

INFLUENCE OF CHEMICAL COMPOSITION OF AMIDE BLOCK ON THE THERMAL PROPERTIES AND STRUCTURE OF TERPOLYMERS

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Abstract

Multiblock terpolymers $-(\text{PBT-b-PTMO-b-PA12.10})_n-$ comprising the polymer systems in which one of the three blocks (PBT) is not soluble in the hard phase of PA12.10 blocks but is slightly soluble in the soft phase of PTMO blocks have been obtained. The DSC and DMTA method was applied to investigate the thermal properties of these polymers and it was found that the PBT block acts as an element that produce stiffness of $-(\text{PBT-b-PTMO-b-PA12.10})_n-$ structure. The terpolymers were compared with the previously described [5] $-(\text{PBT-b-PTMO-b-PA12})_n-$ elastomers, in which the rigid PBT block ($\text{DP} > 7$) dissolves in the hard phase of PA12 blocks and partly dissolves in the soft phase.

It was found that even a small change in the chemical structure of the amide block influences significantly on the structure, phase separation and the properties of terpolymers.

Keywords: DMTA, DSC, multiblock terpolymers, mutual solubility of soft and hard blocks, phase structure, thermal properties

Introduction

A polymeric material, which demonstrates the ability to almost instant return to the original form after a large deformation and can be subjected to processing by analogous methods as the thermoplastic plastics is termed as the thermoplastic elastomer.

A part of the multiblock polymers of the type $-(\text{A}_x \text{B}_y)_n-$, $-(\text{A}_x \text{B}_y \text{C}_z)_n-$ can be included to a group of the thermoplastic elastomer. In order to be a good thermoplastic elastomers, the multiblock polymer should possess:

- linear or slightly branched molecule (which determines the thermoplasticity),
- strictly define differences in the chemical composition of the blocks causing that these blocks termed as the flexible (soft) and rigid (hard) exist in the different thermodynamical states at the same temperature (a thermodynamic condition of the phase separation enabling the formation of the heterophase structure),
- an appropriate phases composition of the system which depends on the type of the blocks and their dimensions. This composition is responsible among others for the

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high-flexible features of copolymer and for a width of elasticity 'plateau' in the temperature spectrum of the Young's modulus (width of 'plateau' determines a range of elastomer application),

- an appropriate dispersion of the phases (microseparation, the possibility of nanostructures formation),
- an adequate density of the intermolecular and interphase links (these links stabilize the nanostructure).

The fulfilment of conditions 3÷5 is dependent on the mutual solubility of the respective blocks. In the systems of multiple repeating sequences (multiplication) of two blocks (multiblock copolymers) the structure is for the most part recognized [1–4]. These are heterogeneous two-phase systems with interface broadening (thin layer). Thus the blocks are insoluble in each other in the multiblock copolymers. Whereas the ternary systems (multiblock terpolymers), being the subject of investigation of our team are considered as a significantly more complex. In these systems a layer termed as the intermediate phase (wide layer) may occur instead of the interface [5–9]. Ukielski [5–7, 9] confirmed that, the size of this intermediate phase will primarily determine the features associated with the conditions 3÷5. For example, an additional third block soluble in the remaining blocks performs a role of the plasticizer of the intermediate phase (reduce the glass transition temperature T_g of this phase), the compatibilizer of the system components and the structure stabiliser. Thereby enables the preparation of the typical thermoplastic elastomers with very good parameters of high elasticity.

Subject of examinations

In aim the proof how the insignificant change of chemical structure, only from three blocks, it can influence on thermal proprieties and structure, the multiblock terpolymers was compared with two series:

- I serie –poly(tetramethylene terephthalate-block-oxytetramethylene-block- lauro-lactam)-(PBT-b-PTMO-b-PA12)_n–,
- II serie –poly(tetramethylene terephthalate-block-oxytetramethylene-block- dodecanemethylene sebacamide)-(PBT-b-PTMO-b-PA12,10)_n–.

The difference between these systems was associated with a small change of the chemical structure of polyamide block. The PA12,10 block has 12 and 8 methylene groups between the amide groups whereas the PA12 block has 11 methylene group between amide groups. The size of the oligoester block PBT (a given degree of polymerization amounted to $DP_{PBT=x=2; 4; 7 \text{ and } 11}$) was varied in both series, whereas the content and the molecular weight of oligoether block PTMO were constant in the compared systems.

Such a small difference in the chemical structure does not influence or has a negligible effect on a value of the solubility parameters of oligoamide blocks [10].

Syntheses of the oligoamide PA12 and PA12,10 blocks and terpolymers –(PBT-b-PTMO-b-PA12)_n–, –(PBT-b-PTMO-b-PA12,10)_n– were previously described in details [5, 6, 11–15].

Experimental

The microcalorimetric examinations were recorded on a DSC-2 (Perkin Elmer) apparatus. The samples were examined in a triple cycle (heating-cooling-heating) in the temperature range from -150 to $+200^{\circ}\text{C}$. Both the heating and cooling rates were $10^{\circ}\text{C min}^{-1}$.

The dynamic mechanical thermal analyses (DMTA) were performed on a Rheovibron DDV-II viscoelastometer in the temperature range from -100 to $+200^{\circ}\text{C}$ at 35 Hz. The storage modulus E' , loss modulus E'' , and loss tangent ($\tan\delta$) were determined.

The tensile data were collected at room temperature with an Instron TMM tensile tester at a cross-head speed of 20 cm min^{-1} .

Hardness (H) measurements were performed on a Shore D apparatus (Zwick, type 3100) according to standard DIN 53505 (ISO 863, PN-80/C- 04238).

The limiting viscosity number ($[\eta]$, LVN) of the poly[ether-block-ester-block-amide] terpolymers in phenol – trichloroethylene (50:50 v/v) was determined by an Ubbelohde viscometer IIA at 30°C .

Results and discussion

Differential scanning calorimetry

The glass transition temperature T_g and the melting temperature T_m of the respective phase in the heterogeneous systems (multiblock polymers, polymer blends) may undergo the deviations from the values of T_g and T_m of the same phase occurring in the homogeneous material. These changes are caused by the factors which disturb the phase structure. In the multiblock polymers composed of the amorphous soft phase and the hard crystalline phase, the depression T_m of the crystalline phase is associated with:

- mutual solubility of the blocks,
- the intermolecular and interfacial interaction.

These factors also influence on the glass transition temperature T_g of the amorphous phase. Additionally, this parameter is affected by stiffness of the block ends caused by the chemical bond (in macromolecule the blocks are chemically bounded and they do not possess free chain ends) [16, 17].

Taking into consideration above the glass transition temperature T_g , a change of the capacity heat Δc_p , crystallisation temperature T_c , crystallisation heat ΔH_c , heat of melting ΔH_m , and the melting temperature T_m of both series of the elastomers were determined by DSC method.

The values of temperatures of the thermal transitions are shown in Figs 1–2, and the compositions and the basic properties of the terpolymers of both series are given in Table 1.

For the terpolymers $-(\text{PBT-b-PTMO-b-PA12})_n-$ of the first series a temperature range of the glass transition extends along with an increase of the molecular mass DP_{PBT} of the ester block, whereas the glass transition temperature T_g of the soft phase increases and the heat of crystallisation of PTMO disappears. This attest to the deteri-

oration of the phase separation of the whole system and ‘contamination’ of the phase of PTMO blocks with other blocks. The endotherm (extreme) determining the heat of melting ΔH_m of the crystalline hard phase decreases and flattens along with an in-

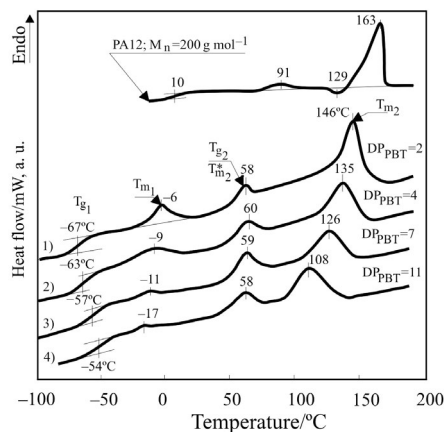


Fig. 1 DSC curves of $-(\text{PBT-b-PTMO-b-PA12})_n-$ terpolymers characterized by different polymerization degree of polyester block DP_{PBT} and constant molecular mass: $\text{PA12}=2000 \text{ g mol}^{-1}$ and $\text{PTMO}=1000 \text{ g mol}^{-1}$ subjected to heating. T_{g1} – glass transition temperatures of soft blocks; T_{m1} – melting temperatures in low-temperature region; T_{g2} , T_{m2}^* – glass transition and melting temperatures in middle-temperature region; T_{m2} – melting temperatures of hard blocks

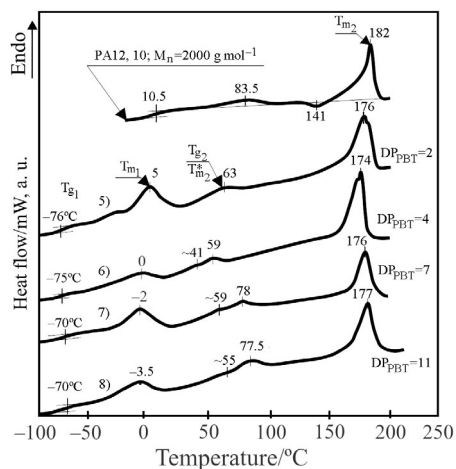


Fig. 2 DSC curves of $-(\text{PBT-b-PTMO-b-PA12.10})_n-$ terpolymers with various polymerization degree of polyester block DP_{PBT} and constant molecular weight: $\text{PA12.10} = 2000 \text{ g mol}^{-1}$ and $\text{PTMO} = 1000 \text{ g mol}^{-1}$ subjected to heating. T_{g1} – glass transition temperatures of soft blocks; T_{m1} – melting temperatures in low-temperature region; T_{g2} , T_{m2}^* – glass transition and melting temperatures in middle-temperature region; T_{m2} – melting temperatures of hard blocks

Table 1 Principal properties of -(PBT-b-PTMO-b-PA12)_n- and -(PBT-b-PTMO-b-PA12.10)_n- terpolymers */

Polymer sample	Molar composition				[η] dL g ⁻¹	H/ Sh D	σ _f MPa	ε _r	ε _{ps,100/} %	ΔC _p J g ⁻¹ K ⁻¹	T _g °C	T _m °C	DP _{PBT}	Series
	PTMO	PA12 or PA12,10	DMT	1,4- butanediol										
1	2	1	3	5	1.52	41	17.7	240	16	0.24	-6 5	146	2	I
2	2	1	5	9	1.67	34	16.1	240	9	0.24	-6 3	135	4	I
3	2	1	8	15	1.48	28	14.3	220	10	0.27	-5 7	126	7	I
4	2	1	12	23	0.89	26	-	215	30	0.26	-5 4	108	11	I
5	2	1	3	5	0.80	42	11.5	199	15	0.09	-7 6	180	2	II
6	2	1	5	9	1.01	54	17.9	176	34	0.04	-7 5	174	4	II
7	2	1	8	15	1.14	40	15.0	200	16	0.15	-7 0	176	7	II
8	2	1	12	23	1.01	41	12.5	184	17	0.17	-7 0	177	11	II

*/rotations were explained in experimental part

crease of DP_{PBT} . The melting temperature T_m decrease from 163°C for a pure block PA12 to 108°C for the terpolymer with the degree of polymerization $DP_{\text{PBT}}=11$. Both these facts confirm that the crystalline phase decreased together with the deterioration of its perfections (excellence). In the copolymers $-(\text{PTMO-b-PA12})_n-$ (two-component system) the following phenomena were not observed: an increase of T_g of the phase composed of PTMO and the depression of T_m of the phase composed of PA12. Hence, it was assumed that PA12 blocks are insoluble in PTMO and the PTMO blocks are insoluble in PA12 [18]. Thus, the observed dependences in the described series of polymers are the results of the solubility of PBT (particularly the low molecular mass fractions) in PTMO and PA12.

A slight decrease of the glass transition temperature T_g of the soft phase with an increase of the DP_{PBT} , that is along with an increase of the contribution of the ester block is characteristic for the second series of polymers. If the soft phase was only composed of unbounded (free) PTMO blocks, its glass transition temperature T_g should amount $T_g = -89^\circ\text{C}$. Therefore, it is assumed, that stiffness of chain ends causes an increase of T_g by about $10 \div 15^\circ\text{C}$. Hence, the glass transition temperature T_g of a pure phase of the PTMO blocks in terpolymers should be in the range from -80 to -75°C . In the discussed group of terpolymers T_g is in the range from -70 to -76°C . This reveals that in the system $-(\text{PBT-b-PTMO-b-PA12,10})_n-$ the soft phase is one-component and has a homogeneous composition and there is a good separation of the soft phase from the hard phase. A small fraction of the PBT blocks in the soft phase occurs in terpolymers with a large content of PBT blocks in the system ($DP_{\text{PBT}}=7$ and 11). The extreme of samples $5 \div 8$, determining the heat of melting ΔH_m of the crystalline hard phase, does not change with an increase of the DP_{PBT} . The melting temperature $T_m=182^\circ\text{C}$ of the pure PA12,10 block in the $-(\text{PBT-b-PTMO-b-PA12,10})_n-$ fluctuates around 175°C . Such a small decrease is probably caused by the interfacial interactions in the system. This means that the crystalline phase did not undergo the deformation, thereby the PTMO and PBT are insoluble in PA12,10 [19].

Dynamic mechanical thermal analysis

The relaxation behavior of all samples was studied by dynamic mechanical thermal analysis (DMTA), measuring the storage modulus E' , the loss modulus E'' and the loss tangent $\tan \delta$. The results are presented in Figs 3 and 4. The loss modulus shows a wide maximum E'' that corresponds to the glass transition of the amorphous phase. When the degree of polycondensation of the PBT block increases, the maxima flatten and shift toward higher temperatures, from -60 to -40°C for the $-(\text{PBT-b-PTMO-b-PA12})_n-$ and from -77 to -70°C for the $-(\text{PBT-b-PTMO-b-PA12,10})_n-$ terpolymers. The $\tan \delta$ curves show that an increased degree of polycondensation of ester block in terpolymers causes an increase in $\tan \delta$ in the range from -30 to -10°C for the $-(\text{PBT-b-PTMO-b-PA12})_n-$, from -40 to $+20^\circ\text{C}$ for the $-(\text{PBT-b-PTMO-b-PA12,10})_n-$ and a shift of the maximum temperature toward higher temperatures. The storage modulus E' shows rapidly decreasing values near T_g and a wide 'plateau' of elastic state. After that, a quick decrease of E' val-

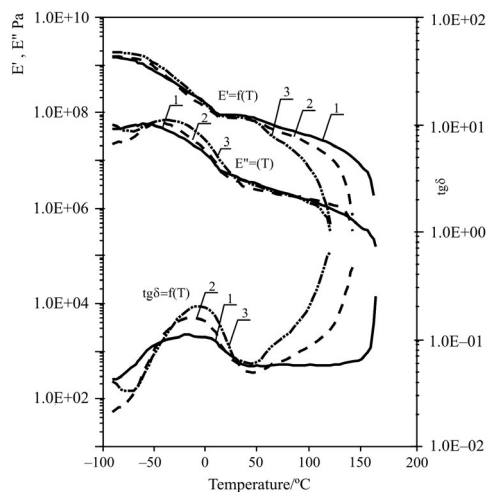


Fig. 3 The storage modulus E' , the loss modulus E'' , and the loss tangent ($\tan\delta$) of $-(\text{PBT-b-PTMO-b-PA12})_n-$ terpolymers vs. temperature

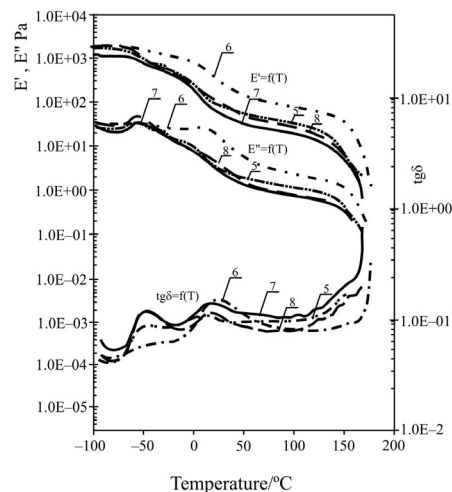


Fig. 4 The storage modulus E' , the loss modulus E'' , and the loss tangent ($\tan\delta$) of $-(\text{PBT-b-PTMO-b-PA12,10})_n-$ terpolymers vs. temperature

ues near the melting temperature is observed. The ‘plateau’ of the elastic state decreases with increasing length of ester block.

A parameter which characterizes the elastic properties is the recovery after elongation ε_{ps} . Good elastomers have $\varepsilon_{ps} \leq 10\%$ at elongation above 100%. This condition is fulfilled in the studied polymers by the samples of terpolymers $-(\text{PBT-b-PTMO-b-PA12})_n-$ with the number 2 and 3 for $DP_{\text{PBT}} < 7$. This allows to consider the terpolymers in which one of the block dissolves or is partly dissolved

(low-molecular fractions) in the two remaining blocks as better elastomers than those with the components which are mutually insoluble in each other.

Conclusions

The results presented in this paper allow to relate the structure and the properties of the three-component multiblock elastomers with the solubility of one component in the two remaining components of the system.

The terpolymers $-(\text{PBT-b-PTMO-b-PA12})_n-$ comprise the systems in which the PBT component with $DP_{\text{PBT}} = < 7$ dissolves both in the phase of PA12 blocks (hard) and the phase of PTMO blocks (soft). Hence, in this system the PBT block acts as a plasticizer, performs a role of compatibilizer at the interphase (probably increases a fraction of the intermediate phase), and simultaneously acts as a stabilizer of the structure [5–7, 9]. Thereby, it enables the nanoseparation and shapes the nanostructure. Terpolymers 1 ÷ 3 are transparent.

The terpolymers $-(\text{PBT-b-PTMO-b-PA12,10})_n-$ exhibit a slight solubility of the PBT block in the flexible block phase and a lack of solubility in the phase of the hard block (PA12,10). Thereby in such three-component system the PBT block acts stiffening (as a filler). A microseparation and a lack of nanostructures occur in these terpolymers. In the external appearance the terpolymers of this group are non-transparent.

For the investigated systems a small change in the chemical structure of the amide block significantly influences on the structure, the phase separation and the properties of terpolymers.

The above conclusions confirm a thesis that the block terpolymers possess good elastic properties in case when one of blocks partly dissolves in the phases formed from the remaining blocks.

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