

SYNTHESIS AND CHARACTERIZATION OF THERMOPLASTIC COPOLY(ESTER-BUTYLENES)

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In this articles a series of thermoplastic poly(ester-butylene) elastomers, based on poly(ethylene-stat-butylene), HO-PEB-OH, as the soft segment and poly(butylene terephthalate), PBT, as the hard segment, were synthesized by a catalyzed transesterification reaction in solution. The incorporation of soft hydrogenated poly(butadiene) segments into the copolyester backbone was accomplished by polycondensation of α,ω -dihydroxyl telechelic HO-PEB-OH, ($PEB \bar{M}_n = 3092$ g/mol) with 1,4-butanediol (BD) and dimethyl terephthalate (DMT) in the presence of a 50 wt-% of high boiling solvent i.e., 1,2,4-trichlorobenzene. The mole ratio of the starting comonomers was selected to result in a constant hard to soft weight ratio of 60:40. The synthesis was optimized in terms of both 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. It was found that the optimal catalyst concentration ($Ti(OBu)_4$) for the synthesis of these thermoplastic elastomers was $0.96 \cdot 10^{-3}$ mol/mol ester and optimal DPPD concentration was 0.5 wt-%. The thermal properties of poly(ester-butylene)s were investigated using differential scanning calorimetry (DSC). The degree of crystallinity was also determined by DSC. The thermal and thermo-oxidative stability were investigated by thermogravimetric analysis (TGA). The rheological properties of poly(ester-butylene)s were investigated by dynamic mechanical spectroscopy in the melt and solid state.

Key words: *thermoplastic elastomers, poly(ester-butylene)s, hydroxyl-terminated poly(ethylene-stat-butylene), polycondensation, thermal analysis, rheology.*

INTRODUCTION

Thermoplastic elastomers have found wide application in many industrial branches as engineering materials thanks to their excellent mechanical and physical properties. These polymers combine the mechanical properties of a chemically cross linked elastomer, for example: elastic recovery, energy of 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 [2], [4], [9], [1], [12].

The thermoplastic and elastic behaviour of these polymers can be explained by their multiphase 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 parts 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 super-molecular structure have been proposed [6],

[11]. The crystalline structure is typically lamellar. Depending on the crystallization conditions, spherulitic crystalline structures can also be formed.

In the present work a series of thermoplastic poly(ester-butylene)s (PTHB)s, based on poly(ethylene-stat-butylene), HO-PEB-OH, as the soft segment and poly(butylene terephthalate), PBT, as the hard segment, were synthesized by two-step catalyzed transesterification reactions in solution. Incorporation of soft hydrogenated poly(butadiene) segments into the copolyester backbone was accomplished by polycondensation of α,ω -hydroxyl telechelic HO-PEB-OH, with 1,4-butanediol and dimethyl terephthalate in the presence of 50 wt-% of a high boiling solvent, i.e., 1,2,4-trichlorobenzene. The mole ratio of the starting components was selected to result in a constant hard to soft segment weight ratio of 60:40. The synthesis was optimized in terms of both the concentration of catalyst, tetra-n-butyl-titanate ($Ti(OBu)_4$), and stabilizer, N,N'-diphenyl-p-phenylene-diamine, as well as the reaction time. The thermal properties of the poly(ester-butylene)s were investigated using differential scanning calorimetry (DSC) and thermogravimetry (TG). The rheological properties of poly(ester-butylene)s were investigated by dynamic mechanical spectroscopy in the melt and solid state.

MATERIAL AND METHODS

MATERIALS

Reagents

Hydroxyl terminated poly(ethylene/butylene), KRATON LIQUID L-2203 (Kraton Polymers UK Ltd) with molecular weight of 3094 g/mol was used as obtained. Dimethyl terephthalate, DMT, was recrystallized from absolute ethanol. PROCEDURE: 50g (0.258 mol) of DMT was dissolved in 400 ml of refluxing absolute ethanol. The solution was cooled and filtered. The isolated crystals of DMT were dried in an oven with a ventilator at about 80 °C. Yield: 47.5g (95%). 1,4-Butandiol (from FLUKA) was purified by vacuum distillation. PROCEDURE: The fraction of 1,4-butandiol boiling between 120 and 122 °C under vacuum of 10 mm Hg (133 Pa) was collected. The redistilled 1,4-butandiol was kept above molecular sieves (4Å).

Catalyst

Tetra n-butyl titanate, $Ti(OC_4H_9)_4$ (from Aldrich), was used as catalyst as a solution in dry 1-butanol (1:9 vol.). 1-Butanol was purified by atmospheric distillation. The fraction boiling between 118 and 120 °C was collected. The redistilled 1-butanol was dried over molecular sieves (4Å). PROCEDURE: In 9 ml dry 1-butanol, 1 ml tetra n-butyl titanate was dissolved. The solution of catalyst was prepared and used under a nitrogen atmosphere.

Stabilizer

N,N'-Diphenyl-p-phenylenediamine, DPPD (BAYER), was used without any further purification.

Solvents

1,2,4-Trichlorobenzene (FLUKA), 1,1,2,2-tetrachloroethylene, (FLUKA) and toluene, (CENTROHEM) were used without any further purification.

EXPERIMENTAL PROCEDURE

Synthesis.

The copolyesters, poly(butylene terephthalate-co-ethylene/butylene terephthalate)s, TPEHBs were synthesized by a two-step catalyzed transesterification. The reactants are α,ω -hydroxyl terminated poly(ethylene/butylene) (KRATON), 1,4-butandiol (BD), dimethyl terephthalate (DMT) and catalyst tetra-n-butyl titanate ($Ti(OBu)_4$). As a heat stabilizer, N,N'-Diphenyl-p-phenylenediamine (DPPD) was used. The synthesis was performed using 1,2,4-trichlorobenzene as solvent.

A typical synthesis procedure was performed as follows: 20.41 g (0.0066 mol) of α,ω -hydroxyl terminated poly(ethylene/butylene), KRATON; 16.22 g (0.18 mol) of 1,4-butanediol; and 29.7 g (0.153 mol) of dimethylterephthalate and 1 ml of a solution (0.96 mmol/mol ester group) of $Ti(OBu)_4$

were charged into a 500 ml glass flask. The solvent, 1,2,4-trichlorobenzene was used in 50 wt % calculated on the reaction mixture (33.7 g). The reaction flask was equipped with a thermometer, magnetic stirrer, nitrogen inlet tube, and a distillation condenser. The excess of the hydroxyl groups relative to the DMT ester groups was 25 mol %. The reaction mixture was heated on a silicone oil bath under a nitrogen atmosphere.

The temperature of the oil bath was set to 160 °C at the beginning of the synthesis and then gradually increased to 220 °C with a step of 10 °C per 10 min. Methanol started to distill over when the temperature of the oil bath was around 140 °C. When the methanol had ceased to distill over, water vacuum was applied in order to remove the solvent. During the solvent removal, the polymer mixture became cloudy. The temperature of the oil bath was raised during one hour to 250 °C. At this point, the thermal stabilizer DPPD (0.33 g, 0.5 wt.-% calculated on the reaction mixture) was added to the reaction mixture. When all of the solvent had been removed, the pressure was reduced (oil pump) to 0.3 mmHg in order to remove the excess of 1,4-butanediol and residual solvent. During this second phase i.e., polycondensation, the temperature of the oil bath was raised to 280 °C (the final temperature of reaction mixture was around 240 °C). The duration of the second (under high vacuum) was 5 hours. At the end of the synthesis, the viscous slurry was cooled in the reactor under nitrogen, and then it was pulled from the reactor (in some cases the flask had to be broken to collect the polymer).

All the other polyesters were synthesized following the same procedure. The synthesis was optimized in terms of the amount of the catalyst and the amount of the stabilizer. The synthesis of the copolyesters TPEHB-6 differed from the others in that it was done in a glass flange-flask instead a round-bottomed flask.

CHARACTERIZATION

Melt viscosity and rheological properties

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 dynamic shear mode between parallel plates, at 230 °C. Dynamic mechanical analysis was performed on polymer discs (the radius of the sample was 25 mm and the thickness was about 1.5 mm), in the temperature range from 180 to + 240 °C, and at frequencies between 0.1 to 100 rad/s.

Dynamic mechanical analysis was performed under torsion rectangular conditions on molded polymer bars ($63.0 \times 12.4 \times 1.0 \text{ mm}^3$) in the temperature range from + 30 to 180 °C. The viscoelastic

properties of the poly(ester-butylene)s are presented as mechanical spectra by following the dependence of the storage (G') and loss (G'') moduli and $\tan \delta$ peak on temperature at a fixed frequency of 6.28 rad/s.

Thermal properties

Differential scanning calorimetry (DSC) was conducted using a Perkin-Elmer DSC-2. The samples of the poly(ether-ester)s were analyzed under a nitrogen atmosphere in the temperature range 50 to 250 °C at a heating rate of 10 °C/min and cooling rate of 40 °C/min.

The TGA curves of the copolyesters were obtained using a Perkin-Elmer TGS-2 at a heating rate of 10 °C/min in either a dynamic air or N₂ atmosphere (flow rate of N₂ 20 ml/min and of air 20 ml/min).

RESULTS AND DISCUSSION

A series of novel thermoplastic poly(ester-butylene)s, based on poly(ethylene-stat-butylene), HO-PEB-OH, as the soft segment and poly(butylene terephthalate), PBT, as the hard segment, was synthesized by a two-step catalyzed transesterification reactions.

The first step, i.e. transesterification reaction, was carried out at normal pressure in the presence of 50 wt-% of a high boiling solvent, i.e. 1,2,4-trichlorobenzene. α,ω -Hydroxyl telechelic HO-PEB-OH, ($\bar{M}_n = 3092$ g/mol), 1,4-butanediol (BD), and dimethyl terephthalate (DMT) were used as the reactants, with a 25 % excess of hydroxyl groups. Tetra-n-butyl-titanate Ti(OBu)₄ was used as the transesterification catalyst. For the second step, i.e. bulk polycondensation, a thermal stabilizer, *N,N'*-diphenyl-p-phenylenediamine (DPPD), was added and the reaction was carried out under vacuum to remove the excess glycol and hence to produce chain extension. The molar ratio of the starting components was selected to result in copolymers with a constant hard to soft weight ratio of 60:40. The final products were multiblock copolymers with a random distribution of the hard and soft segments. The reaction scheme for the synthesis and chemical structure of the segmented poly(ester-butylene)s based on terephthalic acid and polyolefines is shown in Figure 1.

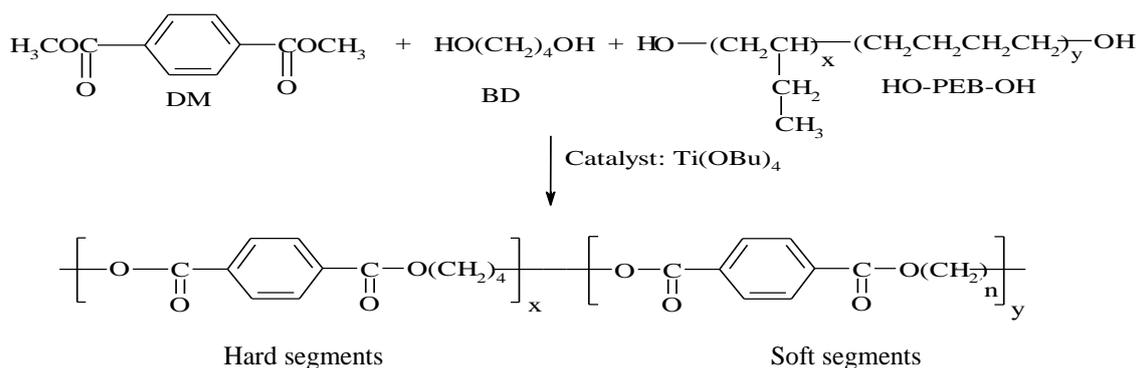


Figure 1: The reaction scheme and chemical structure of the poly(ester-butylene)s, where x is the mole fraction of hard segments and y is the mole fraction of soft segments.

OPTIMIZATION OF THE SYNTHESIS OF TPEHB

In this work, the effect of the concentration of the catalyst, tetra-n-butyl-titanate (Ti(OBu)₄) (1.0 – 2.0 mmol/mol ester) and the thermal stabilizer *N,N'*-diphenyl-p-phenylenediamine, DPPD (0.5 - 1 wt %) on the formation of the poly(ester-butylene)s was investigated. The formation of the poly(ester-butylene)s was monitored by measuring the intrinsic and complex melt viscosities of the obtained polymers. The reaction conditions, intrinsic viscosities and complex dynamic viscosities are shown in Table 1.

Poly(ester-butylene)s are not soluble in common organic solvents, such as THF or chloroform, that are usually used for GPC analysis. Therefore the molecular weight of the prepared polymers were determined by measuring the inherent and intrinsic viscosity of the polymers in a mixture of phenol/tetrachloroethylene/toluene, as well as by complex dynamic melt viscosities. Poly(ester-butylene)s having an intrinsic viscosity between 0.31 and 0.38 dl/g were obtained. The values of the complex dynamic viscosity η^* at 240 °C were in the range from 21 to 100 Pas.

Table 1: Reaction conditions, intrinsic viscosity numbers and complex dynamic viscosities

Polymer	Catalyst, mmol/mol ester	Thermal stabilizer, wt. %	Methanol ^a , %	Vacuum, mm Hg	[η], dl/g	η^* , Pas (240 °C, 1 Hz)
TPEHB1	0.96	0.5	88.7	0.1	0.348	47.1
TPEHB2	1.44	0.5	100	0.3	0.337	40.1
TPEHB3	1.92	0.5	88.7	0.2	0.312	59.8
TPEHB4	0.96	0.75	87.1	0.1	0.372	100.4
TPEHB5	0.96	1.0	80.6	0.1	0.340	21.2
TPEHB6	0.96	0.5	72.6	2	0.378	31.6

^a theoretically volume of methanol, V = 12.4 ml.

ANALYSIS OF HOMOGENEITY OF THE TPEHBS

The presence of unreacted KRATON homopolymer or KRATON-rich fractions was studied by extracting the samples with chloroform. The extraction was carried out in a Soxhlet apparatus for 24h. PBT and block copolymer are insoluble in chloroform. KRATON and block copolymer with very low PBT content are,

however, soluble and are therefore extractable. These values are given in Table 2. expressed as weight fraction of the sample that is soluble in chloroform as well as fraction that was remained as insoluble after the 24hr. The wt-% of the soluble and insoluble fraction are given in Table 2, together with the wt % of HS in each fraction.

Table 2: Results obtained by extraction of the poly(ester-butylene)s with chloroform.

Polymer	Soluble fraction, wt-%	Insoluble fraction, wt-%	HS in soluble fraction, wt-% ^{a)}	HS in insoluble fraction, Wt-%
TPEHB1	28	72	30	70
TPEHB2	54	46	48	61
TPEHB3	52	48	-	-
TPEHB4	38	62	-	-
TPEHB5	41	59	44	74
TPEHB6	49	51	-	-

^{a)}determined as the difference between the starting and insoluble fraction polymer composition

On a basis of the results presented in Table 2., it is obvious that the content of KRATON-rich fractions is very high for almost the all samples. It can be concluded that in spite of the fact that the reaction was carried out in the presence of a solvent in order to compatibilize the immiscible components, phase separation occurred, as was reported by [10].

DSC ANALYSIS

The synthesized poly(ester-butylene)s were partly crystalline polymers, for which melting temperatures were observed by DSC. From the obtained thermograms, the heats of fusion were determined. The DSC thermograms of the synthesized poly(ester-butylene)s recorded during heating and cooling are shown in Figure 2. And 3.

The shape of the endothermic peaks of these polymers indicates that melting of the crystallites occurs in the temperature range of 200 to 230 °C.

Comparing the first-heating thermograms of the TPEHBs, the difference between polymers TPEHB1, TPEHB5 and TPEHB6 on the one hand, and TPEHB2, TPEHB3 and TPEHB4 on the other side, it can be noticed that TPEHB2, TPEHB3 and TPEHB4 have broader melting peaks than the other polymers, which means that they have a broader crystallite size distribution. Also the thermograms of these three polymers have a shoulder peak in the high temperature region of the melting in both I and II runs, which is not the case for other polymers.

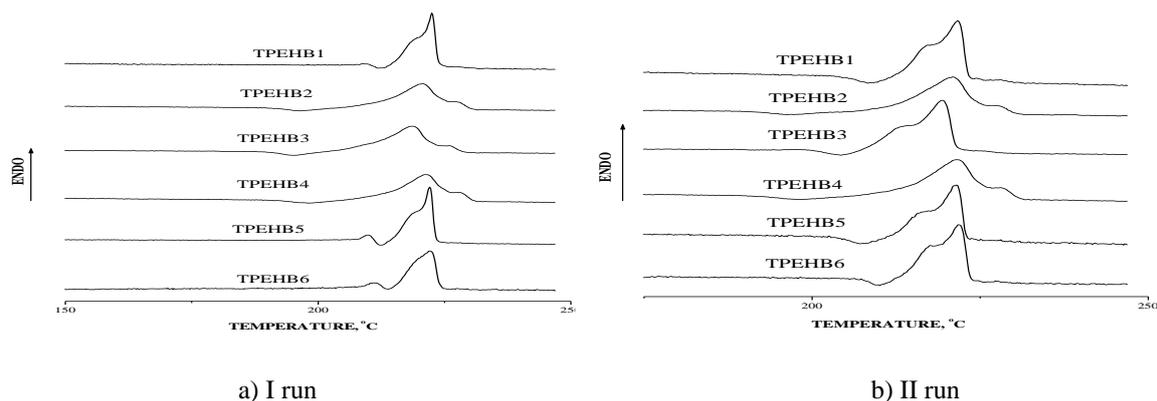


Figure 2: DSC curves of the poly(ester-butylene)s , a) the first and b) second heating

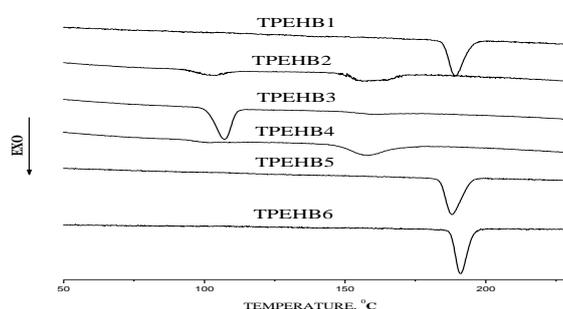


Figure 3: DSC curves of the poly(ester-butylene)s in the cooling process

Similar differences can also be seen in the cooling runs. Unlike TPEHB1, TPEHB5 and TPEHB6 that show only one peak in the cooling process, samples TPEHB2, TPEHB 3 and TPEHB4 have, surprisingly, two peaks during cooling. The only component that can crystallize is PBT. Two crystallization peaks for these polymers can be attributed to crystallization of PBT in the two different phases. PBT in PBT-rich phase can crystallize faster and probably has a higher crystallization temperature, while PBT in the KRATON-rich phase is more constrained and because of that possesses a lower crystallization temperature. The supercooling of the hard segments ($\Delta T_h = T_m - T_c$) of the samples TPEHB1, TPEHB5 and TPEHB6 was around 31-32 °C,

indicating that the segments crystallize quickly. The fact that the rate of crystallization of the hard segments was slower in the TPEHB2, TPEHB 3 and TPEHB4 samples was confirmed by the supercooling in the range from 57 and 63 °C. PBT, which is considered to be a fast crystallizing polymer, has a supercooling of 36 °C.

The melting and crystallization temperatures are given in Table 3. The melting temperatures were determined as the temperature of the main peak in the DSC curves from the first heating scan.

It is obvious that the polymers do not differ much in their melting temperature in the first heating, as well as in the second heating

Table 3: Thermal properties and degree of crystallinity of the poly(ester-butylene)s

Polymer	$T_m, ^\circ\text{C}$	$\Delta H_{th}, \text{J/g}$	$T_d, ^\circ\text{C}$	$T_{dl}, ^\circ\text{C}$	$\Delta H_c, \text{J/g}$	$w_c, \%$	$(w_c)_{PBT}, \%$
TPEHB1	220(222)	26.3(30.9)	189	/	29.1	18.2(21.4)	30.8(36.2)
TPEHB2	221(221)	32.6(31.5)	158	104	26.8	22.6(21.8)	41.8(40.4)
TPEHB3	218(220)	32.6(32.2)	161	107	30.9	22.6(22.3)	44.2(43.7)
TPEHB4	221(221)	33.8(33.3)	158	103	25.7	23.3(23.0)	37.8(37.2)
TPEHB5	222(221)	26.0(25.3)	188	/	32.6	18.0(17.5)	29.5(28.7)
TPEHB6	222(222)	28.7(28.5)	191	/	30.4	19.9(19.7)	33.7(33.4)

It can be seen that with increasing content of hard segments, the melting temperature also increased. Such a dependence of the melting temperature on the content of hard segments has already been reported in the literature for poly(tetramethyleneoxide) and polyisobutylene soft segments based thermoplastic elastomers [6].

From the obtained thermograms, the enthalpy of fusion was calculated as the area of the melting peak. The results are given in Table 3. The enthalpy of melting is in range from 26.0 to 33.8 J/g in the first run and from 25.3 to 33.3 J/g in the second run.

The overall degree of crystallinity was calculated as the ratio of the observed heat of fusion and the theoretical heat of fusion of perfectly crystalline PBT [8].

$$w_c = \Delta H_m / \Delta H_m^0$$

where ΔH_m is the observed heat of fusion and ΔH_m^0 (144.5 J g⁻¹) is the theoretical heat of fusion for perfectly crystalline PBT

The crystalline fraction of the hard segments was calculated from the equation:

$$(w_c)_{PBT} = \Delta H_m / (w_h \Delta H_m^0)$$

where w_h is the weight fraction of the hard segments in the poly(ester-butylene)s, determined from their ¹H NMR spectrum.

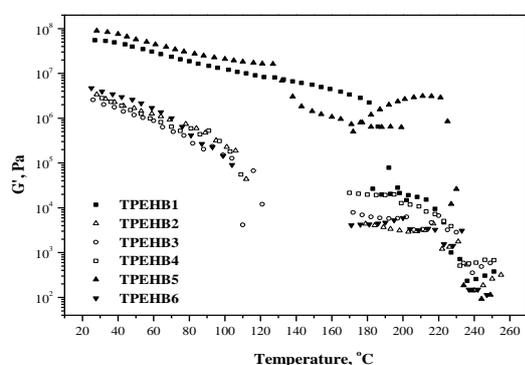


Figure 4: Plots of G' (measured at 6.28 rad/s) versus temperature for the series of poly(ester-butylene)s

The temperature dependence of the storage modulus and loss modulus shows, in the examined range, three region of viscoelastic behavior: a glass transition region of amorphous phase rich in PBT, a rubbery plateau region and a rubbery flow region.

The viscoelastic parameters of importance for thermoplastic poly(ester-butylene)s, which include the glass transition temperature of the PBT rich region, the value of G' at 30 and 50 °C in the rubbery plateau region are given in Table 4. The

The degree of crystallinity, calculated from the DSC data is also given in Table 3. The degree of crystallinity is not very high and these results indicate that only a small fraction of the PBT crystallizes and that some of the short segments are incorporated into the amorphous phase. From the values of the degree of crystallinity, the similarity between TPEHB1, TPEHB5 and TPEHB6 on the one hand and TPEHB2, TPEHB3 and TPEHB4 on the others can be seen again.

It can be seen that with increasing hard segment content the degree of crystallinity of the whole sample, as well as the degree of crystallinity of PBT, decreases. The explanation for this unexpected behavior can be found in the higher viscosity of the melt with increasing hard segment content. The crystallization is suppressed if the viscosity of the melt is higher.

RHEOLOGICAL BEHAVIOUR OF THE TPEHBS

The viscoelastic properties of the poly(ester-butylene)s are presented as mechanical spectra by following the dependence of the storage (G') and loss (G'') shear moduli (Figure 4. and 5) versus temperature, in the range from 30 to 250 °C, at a frequency of 6.28 rad/s. The rheological measurements were performed with two different geometries i.e. rectangular bars and parallel plates (above 160 °C).

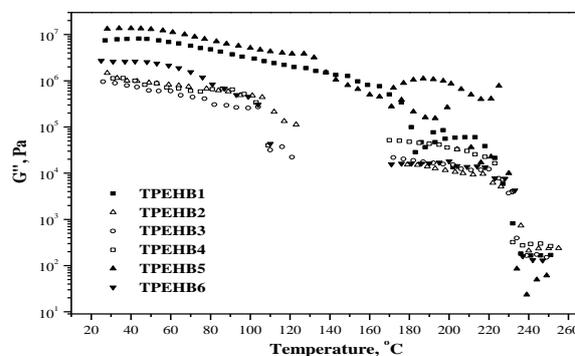


Figure 5: Plots of G'' (measured at 6.28 rad/s) versus temperature for the series of poly(ester-butylene)s

storage modulus of the poly(ester-butylene)s in the rubbery plateau increases with increasing content of hard segments due to the increasing content of crystallizable PBT. The increase in the shear rubbery modulus is attributed to an increase in the PBT crystallinity and consequently to an increase in the physical crosslink density, which makes the polymer stiffer in the rubbery plateau. The storage modulus of four samples, TPEHB2, TPEHB3, TPEHB4 and TPEHB6, dropped sharply with

temperature. The values of G' at 30 and 50 °C of these samples are in the range of 1.1- 1.6 10^6 Pa, and are lower by one decade compared to the samples TPEHB1 and TPEHB5. The very low rubbery modulus of these samples, besides the low molecular weight might also be caused by the

lower modulus of hydrogenated poly(butylene)s itself. It was reported that thermoplastic elastomers with similar soft, nonpolar segments showed lower values of G' compared to copolyesters with poly(tetramethylene oxide), PTMO.

Table 4: Rheological properties of the poly(ester-butylene)s

Sample	Content of PBT, wt-%	G' (30 °C), Pa	G' (50 °C), Pa	$T_{G'=G''}$ °C
TPEHB1	59	5.4×10^7	3.7×10^7	233
TPEHB2	54	3.1×10^6	1.6×10^6	248
TPEHB3	51	2.1×10^6	1.1×10^6	231
TPEHB4	62	2.9×10^6	1.4×10^6	229
TPEHB5	61	8.7×10^7	5.7×10^7	225
TPEHB6	59	4.0×10^6	2.4×10^6	236

Another important parameter is the crossing temperature T_{cr} at which $G'=G''$, i.e. $\tan \delta = 1$. Below the crossing temperature, the behavior of the poly(ester-butylene)s is mainly elastic, i.e. $G' > G''$, and above this temperature the behavior changes to viscous $G'' > G'$. The crossing temperature T_{cr} corresponds to the starting temperature of the melting process.

From the complex dynamic viscosity measurements it could be concluded that the synthesized poly(ester-butylene)s at 240 and 235 °C show pseudoplastic behavior (Figure 6). While, the melts of the more homogeneous samples i.e. TPEHB1, TPEHB5 and TPEHB6, had lower viscosities compared to the less homogenous samples, TPEHB2, TPEHB3 and TPEHB4 samples.

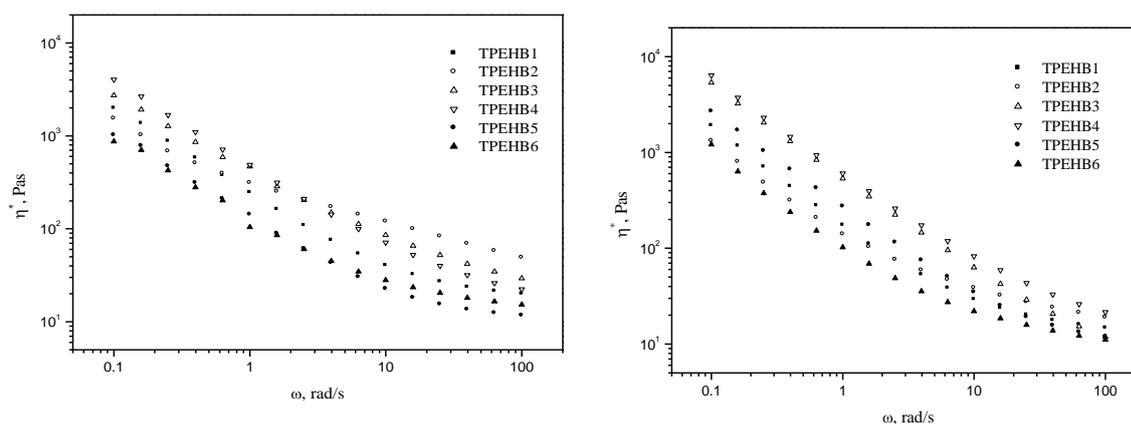


Figure 6: Complex dynamic viscosity vs. frequency at 240 and 235 °C of the poly(ester-butylene)s

THERMOGRAVIMETRIC ANALYSIS OF THE TPEHB5

The thermal stability of the synthesized poly(ester-butylene)s was investigated by thermogravimetric analysis under dynamic nitrogen and air atmospheres. The TG curves of the poly(ester-butylene)s synthesized with different contents of catalyst and heat stabilizer are shown in Figure 7.

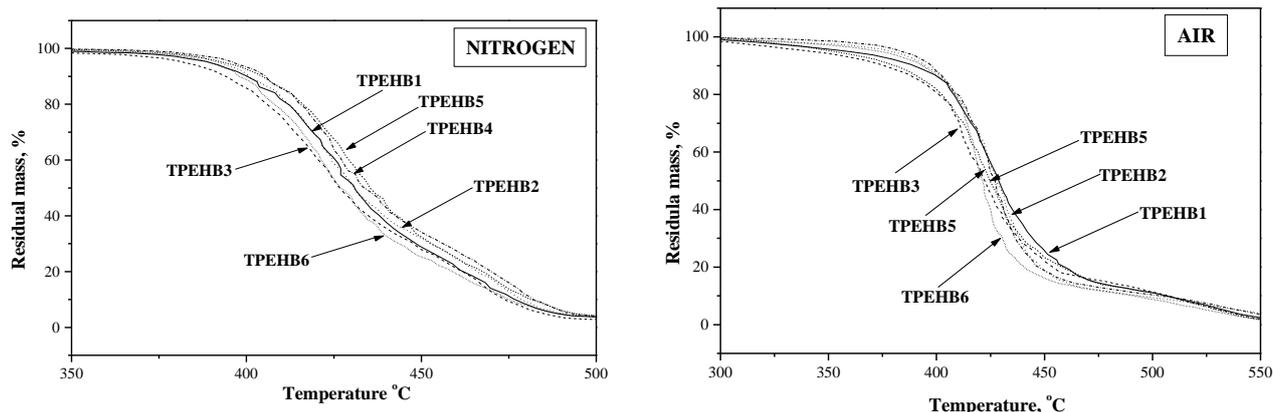


Figure 7: TG curves of the poly(ester-butylene)s

The thermal behavior of all samples is very similar and the curves show that the mechanism of degradation is complex in all cases. The degradation of the poly(ester-butylene)s starts between 393 and 406 °C under nitrogen and between 375 and 397 °C in an air atmosphere (Table.5). The thermal stability of the synthesized poly(ester-butylene)s, i.e., presented as the temperature of the start of degradation depends on the concentration of catalyst and heat stabilizer.

Table 5: Thermal stability of the synthesized poly(ester-butylene)s

Sample	Thermal stabilizer. wt. %	Catalyst mmol/mol ester	T _{10%} in N ₂	T _{50%} in N ₂	T _{10%} in air	T _{50%} in air	% residual weight, in N ₂ at 500 °C
TPEHB1	0.5	0.96	401	431	390	428	3.7
TPEHB2	0.5	1.44	401	431	394	428	3.8
TPEHB3	0.5	1.92	393	427	375	422	2.9
TPEHB4	0.75	0.96	406	432	397	428	4.1
TPEHB5	1.0	0.96	405	435	381	425	4.2
TPEHB6	0.5	0.96	398	428	393	420	3.8

The results confirmed the expectation that the thermal stability of these polymers would increase with increasing content of the heat stabilizer and decreases with increasing concentration of catalyst. The same trend was observed for the temperatures of 50 wt % weight loss, which lie between 427 and 435 °C in an inert atmosphere, and between 420 and 428 °C in an air atmosphere. The residual weights at 500 °C in nitrogen were 2.9 – 4.2 % .

The results show that the thermal stability of the poly(ester-butylene)s, i.e., the start of degradation is 30 °C higher compared to thermoplastic poly(ester-ether) elastomers based on PTMO poly(tetramethylene oxide) stabilized with the same heat stabilizer^{ref}.

Conclusions

A series of thermoplastic poly(ester-butylene)s elastomers based on α,ω -dihydroxyl poly(ethylene-stat-butylene), HO-PEB-OH ($\overline{M}_n = 3092$ g/mol), 1,4-butanediol and dimethyl terephthalate, was synthesized. A two stage polymerization procedure involving transesterification and melt polycondensation could be employed for the introduction of nonpolar soft segments into the polyester chains. Due to the strong tendency of phase separation, the presence of a solvent was necessary at the start of the reaction. It was found that the optimal polymerization conditions, obtained on the bases of the molecular weight of the polymer chains and the homogeneity of the samples are: a reaction time of 5 h at 240 °C under

vacuum, in the presence of 1.0 mmol/mol ester group $\text{Ti}(\text{O}i\text{Bu})_4$ and a DPPD concentration of 1.0 wt %.

The synthesized poly(ester-butylene)s were partly crystalline polymers, the melting temperature and enthalpy of melting of which increased with increasing the content and length of the hard PBT segments. The degree of crystallinity calculated from DSC curves was in the range from 18.0 to 23.4 %, which is in agreement with literature data for other types of copolyester elastomers.

DSC analysis as well as rheological measurements of the solid samples and melts confirmed that the series of synthesized poly(ester-butylene)s, based on their behavior and homogeneity, could be divided in two types. Samples TPEHB1, TPEHB5 and TPEHB6 differ from samples TPEHB2, TPEHB3 and TPEHB4 in the shape and range of melting, as well as in the shape and number of cooling peaks

and also in the rate of crystallization. The rubbery modulus of the first types was one decade higher than that of the second types due to the greater degree of crystallinity of the PBT in the former which results in a higher physical crosslink density, making the polymers stiffer. While in the molten state, these polymers showed lower melt viscosities compared to the less homogeneous samples.

The thermal stability of the synthesized poly(ester-butylene)s depends on the concentration of catalyst and heat stabilizer, i.e. as expected it increases with increasing content of heat stabilizer and decreases with increasing concentration of catalyst.

The thermal stability of the poly(ester-butylene)s, expressed as the start of degradation, is 30 °C higher compared with thermoplastic poly(ester-ether) elastomers based on PTMO poly(tetramethylene oxide) stabilized with the same heat stabilizer.

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