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Poly(ether–ester)s modified with different amounts of fumaric moieties

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Abstract

A series of novel poly(ether–ester)s modified with fumaric moieties is synthesized by transesterification in the melt of dimethyl terephthalate (DMT), dimethyl fumarate (DMF), 1,4-butanediol (BD) and poly(tetramethylene oxide) (PTMO, $\bar{M}_n = 1000$ g/mol). The effect of the introduction of double bonds into both the hard and soft segments and their content on the structure and the thermal and rheological properties of the synthesized polymers are investigated. The introduction of double bonds into the polymer main chains increases the molecular weight of the copolyesters, but reduces the crystallinity of the hard segments and related properties such as modulus and hardness. The presence of double bonds improves the high temperature properties and thermal stability, especially the thermo-oxidative one, lowers the melting and crystallization temperature and increases the glass transition temperature. The incorporation of fumaric moieties into the macrochains improves the adhesive strength of the polymer to a metal surface. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Thermoplastic elastomers; Poly(ether–ester)s; Fumaric residue

1. Introduction

Thermoplastic elastomers have found wide applications in many industrial branches as engineering materials thanks to their excellent mechanical and physical properties. These polymers combine the mechanical properties of chemically crosslinked elastomers, for example: elastic recovery, energy absorption and good flexibility at low temperatures, with those of plastics, such as great impact strength and modulus. Above the glass transition or melting temperature of the hard segment, thermoplastic elastomers may be processed as conventional thermoplastic materials [1–3].

The thermoplastic and elastic behaviour of these polymers can be explained by their multiphasic structure, which is a consequence of the chemical nature and incompatibility of the two types of segments, hard and soft, which are built into the polymer chains. For example, poly(ether–ester)s consist of poly(butylene terephthalate) (PBT) as the hard segments which are dispersed in an amorphous matrix consisting of the soft polyether segments and the non-crystalline part of the hard segments. Upon crystallization, the hard segments are organized into domains, creating a physical network, which provides dimensional stability and minimizes cold flow. The existence of a two-phase morphology of these polymers, which is the result of the two types of segments, was confirmed by thermal analysis and electron microscopy and different models of the supermolecular structure have been proposed [4–6]. The crystalline structure is typically lamellar. Depending on the crystallization conditions, spherulitic crystalline structures could also be formed.

Polyester based thermoplastic elastomers, in which the hard segments are partially crystalline poly(tetramethylene terephthalate), have been synthesized [7–9]. The soft segments in these copolymers are based on poly(tetramethylene oxide) glycol, generally of molecular weight about 1000. These polymers are available as commercial products. The introduction of isophthalic and phthalic acids into the polymer chains changes the block length distribution of the hard segments, which results in changes of the melting temperatures and mechanical properties of the synthesized poly(ether–ester)s. Variation of the length of the soft segments in poly(ether–ester)s can change the mechanical properties of the polymers, such as tensile stress, hardness and elongation at tensile break. Increasing the content of the soft segments decreases the melting temperature and enthalpy of fusion of poly(ether–ester)s.

Poly(ether–ester)s based on PBT and poly(ethylene oxide) (PEO) [10–13], generally have poorer properties than those containing PTMO as the soft segments, but they also possess some advantages, the most important being their hydrophilic character, which makes them attractive candidates for application in the textile industry.

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The resistance to hydrolytic and thermal degradation increases when poly(hexamethylene oxide) and poly(decamethylene oxide) are introduced as the soft segments [14].

It has been reported that unsaturated units, such as isolated –C≡C– bonds, were incorporated into the copolyester backbone through the diol component, i.e. 1,4-butanediol, in order to improve the thermal stability, such as lower flammability, increased oxygen index and char formation, of thermoplastic elastomers [15,16]. Also, segmented thermoplastic elastomers containing double bonds derived from dimethyl terephthalate (DMT), 1,4-butanediol, 2-butene-1,4-diol and poly(tetramethylene oxide) were found to crystallize faster and have higher molecular weights compared to unmodified thermoplastic elastomers [17].

In our previous papers, the use of fumaric acid derivatives in the copolyester synthesis, which enables the introduction of unsaturated reactive sites into the polymer chain, was presented [18,19]. The introduction of reactive double bonds into the main chain allows the polymer to be crosslinked subsequently which would result in a diminished cold flow and an improvement of some other mechanical and thermal properties of poly(ether–ester)s modified with fumaric acid residues compared to their saturated counterparts. It has also been reported that the introduction of double bonds into some copolyesters results in polymers having fibre-forming properties [20] and gives the opportunity of reaction with the polyester matrix in composites. The *trans* double bond from fumaric acid is very reactive due to the adjacent carbonyl group, which permits ready crosslinking, but requires control over the polymer synthesis and an understanding of the effect of the polymer structure on its physical properties and thermal degradation.

In our previous paper, the synthesis and characterization of a series of poly(ether–ester)s modified with 10 mol% fumaric acid was reported. The effect of the concentration of catalyst, tetra-*n*-butyl-titanate ($Ti(OBu)_4$) and stabilizer, *N*,*N*′-diphenyl-*p*-phenylenediamine, DPPD, as well as the reaction time and temperature were investigated in order to optimize the polymerization conditions and to prevent crosslinking through the unsaturated double bonds of fumaric acid during the melt polycondensation [19].

In this article, the synthesis, structure and properties of a new series of thermoplastic elastomer of the copolyester type modified with different contents of fumaric moieties is reported. The level of fumaric unsaturation in the poly(ether–ester)s chains was varied between 1 and 20 mol%. The mole ratio of the starting components was selected to result in a constant hard to soft segment weight ratio of 56:44.

2. Experimental part

2.1. Reactants

Poly(tetramethylene oxide) (PTMO), number average molecular weight of 1000 g/mol (from Merck) was used as received. Dimethyl terephthalate (DMT) was recrystallized from absolute ethanol. 1,4-Butanediol (1,4-BD) was purified by vacuum distillation. Dimethyl fumarate (DMF) (from Aldrich) was used as received. Butan-1-ol was purified by distillation. Tetra-*n*-butyl titanate, $Ti(OC_4H_9)_4$ (from Aldrich) was used as a solution in dry butan-1-ol (1:9 vol). *N*,*N*′-Diphenyl-*p*-phenylenediamine, DPPD (from Bayer) was used as received.

2.2. Synthesis

The poly(ether–ester)s were synthesized by a two-step, catalysed melt transesterification reaction. All the polymers were synthesized in the same manner under optimal conditions [19]: maximal temperature 230 °C; amount of antioxidant, DPPD, 1 wt% of the reaction mixture; amount of catalyst 2.0 mmol/mol ester. In these series the mole percent of DMF in the reaction mixture was changed: 1, 5, 10, 15 and 20 mol%. All the syntheses were performed in a 1000-ml glass reactor. The first step, transesterification, was carried out at 160 °C under nitrogen at normal pressure. After the first step, the volume of methanol was measured and then antioxidant DPPD was added (1 wt%) to the reaction mixture and vacuum was applied. The temperature of the reaction mixture was increased over one hour to the maximal temperature, 230 °C. The second step, polycondensation, was carried out by heating the reaction mixture at the maximal temperature, 230 °C, under vacuum to remove the excess 1,4-butanediol. The end of the synthesis was indicated by a rapid increase in the viscosity of the reaction mixture. The viscous slurry was cooled under nitrogen, and then pulled from the reactor.

2.3. Characterization

The composition and structure of the copolyesters were determined by ^1H NMR (Varian-GEMINI 200 MHz) and ^{13}C NMR (50 MHz) spectroscopy from solution in $CDCl_3$ using tetramethylsilane (TMS) as the reference standard at 298 K. The signal of the internal protons from the methyl groups in the residue of BD at the end of the polymer chain $-(CH_2)_2-CH_2-OH$ appears at $\delta = 1.26$ ppm. The complex region from 1.25 to 2.0 ppm contains the resonance of the internal aliphatic protons in the BD residues and poly(tetramethylene oxide). The signals of the aliphatic protons on the carbon atoms connected with oxygen $-CH_2-O-CH_2-$, in the residue of the polyether, appear at $\delta = 3.4$ ppm. The triplet from 3.70 to 3.75 is due to the $-CH_2-OH$ end groups. The protons from the methyl groups which are connected to esters groups, $-OOC-CH_2-$, give peaks at $\delta = 4.2$–4.4 ppm. Proton resonances at $\delta = 6.8$ ppm from the fumaric protons $-CH{=}CH-$, and at $\delta = 8.2$ ppm from the aromatic protons were observed.

The chemical shifts in the ^{13}C NMR spectra of the poly(ether–ester)s at $\delta = 165.69$ ppm and at $\delta = 164.80$ ppm are from carbonyl atoms from the terephthalic and fumaric acids, respectively. The signals from the substituted aromatic carbons appear as one peak at $\delta = 133.98$ ppm, and those of unsubstituted aromatic carbons at $\delta = 129.51$ ppm. The peak at $\delta = 133.56$ ppm is from unsaturated carbon atoms from fumaric acid. The ether carbon atoms from PTMO give two peaks at $\delta = 70.55$ ppm and $\delta = 70.40$ ppm. The peaks at $\delta = 64.78$ ppm and $\delta = 65.26$ ppm originate from the carbons in the residue of BD and PTMO connected with carbonyl groups, respectively. The internal methyl carbonyl atoms from BD and PTMO appear at $\delta = 25.22$ ppm and $\delta = 25.41$ ppm, respectively.

The inherent viscosities of the polymers were determined in *m*-cresol solution (0.5 g/dl) at 30 ± 0.5 °C using an Ostwald capillary viscometer.

Differential scanning calorimetry (DSC) was conducted using a Perkin–Elmer DSC-2. The samples were analysed under a nitrogen atmosphere (the flow rate was 25 cm^3/min) in the temperature range 50–250 °C at a heating and a cooling rate of 10 K/min. Samples for DSC analyses are prepared from the melt. The weight of the samples was approximately 10 mg. The DSC analyses were carried out in covered aluminium pans.

WAXS analysis was carried out using a Philips PW 1710 X-ray diffractometer with Cu K_α target (tube: 40 kV, 30 mA, $\lambda = 0.154178$ nm). The degree of crystallinity was calculated by peak deconvolution and subsequent determination of the relative areas under the amorphous halo and the crystalline peaks of the X-ray diffraction scans. The ratio of the area under the crystalline peaks to the total (amorphous and crystalline) area gave the degree of crystallinity.

The TG curves of the copolyester were obtained using a Perkin–Elmer TGS-2 instrument under a dynamic atmosphere of O_2 or N_2 (the flow rate in both cases were 25 cm^3/min), at a heating rate of 10 K/min. The average weights of the samples was around 7 mg.

Dynamic mechanical analysis was performed using a Rheometrics mechanical spectrometer RMS-605. The complex dynamic viscosity (η^*) of the polymer melts was recorded in the shear mode between parallel plates at constant temperature, 220 °C, the frequency was varied from 0.1 to 100 rad/s. The radius of the samples was 25 mm and the thickness was about 1.0 mm. The dynamic mechanical analysis was performed under torsion rectangular conditions on moulded polymer bars ($63.0 \times 12.4 \times 1.0$ mm^3) in the temperature range from −80 to +150 °C. The viscoelastic properties of the poly (ether–ester)s are presented as mechanical spectra by following the dependence of the storage (G') and loss (G'') moduli and tan δ peak on temperature at a fixed frequency of 6.28 rad/s. The temperature of the maximum of tan δ is taken as the glass transition temperature.

The hardness measurements were performed using a Shore D apparatus (Zwick Z7-2A C.KG.) on moulded polymer discs. The radius of the sample was 25 mm and the thickness was about 3 mm. The results of the measurements were registered one second after penetration of the needle into the sample.

The measurements of the adhesive shear strength were carried out with a crosshead speed of 20 mm/min at room temperature using a Zwick tensile testing machine. The specimen with plain lap joints (20×20 mm^2 and thickness varied from 0.01 to 0.3 mm) were prepared by pressing the polymer melts between aluminum substrates. The dimensions of the aluminum substrates were ($100 \times 20 \times 1$ mm^3). The results were obtained as the average of five measurements on five to six different thickness of polymer films.

3. Results and discussion

A series of thermoplastic poly(ether–ester)s copolymers based on poly(butylene terephthalate), PBT, or poly(butylene fumarate), PBF, as the hard segment, and poly(tetramethylene oxide terephthalate) or poly(tetramethylene oxide fumarate) as the soft segment, was synthesized by catalysed melt transesterification. Poly(tetramethylene oxide) (PTMO, $\bar{M}_n = 1000$ g/mol), 1,4-butanediol (BD), dimethyl terephthalate (DMT) and dimethyl fumarate (DMF) were used as the reactants. The antioxidant, *N*,*N*′-diphenyl-*p*-phenylenediamine (DPPD) was used as a stabilizer during the syntheses. The molar ratio of the starting components was selected to result in copolymers with a constant hard to soft weight ratio of 56:44. The final products are multiblock copolymers with a random distribution of the hard and soft segments. The chemical structure of the segmented poly(ether–ester)s based on terephthalic and fumaric esters is shown in Fig. 1.

3.1. NMR analysis of the composition and structure of the copoly(ether–ester)s

The molecular structure of the poly(ether–ester)s was conformed by ^{13}C and ^1H NMR spectroscopy. The ^1H NMR spectrum of the poly(ether–ester) TPE-20 is shown in Fig. 2. The poly(ether–ester)s composition and molecular weights were determined from the ^1H NMR by integrating the corresponding proton resonances.

^1H NMR analysis confirmed that fumarate moieties are incorporated into the polymer chains, in the hard as well as

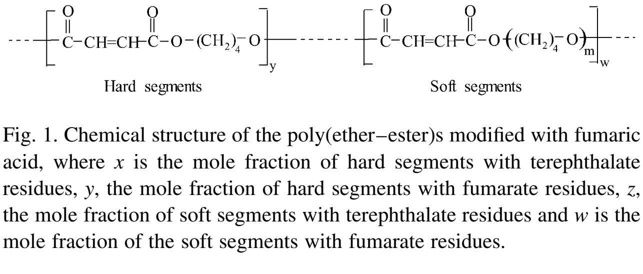

Fig. 1. Chemical structure of the poly(ether–ester)s modified with fumaric acid, where *x* is the mole fraction of hard segments with terephthalate residues, *y*, the mole fraction of hard segments with fumarate residues, *z*, the mole fraction of soft segments with terephthalate residues and *w* is the mole fraction of the soft segments with fumarate residues.

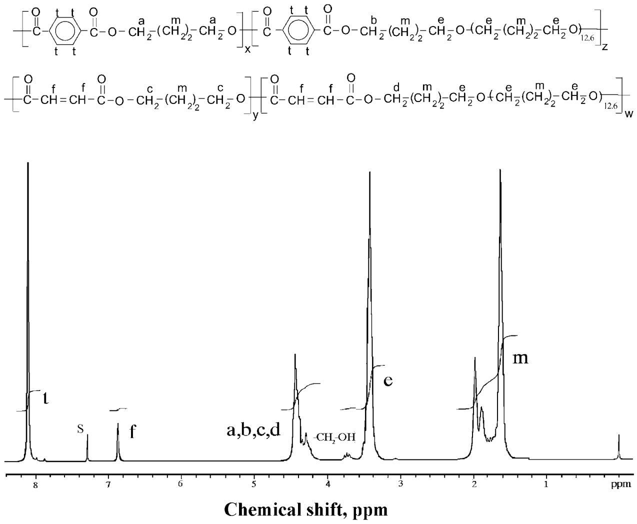

Fig. 2. ^{1}H NMR spectrum and structure of poly(ether–ester) TPE-20 (S = solvent, $CHCl_3$ in $CDCl_3$).

in the soft segments. The mole fractions of fumaric acid in the poly(ether–ester)s were calculated from the ^{1}H NMR spectra. The fumarate residues are incorporated into the macrochains in an amount about 2–3% less than was to be expected from starting mixture compositions, which is in the range of experimental error. It could be concluded that the compositions of the copolyesters were in good agreement with those expected from the composition of the feed.

In a recent study, it was also shown that the extent of double bond saturation, in the synthesis of fumarate-based polyesters, increases with reaction temperature and diol concentration, as well as with the strength and concentration of the catalyst [21]. The key to a successful synthesis of high molecular weight poly(ether–ester)s modified with an unsaturated acid is the combination of a highly effective catalyst and a heat stabilizer, as well as the proper choice polymerization conditions which would protect the fumaric double bonds.

The mole percents of the hard segments were calculated simply by subtraction of the content of the soft segments from 100 mol%. The mole percents of the soft segments were calculated using the equation

$$\text{Content of the soft segments (mol\%)}$$

$$= [I(e)/50.56]/[I(t)/4 + I(f)/2] \times 100$$

where $I(e)$ is the intensity of the signal from protons on carbon atoms connected to the oxygen in the polyethers ($\delta = 3.4$ ppm) and 50.56 is the number of ether protons in the residue of the poly(tetramethylene oxide) ($\bar{M}_n = 1000$ g/mol), $I(f)$ is the intensity of the signals of the fumaric protons and $I(t)$ the intensity of the signals of the aromatic protons.

The mole and weight fractions of the hard segments in the polymers were in the range from 82.3 mol% (47.5 wt%) for TPE-0 to 86.1 mol% (54.0 wt%) for TPE-20. It could be concluded that the introduction of double bonds into the main chain increases the total content of the hard segments of the poly(ether–ester)s (Table 1). The average length of the hard segments is calculated from the ratio of the integral intensities. These calculations are based on the assumption that the soft segment lengths do not change during the polycondensation and that they are equal to the length of the starting PTMO. The average degree of polymerization of the hard segments, both PBT and PBF, calculated on 1 mol PTMO, i.e. soft segment, in the polymer chain was between 4.65 and 6.19, indicating an increase in the length of the hard segments with increasing incorporation of fumarate residues.

The amounts of DMT (x and z) and DMF (y and w) which are incorporated into the hard and soft segments of the polymer chains, respectively, calculated from the ^{1}H NMR analysis, are presented in Fig. 3 as a function of fumarate concentration in the polymer. From the values x, y, z, and w, it can be concluded that both the terephthalate and fumarate react with BD rather than with PTMO, thus giving hard segments.

The average number of the repeating units, b, was calculated using the following equation:

$$I(\text{–}CH_2OH)/I(t) = 4/[4 \times n(\text{DMT}) \times b]$$

Table 1

Content of fumarate and hard segments determined from the ^{1}H NMR spectra, and the viscosity of the synthesized poly(ether–ester)s

Sample[a]	Content of fumarate (mol%)	mol/1 mol PTMO			Hard segment			η_{inh} (dl/g)	η^* (Pa s) 220 °C
		DMT	DMF	BD[b]	On 1 mol PTMO	mol%	wt.-%		
TPE-0	0	5.64	–	4.55	4.65	82.3	47.5	0.55	30
TPE-1	0.93	5.90	0.055	5.14	4.95	83.2	49.1	0.67	39
TPE-5	2.20	5.56	0.125	4.32	4.68	82.4	47.6	0.60	21
TPE-10	8.93	6.04	0.592	7.43	5.62	84.9	52.0	0.91	358
TPE-15	13.2	6.14	0.932	5.25	6.09	85.9	53.7	0.70	595
TPE-20	17.7	5.90	1.268	7.25	6.19	86.1	54.0	0.73	532

[a] The number at the end of each sample designation denotes the initial mole fraction of fumarate in the reaction mixture.

[b] The content of butanediol at the beginning of the synthesis was 6.74 mol/mol PTMO.

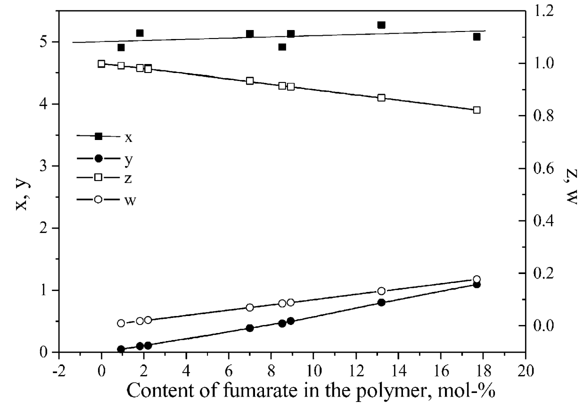

Fig. 3. Content of fumarate in the hard and soft segments in the poly-(ether–ester)s based on ^{1}H NMR analysis.

The molecular weight of the repeating units, $\bar{M}_{ru}$, was calculated from the x, y, z, w values:

$$\bar{M}_{ru}\ (\text{g/mol}) = x \times 220 + y \times 182 + z \times 1130 + w \times 1082$$

The number average molecular weight of the polymer, $\bar{M}_n$, was calculated using the following equation:

$$\bar{M}_n\ (\text{g/mol}) = \bar{M}_{ru} \times b + 2M(\text{–O(CH}_2)_4\text{–OH}),$$

$$M(\text{–O(CH}_2)_4\text{–OH}) = 178\ \text{g/mol}$$

The calculated values of b, $\bar{M}_{ru}$ and $\bar{M}_n$ are given in Table 2.

Poly(ether–ester)s having an inherent viscosity between 0.55 and 0.91 g/dl were obtained. The values of the Newtonian complex viscosity η^* at 220 °C, which could also be used as an indicator of the molecular weight of the poly(ether–ester)s, are in the range from 30 to 530 Pa s. The copolyesters modified with fumaric acid have higher values of inherent viscosity compared to the unmodified poly (ether–ester)s. Significant increases of the complex viscosity, η^*, were observed for the poly(ether–ester)s modified with the higher contents of fumaric acid (Table 1). The number average molecular weights of the poly(ether–ester)s in the series ranged from 8000 g/mol (TPE-0) to 9400 g/mol (TPE-10). The number average molecular weights, $\bar{M}_n$, of the poly(ether–ester)s were also deduced from the content of end groups, determined from ^{1}H NMR measurements, with the assumption that there is a hydroxyl group at the end of every polymer chain. The molecular weights of this series of poly(ether–ester)s modified with fumaric moieties are lower compared with those of commercially available polymers. Nevertheless, they exhibit macromolecular behaviour and have good mechanical properties.

3.2. Thermal properties of the copoly(ether–ester)

The synthesized poly(ether–ester)s are partly crystalline polymers, for which melting and glass transition temperatures were observed by DSC, as well as by TMA and dynamic mechanical analysis. The DSC thermograms of the synthesized poly(ether–ester)s recorded during heating and cooling are shown in Fig. 4a and b. The shape of the endothermic peaks of these polymers indicates that melting of the crystallites occurs in the temperature region of 160–220 °C. The melting temperatures were determined as the temperature of the main peak in the DSC curves from the first heating scan. The DSC curves illustrate a significant shift of the melting temperatures to lower temperatures with increasing fraction of fumaric acid, from 201 °C (TPE-0) to 167 °C (TPE-20). The multiple peaks which occur in all thermograms indicate the presence of crystallites of different size and perfection due to the irregularity of the length of the hard-segments or due to the effect of crystal reorganization which occurs during heating, and results in the appearance of a small peak at higher temperatures [22]. The presence of fumaric acid residues in the polymer chains introduce flexibility into the polymer chains and lowers the melting temperatures and degree of crystallinity compared to terephthalic acid. Multiple melting peaks are also observed in semicrystalline homopolymers, such as PBT and PET, as well as in unmodified thermoplastic elastomers [23,24]. The enthalpy of melting are in range from 18.8 J/g (TPE-20) to 34.0 J/g (TPE-5) in the first run and from 19.4 J/g (TPE-20) to 31.7 J/g (TPE-0) in the second run. The enthalpy of melting decreases with increasing fumaric content, suggesting that the crystal growth of poly(butylene terephthalate) could be disturbed by the incorporation of the fumaric units. The incorporation of unsaturated double bonds has the same effect on the temperature and enthalpy of crystallization, i.e. both of them decrease with increasing degree of unsaturation.

The weight fraction of hard segments that are incorporated in the crystals was calculated from the

Table 2
The composition and average molecular weight, $\bar{M}_n$ of the poly(ether–ester)s determined from their ^{1}H NMR spectra

Sample	Content of fumarate (mol%)	x	y	z	w	$\bar{M}_{om}$ (g/mol)	b	$\bar{M}_n$ (g/mol)
TPE-0	0	4.64	–	0.999	–	2150	3.57	8030
TPE-1	0.93	4.91	0.046	0.991	0.0093	2218	2.83	6630
TPE-5	2.20	4.58	0.103	0.978	0.022	2155	1.86	4360
TPE-10	8.93	5.13	0.503	0.911	0.089	2345	4.07	9740
TPE-15	13.2	5.27	0.800	0.868	0.132	2429	2.38	6140
TPE-20	17.7	5.08	1.091	0.822	0.177	2436	2.29	5930

Table 3
Degree of crystallinity and heats of fusion of the poly(ether–ester)s determined by DSC

Sample	Content of fumarate (mol%)	T_m (°C)	ΔH_m (J/g)		$\Delta H_m^{0\,a}$ (J/g)	T_c (°C)	ΔH_c (J/g)	w_c		
			I run	II run				I run	II run	WAXS
TPE-0	0	201	32.6	31.7	150	164	31.8	0.457	0.444	0.437
TPE-1	0.93	198	32.1	32.4	149.4	156	30.1	0.437	0.441	–
TPE-5	2.20	191	34.0	30.1	148.6	152	28.5	0.480	0.426	0.386
TPE-10	8.93	184	24.0	24.7	144.1	143	23.7	0.320	0.330	0.376
TPE-15	13.2	174	24.1	24.5	142.9	138	22.6	0.314	0.314	0.437
TPE-20	17.7	167	18.8	19.4	137.4	124	20.7	0.239	0.260	0.336

[a] The theoretical value of heat of fusion calculated on the basis of the group contribution, method [25].

equation

$$w_c = \Delta H_m/(w_h \Delta H_m^0)$$

where ΔH_m^0 is the enthalpy of melting of a copolyester calculated on the basis of the group contribution taking into account the composition of the copolymer determined from its ^{1}H NMR spectrum; ΔH_m, the enthalpy of melting of the poly(ether–ester)s from DSC data and w_h, the weight fraction of the hard segments in the poly(ether–ester) determined from its ^{1}H NMR spectrum.

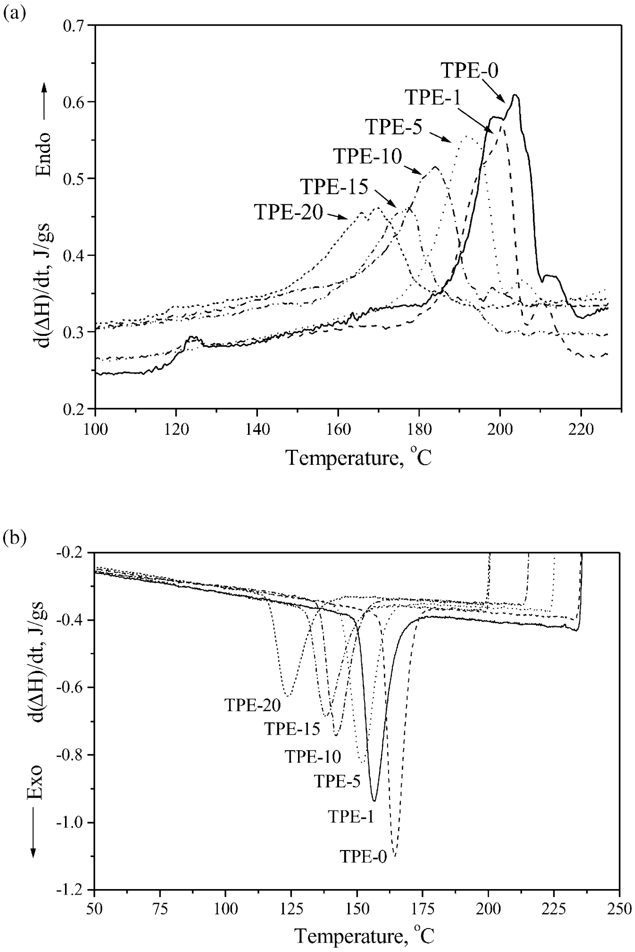

Fig. 4. DSC curves of the poly(ether–ester)s with different contents of fumaric moieties in the polymer chains. (a) Heating rate 10 K/min and (b) cooling rate 10 K/min.

The theoretical ΔH_m^0 values for PBT and PFT are 150.0 and 65.7 J/g, respectively, calculated on the basis of the group contribution method proposed by Van Krevelen [25].

The degree of crystallinity calculated from DSC data and enthalpy of melting are given in Table 3. In the second run the positions of the endothermic peaks do not change and the melting temperatures are the same, but the degree of crystallinity changes by a few percent. The shapes of the endothermic peaks are almost identical, because of that they are not presented in Fig. 4a. It was observed that there is an increase in the degree of crystallinity in the second run with increasing level of fumaric, unsaturation which is the consequence of better conditions for crystallization. The degrees of crystallinity of the poly(ether–ester)s modified with fumarate residue vary between 0.25 and 0.5, which is in agreement with the values reported in the literature (Fig. 5) [7,26]. These results indicate that only fraction of the PBT and PBF segments crystallize and that some of their short segments are incorporated into the amorphous phase [6,7,26].

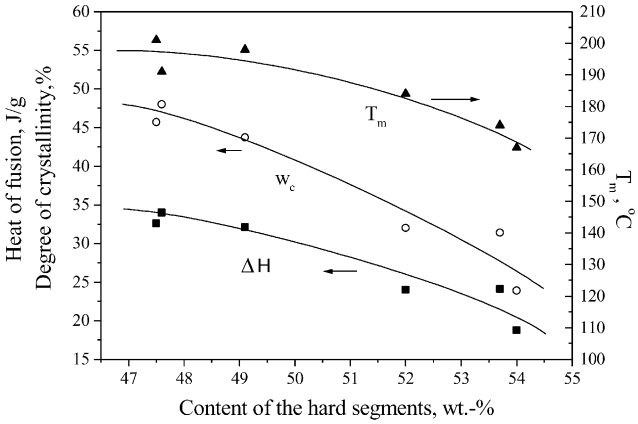

Fig. 5. Change in the melting temperatures, heat of fusion and degree of crystallinity measured by DSC with changing content of fumaric moieties in the poly(ether–ester)s.

3.3. WAXS analysis of the copoly(ether–ester)s

For poly(butylene terephthalate) two crystal modifications (α- and β-forms) have been described and their crystal structures have been analyzed by X-ray diffraction [27]. The transition between the two modifications takes place reversibly by mechanical deformation: from the α-form to the β-form by elongation and inversely by relaxation. The primary modification is the α-form which belongs to the triclinic system with unit cell parameters: $a = 4.83$ Å, $b = 5.94$ Å, c (fibre axis) $= 12.95$ Å, $\alpha = 99.7°$, $\beta = 115.2°$ and $\gamma = 110.8°$.

The positions of peak maxima in the diagram of PBT, synthesized in the same way as the series of poly(ether–ester)s, are very similar to the literature data [28]. Deviations are not greater then 0.2° for 2θ, but deviations of peak intensities are bigger which could be the result of sample shape (discs). The highest peak in difractograms, which has Miller indices $h = 1$, $k = 0$ and $l = 0$ appears at lower 2θ values than for PBT, which means that the values of parameter a for synthesized polymers are greater than the one for pure PBT.

The diffractograms of the poly(ether–ester)s are very similar to the diffractogram for PBT. The main peaks are almost at the same values of 2θ as for PBT, and from the literature data it can be seen that all the poly(ether–ester)s are in the α-form. From Fig. 6 it is obvious that with increasing level of fumaric acid in the polymers the area of the crystalline peaks is reduced compared to the peaks from PBT. This means that the higher the content of fumaric acid the more amorphous is the polymer. The degree of crystallinity of the poly(ether–ester)s decreased with increasing content of fumaric acid, as was confirmed by the results from DSC analysis.

3.4. TG analysis of the copoly(ether–ester)s

The thermal stability of the synthesized poly(ether–ester)s was investigated by thermogravimetric analysis under dynamic nitrogen and oxygen atmospheres. The TG curves of the synthesized poly(ether–ester)s with different contents of fumarate residues are shown in Fig. 7. The thermal behaviour of all the samples is very similar and the curves show that the mechanism of degradation is complex in all cases.

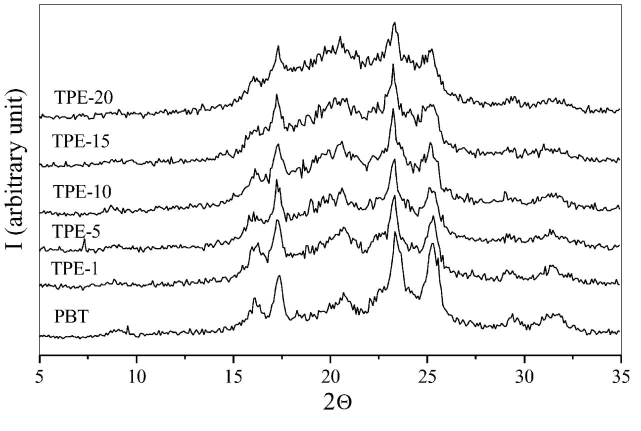

Fig. 6. Diffractograms of the poly(ether–ester)s with various contents of fumaric moieties.

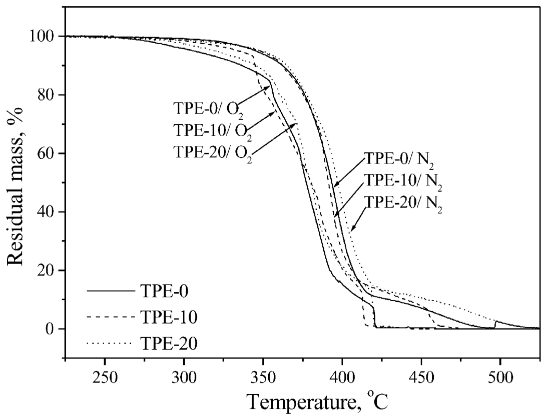

Fig. 7. TG curves for the poly(ether–ester)s TPE-0, 10 and 20.

The degradation of the polymers starts between 362 and 369 °C in the absence of oxygen and between 317 and 347 °C in the presence of oxygen (Table 4). The poly(ether–ester)s with different contents of fumarate moieties start to degrade at higher temperatures in an oxidative atmosphere than the unmodified poly(ether–ester), TPE-0. The reason for such behaviour may be not only due to the presence of fumarate residues, but also due to the difference in molecular weights of the polymers.

The same explanation could be valid for the temperatures of 50 wt% weight loss, which lies between 391 and 397 °C in an inert atmosphere, and between 376 and 381 °C in an oxidative atmosphere. Above 400 °C, the poly(ether–ester)s with higher contents of fumarate degrade slower than the unmodified poly(ether–ester). The reason for this is probably the presence of crosslinking. This behaviour is probably the result of the different contents of the reactive double bonds in the chains of the macromolecules which influence the mechanism of degradation and contribute to crosslinking at higher temperatures.

3.5. Hardness and adhesion of the copoly(ether–ester)s

The results of hardness measurements show that the hardness of the synthesized poly(ether–ester)s decreases with increasing content of fumarate residues, from 54 ShoreD for TPE-0 to 41 ShoreD for TPE-20 (Table 5). The decrease in the hardness results from the incorporation of the double bonds in the polymer chains which increases the flexibility of the chains and lowers the degree of crystallinity.

In many standards for testing materials, adhesive strength is defined as the external force necessary to break the joint, which is divided by a binding area. The adhesive strength, in this case, is defined as the external force required to separate the aluminum specimens bonded with

Table 4
Thermal stability of the synthesized poly(ether–ester)s

Sample	$T_{10\%}$ in N_2 (°C)	$T_{50\%}$ in N_2 (°C)	$T_{10\%}$ in O_2 (°C)	$T_{50\%}$ in O_2 (°C)	Residual weight in N_2 at 450 °C (wt%)
TPE-0	362	393	337	377	7.0
TPE-1	369	396	317	376	8.0
TPE-5	368	391	347	376	5.7
TPE-10	362	391	345	381	7.7
TPE-15	365	394	347	381	12.0
TPE-20	365	397	345	380	11.0

Table 5
Hardness and adhesive strength of the synthesized poly(ether–ester)s

Sample	Content of fumarate (mol%)	T_g (TMA) (°C)	Hardness ShoreD	Adhesive strength (MPa)
TPE-0	–	−74	54	2.2
TPE-1	0.93	−66	54	2.5
TPE-5	2.20	−48	51	2.7
TPE-10	8.93	−64	47	3.5
TPE-15	13.2	−60	47	2.6
TPE-20	17.7	−63	41	3.3

thermoplastic elastomers divided by a binding area. Also it was shown that the adhesive shear strength of the poly(ether–ester)s to the metal substrate increases with increasing level of fumarate unsaturation. The values of the adhesive strength of the synthesized poly(ether–ester)s are between 2.2 MPa for TPE-0 and 3.5 MPa for TPE-10, when the thickness of the adhesive layers was 0.10 mm (Table 5).

3.6. Rheological behaviour of poly(ether–ester)s modified with fumarate residues

The viscoelastic properties of the poly(ether–ester)s are presented as mechanical spectra by following the dependence of the storage (G') and loss (G'') shear moduli and tan δ (Figs. 8 and 9) versus temperature at a frequency of 6.28 rad/s.

The temperature dependence of the storage modulus, the loss modulus and tan δ shows four regions of viscoelastic behaviour: a glassy region, a glass transition region, a rubbery plateau region and a rubbery flow region. The viscoelastic parameters of importance for thermoplastic poly(ether–ester)s include the zero shear modulus G'_0, the value of G' at 50 °C in the rubbery plateau region, and the glass transition temperature. In the prepared series of poly (ether–ester)s, the storage modulus decreases with increasing content of fumarate due to the decreasing degree of crystallinity. Another important parameter is the crossing temperature T_{cr} at which G' is equal to G'', i.e. tan $\delta = 1$. Below the crossing temperature, the behaviour of the poly (ether–ester)s is mainly elastic, i.e. $G' > G''$, and above this temperature the behaviour changes to viscous ($G'' > G'$). The crossing temperature T_{cr}, which corresponds to the starting temperature of the melting process determined by DSC, decreases with the content of fumaric moieties in the polymer chain.

Table 6
Rheological properties of the poly(ether–ester)s modified with fumarate in the glass transition region

Sample	Content of fumarate (mol%)	T_g (°C)			Characteristics of damping peak, tan δ			G'_0 (Pa)	$G'_{50\,°C}$ (Pa)	$T_{G'=G''}$ (°C)
		G''_{peak}	Infl. G'	tan δ_{peak}	h[a]	w[b] (°C)	S[c]			
TPE-1	0.93	−50	−43	−43	0.097	35.3	3.41	1.0×10^9	4.8×10^7	213
TPE-5	2.20	−58	−36	−36	0.097	44.9	4.35	4.2×10^8	3.5×10^7	210
TPE-10	8.93	−61	−37	−37	0.112	48.0	5.38	1.0×10^9	5.6×10^7	–
TPE-15	13.2	−56	−34	−34	0.126	40.5	5.11	8.4×10^8	5.3×10^7	190
TPE-20	17.7	−59	−36	−36	0.146	45.6	6.66	5.3×10^8	2.7×10^7	180

[a] Amplitude of tan δ.
[b] Width at half height.
[c] Area or surface.

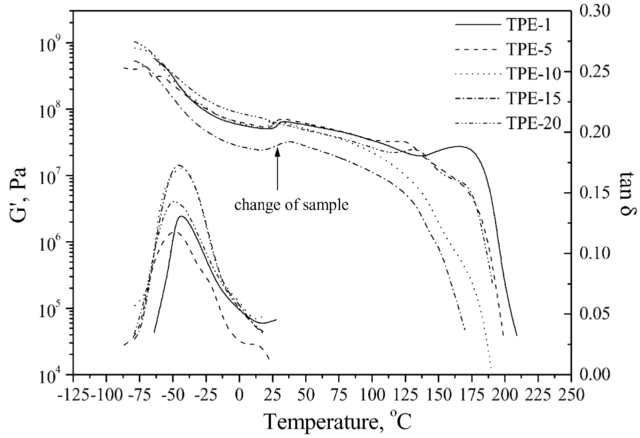

Fig. 8. Storage (G') modulus and tan δ (measured at 6.28 rad/s) versus temperature for the series of poly(ether–ester)s.

A broad glass transition is observed in the temperature range between −80 and 10 °C, which is characteristic for thermoplastic poly(ether–ester)s [7,26]. The glass transition temperature was determined either from the loss modulus peak temperature, G''_{peak}, or the maximum tan δ, or as the inflection point of the turndown of the modulus G' in the glass transition region. From Table 6 it can be seen that the glass transition temperature depends on the method of determination with the G''_{peak} maximum giving the lowest value. All the synthesized poly(ether–ester)s showed only one glass transition temperature which is due to the glass transition occurring in the non-crystalline phase of the sample consisting of a mixture of soft segments and non-crystallized hard segments of varying length. Polymers with a higher content of fumarate residues exhibit higher T_g than the unmodified poly(ether–ester). The increase of T_g with increasing content of the fumarate residues in the main chains is due to the increasing content of the non-crystalline hard segments, which give a higher percent of pseudo-crosslinking.

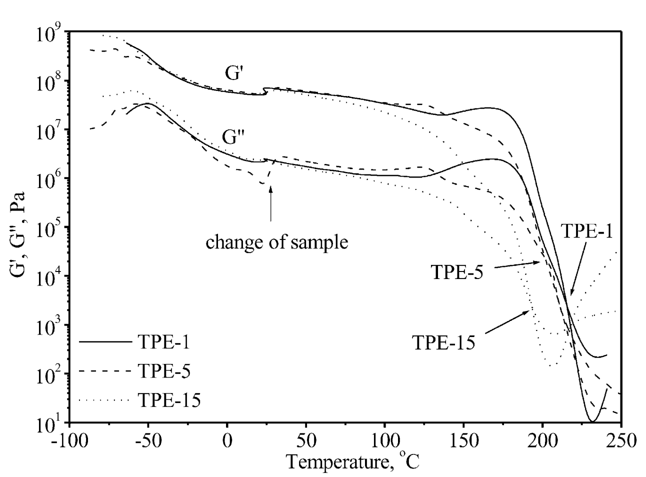

Fig. 9. Plots of G' and G'' (measured at 6.28 rad/s) versus temperature for the series of poly(ether–ester)s.

The damping peaks of the series of poly(ether–ester)s with different content of fumarate are shown in Fig. 9. It can be concluded that both the amplitude and width at half-height (WHH) of the tan δ loss peak depend on the cross-linking density. As shown in Fig. 9, the amplitude and the WHH increase with decreasing degree of pseudocross-linking. It can also be seen that in the series of polymers, the tan δ peak broadens with increasing content of fumarate, indicating the lower crosslink density, i.e. higher damping. Such behaviour has already been attributed to a shortening of the kinetic chain fragments due to crosslinking, crystallization or spatial hindrances [13,29]. In the case of poly(ether–ester)s modified with fumarates, the increase of the damping effect is probably due to the decrease of the degree of crystallinity with increasing content of fumarate and segmental mobility.

4. Conclusion

The melt polycondensation of methyl esters of terephthalic acid with polyols and glycols, which was successfully applied to the synthesis of poly(ether–ester)s, has been extended for the introduction of different levels of unsaturated double bonds in both the hard and soft segments of the polyester chain. The introduction of double bonds into the main chain increases the molecular weight of the copolyesters, but reduces the crystallinity of the hard segment and related properties such as storage shear modulus and hardness. The presence of the double bonds improves the high temperature properties and thermal stability, especially the oxidative one, but lowers the melting and crystallization temperature. The introduction of fumaric moieties improves the adhesive strength of the polymer to metal surface and increase damping, which makes these thermoplastic elastomers excellent candidates for thermoplastic metal coating. Also, these copolyesters, due to their fibre-forming properties, could be used for the formation of elastomeric fibres with reactive double bonds capable of reacting with the polymeric matrix in composites. The influence of the content of unsaturated bonds on the rheological properties, presented as master curves, as well as microphase separation of these poly(ether–ester)s, which occurs during melting, will be discussed in a forthcoming publication.

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