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The influence of antioxidant and post-synthetic treatment on the properties of biodegradable poly(butylene succinate)s modified with poly(propylene oxide)

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Abstract: Novel poly(ester–ether)s based on poly(butylene succinate) (PBS) as the hard segments and 30 mass % of poly(propylene oxide) (PPO) as the soft segments were synthesized with varying amount of the antioxidant (*N,N'*-diphenyl-*p*-phenylenediamine, DPPD). The influences of the addition of DPPD and the impact of post-synthetic treatment by precipitation on the molecular structure, thermal and physical properties, as well as on the storage stability of the biodegradable aliphatic copolyesters, were investigated. The structure and composition of the copolymers were determined by means of ^{1}H-NMR spectroscopy. The molecular weight and polydispersity of the poly(ester–ether)s were evaluated from solution viscosity and GPC measurements. The thermal properties and stability were evaluated, respectively, by means of DSC and non-isothermal thermogravimetry in an inert nitrogen atmosphere. The biodegradability potential of the polymers was studied in hydrolytic and enzymatic degradation tests with *Candida cylindracea* lipase by monitoring the weight loss of polymer films after incubation. The weight losses of the samples increased with time and were in the range from 1 to 5 mass % after 4 weeks. GPC analysis confirmed that there were changes in the molecular weight of the copolyesters during both hydrolytic and enzymatic degradation tests, leading to the conclusion that the degradation mechanism of poly(butylene succinate)s modified with PPO occurred through surface erosion and bulk degradation.

Keywords: poly(ester–ether), poly(butylene succinate), poly(propylene oxide), biodegradable, antioxidant, enzymatic degradation.

INTRODUCTION

Due to their low cost, easy processing and resistance to degradation under environmental conditions, the use of synthetic polymeric materials has been growing progressively in the past few decades. However, environmental concerns about the waste resulting from these materials, especially those from short-term applications, has become the centre of attention in the last decade. Replacement

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of the currently used bioresistant polymeric materials with biodegradable polymers is one of the solutions for global waste problems.[1,2] Only a few types of synthetic polymers can be considered as potential biodegradable materials, mainly ones with hydrolysable groups incorporated into the polymeric chain.[3,4] Aliphatic polyesters, with hydrolysable ester units within the polymeric chain are recognised as one of the most promising polymers for the development of ecologically friendly materials.[5,6] Intense interest in these polymers as degradable thermoplastic exists also for medical application, where there is a need for materials which will be eliminated after time-limited applications, for example in surgery and in formulations for controlled drug release.[7–9] The development of aliphatic polyesters as biodegradable materials has advanced to such a high level that some polymers belonging to this class have already found commercial application, such as poly(glycolic acid) (PGA), poly(L-lactic acid) (PLLA), poly(ε-caprolactone) (PLC) and different poly(hydroxyalkanoates).

The properties of aliphatic polyesters in terms of time-tunable degradability and mechanical properties can be further developed, usually by copolymerization, in order to fulfil different application demands. For some applications, elastomeric materials are more suitable than relatively hard ones, such as aliphatic crystalline polyesters. Biodegradable thermoset elastomers were synthesized from a star copolymers of ε-caprolactone and *D,L*-lactide and also from copolymers of poly(ethylene oxide) and citric acid.[10,11] All these formulations involve crosslinking during the final stage of thermoset preparation. One of the developed ways to obtain thermoplastic elastomers without chemical crosslinking is copolymerization with flexible polyethers.[12,13] In addition to altered mechanical properties, copolymerization with polyethers has the advantage of introducing hydrophilic groups, which render the so-obtained polymers more susceptible to biodegradation. Among different polyethers, poly(ethylene oxide), PEO, and poly(tetramethylene oxide), PTMO, were used to modify the properties of not only aliphatic, but also of aliphatic/aromatic polyesters. For example, PEO was used as the soft segments in a number of cases, *i.e.*, in combination with poly–(lactic acid), poly(butylene terephthalate), poly(butylene succinate) and poly(ε-caprolactone).[14–19] The less hydrophilic PTMO was also used as a constituent part of the soft segments in copolymerization with aromatic and aromatic/aliphatic polyesters.[20–22] In previous studies, it was shown that poly(butylene succinate), PBS, modified with flexible PEO segments has better biodegradability properties compared to PBS modified with PTMO, due to the increased hydrophilicity of the former.[16] However, the oxidative instability of poly(ester–ether)s with PEO is also much more pronounced in comparison to poly(ester–ether)s with PTMO. There has been a report on aliphatic polyesters with poly(propylene oxide) as a building part of the soft segments in biodegradable aliphatic copolyesters.[23] This study showed that the investigated poly(ester–ether)s with PPO had in some ins-

tances even better biodegradability profiles compared to the corresponding ones with PEO.

The main disadvantage of segmented polymers with polyethers as soft segments is their long-term instability under environmental conditions. The oxidative reactions of the ether bonds *via* a free-radical mechanism lead to chain scission and can be thermo-, photo- or γ-radiation initiated. Thus, some attempts to improve the oxidative instability during storage of polymers with PEO included the use of the antioxidant vitamin E as well as commercially available hindered phenols.[24] Hindered amines, such as *N*,*N*'-diphenyl-*p*-phenylenediamine, are also used as radical scavengers where oxidative reactions are expected to occur, such as in the rubber processing and in biomedical applications.[25,26]

In this work poly(ester–ether)s with PPO in the soft segments and poly(butylene succinate) as the hard segments were synthesized and their properties including biodegradability compared to those previous prepared copolymers based on PBS but with PEO or PTMO as the soft segments. Poly(propylene oxide), with a methyl group as a side-group in the repeating units, is a logical extension of our previous studies. The influence of the amount of antioxidant, *N*,*N*'-diphenyl-*p*-phenylenediamine, DPPD, on the long-term stability and overall properties, including biodegradability, was investigated. Since the stability of the polymers, as well as biodegradability depends on the form in which the polymers are stored, the influence of post-synthetic treatment through precipitation was also evaluated.

EXPERIMENTAL

Materials

Dimethyl succinate (Alfa AESAR, GC > 98 %) was used as received. α,ω-Hydroxyl terminated poly(propylene oxide), PPO, with a molecular weight of 1200 g mol^{-1}, (Fluka) was used as obtained. 1,4-Butanediol (MERCK) was purified by vacuum distillation. Titanium-tetrabutoxide, $Ti(OBu)_4$, (Aldrich) was used as a solution in dry *n*-butanol (1:9 v/v). The antioxidant *N*,*N*'-diphenyl–*p*-phenylendiamine, DPPD, (Bayer) was used as received. *Candida cylindracea* lipase was purchased from Sigma.

Synthesis of the polyesters

The aliphatic poly(ester–ether)s, PBSPPOs, were synthesized by a two step transesterification reaction in the bulk, starting from dimethyl succinate, 1,4-butanediol and 30 mass % of α,ω-hydroxyl-terminated poly(propylene oxide) (PPO, M_n = 1200 g mol^{-1}). The diol component was used in a 15 mol % excess over the dimethyl ester. A series of PBSPPOs without antioxidant and with 0.5 and 1 mass % of DPPD as the antioxidant were synthesized. As an example, the synthesis of a poly(ester–ether) without stabilizer, PBSPPO-0, is described. A three-necked laboratory reactor equipped with a condenser, nitrogen inlet tube, magnetic stirrer and thermometer was charged with 40.88 g (0.28 mol) of dimethyl succinate, 18.24 g (0.152 mol) of poly(propylene oxide) and 27.36 g (0.304 mol) of 1,4-butanediol. The reaction mixture was purged with nitrogen and the reaction was started by the introduction of 0.075 g (0.221 mmol) of $Ti(OBu)_4$, as catalyst. The reaction mixture was heated quickly to 150 °C and then gradually (1 °C min^{-1}) to the final reaction temperature of 220 °C. The methanol formed during the first stage was distilled off. The second phase of reaction was carried out with a second portion of catalyst (0.221 mmol), under vacuum ($p \approx 0.5$ mm Hg).

For the different composition of the reaction mixture and applied vacuum, different reaction times from 24 to 54 h were required in order to obtain polymers of high molecular weight. After completion of the reaction, the poly(ester–ether) was cooled in the reactor to room temperature under nitrogen. One portion of the poly(ester–ether) was precipitated from chloroform into methanol (PBSPPO-0-P) and dried under vacuum, while the rest was stored and used further without precipitation (PBSPPO-0). All the other polyesters were synthesized in the manner described above. The other two PBSPPOs in the series were synthesized with 0.5 mass % (PBSPPO-0.5) and 1 mass % (PBSPPO-1) of DPPD. The numbers in the abbreviations of poly(ester–ether)s indicate the mass percent of antioxidant, while for the precipitated samples, the letter P is used at the end of the abbreviation.

Characterization of the polyesters

^{1}H-NMR spectra were recorded in $CDCl_3$ solution with tetramethylsilane as the reference standard using a Varian-GEMINI-200 (200 MHz) instrument. The ^{1}H-NMR spectra of these polymers showed characteristic peaks: protons from the succinic acid appear at δ = 2.63 ppm, protons from the methylene group in the poly(propylene oxide) which were attached to the ether group at δ = = 3.52–3.62 ppm, and central and terminal protons from the 1,4-butanediol at δ = 1.64–1.77 ppm and δ = 4.09–4.12 ppm, respectively. Protons from the methylene group in poly(propylene oxide) which were attached to the ester group appear at δ = 4.09–4.30 ppm, and in the same region a signal from the terminal methylene protons in 1,4-butanediol appears. Protons from methylene group of the poly(propylene oxide) appear at δ = 3.41–3.45 ppm and the signal of the protons from the methyl group of the poly(propylene oxide) appear at δ = 1.15–1.25 ppm. The compositions of the polyesters were calculated from the relative intensities of the peaks characteristics for the succinic acid residue and for the protons from the side methyl groups of the poly(propylene oxide).

The viscosities of solutions of the polymers in chloroform were measured at 25 °C using an Ubbelohde viscometer. The intrinsic viscosity, [η], was calculated from these measurements.

Gel permeation chromatography (GPC) was performed using a Waters 2414 instrument at 30 °C, with four Styrogel columns and a refractive index detector. The columns cover a range of molar masses from 2500 g mol^{-1} to 1 million g mol^{-1}. Calibration was performed with poly(methyl methacrylate) standards. Chloroform was used as the eluent at a flow rate of 1 ml min^{-1}. The copolyesters were injected onto the column as 10 mg ml^{-1} solutions with a 200 μl loop. The number-average (M_n) and weight-average molecular weights (M_w) and polydispersity indexes were evaluated from these measurements using Waters Breeze software.

Differential scanning calorimetry (DSC) was performed using a TA Instruments SDT Q600 analyser under a nitrogen atmosphere in the temperature range from 30 to 160 °C at a heating and cooling rate of 10 °C min^{-1}. The polyester samples were scanned from 30 to 160 °C, then cooled to 30 °C and heated again to 160 °C. The melting temperatures were determined from the initial scan as the temperature of the maximum of the main endothermic peak in the DSC curves.

The TA Instruments SDT Q600 was also used for thermogravimetry. Non-isothermal experiments were performed in the temperature range 30–500 °C at a heating rate of 10 °C min^{-1}. The thermal stability of the poly(ester–ether)s was studied under a dynamic atmosphere of nitrogen (the flow rate was 100 cm^3 min^{-1}).

The moisture uptake of the poly(ester–ether)s was measured as the increase in the mass of polymer films, which were placed in a chamber above a saturated solution of K_2SO_4, giving a relative humidity of 97 %, for 7 days at room temperature.

Enzymatic and hydrolytic degradation tests were performed on poly(ester–ether)s films. The polymer films were obtained by hot pressing at 20 °C above the melting temperature. In addition, the films were stored at ambient temperature for at least three weeks before characterization in order to attain equilibrium crystallinity. The films (10×40 mm^2 and about 150 μm thick) were incubated in a phosphate buffer solution (pH ≈ 7.00) (hydrolytic degradation) or with 2 mg ml^{-1} li-

pase from *Candida cylindracea* (enzymatic degradation) in an incubator at 37 °C. The enzymatic and hydrolytic degradation tests of the poly(ester–ether)s films were run in duplicate. Every 7 days, the enzyme solution was replaced with a freshly prepared one. The films were removed either from the enzymatic or buffer solution after selected time intervals, washed with distilled water, and dried under vacuum at room temperature to constant weight. The extent of biodegradation was quantified as the percent weight loss of the polymeric films.

The surfaces of the samples were observed using an optical microscope "Carl Zeiss Jena" in reflected light before and after hydrolytic and enzymatic degradation, without any further mechanical treatment.

RESULTS AND DISCUSSION

Synthesis and stabilisation of poly(ester–ether)s

Aliphatic poly(ester–ether)s with poly(propylene oxide) as the soft segments and poly(butylene succinate) as the hard segments were synthesised with varied amount of the antioxidant *N,N*'-diphenyl-*p*-phenylenediamine (DPPD). In addition to the influence of the different amounts of antioxidant, the influence of post-synthetic treatment of the obtained polymers on the properties of the poly(ester–ether)s was also investigated.

All poly(ester–ether)s in the series with varying amount of DPPD and constant amount of the soft segments (5.5 mol % or 30 mass %) were synthesised according to the well-established transesterification reaction procedure for obtaining polyesters of high molecular weight.[16] Starting from dimethylsuccinate, 1,4-butanediol and poly(propylene oxide) (M_n = 1200 g mol^{-1}) and using a $Ti(OBu)_4$ as the catalyst, oligomeric chains were produced in the first phase of reaction under atmospheric pressure and nitrogen atmosphere. Thereafter, a vacuum was applied in order to produce chain extension and to obtain polymers of high molecular weight with the addition of the antioxidant DPPD. Longer reaction times for the second phase of the reaction, *i.e.*, polycondensation, were required compared to those for the homopolyester, PBS.[17] These results are in agreement with the fact that the reaction rate decreases due to the higher transesterification activation energy of dimethyl succinate and PPO compared to dimethyl succinate with 1,4-butanediol.[27,28]

The structure and composition of the synthesized poly(ester–ether)s were confirmed by ^{1}H-NMR spectroscopy (Fig. 1). Using the intensity ratio of the methylene protons peak from the succinic acid residue (signal a in Fig. 1) and the methyl protons peak from the side group in the poly(propylene oxide) units (signal g in Fig. 1), the mol and mass fraction of soft segments in the polymer chain were determined. As can be seen from the results presented in Table I in all cases, good agreement with the theoretical composition based on the feed composition was achieved. Thus, the presence of the antioxidant did not influence the composition of the synthesised poly(ester–ether)s. Secondly, in all three cases, the composition of the polymer chains was not altered through precipitation, indicating that the formation of the polymers during the course of the synthesis

was uniform, and that there was no preferential incorporation of either diol units; thus finally random copolymers were obtained.

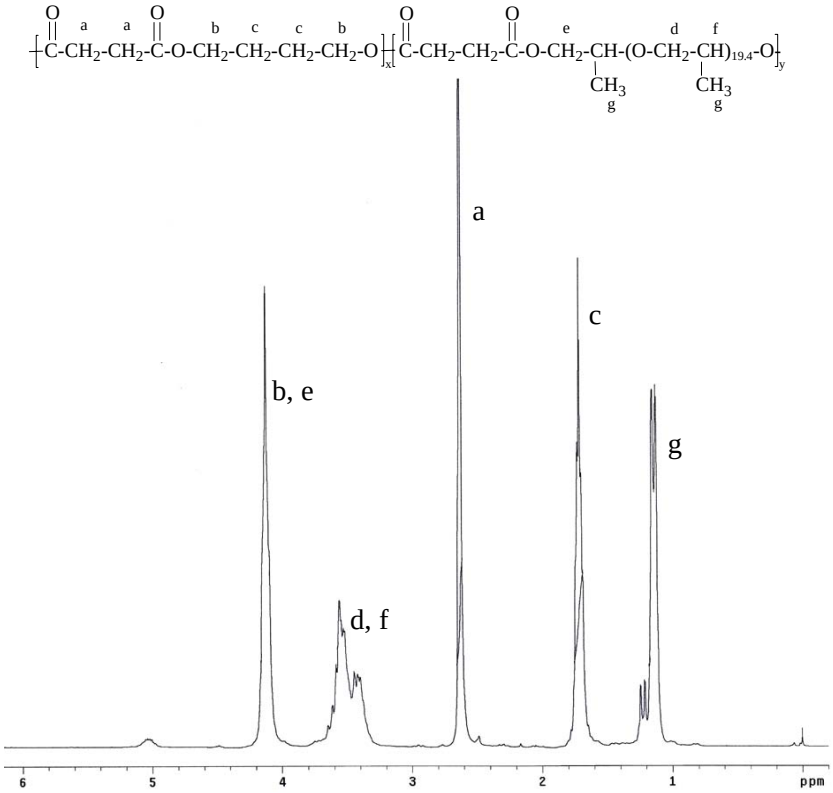


Fig. 1. ^{1}H-NMR spectrum of the poly(ester–ether) PBSPPO-0 in $CDCl_3$.

TABLE I. Composition of poly(ester–ether)s determined from the ^{1}H-NMR spectra

Polymer	Mass fraction of soft segments mass %		Mole fraction of soft segments mol %		L_n
	Theoretical	Experimental	Theoretical	Experimental	
PBSPPO-0	30	29.6	5.5	5.9	17.0
PBSPPO-0-P		29.3		5.4	18.4
PBSPPO-0.5		29.3		5.2	19.1
PBSPPO-0.5-P		29.2		5.2	19.3
PBSPPO-1		29.7		6.0	16.7
PBSPPO-1-P		29.8		6.2	16.2

Under the assumption that the length of the soft segment is one, and taking into account the fact that the copolymers are random, the average length of the hard poly(butylene succinate) segments was calculated from the mole fraction of PBS in the copolymer, using the formula:

$$L_n = \frac{1}{1 - x_{PBS}} - 1$$

The values are included in Table I. In previous studies on the biodegradebility of poly(ester–ether)s with PTMO as the soft segments, it was shown that there is an optimal hard segment length for promoting catalytic action of *Candida cylindracea* lipase,[22] which was also used in the present work. The compositions of the PBSPPOs in this study were designed to obtain poly(ester–ether)s with hard segments of 17 to 18 PBS units, in order to have the optimal catalytic action of the chosen enzyme. As can be seen from the data in Table I, the average sequence length of the PBS hard segments was between 16 and 19, depending on the molar fraction of the soft PPO segments, which varied from 5.5 to 6.2 mol %.

The results of characterisation in terms of the size of polymeric chain, *i.e.*, intrinsic viscosities and molecular weights obtained in GPC analysis, are summarised in Table II. The values of intrinsic viscosities of the synthesized copolyesters were from 78.9 to 101.5 $cm^3\ g^{-1}$. With increasing content of the antioxidant, the molecular weights of the synthesised poly(ester–ether) increased. While for the lower content of DPPD (0.5 %), only a moderate increase was observed, for the higher content of DPPD (1 %), the increase in molecular weight was much more pronounced. It can be concluded that some thermal degradation reactions occurred during the synthesis, although, under the chosen reaction conditions (vacuum at 220 °C), appreciable degradation of the polymers is not to be expected. These thermal degradation reactions could be efficiently prevented by the use of DPPD.

TABLE II. Intrinsic viscosity, molecular weights and molecular weight distribution of the synthesized poly(ester–ether)s

Polymer	$[\eta]^a$ / $cm^3\ g^{-1}$	$[\eta]^b$ / $cm^3\ g^{-1}$	$M_n{}^b$ / 10^4 g mol^{-1}	$M_w{}^b$ / 10^4 g mol^{-1}	$M_w/M_n{}^b$
PBSPPO-0	78.9	74.9	2.72	5.16	1.90
PBSPPO-0-P	82.6	13.8	0.49	0.92	1.88
PBSPPO-0.5	79.6	68.1	2.71	4.61	1.70
PBSPPO-0.5-P	84.2	77.1	2.69	4.67	1.74
PBSPPO-1	87.5	81.5	3.34	6.28	1.88
PBSPPO-1-P	101.5	94.0	3.17	5.72	1.81

[a]Determined for the as-prepared samples; [b]determined after 8 months of aging at room temperature

In this study, it was shown that relatively high-molecular weight poly(ester––ether)s based on PPO could be synthesized using a highly effective catalyst, *i.e.*, tetra-*n*-butyl-titanate, and the molecular weight increased with increasing content of antioxidant, as well as by precipitation leading to the elimination of low-molecular weight fractions. All the synthesized copolymers exhibited macromolecular behaviour and were suitable for the preparation of elastomeric, flexible and tough films by the melt-press method.

As can be seen from the values of the intrinsic viscosities after 8 months of aging, the poly(ester–ether)s are prone to degradation under ambient conditions, as shown in previous studies.[17,22] This can also be seen from GPC measurements which were made after 8 months of aging. This is especially the case for PBSPPO-0-P, which was precipitated after the synthesis. Probably, the reason is in addition to the absence of antioxidant, the morphology of the sample, which was in the form of a powder with a high surface to volume ratio. The results obtained for the samples with DPPD show that the oxidative degradation could be suppressed, although not completely prevented, even with the highest employed amount of DPPD. For complete prevention of the oxidative degradation of poly–(ester–ether)s, higher quantities than 1 mass % of DPPD are recommended.

Thermal properties of the poly(ester-ether)s

The thermal properties of poly(ester–ether)s were characterized by DSC analysis in terms of melting temperatures and enthalpies of melting. Poly(butylene succinate) homopolymer is a crystalline polyester with a melting temperature of 115–117 °C. The main disadvantage of the copolymers of this polyester is that the melting temperatures are usually decreased to below 100 °C. The composition of the poly(ester–ether) was chosen to be such as to obtain polymers with a melting temperature above 100 °C, which is important from the technical point of view. The melting temperatures of all the synthesized poly(ester–ether)s were in temperature region from 104 to 109 °C, irrespective of the presence of a heat stabiliser or post-synthetic treatment (Fig. 2 and Table III).

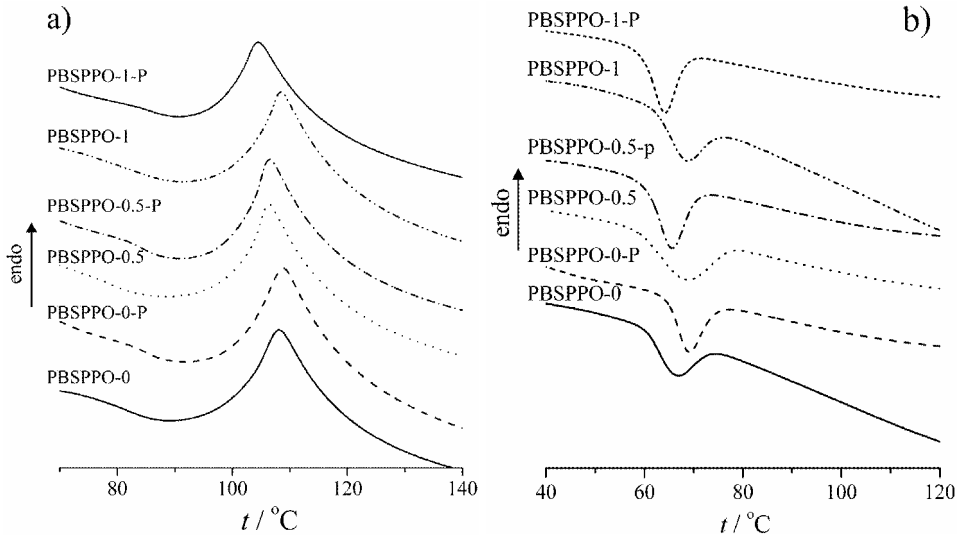


Fig. 2. DSC thermograms of the poly(ester–ether)s obtained in the initial heating scan (a) and subsequent cooling (b); heating and cooling rate 10 °C min^{-1}, nitrogen atmosphere.

TABLE III. Thermal properties of the poly(ester–ether)s

Polymer	T_{mI} / °C	ΔH_{mI} / J g^{-1}	T_{mII} / °C	ΔH_{mII} / J g^{-1}	T_c / °C	X_c[a] / %	x_{cPBS}[b] / %
PBSPPO-0	108.5	56.8	107.9	48.4	65.8	51.4	73.1
PBSPPO-0-P	109.5	60.3	109.2	51.7	68.9	54.6	77.2
PBSPPO-0.5	106.5	54.2	105.6	48.9	67.8	49.0	67.2
PBSPPO-0.5-P	106.7	55.2	106.0	53.9	65.3	49.9	68.9
PBSPPO-1	108.7	55.8	108.1	46.0	67.8	50.5	71.9
PBSPPO-1-P	104.8	45.9	104.7	41.2	64.0	41.5	58.6

[a]Determined as the ratio of the apparent to theoretically calculated enthalpy of melting for perfectly crystalline PBS; [b]degree of crystallinity of PBS, calculated using the experimentally determined mass fraction of PBS in the poly(ester–ether)s

The presence of the antioxidant and the thus obtained differences in the molecular weights of the samples did not have a significant influence on the melting temperatures. The post-synthetic treatment by precipitation, in which smaller molecular weight fractions were removed, also did not have a great impact on the melting temperatures, except in the case of the polyester with the highest content of DPPD. As the largest difference in the values of the intrinsic viscosities before and after precipitation was observed in the case of this poly(ester–ether), the differences in the melting temperatures can be ascribed to changes in the molecular weight and polydispersity between the treated and untreated sample.

Similar tendencies as those in the case of melting temperatures were observed for the enthalpies of melting, ΔH_m, and, consequently, the total degrees of crystallinity, x_c. The enthalpies of melting were used to calculate the total degrees of crystallinity as the ratio of the observed enthalpy to that theoretically calculated on the basis of the group contribution method,[29] of perfectly crystalline PBS (ΔH_m^0 = 110.5 J g^{-1}). The total degree of crystallinity of the poly(ester–ether)s was in the range from 41.5 to 54.6 %.

For the untreated samples obtained with different amount of DPPD, the differences in the degree of crystallinity were just a few percent, which were in the range of experimental error of the determination of the degree of crystallinity by the DSC method. For the samples which were precipitated, the degree of crystallinity decreased following the trend of increasing molecular weight in the series. Except for the sample with the highest content of DPPD, the degree of crystallinity of the other samples rose slightly after precipitation. As the lower molecular weight fractions were removed, the sample with a narrower molecular weight distribution forms a more uniform and perfect crystal structure with fewer defect, which can disturb crystalline growth and overall degree of crystallinity. In addition, all the investigated samples showed a single endothermic peak on heating, which is an indication of the perfection of the crystallite size distribution. The biggest change in the degree of crystallinity due to the post-synthetic treatment and in the opposite direction from the other PBSPPOs was observed for the

sample with 1 mass % of DPPD. The reason for the decrease of almost 10 % in the degree of crystallinity after precipitation for this sample is probably due to the high molecular weight of the precipitated sample, as judged from the value of the intrinsic viscosity. The enthalpies of melting for this sample remained very low also in the second DSC run, which indicates retarded crystallisation, probably due to the increased viscosity of this sample because of its high molecular weight. All the poly(ester–ether)s exhibited a total degree of crystallinity which were greatly reduced compared to usually observed values for pure PBS determined by DSC, which is around 80 %.[17,22] Since biodegradability depends strongly on the degree of crystallinity, as shown in a number of studies, the obtained poly(ester–ether)s should have improved biodegradability properties compared to PBS, while still maintaining optimal thermal properties.

The degree of crystallinity relative to the mass fraction of hard crystallisable PBS segments, x_{cPBS}, were in the range 58.6 to 77.2, which means that only 59 to 77 weight % of the PBS segments in the poly(ester–ether)s crystallized. From the values of x_{cPBS}, it is clear that the presence of the soft polyether segments disturbs the crystal growth of hard PBS segments. However, the presence of polyether in polymeric chains does not affect the rate of crystallisation compared to pure PBS. The supercooling ($\Delta T_h = T_m - T_c$), the difference between the melting and crystallisation temperature, which is an indicator of the rate of crystallisation, was around 40±2 °C, which is close to the value for pure PBS, which has a ΔT_h value of 38 °C and is considered to be a fast crystallising polymer.

Thermal stability of the poly(ester-ether)s

From the processing and application standpoint, as well as from the interest in chemical recycling, it is important to evaluate thermal stability of new polymeric materials. The poly(ester–ether)s were investigated by non-isothermal thermogravimetry (TG) in order to determine their thermal stability and degradation behaviour. All the poly(ester–ether)s showed a single peak in the differential thermogravimetry (DTG) curves, indicating that there is no difference in the mechanism of the degradation between the poly(ester–ether)s obtained in the presence of different contents of DPPD or between the samples which had undergone post-synthetic treatment by precipitation.

The temperatures at which the poly(ester–ether)s had lost 5 % of their initial mass, which is considered as the beginning of degradation, and the temperatures at the maximum degradation rate, as well as the residual mass at 450 °C are summarised in Table IV. As can be seen from the data presented in Table IV, there is slight difference in the thermal stability between polymers obtained in the presence of DPPD and without antioxidant, the later being more stable.

The only exception is the sample obtained with highest amount of DPPD and without any post-synthetic treatment. There were no differences observed in the

mass remaining at the end of degradation, showing that the differences observed could not be ascribed to the presence of the volatile DPPD, which was present in such a low content. Overall, the observed unexpected differences between poly(ester–ether)s obtained under different conditions could not be explained with the present available set of data. However, the differences between the samples are so small that the whole series can be compared with other polyesters intended for the same application. Poly(ester–ether)s based on PPO exhibit improved stability compared to almost all well known hydroxyalkanoic acid based polyesters, investigated in similar TG experiments.[30] The thermal stability of the poly(ester–ether)s modified with PPO is comparable to the most stable poly(hydroxylalkanoate)s, poly(δ-valerolactone) and poly(ε-caprolactone).

TABLE IV. $T_{5\%}$, T_d^{max} and residual mass at 450 °C obtained by thermogravimetry

Polymer	$T_{5\%}$ / °C	T_d^{max} / °C	Residue at 450 °C, mass %
PBSPPO-0	349.6	400.8	4.2
PBSPPO-0-P	349.9	401.4	2.5
PBSPPO-0.5	327.5	385.3	1.9
PBSPPO-0.5-P	328.3	382.6	3.5
PBSPPO-1	349.5	401.0	4.5
PBSPPO-1-P	336.6	384.1	2.4

Biodegradability tests

Hydrolytic degradation of the poly(ester–ether)s in phosphate buffer solution and in the presence of the lipase from *Candida cylindracea* on polymer films was followed by mass loss during degradation and changes in the molecular weight by GPC analysis, as well as by optical microscopy of the surface of the degraded and non-degraded samples. All samples were included in the study except for PBSPPO-0-P, which was to fragile due to oxidation that films of sufficient strength could not be obtained.

Among all other factors which can affect biodegradability through scission of hydrolysable bonds within a polymeric chain, hydrophilicity is the one which can greatly influence the rate and extent of degradation. With the introduction of polyether soft segments, the hydrophilicity of so obtained poly(ester–ether) is increased, and as shown in a number of studies, the biodegradability is thus improved.[21] Moisture-uptake tests were performed on the novel poly(ester–ether)s synthesized within the framework of this study in order to investigate the influence of the presence of the aromatic antioxidant, as well as the influence of post-synthetic treatment on the hydrophilicity of the obtained copolymers. The results obtained for moisture uptake of polymeric films after 7 days of incubation in an atmosphere of relative humidity 97 % are presented in the Fig. 3.

It is obvious that with increasing content of the aromatic, hydrophobic DPPD, the absorption of moisture was decreased for both the precipitated and unpreci-

pitated samples. A possible explanation is that the presence of the aromatic antioxidant renders the surface of the samples more hydrophobic, which results in a decreased moisture uptake with increasing content of DPPD. It is also apparent that the samples obtained from the poly(ester–ether)s which were precipitated absorbed more water than the untreated ones when the poly(ester–ether)s were synthesized in the presence of DPPD. Some of the DPPD was obviously lost during the precipitation procedure which resulted in the observed difference between the precipitated and unprecipitated samples. Compared to the poly(ester––ether)s containing poly(ethylene oxide) soft segments of comparable molecular weight to that of the PPO employed in this study, the presently investigated poly–(ester–ether)s were less hydrophilic and the differences within the series were smaller. Thus, the biodegradability cannot be mainly determined by the slightly increased hydrophilicity compared to PBS found in some of previous studies.[16,21]

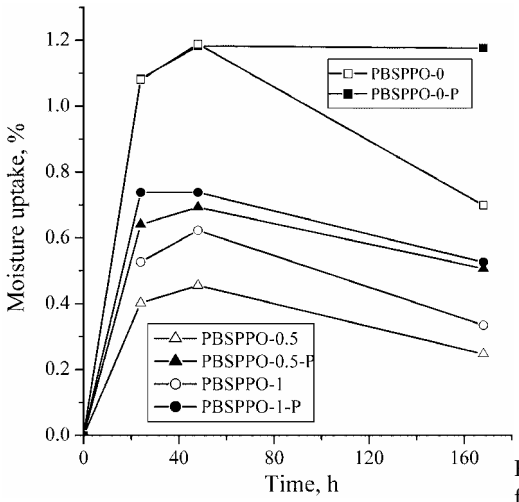


Fig. 3. Moisture uptake of the poly(ester–ether) films incubated in a 97 % humidity atmosphere.

The weight losses of the poly(ester–ether)s based on PPO in the hydrolytic tests increased with time and were from 1 to 5 mass % after 28 days. A mild catalytic activity of the lipase from *Candida cylindracea* was confirmed since in all cases the weight losses in the tests conducted with the enzyme were slightly higher than those observed in the tests performed in buffer solution without the enzyme. The weight losses of the poly(ester–ether) samples with different contents of antioxidant incubated in the enzyme buffer solution for 28 days are presented in Fig. 4. The highest weight losses are observed for the poly(ester–ether) obtained without the addition of the antioxidant, which is in agreement with the assessment of the hydrophilicity obtained in the moisture-uptake tests. Nevertheless, all samples showed similar rates of weight loss within the investigated timeframe, which were much higher compared to poly(butylene succinate) investigated in a similar manner in previous studies.[16,17,22] The same explanation which con-

nects the increased degradability of poly(ester–ether)s compared to PBS homopolyester of increased flexibility and decreased crystallinity for the copolymer also holds in this case. Since the degrees of crystallinity were similar for all samples and the hydrophilicity was not greatly affected by the presence of the hydrophobic DPPD, the degradation rates were, as expected, of a similar magnitude.

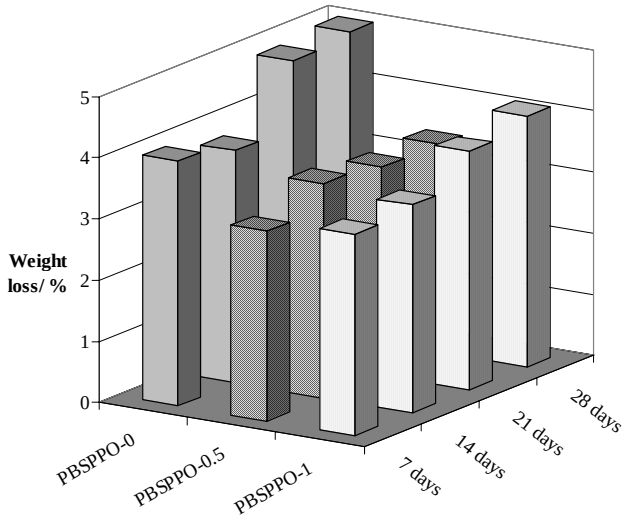


Fig. 4. Weight losses in the enzymatic degradation tests of the poly(ester–ether)s with different contents of DPPD.

The precipitated and unprecipitated samples were also compared for the poly(ester–ether)s obtained in the presence of the antioxidant DPPD (Fig. 5). While the post-synthetic treatment did not have any influence on the degradability of the samples with the lower content of DPPD, the poly(ester–ether) obtained with 1 % of DPPD exhibited a greatly reduced susceptibility toward degradation after precipitation, and was the least degradable sample of all the ones investigated. As can be seen from the values of the intrinsic viscosity, this sample showed the highest relative increase in molecular weight after precipitation. It can be concluded that in this case the biodegradability depended strongly on the molecular weight, since the degradability was greatly reduced after the lower molecular weight fractions had been removed.

The results obtained in GPC measurement before and after hydrolytic and enzymatic degradation tests on the samples incubated for 28 days show that the enzymatic degradation proceeds *via* bulk degradation of the polymeric films, since a decrease in molecular weight was observed after the degradation experiments (Fig. 6). This was not the case, however, when the weight losses were small, as in the case of PBSPPO-1-P, where no change in molecular weight was observed (Fig. 6b).

The structure of the surface of poly(ester–ether)s films was inspected by optical microscope before and after degradation. In all the samples, a spherulite

structure was clearly visible. The poly(ester–ether) with the highest amount of DPPD appeared to have spherulites of the smallest size of all the samples. There was no change in the structure observed for the precipitated samples in comparison to the unprecipitated ones. Upon incubation in buffer solution with or without the addition of the lipase, no visible cracks or holes were detected. Although the degradation proceeds *via* bulk degradation the extent of weight loss in the investigated timeframe was so small that no observable erosion could be detected. Representative images of the surface of the polymeric films before and after hydrolytic and enzymatic degradation are presented in Fig. 7.

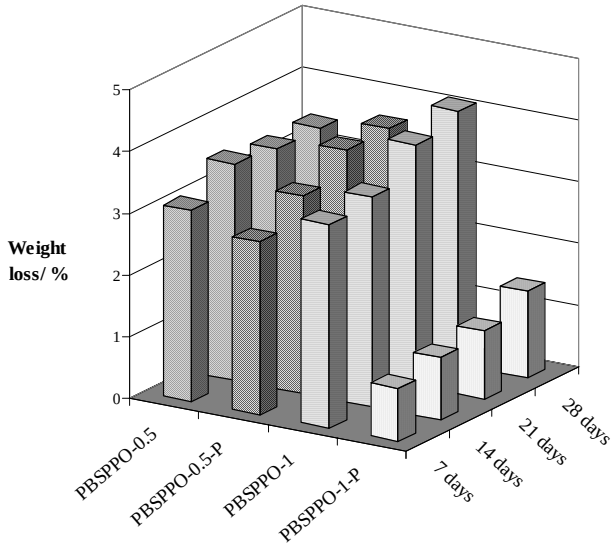


Fig. 5. Weight losses in the enzymatic degradation tests of unprecipitated and precipitated poly(ester–ether)s with different contents of DPPD.

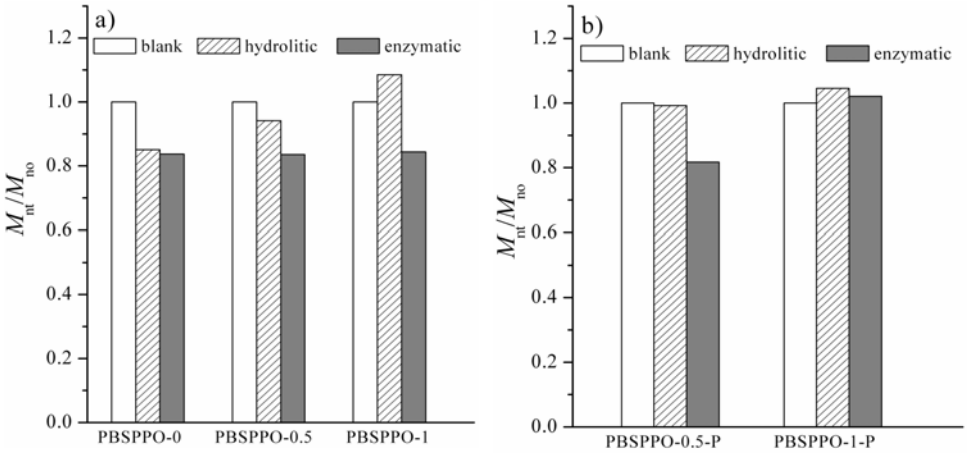
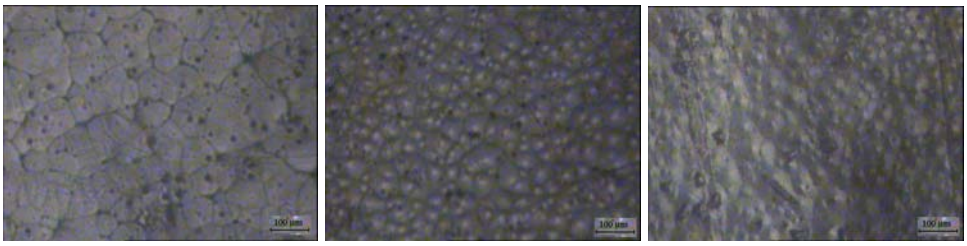


Fig. 6. Change in the number average molecular weight after 28 days of incubation (M_{nt}) in buffer solution (hydrolytic) or enzyme solution (enzymatic) relative to the initial number molecular weight, M_{no}; a) untreated samples, b) samples after precipitation.



a b c

Fig. 7. Surface appearance of the poly(ester–ether) PBSPPO-0 before (a) and after hydrolytic (b) and enzymatic (c) degradation for 28 days.

CONCLUSIONS

High molecular weight poly(ether–ester)s based on poly(butylene succinate) as the hard segments and poly(propylene oxide) as the soft segments were successfully synthesized by a catalysed transesterification reaction in the melt. The number average molecular weights, M_n, of the copolyesters in the series were above 27000 g mol^{-1}, while the polydispersity index, M_w/M_n, was in the range 1.7 to 1.8. The molecular weights of synthesized copolyesters increased both in the presence of antioxidant (*N*,*N*'-diphenyl-*p*-phenylenediamine, DPPD) as well as by precipitation of the polymers. The oxidative degradation of poly(ester–ether)s based on PPO could be suppressed, although not completely prevented, even with highest amount of added antioxidant DPPD. For complete prevention of the oxidative degradation of the copolyesters, higher quantities of DPPD are recommended.

The melting temperatures of the poly(ether–ester)s based on PPO were lower than that of PBS but above 100 °C, which is important for their possible application. The copolymers exhibited macromolecular behaviour and were suitable for the preparation of flexible and tough films by the melt-press method. The total degree of crystallinity of the poly(ether–ester)s was in the range of 41 to 55 %, *i.e.*, lower than the degree of crystallinity of the homopolyester (PBS). The degree of crystallinity calculated with respect to the weight fraction of PBS segments (x_{cPBS}) in the poly(ether–ester)s indicated a decreasing tendency of crystallization of the hard segments with increasing molecular weight of the synthesized copolyesters.

Incubation in a buffer solution for 4 weeks resulted in mass losses from 1 to 5 %, depending on the content of antioxidant and post-synthetic treatment. Enzymatic degradation in the presence of lipase from *Candida cylindracea* was slightly increased compared to hydrolytic degradation. The enzymatic degradation showed that the introduction of the soft PPO segments into the polymer chains increased the degradability compared to PBS, showing the dependence of the amount of degradation on the chain structure, *i.e.*, molecular weight and hydrophilicity. GPC Analysis confirmed that there were changes in the molecular weight of the copolyesters during both hydrolytic and enzymatic degradation tests, leading to

the conclusion that the degradation mechanism of the poly(ester–ether)s based on PPO occurs through surface erosion and bulk degradation.

High molecular weight poly(ester–ether)s based on PBS and hydrophilic poly(propylene oxide) show promise as biodegradable elastomers, having satisfactory thermal and mechanical properties and simultaneously good biodegradability.

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И З В О Д

УТИЦАЈ АНТИОКСИОДАНСА И НАЧИНА ИЗДВАЈАЊА ПОЛИМЕРА НА СВОЈСТВА БИОДЕГРАДАБИЛНИХ ПОЛИ(БУТИЛЕН СУКЦИНАТА) МОДИФИКОВАНИХ ПОЛИ(ПРОПИЛЕНОКСИДОМ)

ДРАГАНА ПЕПИЋ, МАРИЈА РАДОИЧИЋ, МАРИЈА С. НИКОЛИЋ и ЈАСНА ЂОНЛАГИЋ

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У оквиру овог рада синтетисани су нови поли(естар–етри) на бази поли(бутилен сукцината) (PBS) као тврдих сегмената и 30 масених % поли(пропиленоксида) (PPO) уграђених у меке сегменте, без и у присуству антиоксиданса *N,N′*-дифенил-*p*-фенилендиамина (DPPD). Изучавао се утицај антиоксиоданса DPPD као и начина издвајања полимера, односно преталожавања на структуру и величину молекула, термичка и физичка својства као и на стабилност биодеградабилних алифатских кополиестара. Структура и састав кополиестара су проверени ^{1}H-NMR спектроскопијом. Величина молекула и расподела величина молекула синтетисаних поли(естар–етара) су одређени вискозиметријом разблажених раствора и GPC анализом. Термичка својства и термичка стабилност поли(естар–етара) су анализирана DSC и неизотермском термогравиметријом у инертној атмосфери азота. Биодеградабилни потенцијал полимера је изучаван у огледима хидролотичке и ензимске деградације у присуству липазе *Candida cylindracea* пратећи промене у маси полимерних филмова током инкубације. Губици су расли са временом и после 4 недеље су били у опсегу од 1 до 5 масених %. GPC анализа је потврдила да постоје промене у моларној маси узорака и у огледима хидролитичке и ензимске деградације на основу чега се може закључити да се механизам деградације поли(естар–етара) на бази PPO одвија кроз ерозију површине и деградацију у маси.

(Примљено 31. јула 2007)

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