J Mater Sci: Mater Med (2011) 22:2673–2684
DOI 10.1007/s10856-011-4463-8

# Synthesis and characterization of hydrolytically degradable copolyester biomaterials based on glycolic acid, sebacic acid and ethylene glycol

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Received: 21 January 2011 / Accepted: 17 October 2011 / Published online: 5 November 2011
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**Abstract** Copolyesters of glycolic acid (G) combined with sebacic acid (S) and ethylene glycol were synthesized in different molar ratios (G: 0–100% and S: 100–0%) and their hydrolytic degradation was studied and correlated with their structures. Based on the FTIR spectra of the homopolyesters and copolyesters and the normalized peak intensity of the $I_{2918}$, $I_{2848}$ and $I_{1087}$ for the corresponding wavenumbers, it is concluded that the $I_{2918}$ and the $I_{2848}$ are in accordance with the mean number degree of polymerization of ethylene sebacate units and the $I_{1087}$ is in accordance with the mean number degree of polymerization of glycolate units. Based on the XRD diffractograms, poly(ethylene sebacate) and poly(glycolic acid) belong to the monoclinic and the orthorhombic crystal system, respectively and both have higher crystallinity than the copolyesters. The experimental data of the hydrolytic degradation were fitted with exponential rise to maximum type functions using two-parameter model and four-parameter model. Three regions can been distinguished for the hydrolytic degradation by decreasing the molar feed ratio of sebacic acid, which are correlated with the changes of crystallinity. Two copolyesters are proposed: first the copolyester with high amount of glycolate units (S10G90) having higher hydrolytic degradation than G100 and second the copolyester with equal amount of glycolate and ethylene sebacate units (S50G50), having lower hydrolytic degradation than G100. These hydrolytically degradable copolyesters are soluble in common organic solvents, opposite to poly(glycolic acid) and could have perspectives for biomedical applications.

## 1 Introduction

Among the polyesters, the category of degradable synthetic aliphatic polyesters is very important, since they were adopted in surgery and in pharmacology 30 years ago and remain among the most widely used degradable synthetic polymers [1–3]. Polyesters such as poly(ε-caprolactone) (ε-PCL), polylactide (PLA), polyglycolide (PGA) and their copolymers have been widely reported to be applied in varied biomedical fields, including drug delivery systems, resorbable sutures, stents and scaffolds for tissue regeneration [2, 4–7]. Biodegradation of polymeric biomaterials involves cleavage of hydrolytically or enzymatically sensitive bonds in the polymer leading to polymer erosion. Depending on the mode of degradation, polymeric biomaterials can be classified into hydrolytically degradable polymers and enzymatically degradable polymers [8]. An in vitro method to evaluate the suitability of a biomaterial before inserting it to a living organism is its hydrolytic degradation [9]. The degradable polymers are insoluble in water but they can degrade by hydrolytic attack of the ester bond [1, 2, 8]. The degradation of the material due to its dissolution is accompanied by mass loss, reduction of the molecular weight, changes in the implant's structural configuration, changes in mechanical properties such as reduction in strength and stiffness etc. [6, 10]. Water access to the ester bond is governed by hydrophobicity of the monomeric units, the crystallinity of the sample and the bulk sample dimensions. Because water rapidly plasticizes these polymers, degradation proceeds through the entire

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mass simultaneously, often ultimately leading to mechanical distortion, cracking, pitting and fissure of the material in uncontrolled ways [1]. The inherent degradability of aliphatic polyesters makes them highly interesting for applications where the effects on the environment are of importance, e.g. packaging, disposable items, and agricultural geomembranes, but they are also of great interest in biomedical applications where temporary aid is needed, typically sutures, bone pins, stents, scaffolds, and in drug delivery matrices [11]. There have been a number of reports that provide strong indications that the degradation kinetics cannot only be described by random chain scissions, but that the end groups may play an important role in the process. The degradation process is influenced by many factors, including water accessibility, molecular mobility, etc. [5, 10, 12–14]. The mechanical properties and the degradation of the polymers are affected by the combined effects of the crystallinity, the molecular weight ($M_w$), the glass transition temperature ($T_g$), and the monomer hydrophobicity [1, 2, 6, 10, 12, 13, 15].

PGA is a highly crystalline polymer, exhibiting a high tensile modulus with very low solubility in organic solvents. The glass transition temperature of the polymer ranges from 35 to 40°C and the melting point can be greater than 200°C. In spite of its low solubility, this polymer has been fabricated into a variety of forms and structures [8, 16]. Except from PGA and PLA homopolymers, extensive research has been performed in developing a full range of poly(lactide-co-glycolide) polymers (PLGA). Different ratios of poly(lactide-co-glycolides) have been commercially developed and are being investigated for a wide range of biomedical applications. The major advantages of these copolymers are that due to the different crystallinity and hydrophobicity of the lactic and glycolic acid components, their application permits the preparation of 'custom made' carriers according to the specific needs [8, 17, 18].

Aliphatic polyester made from diacids (e.g. adipic acid) [15, 19] and sebacic acid [21, 22] and diols is expected to be one of the most economically competitive biodegradable polymers and it can be degraded and digested completely by microorganisms [15]. Studies, on the crystal structure, polymorphism, spherulitic characteristics and hydrolytic degradation of poly(ethylene adipate) [5, 19], poly(butylene adipate) [7] or degradation of poly(propylene adipate) have been reported [20]. Moreover, the crystal structure, melting behaviour or enzymatic degradation of copolymers of poly(ethylene succinate), poly(butylene succinate) and poly(propylene succinate) have been also reported [21, 22].

In our previous work [19] we studied the synthesis and the hydrolytic degradation of copolyesters based on glycolic acid combined with adipic acid and ethylene glycol in different molar ratios. It was found that these copolyesters are easily processed by solvent-based methods, since they are soluble in many common organic solvents, opposite to poly(glycolic acid) and their degradation behavior is different. Under this scope, it would be interesting to investigate other commonomers with more methylene groups in their backbone, such as sebacic acid, $HOOC(CH_2)_8COOH$, which is an intermediate product of x-oxidization of long-chain aliphatic acids. Compared with short-chain aliphatic acid, sebacic acid is more suitable for the preparation of polyesters, as short-chain aliphatic acids tend to intramolecular condensation. The Food and Drug Administration (FDA) of the United States has approved some sebacic acid-based polymers in biomedical applications [23]. The aim of this paper is to synthesize and characterize hydrolytically degradable copolyester biomaterials based on glycolic acid in combination with sebacic acid and ethylene glycol. Besides the scientific importance of the new synthesized copolyesters, some applications of them could be as biomaterials, e.g. in tissue engineering scaffolds and drug release.

## 2 Experimental

Glycolic acid, $HOCH_2COOH$ (p.a., Fluka), sebacic acid, $HOOC(CH_2)_8COOH$ (p.a., Merck) and ethylene glycol, $HO(CH_2)_2OH$ (p.a., Merck) were used as monomers. The polyesterification was carried out in a 0.5 l vapor reflux reactor by the azeotropic distillation method according to a proper procedure previously described in detail [19, 24]. Since glycols are generally volatile and they co-distill with the water, the initial amount of glycol was in a molar excess of 10% over the stoichiometry (i.e. the molar ratio of ethylene glycol to the sebacic acid was 1.10: 1). Toluene (p.a. Merck) was used as the azeotropic agent in a ratio of 3.5 wt. % over the total weight of the monomers. The polyesters were produced by prolonged heating of the reaction mixture at temperatures up to 215°C. The acid number (A.N.) of the polyesters, dissolved in toluene/methanol (1/2 v/v), was determined by titration with 0.5 N KOH alcoholic solution, indicating the progress of the polyesterification. The molecular weight of the polyesters, $M_n$, was estimated from the A.N. using the equation [19, 24]:

$$\overline{M}_n = \frac{56000}{A.N.} \quad (1)$$

The hydrolytic degradation of polyesters was studied in deionized water at 50°C by using an amount of 2 g of polyester as specimen in the form of tablet (diameter: 20 mm, height: about 1 mm) by exerting pressure (94 MPa for 30 s). In the case of viscous liquid polyester (S20G80, see below) the polyester could not be pressed into tablet, so it was used as is. The proportion of the initial weight of polyester to water volume was equal to 1 g : 150 ml and its weight loss was determined by weighting the tablet at certain time intervals (experimental error: ± 5%). The weight loss versus time curves for each polyester is the mean values of at least three different experiments.

The two homopolyesters of poly(ethylene sebacate) and of poly(glycolic acid) were produced by polyesterification of ethylene glycol with sebacic acid and glycolic acid, respectively. Copolyesters were produced by polyesterification of ethylene glycol, sebacic acid and glycolic acid, in different molar ratios.

The polyesters were characterized by Fourier Transform Infrared Spectroscopy (FTIR) with a Perkin Elmer GX, in the form of tablets with KBr. The number of scans was 10 and the resolution 1 $\mathrm{cm}^{-1}$. Furthermore, their crystal structure was studied by X-Ray Diffraction (XRD) with a Siemens D5000 diffractometer using samples in the form of powder, with $\mathrm{CuK}_\alpha$ radiation and scan rate of 0.02° per second.

## 3 Results and discussion

Table 1 presents the monomers used for the synthesis of homopolyesters and copolyesters and their characteristics. At room temperature, S100 and G100 are solid and the copolyesters are wax-like solids, except of S20G80, which resembles to viscous liquid. The acid number (A.N.) of the polyesters is below 40, as is valid for commercial polyesters [19, 24] and their molecular weight ($\overline{M_n}$) is between 1,470 and 2,500. The mean number degree of polymerization of polyesters is determined as:

$$\overline{X_n} = \frac{\overline{M_n}}{m_o} \tag{2}$$

where $m_o$ is the molecular weight of the mean structural unit. For the homopolyester S100, the corresponding $m_o$ is equal to $m_{o,S} = 184$ (ethylene sebacate structural unit) and for the homopolyester G100 is equal to $m_{o,G} = 58$ (glycolate structural unit). For the copolyesters, the corresponding $m_{o,S}$ and $m_{o,G}$ are determined supposing that the ratio between both structural units is equal to the feed ratio of the monomers, i.e. it is valid the rule of mixture.

$$\overline{X_{n,S}} = \frac{f_S \cdot \overline{M_n}}{m_{o,S}} \tag{3}$$

and

$$\overline{X_{n,G}} = \frac{f_G \cdot \overline{M_n}}{m_{o,G}} \tag{4}$$

where $\overline{X}_{n,S}$, $\overline{X}_{n,G}$ is the mean number degree of polymerization of ethylene sebacate and glycolate, respectively and $f_S$, $f_G$ is the molar feed ratio of sebacic acid and glycolic acid, respectively, i.e. $f_S + f_G = 1$. The values of $\overline{X}_{n,S}$, $\overline{X}_{n,G}$ of the polyesters are presented in Table 1.

New materials have been synthesized as copolymers based on glycolic acid without using catalyst, in order to have solubility, different hydrolytic degradation behavior, lower cost etc. compared to polyglycolide (PGA). The prerequisite of not using catalyst excludes the ring opening polymerization which surely leads to high molecular

**Table 1** Monomers used for the synthesis of polyesters, their acid number (A.N.), molecular weight ($M_n$) and mean number degree of polymerization

| Code of polyesters[a] | Monomers (mol) | | | Acid number A.N. | Molecular weight $\overline{M_n}$ | Mean number degree of polymerization of: | |
|---|---|---|---|---|---|---|---|
| | Sebacic acid (S) | Glycolic acid (G) | Ethylene glycol $Et(OH)_2$ | | | Ethylene sebacate $\overline{X}_{n,S}$ | Glycolate $\overline{X}_{n,G}$ |
| S100 | 100 | – | 110 | 30 | 1867 → 1870 | 10.2 | – |
| S80G20 | 80 | 20 | 88 | 23 | 2435 → 2450 | 10.6 | 8.4 |
| S60G40 | 60 | 40 | 66 | 35 | 1600 → 1600 | 5.2 | 11.0 |
| S50G50 | 50 | 50 | 55 | 35 | 1600 → 1600 | 4.3 | 13.8 |
| S40G60 | 40 | 60 | 44 | 32 | 1750 → 1750 | 3.8 | 18.1 |
| S20G80 | 20 | 80 | 22 | 38 | 1474 → 1470 | 1.6 | 20.3 |
| S10G90 | 10 | 90 | 11 | 34 | 1647 → 1650 | 0.9 | 25.6 |
| G100 | – | 100 | – | [b] | [b] | – | [b] |

[a] The codes of the corresponding degraded polyesters are the same as the initial code by adding the symbol –D (e.g. for the polyester S100 the corresponding degraded polyester is symbolized as: S100-D)

[b] Polyester G100 is insoluble in solvents (e.g. toluene/methanol)

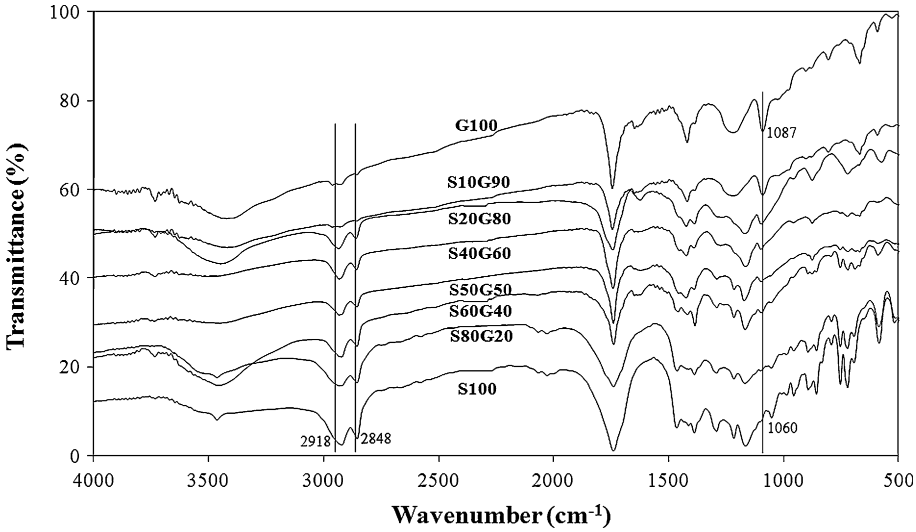


**Fig. 1** FTIR spectra of the initial homopolyesters and copolyestres

weight. The synthesis process without the addition of catalysts or additives avoids the possible toxic effects in biomedical applications [25]. These materials (Table 1) have low molecular weight, opposite to commercial polylactide (PLA), PGA and their copolymers which are synthesized by ring-opening polymerization [6, 8, 12]. On the other hand, poly(ethylene sebacate) are novel biodegradable polyesters [5, 26], with applications such as biomaterials, in drug carriers by loading proper drug molecules, in the form of nanoparticles etc. [26–28]. Furthermore, commercial polyesters with low molecular weights, such as poly[di(ethylene glycol) adipate] ($M_n = 500$–2,500) and poly(2-ethyl-1,3-hexanediol sebacate) ($M_n = 800$) are available [29] having applications as macromonomers [30], in blending [31] and other formulations, as biodegradable polyesters, as polymeric thickeners in dielectric heat transfer fluids, as viscosity builder for high performance fluids, lubricants and greases [29].

The FTIR spectra of the polyesters are shown in Fig. 1. The homopolyesters S100 and G100 exhibit the absorption bands of the corresponding stretching vibrations : –OH from ethylene glycol or glycolic acid (at 3,400–3,200 $cm^{-1}$), $–CH_2–$ (at 2980–2850 $cm^{-1}$) and > C=O from ester groups (at 1755 $cm^{-1}$) [19, 32, 33]. Also, there is an absorption band of $–CH_2–$ bending vibrations at around 1,470 $cm^{-1}$ and a less intense peak of the carboxylic -OH bending vibrations at 1,415 $cm^{-1}$. A peak arising from C–O stretching vibrations of carboxyl groups appears at around 1,295 $cm^{-1}$ [19, 33]. Moreover, the peaks at around 1,210, 1,150 and 1,060 $cm^{-1}$ (or at 1,087 $cm^{-1}$ for G100) can be assigned to C–O stretching modes in ester and oxymethylene groups, respectively [33]. Finally, the absorption bands at 952, 900, 860, 750 and 730 $cm^{-1}$ are attributed to –C–H rocking vibrations [19, 32, 33].

According to Fig. 1, the FTIR spectra of the homopolymers S100 and G100 differ significantly in three wavenumbers [32, 34].

1. The band of $–CH_2–$ at 2,918 $cm^{-1}$ is very strong in S100 spectrum and very low in G100.
2. The band of $–CH_2–$ at 2,848 $cm^{-1}$ is strong in S100 spectrum and very low in G100.
3. S100 exhibits the band of C–O due to the ester groups at 1,060 $cm^{-1}$, whereas G100 exhibits the corresponding band at higher wavenumber, i.e. at 1,087 $cm^{-1}$.

These differences in the FTIR spectra can be used to quantify the differences between the structure of the copolyesters. The first two peaks (at 2,918 and 2,848 $cm^{-1}$) are attributed to the ethylene sebacate structural units and the peak at 1,087 $cm^{-1}$ to the glycolate units. Thus, their intensity can be used to correlate the contribution of the ethylene sebacate and the glycolate units of the polyesters. The peak intensity (I) of the above mentioned bands of the polyesters (Fig. 1) was normalized using the >C=O peak at 1,750–1,735 $cm^{-1}$ as internal standard (in order to correct the differences between the thickness of KBr polyester discs). The dependence of the normalized peak intensity of the $I_{2918}$, $I_{2848}$ and $I_{1087}$ versus molar feed ratio of sebacic acid (%) is presented in Fig. 2. Starting from S100 and by decreasing the molar ratio of sebacic acid down to 0% (i.e. polyester G100), $I_{2918}$ and $I_{2848}$ decrease gradually, which is in accordance with the mean number degree of polymerization of ethylene sebacate units ($\overline{X}_{n,S}$). On the other hand, the intensity $I_{1087}$ of G100 decreases with increasing molar ratio of sebacic acid (i.e. by decreasing the molar ratio of glycolic acid), which is in accordance with the mean number degree of polymerization of glycolate units ($\overline{X}_{n,G}$). It is noticed that the

**Fig. 2** Dependence of the normalized peak intensity of $I_{2918}$, $I_{2848}$ and $I_{1086}$ and mean number degree of polymerization of glycolate units ($\overline{X}_{n,G}$) versus molar feed ratio of sebacic acid (%)

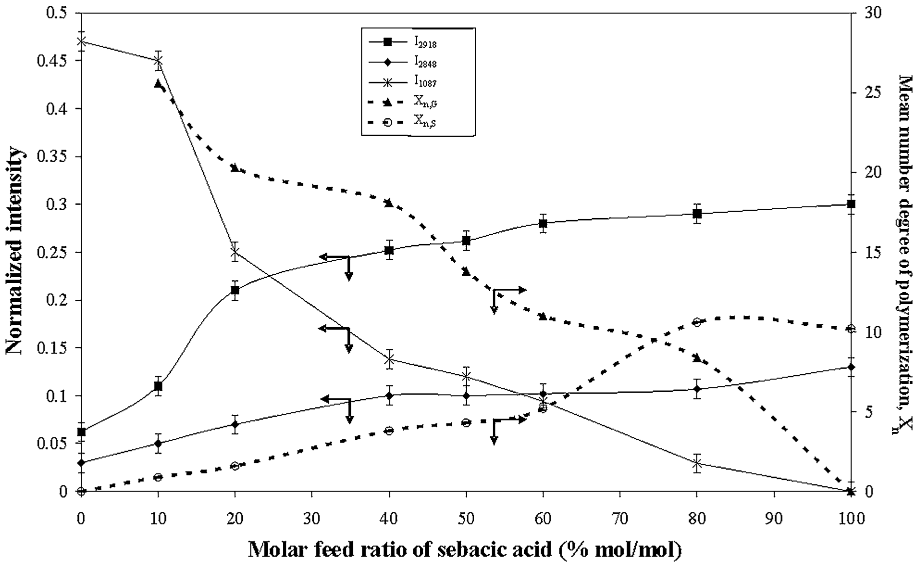
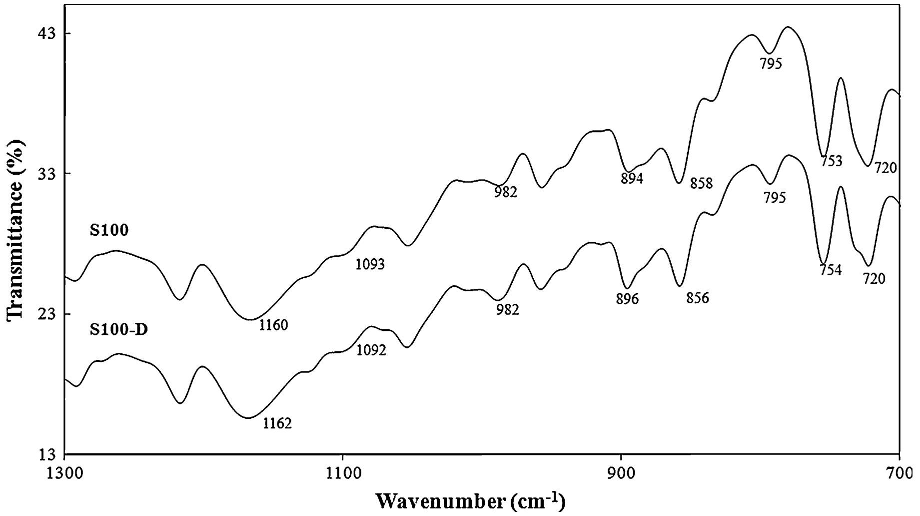


**Fig. 3** FTIR spectra of the initial and degraded S100 polyester



peak at 1,087 cm$^{-1}$ is attributed to the C–O ester groups of glycolate units and not to ethylene sebacate.

According to the literature [19, 33], the region between 1,200 and 700 cm$^{-1}$ can be utilized to evaluate the extent of degradation of polyesters after their hydrolysis. Specifically, the bands at 713, 753, 850 cm$^{-1}$ are associated with the amorphous regions, in opposite to 806, 901 and 972 cm$^{-1}$ which are associated with the crystalline phase. Furthermore, the two broad intense peaks at 1,142 and 1,077 cm$^{-1}$ can be attributed to C–O stretching modes in the ester and oxymethylene groups, respectively and are associated mainly with ester and oxymethylene groups originating in the amorphous domains. Hydrolysis could cause both of these C–O stretching modes to substantially decrease in intensity.

Figures 3 and 4 show the FTIR spectra of the initial polyesters S100, S50G50 and the corresponding hydrolytically degraded S100-D and S50G50-D, respectively. For the initial polyester G100 and the corresponding hydrolytically degraded [19], the absorption band at 1,090 cm$^{-1}$ due to the amorphous region decreases after hydrolysis, whereas the absorption bands at 972, 901 and 806 cm$^{-1}$ due to the crystalline region increase [19]. Concerning the initial polyester S100 and the corresponding degraded (Fig. 3), the absorption bands attributed to the crystalline region at 982 and 894 cm$^{-1}$ increase. More profound are the differences in the case of copolyester S50G50 (Fig. 4), which is hydrolytically degraded to a higher degree than S100 (see below). The intense absorption band at 1,172 cm$^{-1}$ due to amorphous region almost disappeared after hydrolysis, whereas the absorption bands at 802, 898 and 976 cm$^{-1}$ due to crystalline region increase. By comparing the FTIR spectra of the initial and the degraded polyester S50G50, it is confirmed that the amorphous region is preferably attacked during hydrolysis.

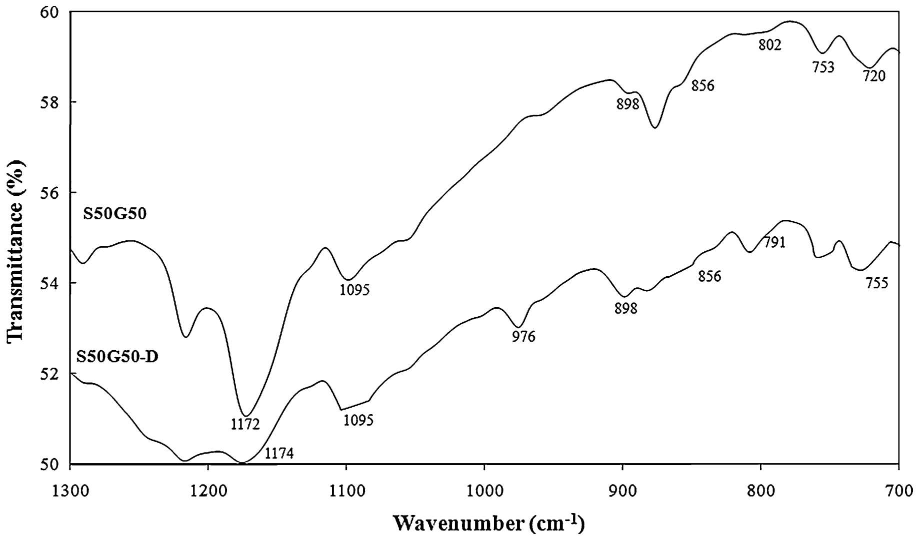


**Fig. 4** FTIR spectra of the initial and degraded S50G50 polyester

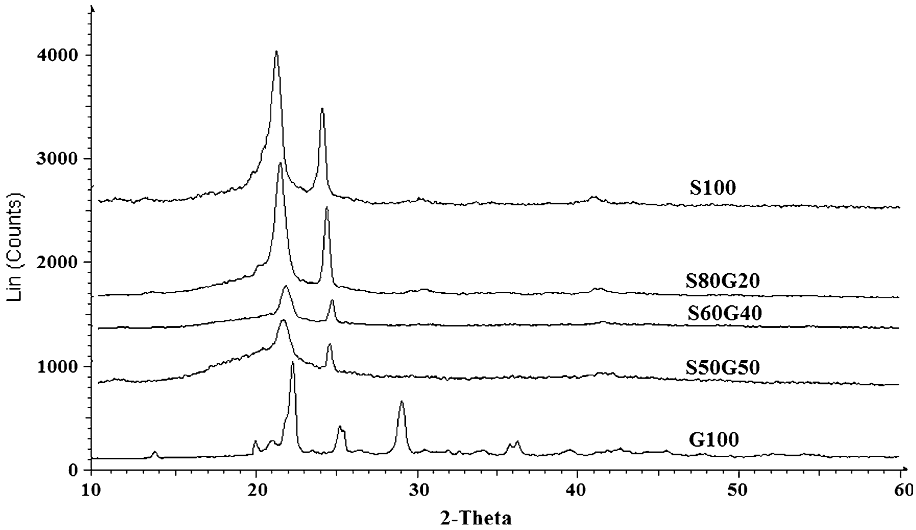


**Fig. 5** XRD of the initial homopolyestres and copolyesters

Figure 5 shows the XRD diffractogram of the homopolyesters (S100 and G100) and the copolyesters (S80G20, S60G40 and S50G50) and Fig. 6 shows the XRD diffractogram representatively for the copolyester S60G40 and the degraded S60G40-D. S100 (Fig. 5) has two main reflections, i.e. at 21.1 and 24.1$^{o}$, and two less intense at 30.1 and 41.1$^{o}$. The main reflections of G100 appear at 22, 25.2 and 29$^{o}$, and the less intense at 19.8, 36.3, 39.5 and 42.6$^{o}$. The reflections of the diffractograms of the homopolymers were indexed [35, 36], in order to define their crystal structure. From the indexing it was found that the crystal system of the homopolymer S100 is the monoclinic with unit cell dimensions: $a = 5.52$, $b = 7.30$, $c = 16.65$ Å and $\beta = 115.0^{o}$, whereas that of G100 is the orthorhombic with the corresponding unit cell dimensions $a = 5.22$, $b = 6.19$ and $c = 7.02$ Å. These values are in accordance with the values reported in the literature which refer to high molecular weight polymers (e.g. polyethylene sebacate with $M_n = 19{,}000$) [35, 37, 38]. It is noticed that the crystal system of degraded homopolymers is the same as that of the corresponding initial. Copolyester S80G20 has two main reflections at 21.5 and 24.3$^{o}$ and two less intense at 30.5 and 41.3$^{o}$, S60G40 has two main reflections at 21.6 and 24.6$^{o}$ and two less intense at 30.9 and 41.6$^{o}$, S50G50 has two main reflections at 21.7 and 24.6$^{o}$ and one less intense at 42.2$^{o}$. Copolyesters S80G20, S60G40 and S50G50 have the same crystal system as S100 (monoclinic) with slight differences in the unit cell dimensions. These differences shift the main peak to slightly higher reflection angles. From the diffractograms, the degree of crystallinity $x_c$ (%), of polyesters was estimated, based on Ref. [39, 40]. The values of $x_c$ are presented in Table 2. Homopolyester S100 and G100, have higher crystallinity than the copolyesters, due to their single type of structural units, i.e. ethylene sebacate and glycolate, respectively. Starting from S100 ($x_c = 58\%$) and by increasing the molar ratio of

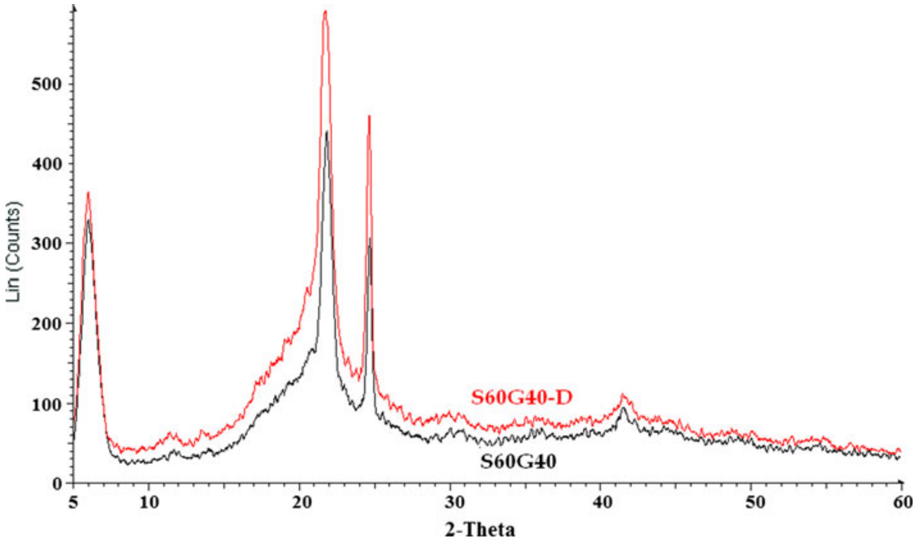


**Fig. 6** XRD of the initial and degraded S60G40 polyester

glycolic acid, the crystallinity of the copolyesters decreases gradually and it reaches the lowest value $x_c = 10\%$ for the copolyester S20G80. The insertion of 10% molar feed ratio of sebacic acid, i.e. copolymer S10G90, leads to an abrupt decrease of the crystallinity, compared to the homopolymer G100. Comparing the crystallinity of every initial polyester with that of the corresponding degraded (Fig. 6; Table 2), the latter have higher crystallinity. This is attributed to the preferable attack and degradation of the amorphous regions during hydrolysis [41] and therefore remain the crystalline regions of the copolyester.

Figure 7 shows the hydrolytic degradation expressed as W ($W = (W_o - W_t)/W_o$, where $W_o$: initial weight of sample and $W_t$: weight of sample at time t) of the polyesters S100, S50G50, S10G90 and G100 versus time. The temperature of 50°C for the hydrolytic degradation is above the glass transition temperature of poly(glycolic acid), which is in the range of 35–40°C [8] and that of poly(ethylene sebacate), which is at −30°C [42]. The hydrolytic degradation of the polyesters increases and after a certain time (equilibrium time, $t_{eq}$) reaches its maximum value of $W_m = (W_o - W_{eq})/W_o$, where $W_{eq}$: weight of sample at equilibrium time. Poly(ethylene sebacate), S100, shows lower degradation, $W_m$, than poly(glycolic acid), G100. This is attributed to the higher crystallinity of S100 and additionally to its more hydrophobic character, containing eight methylene groups between the carboxylic groups, in comparison to G100, containing only one methylene group per monomer unit. The copolyester S50G50 shows lower degradation, $W_m$, than the copolyester S10G90, due to its higher crystallinity and hydrophobic character.

The experimental data can be fitted with exponential rise to maximum type functions [19]. As a first approximation, a simple model with two parameters was used for the fitting:

**Table 2** Degree of crystallinity, $x_c$(%), of initial and degraded polyesters

| Code of polyesters | Degree of crystallinity, $x_c$ (%) |
|---|---|
| S100 | 58 |
| S100-D | 59 |
| S80G20 | 47 |
| S80G20-D | 49 |
| S60G40 | 42 |
| S60G40-D | 45 |
| S50G50 | 40 |
| S50G50-D | 46 |
| S40G60 | 26 |
| S40G60-D | 36 |
| S20G80 | 10 |
| S20G80-D | 29 |
| S10G90 | 23 |
| S10G90-D | 32 |
| G100 | 53 |
| G100-D | 55 |

$$\frac{W_o - W_t}{W_o} = a \cdot (1 - \exp(-b \cdot t)) \quad (7)$$

where: a = pro-exponential parameter; b = empirical parameter for the fitting of the experimental data ($h^{-1}$); t = time (h). From Eq. 7, when time $t \to \infty$, then $\exp(-bt) \to 0$, thus the maximum degradation according to the model, $W_a$, corresponds to the parameter a. In Fig. 7 the two-parameter model is shown with the dotted lines.

As a second approximation, a more complex, four-parameter model was used for the fitting:

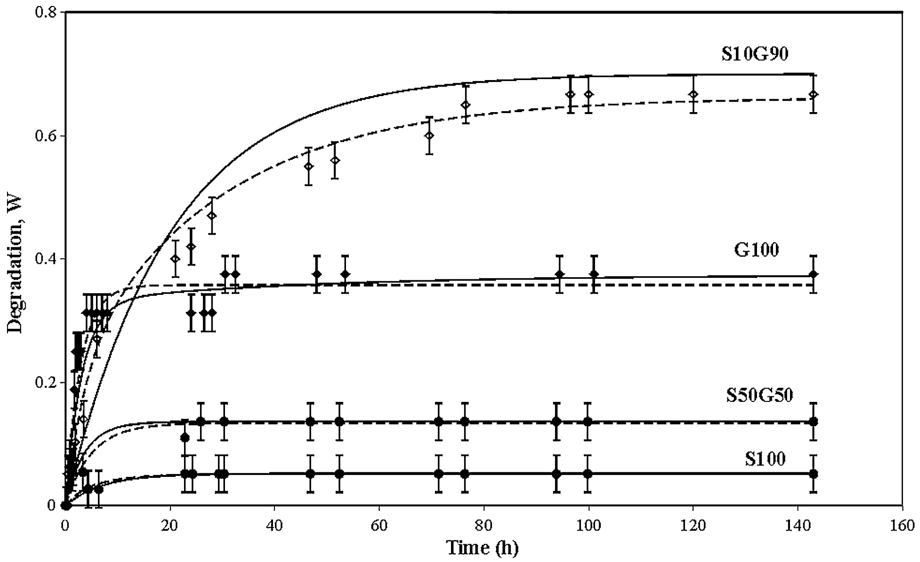


**Fig. 7** Hydrolytic degradation W, of the polyesters S100, S50G50, S10G90 and G100 versus time [W = ($W_o$−$W_t$)/$W_o$, where $W_o$ initial weight of sample and $W_t$ weight of sample at time t] Experimental data (*points*) and their fitting with two (*dotted lines*) or four parameter (*continuous lines*) models

$$\frac{W_o - W_t}{W_o} = a \cdot (1 - \exp(-b \cdot t)) + c \cdot (1 - \exp(-d \cdot t)) \quad (8)$$

where: a, c = pro-exponential parameters; b and d = empirical parameters for the fitting of the experimental data ($h^{-1}$). From Eq. 8, when time t → ∞, then exp(−bt) → 0 and exp(−dt) → 0, thus the maximum degradation according to the model, $W_{a+c}$, corresponds to the sum of the parameters a, c. In Fig. 7 the four- parameter model is shown with the continuous lines.

The experimental data of the hydrolytic degradation and the parameters of Eqs. 7 and 8 for the polyesters are summarized in Table 3. The polyester S100 shows the lowest value of $W_m$. The latter increases by increasing the molar feed ratio of glycolic acid up to 60% (S40G60). By further increase of glycolic acid up to 100% (G100) the $W_m$ decreases. The relative variation between the experimental maximum degradation $W_m$ (Table 3, column 3) and the maximum degradation according to the two- parameter model, $W_a$ (Table 3, column 4), expressed as [($W_m$−$W_a$)/$W_m$]×100 (Table 3, column 6), is up to 17.2% (in absolute value). On the other hand, the corresponding values for the four- parameter model, $W_{a+c}$ (Table 3, column 11), is much lower, i.e. up to 3.3% (in absolute value). The two-parameter model describes very well mainly the initial part of the degradation (up to the initial 10 h), whereas the four-parameter model is appropriate for fitting hydrolytic degradation on the entire time period. This was also observed in copolyesters of glycolic acid with adipic acid and ethylene glycol [19].

Apart from the fitting of the experimental data using the two- and four- parameter models, it is important to determine the kinetics of the hydrolytic degradation of the polyesters. The latter is a complicated phenomenon which belongs to the heterogeneous, non- catalyzed reactions. These reactions take place between the solid state of the polyester and the liquid phase of the water and, indeed, between an ester group containing into the macromolecule of polyester and a molecule of water [19, 43]. The chemical reaction rate which is used in single phase reaction systems can be used also for multiphase reaction systems (as in the hydrolytic degradation of the polyester) and is then characterized as effective reaction rate [44]. Below, the chemical reaction rate is used under this meaning. This is a kinetic approach based on the liquid–solid systems, taking also into consideration the surface of the solid polyesters in the form of tablet [45]. Based on kinetics analysis that has been already described in detail [19], the hydrolysis can be described from the following equation:

$$dW = -k \cdot S \cdot m_0 \cdot C \cdot dt \quad (9)$$

where W: weight of polyester (g), k: rate constant of hydrolytic degradation, S: surface of the solid polyester in the form of tablet ($6.91.10^{-4} m^2$), $m_o$: molecular weight of the mean structural unit, C: concentration of water, i.e. 1/18 mol/g or 55.5 mol/kg.

For the polyester S100, $m_o$ is equal to $m_{o,S} = 184$ (ethylene sebacate structural unit) and for the polyester G100 is equal to $m_{o,G} = 58$ (glycolate structural unit). For the copolyesters:

$$m_o = f_S \cdot m_{o,S} + f_G \cdot m_{o,G} \quad (10)$$

Taking S, $m_o$ and C as constants and integrating Eq. (9) between t = 0 → W = $W_o$ up to t = t → W = $W_t$, we have:

$$W_o - W_t = k \cdot S \cdot m_0 \cdot C \cdot t = K \cdot t \quad (11)$$

where:

$$K = k \cdot S \cdot m_0 \cdot C \quad (12)$$

**Table 3** Results of hydrolytic degradation of polyesters at 50°C : experimental data, their fitting with two- or four-parameter model and calculated rate constant for the degradation

| Code of polyesters | Equilibrium parameters of the experimental data | | Two-parameter model (Eq. 7) | | | Four-parameter model (Eq. 8) | | | | | | Rate constant (k) of hydrolytic degradation at 50°C based on: | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | Two-parameter model | | Four- parameter model | |
| | Equilibrium time $t_{eq}$ | Degradation at maximum, $W_m$ | $A = W_a$ | b | $\frac{W_m - W_a}{W_m} * 100$ | a | b | c | d | $a + c = W_{a+c}$ | $\frac{W_m - W_{a+c}}{W_m} * 100$ | k | | k | |
| | (h) | | | $(h^{-1})$ | | | $(h^{-1})$ | | $(h^{-1})$ | | (%) | $(kg/m^2 \times s)$ | $(s^{-1})$ | $(kg/m^2 \times s)$ | $(s^{-1})$ |
| (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) | (11) | (12) | (13) | (14) | (15) | (16) |
| S100 | 14.0 | 0.050 | 0.0518 | 0.1382 | −3.6 | 0.0300 | 0.2560 | 0.0214 | 0.1150 | 0.0514 | −2.8 | 2.60E−07 | 7.34E−07 | 9.96E−07 | 3.53E−07 |
| S80G20 | 16.0 | 0.098 | 0.0976 | 0.2477 | +1.0 | 0.0395 | 0.4166 | 0.0583 | 0.1718 | 0.0978 | +0.5 | 2.52E−06 | 8.49E−07 | 2.56E−06 | 8.63E−07 |
| S60G40 | 22.8 | 0.100 | 0.1000 | 0.2396 | +1.0 | 0.0500 | 0.2860 | 0.0500 | 0.1700 | 0.1000 | 0.0 | 3.05E−06 | 1.05E−06 | 3.20E−06 | 1.20E−06 |
| S50G50 | 23.6 | 0.136 | 0.1333 | 0.2008 | +2.2 | 0.1220 | 0.2860 | 0.0140 | 0.1700 | 0.1360 | 0.0 | 3.18E−06 | 1.19E−06 | 4.53E−06 | 1.69E−06 |
| S40G60 | 71.3 | 0.918 | 0.9480 | 0.0358 | −3.3 | 0.8000 | 0.0450 | 0.1160 | 0.0130 | 0.9160 | +0.2 | 5.37E−06 | 2.01E−06 | 5.74E−06 | 2.14E−06 |
| S20G80 | 93.3 | 0.877 | 0.7258 | 0.0961 | +17.2 | 0.7600 | 0.0450 | 0.1460 | 0.3300 | 0.9060 | −3.3 | 1.31E−05 | 4.41E−06 | 1.18E−05 | 3.96E−06 |
| S10G90 | 84.6 | 0.667 | 0.7562 | 0.0361 | −12.4 | 0.4520 | 0.0350 | 0.2100 | 0.2700 | 0.6620 | +1.1 | 1.33E−05 | 4.70E−06 | 1.54E−05 | 4.84E−06 |
| G100 | 30.5 | 0.375 | 0.0518 | 0.1382 | +4.5 | 0.327 | 0.327 | 0.046 | 0.025 | 0.373 | −0.5 | 1.88E−05 | 7.22E−06 | 1.68E−05 | 6.45E−06 |

$W_m = (W_o - W_{eq})/W_o$, where $W_o$ initial weight of sample and $W_{eq}$ weight of sample at equilibrium time

$W_a$ maximum degradation according to the two-parameter model

$W_{a+c}$ maximum degradation according to the four-parameter model

By plotting ($W_o - W_t$) versus t, using the initial linear part of the fitting curve (i.e. up to 5 h), the constant K is determined from the slope of the straight line. Then, the rate constant of polyester degradation k is determined from Eq. 12 in units of kg/(m$^2$ s) or in s$^{-1}$ by multiplying with S and dividing by the initial weight $W_o$ ($1.8 \times 10^{-3}$ kg). In the kinetics study only the initial time period is used, where the concentration is nearly equal to the initial, whereas afterwards the concentration changes with the progress of the phenomenon. Thus, for the calculation of the rate constant for the degradation, k, only the data from the initial linear part (which corresponds at time of about 3 h) was used [19]. The results of the kinetics of the hydrolytic degradation for the polyesters are presented in Table 3 (columns 13, 14 for the two- parameter model and columns 15, 16 for the four-parameter model). The values of k calculated from the two models are similar. Thus, the two models, which were used for the fitting of the experimental data, can be used to determine the kinetics of the hydrolytic degradation of the polyesters.

Figure 8 shows the dependence of k (s$^{-1}$), calculated with four- parameter model, of the polyesters versus molar feed ratio of sebacic acid (%). By decreasing the molar feed ratio of sebacic acid from 100 (S100) to 0% (G100) the values of k increase. Specifically, from S100 to S40G60 k increases linearly, and then up to G100 again increases linearly but with a higher rate, almost three times higher (the slope of the first straight line is $3 \times 10^{-8}$ and that of the second is $1 \times 10^{-7}$).

The hydrolytic degradation of the polyesters is affected mainly by the crystallinity of the polyester, and by the number of ester groups contained in the macromolecule, indicating hydrophobicity. The hydrophobicity of the macromolecule and the flexibility of the macromolecular backbone are factors, which both influence the access of water in the vicinity of the ester groups where the hydrolysis reaction takes place [19]. Figure 9 shows the dependence of degree of crystallinity, $x_c$(%), and the maximum degradation, $W_m$, of the polyesters versus molar feed ratio of sebacic acid (%). Concerning the two homopolymers, the maximum degradation $W_m$ of S100 is much lower than that of G100. The crystallinity of S100 is slightly higher than that of G100 and therefore, the lower crystallinity indicates higher amorphous region which is more preferably attacked during hydrolysis [41]. However, the main reason for the different hydrolytic degradation of the two polyesters is the fact that sebacic acid is more hydrophobic than glycolic acid [23]. Three regions can been distinguished by decreasing the molar feed ratio of sebacic acid: first region: 100–50% sebacic acid, where $x_c$ decreases and $W_m$ increases slightly. Second region: 50–20% sebacic acid, where $x_c$ decreases and $W_m$ increases abruptly having high values (i.e. approx. 90% for copolyesters S20G80 and

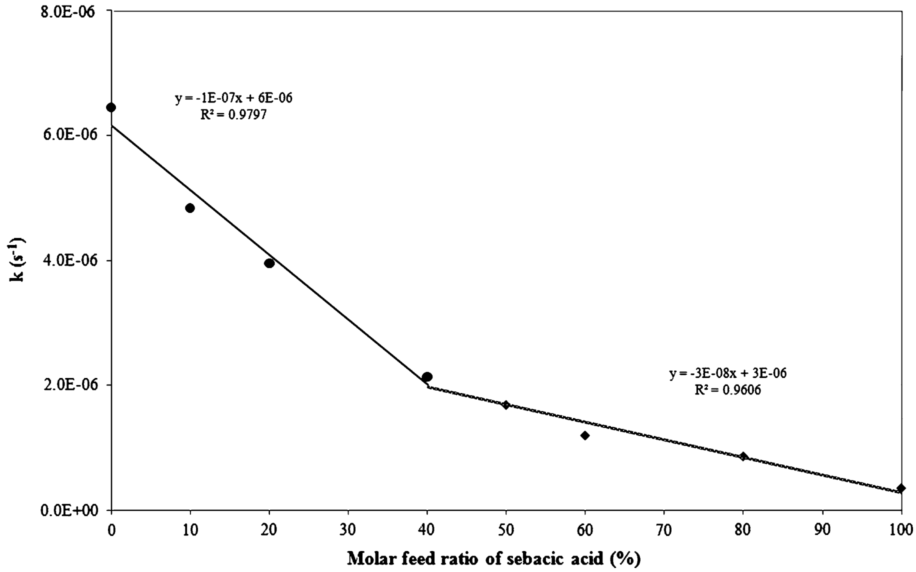


**Fig. 8** The dependence of rate constant of degradation, k ($s^{-1}$), calculated with four-parameter model, of the polyesters versus molar feed ratio of sebacic acid (%)

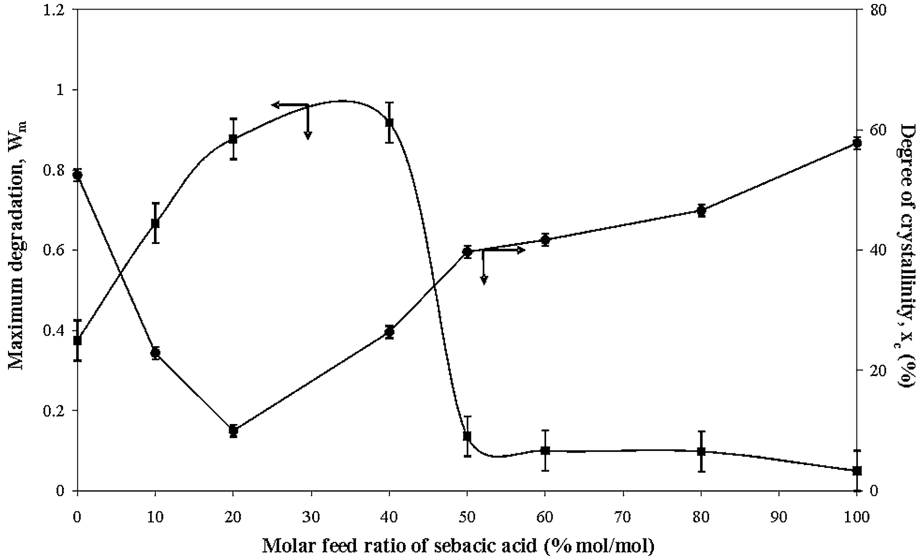


**Fig. 9** The dependence of degree of crystallinity, $x_c$(%), and the maximum degradation, $W_m$, of the polyesters versus molar feed ratio of sebacic acid (%)

S40G60). Third region: 20–0% sebacic acid, where $x_c$ increases and $W_m$ decreases considerably. Copolyesters S10G90, S20G80 and S40G60 having the lowest crystallinity ($x_c$ = 23, 10 and 26%, respectively) show the highest degradation ($W_m$ = 0.667, 0.877 and 0.918, respectively). Compared to similar copolyesters with adipic acid instead of sebacic acid [19], the latter have lower degradation rate constants and lower maximum degradation, due to the more hydrophobic nature of sebacic acid compared to that of the adipic acid [46].

The copolyesters synthesized are biocompatible, since sebacic acid-based polymers have been approved for biomedical applications. The copolymerization of glycolic acid with sebacic acid and ethylene glycol leads to copolyesters with modified structure compared to the poly(glycolic acid) and therefore to different hydrolytic degradation behaviour. Taking into consideration a higher or lower hydrolytic degradation of copolyesters compared to that of poly(glycolic acid), two copolyesters are proposed: First. The copolyester with high amount of glycolate units (S10G90), which has low crystallinity ($x_c$ = 23%), high maximum degradation ($W_m$ = 66.7%) and high rate constant of polyester degradation ($k = 4.84 \times 10^{-6}\ s^{-1}$). Second. The copolyester with equal amount of glycolate and ethylene sebacate units (S50G50), which has high crystallinity ($x_c$ = 40%), low maximum degradation ($W_m$ = 13.6%) and low rate constant of polyester degradation ($k = 1.69 \times 10^{-6}\ s^{-1}$). Moreover, these copolyesters are soluble in common organic solvents, opposite to poly(glycolic acid). These hydrolytically degradable and biocompatible copolyesters could have perspectives as biomaterials for biomedical applications (as already described). Another kind of copolyesters with higher molecular weight and better mechanical properties can be further synthesized using the present copolyesters as precursors. The latter will be fed into a specific reactor, like that used for the production of high molecular weight poly(ethylene terephthalate), by following a second step of polyesterification. This procedure constitutes another research task, including also the study on the effect of the degree of polymerization to the crystallographic and the hydrolytic behaviour of these copolyesters.

## 4 Conclusions

Copolyesters of glycolic acid combined with sebacic acid and ethylene glycol were synthesized and their hydrolytic degradation was studied and correlated with their structures. Based on the FTIR spectra of the homopolyesters and copolyesters and the normalized peak intensity of the $I_{2918}$, $I_{2848}$ and $I_{1087}$ for the corresponding wavenumbers, it is concluded that the $I_{2918}$ and the $I_{2848}$ are in accordance with the mean number degree of polymerization of ethylene sebacate units and the $I_{1087}$ is in accordance with the mean number degree of polymerization of glycolate units. The region between 1,200 and 700 $\mathrm{cm}^{-1}$ was utilized for evaluating the extent of degradation of polyesters after their hydrolysis. The absorption bands attributed to the amorphous region decrease after hydrolysis, whereas those attributed to the crystalline region increase. Based on the XRD diffractograms, poly(ethylene sebacate), S100, and poly(glycolic acid), G100, belongs to the monoclinic and the orthorhombic crystal system, respectively and both have higher crystallinity than the copolyesters. The copolyesters after their hydrolytical degradation have higher crystallinity. The experimental data of the hydrolytic degradation were fitted with exponential rise to maximum type functions using two-parameter model, which describes very well mainly the initial part of the degradation, and four-parameter model, which is appropriate for fitting the hydrolytic degradation on the entire time period. Three regions can been distinguished for the hydrolytic degradation (maximum degradation $W_m$ and the rate constant of polyester degradation k) by decreasing the molar feed ratio of sebacic acid, which are correlated with the changes of crystallinity ($x_c$). Two copolyesters are proposed: first the copolyester with high amount of glycolate units (S10G90) (low $x_c$, high $W_m$ and high k) having higher hydrolytic degradation than G100 and second the copolyester with equal amount of glycolate and ethylene sebacate units (S50G50) (high $x_c$, low $W_m$ and low k), having lower hydrolytic degradation than G100. These hydrolytically degradable copolyesters are soluble in common organic solvents, opposite to poly(glycolic acid) and could have perspectives as biomaterials for biomedical applications.

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