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THERMAL PROPERTIES OF MULTIBLOCK THERMOPLASTIC ELASTOMERS WITH OLIGOAMIDE SOFT BLOCKS DERIVED FROM DIMERIZED FATTY ACID

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Two series of multiblock copolymers, poly(ester-*block*-amide)s (PEA) and poly(amide-*block*-amide)s (PAA), with the same type of oligoamide soft block were obtained. Oligoamide soft block was prepared from dimerized fatty acid and 1,6-hexamethylenediamine. Oligo(butylene terephthalate) (PBT) was used as oligoester hard block in the first series and oligolaurolactam (PA12) was oligoamide hard block in the second one. The thermal and mechanical properties of these copolymers have been investigated as functions of temperature and the hard/soft block ratio. DSC and DMTA revealed that the copolymers behaved as thermoplastic elastomers.

Keywords: *dimerized fatty acid, DMTA, DSC, multiblock copolymers, mutual miscibility of soft and hard blocks, phase structure, thermal properties*

Introduction

Thermoplastic elastomers (TPE) are very interesting group of structural polymers, and their characteristics are a subject of intensive studies undertaken by numerous research teams throughout the world [1–11].

The properties of thermoplastic elastomers are influenced by an appropriate phase structure and its thermal reproducibility in the heating-cooling cycles, functional mechanical features (e.g. a large reversible deformation) as well as the processability (the possibility of repeated melting and solidification) [1–4].

A macromolecule of the block elastomers consists of soft and hard blocks distributed alternately. These blocks differ considerably in the physical and chemical properties. The soft blocks are capable of the formation of matrix (soft phase). The hard blocks, as a result of aggregation form the domains of these blocks, constituting the hard phase [1–4].

The phase structure of multiblock thermoplastic elastomers can be investigated by thermal and mechanical analysis (e.g. DSC and DMTA technique). The glass transition temperature T_g and the melting temperature T_m of the respective phase in the heterogeneous systems (multiblock polymers, polymer blends) can be different from T_g and T_m of the same phase in the homogeneous material. The reasons of such phenomenon are mutual miscibility of units, the intermolecular and interfacial interaction [5–13].

Experimental

Materials

In present work, two series of multiblock thermoplastic elastomers were characterized:

- I series – poly(ester-*block*-amide)s (PEA), $–[PBT–b–PA6.36]_n–$
- II series – poly(amide-*block*-amide)s (PAA), $–[PA12–b–PA6.36]_n–$

The dependence of the thermal and mechanical properties on the mutual block miscibility and the molecular mass of soft block is presented.

Copolymers were obtained in the process of melt polycondensation. Syntheses of oligoamide soft block (PA6.36), oligoamide hard block (PA12) and PEA and PAA copolymers were previously described in details [5, 7, 11].

Characterisation of copolymers is summarised in Table 1.

Methods

The microcalorimetric measurements were recorded on a TA Instruments (DSC-910), apparatus. The samples were examined in a triple cycle (heating-cooling-heating) in the temperature range from –150 to +200°C. The heating and cooling rates were 10°C min^{-1}. The dynamic mechanical thermal analyses (DMTA) were performed on a DMTA Polymer Laboratories Mk-II apparatus in the temperature range from –120 to+200°C (heating rate 1°C min^{-1}) at

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Table 1 Characterisation of PEA and PAA multiblock copolymers

	Molecular mass of			Hard segment content W_h / %	Soft segment content W_s / %
	PBT	PA12	PA6.36		
I series PEA	4910	–	1224	80	20
	1880	–	1224	60	40
	1260	–	1224	50	50
	870	–	1224	40	60
	360	–	1224	20	80
II series PAA	–	2000	1224	80	20
	–	2000	1224	60	40
	–	2000	1224	50	50
	–	2000	1224	40	60
	–	2000	1224	20	80

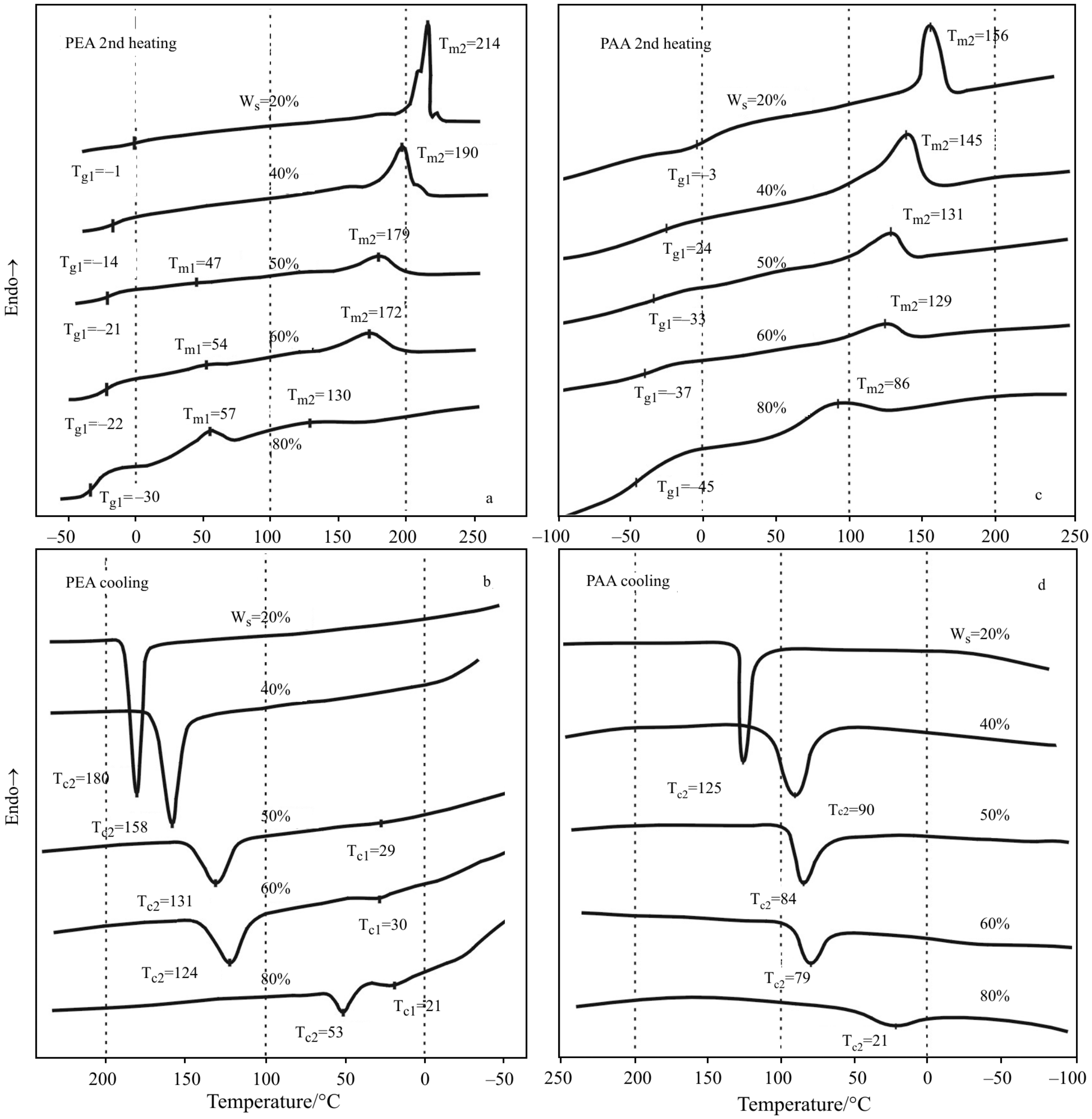

Fig. 1 DSC curves of cooling and 2nd heating of PEA (Fig. 1a, 1b) and PAA (Fig. 1c, 1d)

1 Hz. The storage modulus *E*', loss modulus *E*'', and loss tangent tan δ were determined.

Results and discussion

The DSC 2nd heating and cooling scans for poly(ester-*b*-amide)s (PEA) and poly(amide-*b*-amide)s (PAA) are shown in Fig. 1.

For the first series of PEA (Fig. 1a), the experimental results clearly show that the synthesised copolymers exhibit two characteristic transition temperatures; low-temperature glass transition attributed to the oligoamide soft block (T_{g1}) and high-temperature melting transition attributed to the oligoester hard block (T_{m2}). An additional transition is attributed to the melting transition of the oligoamide soft block (T_{m1}) associated with annealing endotherm [10]. A decrease in the oligoamide soft block concentration to 40 mass% causes that the melting point of the soft block is not detectable.

At the same time (Fig. 1b), can be observed well-defined crystallization temperatures of hard oligoester blocks (T_{c2}) and crystallization temperatures of soft oligoamide blocks (T_{c1}). The increasing values of T_{g1} testify to enhanced mutual miscibility between the soft block phase and the hard block phase in the investigated polymer systems.

The curves of poly(amide-*b*-amide)s (Fig. 1c) show the glass transitions (T_{g1}) in low temperature range from –45 to –3°C associated with the soft blocks concentration and attributed to the amorphous soft blocks phase. The endotherms on the curves in the range from 86 to 156°C, can be related to the melting transition of PA12 hard blocks domain (T_{m2}). The maxima decrease and flatten along with increasing content of the soft block. This phenomenon confirms the disturbance of PA12 crystalline structure by PA6.36 soft blocks.

The crystallization transition of hard blocks appears in all prepared polymers (Fig. 1d). For this series, the DSC curves do not indicate on a thermal effect related to melting and crystallization of soft oligoamide block. Therefore the soft oligoamide phase does not crystallize in presence of PA12. Oligoamide hard block is like a plasticizer of the amorphous phase in this arrangement. Probably low-molecular fractions of hard and soft blocks dissolve each other, which disturbs the crystalline structure and causes a decrease of T_{m2} hard phase.

In order to better illustrate the differences in both series, a comparison of melting and crystallization temperatures is presented on Fig. 2.

Figures 3 and 4 show the results of dynamic mechanical thermal analysis. The relaxation behaviour of all samples was studied by DMTA, measurements of the storage modulus *E*', the loss modulus *E*'' and the loss tangent (tan δ) as functions of the temperature.

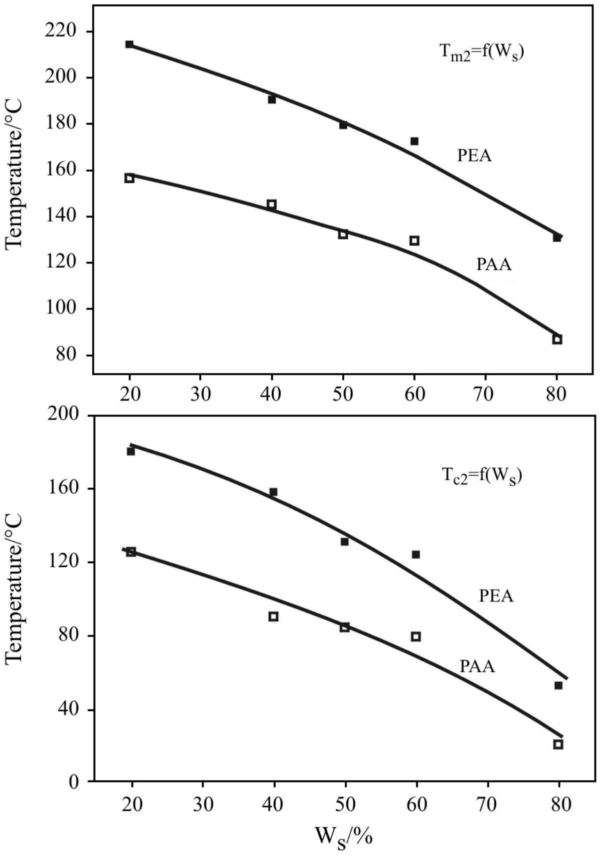

Fig. 2 Melting (T_{m2}=f(W_s)) and crystallization (T_{c2}=f(W_s)) temperatures of hard block *vs.* soft block content

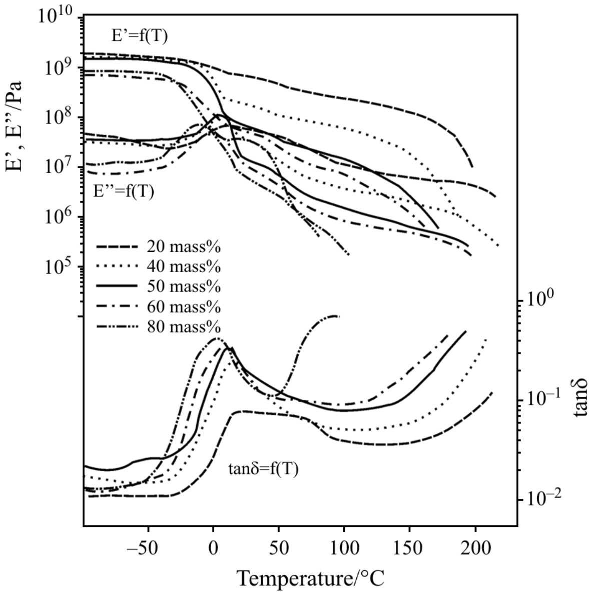

Fig. 3 Storage modulus (*E*'), loss modulus (*E*'') and loss tangent (tan δ) *vs*. temperature for PEA varying in the soft blocks content

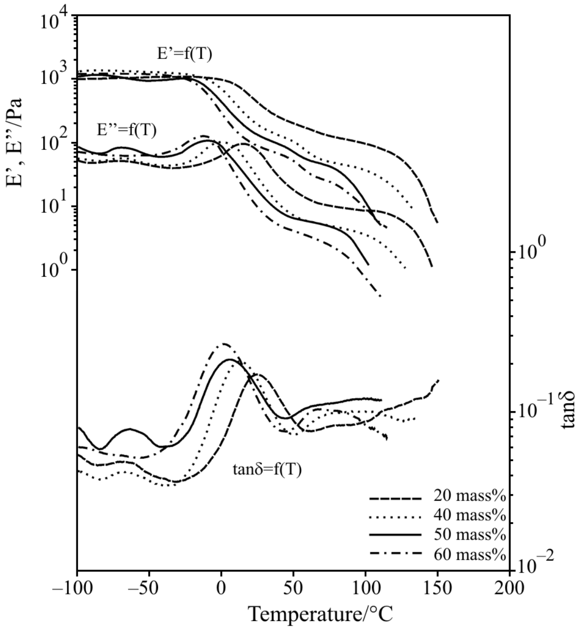

Fig. 4 Storage modulus (*E*'), loss modulus (*E*'') and loss tangent (tan δ) *vs.* temperature for PAA varying in the soft blocks content

At low temperatures the storage modulus *E*' of the PEA is typical for polymers in the glassy state (Fig. 3). As the temperature is increased, *E*' decreases slightly during the transition from the glassy to the rubber-like state. In a high-temperature region, a distinct drop of *E*' can be related to the transition from the high-elasticity state to the plastic state. The drop of *E*' is tentatively assigned to the movement of relatively short crystalline stems and melting of hard blocks crystallite.

The loss modulus *E*'' and the loss tangent (tan δ) for copolymers show only one maximum at low temperatures attributed to the high homogeneity with the amorphous oligoamide phase (relaxation transition associated with a low-temperature glass transition). Broadening and shifting of tan δ maximum with increasing temperature for PEA of lower soft block concentration is ascribed to the presence of PBT sequences in the amorphous phase of soft blocks.

The DMTA results for the second series (PAA) are presented in Fig. 4. The loss modulus shows a wide maximum *E*'' that corresponds to the glass transition of the amorphous phase. When the concentrations of the oligoamide soft block decrease, the maximum flattens and shifts toward higher temperatures, from –25 to +10°C. The tan δ curves show that a decreased soft block content in polymers causes an increase in tan δ in the range from –20 to+40°C and a shift of the maximum temperature toward higher temperatures. The values of storage modulus *E*' show rapid decreases near T_g and a wide 'plateau' of the elastic state is observed. After that, a sharp decrease the *E*' values near the melting temperature is observed. The 'plateau' of the elastic state decreases with increasing length of oligoamide soft block.

The glass transition temperatures observed by DSC method (T_{g1}) and the relaxation processes observed by DMTA method (E''max, tan δ max) are compared in Fig. 5. In general, the glass transition temperature for both series of the copolymers decreases significantly as the soft blocks concentration is increased. This phenomenon indicates a mutual miscibility of the blocks and an increase of the interphase. At the same time, copolymers from the PEA series exhibit higher glass transition temperatures than those from the PAA series.

A similar behaviour is observed for the loss modulus *E*'' and the loss tangent (tan δ) maximum at-

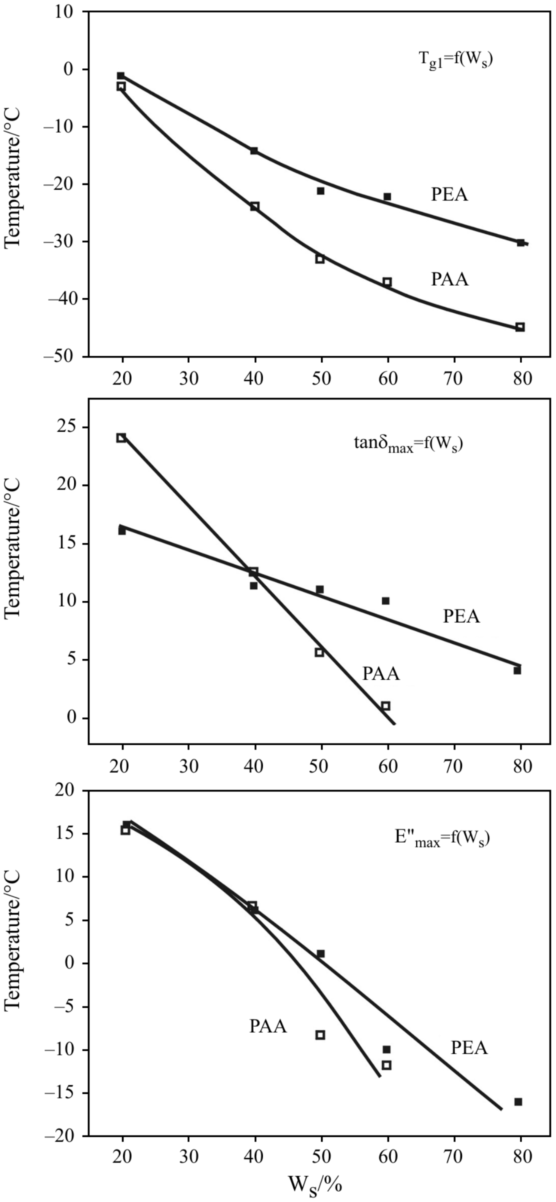

Fig. 5 Comparison of glass transition temperatures obtained from DSC as T_{g1} and from DMTA as tan δ_{max} or E''_{max}

tributable to the soft oligoamide phase. The temperatures of relaxation transition decrease with increasing the soft block concentration. This effect testifies about the interaction between the amorphous hard phase and amorphous soft phase.

Conclusions

The multiphase structure of investigated copolymers was confirmed by DSC and DMTA method of measurements (series exhibit two characteristic transitions: glass of soft phase and melting of hard phase).

Both series of copolymers show temperatures of the glass transition (T_{g1}) in low-temperature range due to the amorphous soft phase created by due soft oligoamide blocks and temperatures of melting transition (T_{m2}) in the high temperature range attributed to crystalline hard phase created by hard blocks, oligoester PBT for PEA series and oligoamide PA12 for PAA series. Therefore the copolymers are thermoplastic elastomers with crystallisable hard block resulting in pseudocrosslinking.

The glass transition of poly(amide-*block*-amide)s is shifted to a low temperature region. Melting point temperatures for PEA hard block phase are higher than for PAA, because of higher melting temperature of PBT.

In the case of poly(amide-*block*-amide)s it can be observed that a mutual miscibility causes a change of microstructure of hard and soft blocks because of the similar chemical structure of both blocks (comparable Hildebrand’s solubility parameters). For poly(ester-*block*-amide)s, when the blocks have another chemical structure, the mutual miscibility is disturbed. It is testified by endotherms (T_{m1}) on DSC curves for PEA with a higher concentration of the soft blocks. These endotherms are result of dissipation of aggregates created in the amorphous phase of amide block. This phenomenon is not observed for PAA, the complete dispersion of amorphous oligoamide soft blocks phases in amorphous oligoamide hard blocks is occurred.

The DSC and DMTA results confirmed thermoplastic elastomer behaviour in the synthesized poly(ester-*block*-amide)s and poly(amide-block-amide)s.

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