

Synthesis, structure and properties of thermoplastic poly(ester–siloxane) elastomers*

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Abstract: Two series of thermoplastic poly(ester–siloxane) elastomers (TPES), with hard segments based on poly(butylene terephthalate) (PBT) and soft segments based on poly(dimethylsiloxane) (PDMS), were synthesized by high-temperature, two-step transesterification reaction in the melt. In series I, the mass ratio of hard and soft segments was kept constant (57:43), while the length of the segments was varied, whereas in series II, the mass ratio of hard and soft segments was varied in range from 70:30 to 40:60, with a constant length of the soft segments. The segmented structure of the poly(ester–siloxane) copolymers was verified by ¹H-NMR spectroscopy of the soluble and insoluble fractions, obtained after extraction of the samples with chloroform. The influence of the structure and composition of the TPES on the melting temperatures and degrees of crystallinity was investigated by differential scanning calorimetry (DSC). The rheological properties were investigated by dynamic mechanical analysis (DMA).

Keywords: thermoplastic elastomers, poly(ester–siloxane)s, carboxypropyl-terminated poly(dimethylsiloxane)s.

INTRODUCTION

Block copolymers belonging to the class of thermoplastic elastomers consist of two types of chemically different segments, hard-crystalline and soft-amorphous segments, and show a phase-separated microstructure. Due to the phase-separated microstructure, thermoplastic elastomers combine the elasticity and flexibility of rubbers and the processability of thermoplastics. The properties of thermoplastic elastomers depend on the chemical nature and incompatibility of the two types of segments, hard and soft, as well as on their mass ratio and respective lengths.^{1,2} Poly(organosiloxane)s

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exhibit many important and interesting properties, such as low-temperature flexibility, high thermal and thermo-oxidative stability, good biocompatibility, low surface energy, ultraviolet resistance and high permeability to many gases.^{3,4} As a result of the described unique combination of the properties of poly(organosiloxane)s, siloxane containing block or segmented copolymers have received special attention for many applications, such as biomaterials, photoresists, gas separation membranes, protective coatings, elastomers and emulsifiers.³

RESULTS AND DISCUSSION

Two series of different thermoplastic poly(ester-siloxane)s (TPES), based on poly(butylene terephthalate) (PBT) and low molecular weight carboxypropyl-terminated poly(dimethylsiloxane)s (PDMS) were synthesized using the so-called catalyzed two-step transesterification reaction in the melt.⁵⁻⁷ The molecular structure of the synthesized TPES copolymers is shown in Fig. 1.

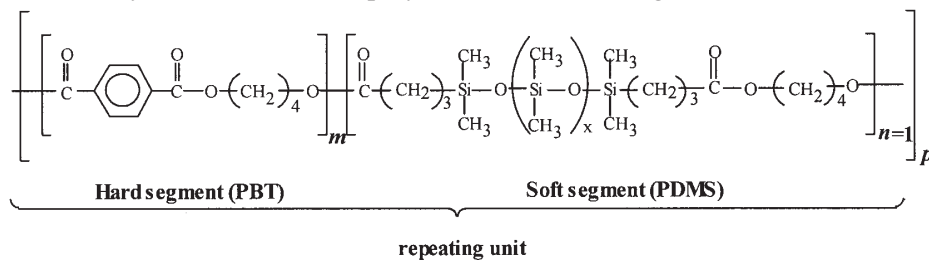


Fig. 1. Molecular structure of the synthesized poly(ester-siloxane) copolymers.

The mass ratio of the PBT and PDMS segments, predetermined by the reaction mixture composition, was 57:43 in the first series, while the length of both the hard and soft segments was varied.⁶ In the second series, the predetermined mass ratio of PBT and PDMS segments was in range from 70:30 to 40:60, with a constant length of the soft segments⁷ (Table I). The structure, composition and size of the TPES macromolecules were investigated by ¹H-NMR spectroscopy, dilute solutions viscometry and complex dynamic melt viscometry. The obtained results are presented in Table I.

TABLE I. Molar masses of the PDMS segments (\bar{M}_n^{PDMS}), mass fraction (%) and degree of polymerization of the PBT segments (m) and the molar masses of the TPES copolymers (\bar{M}_n^{TPES}) (determined from ¹H-NMR spectra); inherent (η_{inh}) and complex dynamic (η^*) viscosities; temperatures of melting (T_m) and degree of crystallinity (w_c^{DSC}) (determined from DSC curves); the microphase separation transition temperature T_{MST} (determined from Han's diagrams)

Sample	\bar{M}_n^{PDMS}	Mass % of PBT (NMR) ^a	m (NMR)	\bar{M}_n^{TPES} (NMR)	η_{inh} dl/g	η^* at 230 °C Pa s	Temperature of melting T_m /°C	w_c^{DSC} %	T_{MST} °C
Series I									
TPES1	600	59.2 (57)	3.8	15400	0.51	5	195	18.5	220
TPES2	920	59.1 (57)	5.9	17700	0.48	140	213	19.1	234

TABLE I. Continued

Sample	\bar{M}_n^{PDMS}	Mass % of PBT (NMR) ^{a)}	m (NMR)	\bar{M}_n^{TPES} (NMR)	η_{inh} dl/g	η^* at 230 °C Pa s	Temperature of melting T_m /°C	w_c^{DSC} %	T_{MST} °C
TPES3	1240	60.0 (57)	8.3	15200	0.38	150	219	20.1	234
TPES4	2220	62.9 (57)	16.9	8300	0.33	100	222	22.6	233
Series II									
TPES30	1080	76.2 (70)	15.4	25000	0.37	240	218	23.3	234
TPES40		69.5 (60)	11.0	34650	0.43	100	216	20.8	233
TPES45		58.7 (55)	6.8	35000	0.45	70	209	17.2	234
TPES50		53.5 (50)	5.5	23670	0.44	65	210	15.0	227
TPES60		39.2 (40)	3.1	10600	0.35	10	205	11.4	230

^{a)}In brackets, the values predetermined by the reaction mixture composition

The composition and structure of the soluble and insoluble fractions, obtained after extraction with chloroform, were identified by analysis of their ¹H-NMR spectra. It is well known that PBT homopolymers and block copolymers are insoluble in chloroform, while the PDMS prepolymer and block copolymers with a very low PBT content are, however, soluble and therefore extractable with chloroform. Examination of the extracted and insoluble fractions by ¹H-NMR spectroscopy showed that both contained aromatic rings from the PBT segments and also PDMS segments. The soluble fractions were enriched in PDMS segments, with rather low contents of PBT segments, while the insoluble fractions were enriched in PBT segments, with rather low contents of PDMS segments. It was concluded that both the extracted and insoluble fractions have a multiblock structure but with short PBT blocks in the soluble and longer PBT blocks in the insoluble fractions.^{6,7} Partial incorporation and distribution of the soft segments in the copolymer chains is probably the result of the high immiscibility of the non-polar PDMS with the polar PBT and phase separation which occurs during the melt transesterification.

The influence of the structure and composition on some of the properties of TPES, such as thermal and rheological, was investigated by differential scanning calorimetry (DSC) and dynamic mechanical spectroscopy (DMA). With increasing mass fraction and degree of polymerization of the PBT segments (m), the melting temperatures (T_m) and also the degree of crystallinity (w_c^{DSC}) shifted gradually to higher values (Table I). The increase in T_m and w_c^{DSC} was a consequence of the increasing size of the crystallites and their degree of regularity with increasing m . An important rheological parameter for phase segregated copolymers, such as poly(ester-siloxane)s, is the microphase separation transition temperature, T_{MST} , (also referred to as the order-disorder transition).⁸ At room temperature, poly(ester-siloxane)s consist of a crystalline PBT-phase which is dispersed in an amorphous PDMS-phase. However, as the temperature is increased above a certain critical value, the size of the PBT-crystallites begins to decrease and the ordered

microdomain structure changes to a disordered homogeneous phase (isotropic melt) at T_{MST} . The microphase separation transition temperatures for the poly(ester-siloxane)s were determined from Han's diagrams (plots of $\log G'$ – the storage shear modulus, versus $\log G''$ – the loss shear modulus) and were in range from 220 to 234 °C (Table I).

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ИЗВОД

СИНТЕЗА, СТРУКТУРА И СВОЈСТВА ТЕМОПЛАСТИЧНИХ
ПОЛИ(ЕСТЕР-СИЛОКСАНСКИХ) ЕЛАСТОМЕРАВЕСНА В. АНТИЋ¹ и ЈАСНА ЂОНЛАГИЋ²

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Две серије термопластичних поли(естер-силоксанских) еластомера (TPES), са твр-дим сегментима на бази поли(бутилентерефталата) (PBT), и меких сегментима на бази поли(диметилсилоксана) (PDMS), синтетизоване су реакцијом високотемпературне двостепене трансестерификације у растопу. У серији I је при константном масеном односу твр-дим и меких сегмената од 57:43 варирана њихова дужина, док је у серији II вариран масени однос твр-дим и меких сегмената у опсегу од 70:30 до 40:60, при константној дужини меког сегмента. Сегментирана структура поли(естер-силоксанских) ко-полимера је потврђена ¹H-NMR спектроскопијом растворних и нерастворних фракција, добијених након екстракције узорака у хлороформу. Утицај структуре и састава TPES на температуре топљења и степен кристаличности је испитан диференцијалном скенирајућом калориметријом (DSC). Реолошка својства TPES испитана су динамичко-механичком спектроскопијом (DMA).

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