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Synthesis and Characterization of Multiblock Copolyesters Containing Poly(dimethylsiloxane) in the Soft Segments

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Summary: Synthesis and thermal properties of poly(aliphatic/aromatic-ester) copolymers containing additionally poly(dimethylsiloxane) (PDMS) chains in the soft segments are discussed. A two step method of transesterification and polycondensation from the melt was carried out in a presence of magnesium-titanate catalyst. An aliphatic dimer fatty acid was used as a component of the soft segments while poly(butylene terephthalate) (PBT) constituted the hard blocks. Effectiveness of the incorporation of PDMS into polymer chain was confirmed by the Soxhlet extraction and infrared spectroscopy of an excess of 1,4-butane diol destilled off from the polycondensation reaction. Multiblock copolymers showed microphase separation as determined by differential scanning calorimetry. Incorporation of a small amount of PDMS (up to 14.5 wt.-%) into polymer chain containg low concentration of hard segments of PBT lead to decrease in crystallinity of such copolymers. This may indicate that semicrystalline PBT are dissolved in the amorphous matrix of the soft segments.

Keywords: dimer fatty acid, multiblock copolymers, poly(butylene terephthalate), poly(dimethylsiloxane), polycondensation

Introduction

Thermoplastic elastomers (TPE) are very interesting class of polymers which possess both plastic and rubbery properties. They are composed from different fragments (segments) of macromolecule which are alternated along the main chain. These are tighted through labile connections being a consequence of glass transition of segments, crystallization, they might be ionic associations or groups connected by the hydrogen bonds. These groups have features of physical cross-links and they are called the "hard segments". In contrast to chemically cross-linked materials, the physical cross-links are reversible and can be disrupted at elevated temperatures or in solvents, which give the material its good processability. Other segments which are characterized by "small" elastic modulus, low glass transition temperature and low bond cohesion energy are called the "soft segments".[1,2]

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By varying the hard/soft segments composition and concentration and additionally using thermal and mechanical conditioning, the physical, mechanical and chemical properties as well as morphology of the multiblock copolymers can be changed. The resulting polymers can behave as classical thermoplasts or polymeric materials of high elasticity or change from crystalline to amorphous polymers.

Widely known examples of multiblock thermoplastic elastomers (TPE) include poly(ester-urethane)s, poly(ether-amide)s, poly(ester-ether)s.[3,4] Polymers containing aliphatic units (derived from aliphatic dicarboxylic acids) and polyester hard segments are also known.[5] Poly(dimethylsiloxane) (PDMS) has also been used in multiblock terpoly(ester-ether-siloxanes),[6,7] poly(siloxane-ester-imides)[8] and thermoplastic poly(ester-siloxane)s[9,10] as a component of the soft segments. Incorporation of highly hydrophobic PDMS into polymer chain impart improved antistick/antiblock and mould release properties as well as improved film and fiber properties.[11,12]

Taking into consideration that the phase behaviour of segmented block copolymers in general, is controlled by the differences in the Hildebrand solubility parameters (δ) it is known that PDMS has one of the smaller solubility parameters (7.3 - 7.6 $(\mathrm{cal/cm^3})^{1/2}$)[13] in comparision with other organic polymers, however aliphatic dimer fatty acid is characterized also by the small solubility parameter, namely 7.9 $(\mathrm{cal/cm^3})^{1/2}$ (calculated based on the Small method).[14] Thus, the formation of one homogenous soft phase is expected in such copolymers.

In this study, the multiblock poly(aliphatic/aromatic-ester) copolymers have been prepared and poly(dimethylsiloxane) has been introduced into polymer melt during the synthesis in order to produce material of highly hydrophobic properties.

Experimental

Synthesis of Polymers

Synthesis of hydrophobized poly(aliphatic/aromatic-ester) copolymers (PEDMS) was carried out by transesterification and polycondensation from the melt. Following materials were used: dimetylterephthalate (DMT) – "Elana S.A." Torun, Poland; 1,4 - butanediol (1,4 -BD) – BASF, Gemany; dimer fatty acid (DFA) – commercial name Pripol 1009, molecular weight 570 g/mol, Uniqema Chemie, BV , Gouda, The Netherlands; poly(dimethylsiloxane) (PDMS) of M_n = 1000 g/mol, Wacker, Germany; magnesium-titanate catalyst, prepared as described in.[21]

The apparatus for polymer synthesis was constructed as a two separated reactors: the upper reactor for the transesterification and the buttom one for the polycondensation. The reactors were connected by a launching tube where the valve was located.

The reaction mixture consisting of DMT, 1,4-BD and magnesium-titanate catalyst (2 g/kg of polymer) was heated to 200 °C with a heating rate of 1.5 °C/min and constant mixing rate (60 rpm) in the reactor for transesterification. The molar ratio of BD and DMT was as 1.8:1. The reaction was stopped when more than 95% of the stoichiometric amount of methanol was evaporated. Under these conditions and under reduced pressure oligomer of butylene terephthalate was obtained.

During the second stage of the reaction a dimer fatty acid was added along with a catalyst and α,ω-disilanol PDMS to the first reactor and the reaction mixture was transferred to the bottom reactor. The polycondensation was carried out at 245-255°C and 0.5-0.6 mm Hg of vacuum. The process was considered complete on the basis of the observed power consumption of the stirrer motor when the product of highest melt viscosity was obtained (up to a constant value of a power consumption by the reactor stirrer).

The reaction mass was extruded into water by compressed nitrogen and extrudate was granulated. The optimum yield from the apparatus was 1 kg of polymer.

Polymers Characterization

The limiting viscosity number (inherent viscosity) $[\eta]$ of the polymers was measured at 30°C using polymer solutions in $PhOH/C_2Cl_3H$/toluene (1:1:2 by vol.).

Granules of the polymer were placed into the extraction thimble and were extracted with refluxing methanol for 6 hours. After extraction polymers were dried in a vacuum oven at 50 °C for 3 hours to constant mass.

IR spectra of 1,4-butanediol destilled off from the polycondensation reaction were recorded on a Specord M80 Carl Zeiss Jena Spectrometer using KBr pellets. Solid samples were characterized by Fourier transform attenuated total reflection infrared spectroscopy (ATR-FTIR). A Nexus FTIR spectrometer (Nicolet Instrument Corporation, U.S.A.) equipped with the Golden Gate Single Reflection Diamond ATR head, (Specac INC, U.S.A.) scanning between 600 and 4000 cm^{-1}.

Water contact angle was measured using an optical bench-type contact angle goniometer (OCA Contact Angle System, Data Physics, USA). Drops of destilled water (3 μl) were deposited onto the compression moulded polymer film surfaces and the direct microscopic measurement of the contact angles was done with the goniometer.

Differential scanning calorimetry (DSC) was performed with a TA Instruments (DSC-2920) apparatus. The samples were dried in a vacuum at 70 °C. The process was carried out in three cycles: heating, cooling, and heating, in the temperature ranges -100 to 220 °C. The rate of heating and cooling was 10 °C/min. Temperature and enthalpy calibration were carried out using an indium standard. The glass transition temperature (T_g) was determined from the temperature diagrams as the temperature corresponding to mid point.

Results and Discussion

Three series of hydrophobized poly(aliphatic/aromatic-ester) (PEDMS) copolymers, containing the ester hard segments of poly(butylene terephthalate)(PBT) and an aliphatic soft segments composed of dimer fatty acid extended with poly(dimethylsiloxane) were synthesiszed. Polymers differed in chemical composition and concentration (mass ratio) of used monomers as presented in Table 1.

Table 1. Composition of PEDMS copolymers containing poly(dimethylsiloxane) (PDMS) of M_n = 1000 g/mol and their inherent viscosities [η].

No	Mass ratio (at feed) (wt.-%)			[η] (dL/g)
	PBT	DFA	$PDMS_{1000}$	
I a	26	74	-	0.9
I b	26	70	4	0.83
I c	26	66.5	7.5	0.86
I d	26	63	11	0.81
I e	26	59.5	14.5	0.82
	PBT	DFA	$PDMS_{4000}$	
II b	26	70	4	0.75
II c	26	66.5	7.5	0.76
II d	26	63	11	0.72
	PBT	DFA	$PDMS_{1000}$	
IIIa	50	50	-	0.94
IIIb	50	47.5	2.5	0.93
IIIc	50	45	5	0.97
IIId	50	42.5	7.5	0.92
IIId	50	40	10	0.94

Extraction of the polymers revealed that polymers contained small amount (about 1%) of extractables which indicates on effectiveness of the PDMS incorporation into the polyester. Infrared spectroscopy has been also used to monitor the incorporation of poly(dimethylsiloxane) into the polymer chain by taking spectra of a low-molecular weight diol (1,4-butanediol) distilled off from the polycondensation reaction. Figure 1 presents spectra of a pure 1,4-butanediol.

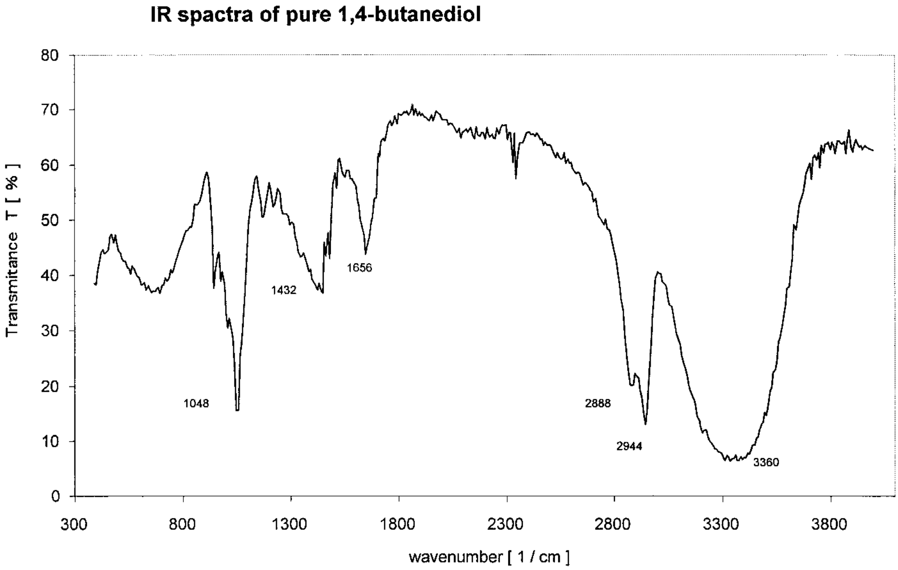

Fig. 1. IR spectra of a pure 1,4-butanediol.

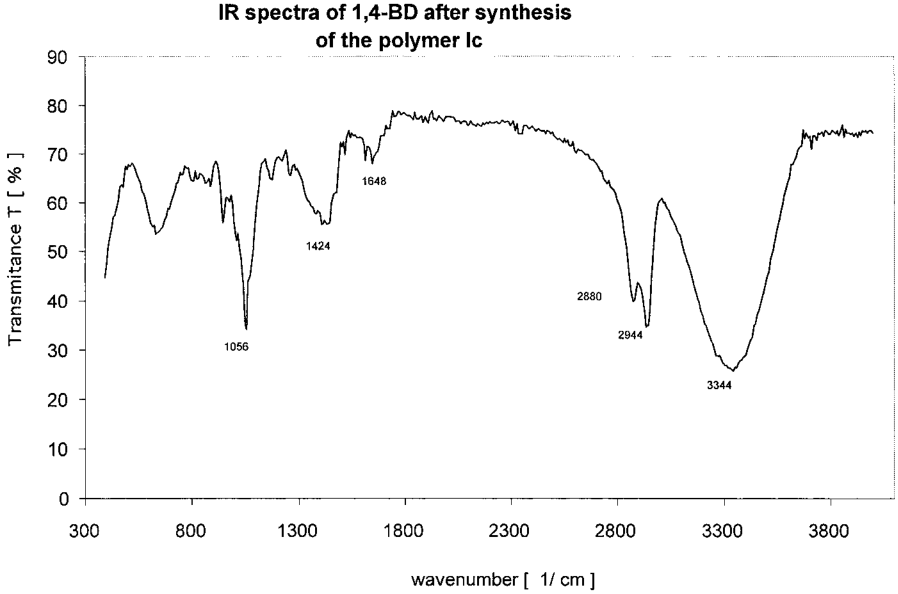

Fig. 2. IR spectra of 1,4-BD destilled from the polycondensation reaction (polymer I c).

Three characteristic bands are present: the bands at 2888 and 2944cm^{-1} correspond to ν(C-H) stretching; the bands at 3360, 1048 and1432 cm^{-1} correspond to O-H bending. This spectra was compared with the spectra (Figure 2) taken for 1,4-butanediol after polycondensation step. Good agreement between chemical structure of a pure 1,4-butanediol and 1,4-BD destilled from the reaction indicate the effectiveness of the synthesis.

The chemical structure of solid PEDMS polymer films was examined by ATRFT-IR spectroscopy. Infrared absorption spectrum shown as example for sample Ic on Figure 3 reveal presence of characteristic PDMS bands: Si-O-Si stretching vibrations at 1015.5 and 1098.8 cm^{-1}; Si-C stretching and CH_3 rocking at 794.1 cm^{-1}; CH_3 symmetric deformation of Si-CH_3 at 1266.4 cm^{-1}; and CH_3 asymetric deformation of Si-CH_3 at 1409.05 cm^{-1}.

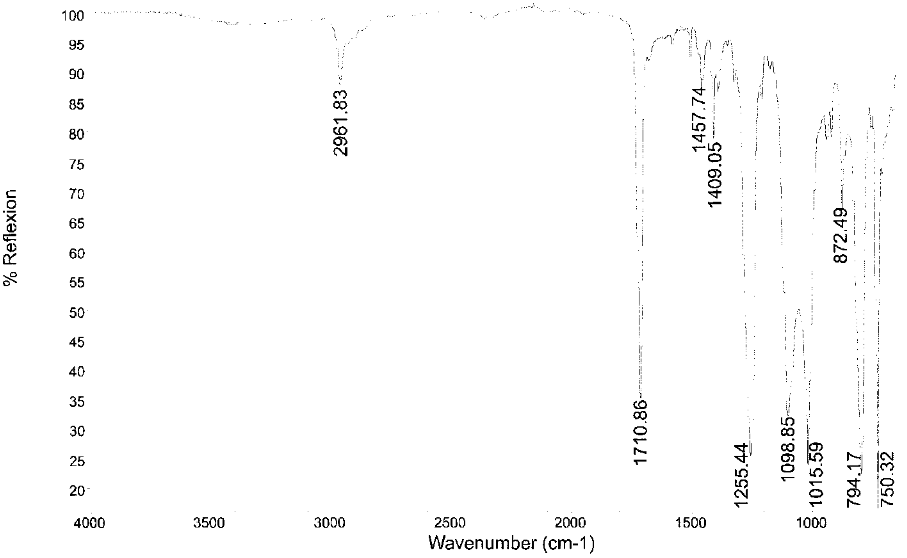

Fig. 3. ATR-FTIR spectra of a PEDMS sample (I c).

As it was discussed in the introduction part, a highly hydrophobic PDMS can be introduced into existing polymer substrates to improve surface properties without changing the bulk properties[15] (a silicon rubber has a water contact angle of 111^{o}).[16] PEDMS copolymers (Figure 4) containing PDMS chains exhibit higher water contact angles compared to non modified. The effect of PDMS molecular weight on hydrophobicity of polymers is not much significant but copolymers containing $PDMS_{4000}$ (M_n = 4000 g/mol) shows the highest values of the contact angle.

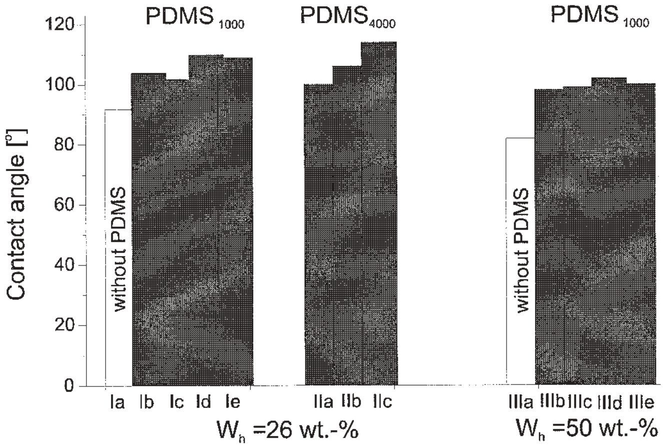

Fig. 4. Water contact angle of PEDMS polymer surfaces.

The PEDMS synthesised are semi-crystalline polymers. Results from differential scanning calorimetry show an appearance of two characteristic temperature transitions: a single low glass transition temperature and a single melting temperature confirming their multiblock structure. However, analysis of the low temperature transition for the „pure" DFA soft segment in series I and II ($P_k = 1$) and DFA-PDMS soft segments material indicate a slight decrease in the T_g of the soft segments (Table 2) what is associated with a higher degree of phase separation.[17] Opposite tendency is observed for the polymers of series III ($P_k = 2.8$) where the shift to higher temperatures is observed (DFA segments are better mixed with the PDMS material). The detected single glass transition, which shifts to higher temperature with increasing PDMS content in series III, indicates that the siloxane and aliphatic units form a homogenous amorphous phase at a PBT weight content of 50 % ($P_k = 2.8$).

Based on the experimental heat of fusion ΔH_m (J/g of polymer) from DSC measurements, the crystalline phase content in the polymer ($W_{c,h}$) was calculated from the following equation:

$$W_{c,h} = \Delta H_m / \Delta H_f \, 100 \qquad (1)$$

where ΔH_m is the heat of melting of the hard segments determined from DSC (Table 2) and ΔH_f is the heat of melting of crystalline PBT phase ($\Delta H_f = 144.5$ J/g).[18]

Table 2. DSC transitions of PEDMS copolymers.

Symbol	Soft segments		Hard segments				
	T_{g1} (°C)	ΔC_p (J/g/°C)	T_{g2} (°C)	T_{m2} (°C)	ΔH_{m2} (J/g)	T_{c2} (°C)	$W_{c,h}$ (%)
I a	-41.7	0.331	53.3	117.2	10.6	24.3	7.3
I b	-41.9	0.374	49.1	102.2	8.8	26.1	6.1
I c	-39.7	0.471	48.4	99.8	9.4	32.5	6.5
I d	-42.1	0.326	48.5	121.9	8.5	43.3	5.8
I e	-42.8	0.361	47.4	126.1	9.3	75.4	6.4
II b	-41.3	0.317	55.1	100.7	9.8	32.3	6.8
II c	-41.7	0.394	52.7	104.7	10.1	26.7	7.4
II d	-42.4	0.436	53.6	96.9	12.5	30.1	8.6
III a	-33.0	0.249	55.7	170.8	16.8	122.3	11.6
III b	-30.8	0.261	51.8	171.1	18.8	114.3	13.0
III c	-28.0	0.268	52.8	173.8	20.7	115.2	14.3
III d	-27.6	0.225	53.8	175.6	21.0	120.1	14.5
III e	-29.3	o.225	48.8	182.1	23.4	132.0	16.1

T_{g1} *- glass transition of the soft segments,*
ΔC_p *- change of the heat capacity at glass transition;*
T_{g2}, T_{m2}, T_{c2} *- glass transition, melting, and crystallization temperatures, respectively, of the hard segments;*
ΔH_{m2} *- melting enthalpy of the hard segments;* $W_{c,h}$ *- mass content of PBT crystallites in the polymer.*

According to the DSC measurements, the crystalline fraction is higher for polymers containing higher amount of PBT hard segments (series III, Table 2). For series I, the crystalline phase content decreases with increasing PDMS_{1000} concentration. These polymers contain a very low amount of crystalline phase (26 wt.-%). This indicate that crystallization behaviour is disturbed by the addition of poly(dimethylsiloxane) (PBT starts to dissolve in the soft amorphous phase). Increase of the molecular weight of PDMS to 4000 g/mol leads to opposite effect: an increase of the crystallinity was observed for series II when the hard segment charge was kept at the some weight level). Addition of the PDMS_{1000} to polymers containing 50 wt.-% of the hard segments increases their crystalinity with increasing PDMS_{1000} content.

Conclusions

The two step method of transesterification to produce an oligomer of poly(butylene terephthalate) and then polycondensation of this product with dimer fatty acid and silanol-terminated poly(dimethylsiloxane)s of different molecular weight has beed succesfully applied for preparation of multiblock copolymers. Their multiblock structure has been confirmed by differential scanning calorimetry. Incorporation of small amount of $PDMS_{1000}$ (up to 14.5 wt.-%) into polymers containing low concentration of crystalline hard segments of PBT has effected polymers crystallinity. This may indicate that semicrystalline PBT dissolves in the amorphous matrix of the soft segments. The influence of the PDMS molecular weight and concentration on mechanical properties, especially on the fatigue behaviour will be discussed in a further publication.

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[1] G. Holden, N.R. Legge, R. Quirk, H.E. Schroeder, editors "*Thermoplastic Elastomers*" Hanser Publishers, Munich Vienna New York 1996, p. 222.
[2] N.R Legge, G. Holden, H.E. Schroeder, editors. „*Thermoplastic Elastomers*", Carl Hanser Verlag, New York 1987.
[3] R. Walker , Ch.P. Rader. editors, „*Handbook of Thermoplastic Elastomers*", van Nostrand Reinhold Comp., New York, 1988, p. 207.
[4] R.J. Cella. *J. Polym. Sci., Polym. Symp.* **1973**, *42*, 727.
[5] M. El Fray , J. Slonecki, *Angew. Makromol. Chem.* **1999**, *266*, 30.
[6] Z. Roslaniec, *Polymer* **1992**, *33*, 1717.
[7] Z. Roslaniec, *Polimery (Warsaw)* **1997**, *42*, 376.
[8] M. Cazacu, C. Racles, A. Vlad , M. Marcu, *Europ. Polym. J.* **2001**, *37*, 2465.
[9] V.V. Antic, M.R. Balaban, J. Djonlagic, *Polym. Int.* **2001**, *50(11)*, 1201.
[10] D.A. Schiraldi, *Polymer Preprints* **2001**, *42(1)*, 221.
[11] P.R. Ginnings, US Patent 4 496 704; 1985.
[12] N. Yamamoto, H. Mori, A. Nakata, M. Suehiro, US Patent 4 894 427, 1990.
[13] O. Olabisi, L.M. Robertson, M.T. Shaw, "*Polymer-Polymer Miscibility*", Academic Press, New York 1979, p. 54.
[14] J.L. Gardon, in: *Encyclopedia of Polym. Sci. & Technol.*, John Willey & Sons, New York, 1965; p. 851
[15] Y. Ikada, *Biomaterials* **1994**, *15*, 725
[16] D.W. Grainger, S.W. Kim, J. Feijen, *J. Biomed. Mater. Res.* **1998**, *22*, 231.
[17] M. El Fray, J. Slonecki, *J. Macromol. Sci. – Phys.* **1998**, *B37(2)*, 143.
[18] Y. Camberlin, J.P. Pascault, *J. Polym. Sci. – Polym. Chem.* **1983**, *21*, 415.