly affects the biodegradable character. Aliphatic-aromatic copolymer (4-12)/PBT-30/70 is characterized as not biodegradable under our conditions because of a mineralization level remaining lower than 5% after 19 days. Similar results are obtained with Ecoflex® upon our experimental window ($T_{min} \sim 3\%$ in 19 days).

The Table 2 summarizes results by the normalized mineralization ratio calculated as:

$$Tm_N = \frac{Tm_{Material}}{Tm_{Cellulose}} x100$$

***Table 2.***
Biodegradation test results expressed through the normalized mineralization level ratio after 19 days under our conditions.

| Sample | Chemical structure | $Tm_N$ (%) after 19 days |
|---|---|---|
| **4–12** | **aliphatic** | **45,3** |
| PBCHD | cycloaliphatic | $\sim 0$ |
| 4-12/PBCHD-30/70 | aliphatic/cycloaliphatic | 62,5 |
| (4-12)/PBT-30/70 | aliphatic/aromatic copolymer | $\sim 0$ |

It could be noticeable that our experimental conditions are rather severe, since mineralization levels were measured during a short period over 19 days at a temperature about ambient temperature (30 °C). The kinetics of degradation has to be high, and data are available compared with those of cellulose in similar conditions.

Moreover, we checked also the biodegradability of a fully cycloaliphatic sample (PBCHD) and an aliphatic/cycloaliphatic copolymer (4-12/PBCHD). See Table 2. Under these conditions, fully aliphatic polyesters exhibit a satisfying biodegradability. On this basis, it could be expected that cycloaliphatic polyesters PBCHD offer a good combination of a high biodegradability and good thermomechanical properties.

First at all, an unexpected result is obtained with the cycloaliphatic homopolymer PBCHD which presents a scarce biodegradability with a dramatically low mineralization level after 19 days of testing (less than 1%). On the contrary, the copolymer 4-12/PBCHD exhibits a very interesting high mineralization level upon 19 days, surprisingly better than those of the parent homopolymer 4-12 (up to 27,6% after 19 days of measurement, see Figure 2).

It is noteworthy that the thermomechanical properties of the PBCHD are modified by varying the *cis/trans* ratio of the 1,4-cyclohexylene ring which strongly influences the crystallinity of the material. The studied PBCHD sample is characterized by a high *trans* content of the 1,4-cyclohexylene ring, about 90% of *trans* stereoisomer which improve chain packing and thus crystal perfection ($T_m$ about 155 °C). Obviously, the crystallinity falls down due to copolymerization in case of 4-12/PBCHD ($T_m$ about 55 °C).[2]

These last results put in evidence that chemical structure is not the only parameter managing the degradability. We assume that the no significant biodegradable character of the considered PBCHD homopolymer is imputed to the sample morphology. To better understand the correlation between biodegradation behavior with chemical structure, it would be necessary to control morphology and crystallisation ratio of materials. A series of PBCHD with various *trans* unit average could give new insights about the effect of physical organization of the polymers onto their biodegradability.

## Discussion

This study points out a question: since materials could undergo both chemical evolution and strong molecular evolution due to oxidative degradation (photoageing) during their life cycle, what's about biodegradability after photoageing under use? While chain scissions could appear as favourable to microorganisms attack, the rigidity of a network could reduce the biodegradability. It is now necessary to get better insights about this and further development has to be done.

At this moment, we could answer that oxidative process induce chemical evolution through the formation of hydroxylated and carbonylated by-products. These species improve the wettability of the material and its hydrophilic character. The Table 3 gives the evolution of contact angle measured after various UV exposure times

***Table 3.***
Contact angle measured upon photoageing in accelerated conditions in case of aliphatic-aromatic copolyesters.

| Sample /UV exposure time (hours) | 0 | 50 | 100 | 150 | 200 |
|---|---|---|---|---|---|
| Ecoflex® | 70° | 57° | 55° | 50° | 38° |
| 4-12/PBT- 30/70 | 74° | 70° | 61° | 58° | 52° |

***Table 4.***
Impact of photoageing on biodegradability of Ecoflex®: biodegradation test results expressed through the normalized mineralization level ratio after 25 days under our conditions.

| UV exposure | 0 hour | 40 hours |
|---|---|---|
| $Tm_N$ (%) after 25 days of biodegradation testing | **6%** | **31,6 %** |

upon accelerated photooxidation in case of aliphatic-aromatic copolyesters. The wettability towards water significantly increases in both cases. Hence, this is expected to act as a benefit for biodegradation.

Elsewhere, biodegradation test were carried out on photooxidized Ecoflex® after 40 hours of exposure in SEPAP device. Whereas the photoageing induces the formation of a threedimensional network, the material is almost fully crosslinked after irradiation during 40 hours, but, a significant increase of the mineralization level is recorded. See Table 4.

## Conclusion

To conclude, the correlation found between chemical structure, composition, and final properties enables the preparation of materials with desired properties in terms of physical performances, according to their final destination.

Up to now materials were chosen to satisfy specific property(ies) in relation with the required application. Nowadays, a specific attention has to be devoted to the durability of this property regarding to the lifetime duration...That's what we call the lifetime durability which consists in a wide and important scientific topic.

Since few years specific attention has to be focused on sustainable development considerations and it is necessary to take into account environmental considerations all along the lifetime use of polymeric materials. It is the reason why we attempted to correlate chemical structure and durability of polymers, including both photodegradability and biodegradability. We are able to predict the behavior of materials upon ageing and the evolution of their properties, regarding to their initial chemical structures. Hence, we are able to design (co)polyesters characterized by well-adapted physical, thermal and mechanical properties, but also, with high photostability and/or high biodegradability.

However, the relationship between the photo- and the bio-degradation upon lifetime use has to be deeply clarified.

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