

THERMAL, MECHANICAL AND DIELECTRIC PROPERTIES OF SOME NEW POLY(AMIDE-*block*-ESTER) THERMOPLASTIC ELASTOMERS

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Received: November 12, 2005

Abstract. Four kinds of poly(amide-*block*-ester)s (PAE) with the same hard blocks of PBT and different soft blocks of selected diamines and dimerized fatty acid were synthesized and results of their investigations are presented. The following experimental techniques were used: differential scanning calorimetry (DSC), dynamic mechanical thermoanalysis (DMTA), and dielectric spectroscopy (DETA). An influence of the particular diamines onto phase structure and physical properties of the investigated PAE is discussed on the basis of the results obtained.

1. INTRODUCTION

Poly(amide-*block*-ester)s (PAE) belong to a group of multiblock copolymers which consist of blocks with different physical properties creating soft and hard phases. If the blocks are immiscible and the hard one exhibit a tendency toward crystallization, the material combines rubber-like properties with the easy processability of thermoplastics and is called thermoplastic elastomer [1-3].

In the presented work, four kinds of poly(amide-*block*-ester)s with the same hard blocks of poly(butylene terephthalate) (PBT) and different soft blocks (polyamides) of selected diamines combined with dimerized fatty acid (DFA) were synthesized and some experimental investigations were performed. The aim of the experiment was to find :

- i. how particular diamines modify the phase structure and physical properties of the copolymers having the same hard phase, and
- ii. which a factor acts most efficiently onto their relaxation properties – either mechanical or dielectric ones.

2. EXPERIMENTAL

2.1. Materials

The following materials were used for the synthesis of multiblock copolymers: dimethyl terephthalate (DMT, ZWCh Elana, Poland), 1,4-butanediol (1,4-BD, BASF), dimerized fatty acid (DFA) Pripol 1009, average molecular weight 575 g·mol⁻¹, (C36)

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(Uniqema, Netherlands), diamines: 1,6-hexamethylenediamine (HMDA), 1,4-cyclohexanediamine (CHMDA) (Aldrich Chemie, Germany) and bis-(3-aminopropyl)-polytetrahydrofuran with molecular weight 750 $\text{g}\cdot\text{mol}^{-1}$ (EA750) and 2100 $\text{g}\cdot\text{mol}^{-1}$ (EA2100) (BASF, Germany).

2.2. Synthesis

Copolymers were obtained by polycondensation in the melt. This was three-step process: (1) oligoamide preparation, (2) transesterification and (3) polycondensation reaction.

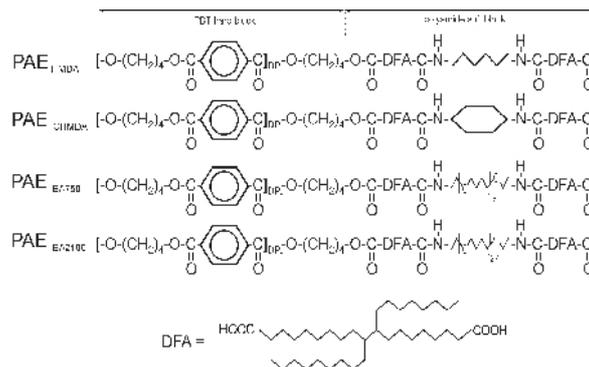
1) The oligoamide preparation was carried out using diamine and dimerized fatty acid (DFA). Four type of diamines were used to this reaction: 1,6-hexamethylenediamine (HMDA), 1,4-cyclohexanediamine (CHMDA), and bis-(3-aminopropyl)-polytetrahydrofurans (EA750 and EA2100) – to yield a series of oligoamides. The reaction started at 100 °C and finished at 220 °C after two hours, when $-\text{NH}_2$ groups became not detectable. The reaction mixture was heated up to 240 °C after the ending of the oligoamide preparation.

2) The transesterification reaction between dimethyl terephthalate (DMT) and 1,4-butanediol (1,4-BD) with molar ratio 1:2 was carried out in the presence of magnesium-titanate catalyst at intensive stirring and programmed temperature raise from 150 to 210 °C with a heating rate of 1.5 °C/min. The reaction finished when more than 95% of the stoichiometric amount of methanol had evaporated.

3) At the third stage, product of transesterification together with the catalyst was added. The polycondensation reaction was carried out at 255-260 °C at the pressure of $\sim 0,4$ hPa. The process was considered to be complete when the highest melt viscosity of the polymer was obtained. The reaction mass was extruded by means of compressed nitrogen into water and then granulated.

In this way, four kinds of the multiblock poly(amide-*block*-ester) elastomers comprising hard blocks of poly(butylene terephthalate) (PBT) and soft segments of different polyamide were synthesized and analysed. The PEA and diamines as well as the correspondent formulae are listed below:

- PAE_{HMDA} - hexamethylenediamine – HMDA, aliphatic
- PAE_{CHMDA} - cyclohexamethylenediamine – CHMDA, cyclic
- PAE_{EA750} - oligoetheroamine with molecular mass 750
- PAE_{EA2100} - oligoetheroamine with molecular mass 2100.



Each kind of these copolymers contains a number of samples varying with the soft segment/hard segment (W_s/W_h) ratio. They are listed in Table 1. together with some characteristic temperatures. More details concerning this synthesis has been published previously [4].

2.3. Measurements

Differential scanning calorimetry (DSC)- measurements in *heating-cooling-heating* cycle were carried out by a Perkin-Elmer DSC-2 set at heating and cooling rate of 10 °C/min. Dynamic thermo-mechanical analysis (DMTA) was performed using a DMTA Polymer Laboratories Mk II apparatus at 1 Hz, within the temperatures range from -110 °C to melting point, with a heating rate of 1 °C/min. The dielectric spectra (DETA) were collected using a Hewlett-Packard HP-4192A Impedance Analyser and a nitrogen temperature control system, within the frequency band from 0.1 to 1000 kHz. Details of the measurement technique have been described earlier [5].

3. RESULTS AND DISCUSSION

3.1. Results of DSC study

Selected plots of DSC for all kinds of the PAE with the W_s value of 50 wt.% are presented in Fig. 1. An essential difference between plots is the result of their specific chemical compositions. The glass transition temperatures are marked on the curves as T_{g1} ; the responsible steps could be seen at higher magnification of the plot scale. Two melting temperatures: T_{m1} (visible only in two PAEs) which corresponds to melting of the soft, amorphous phase melting, and T_{m2} – to the hard, mostly crystalline phase melting. The values of these temperatures for all PAE are collected in Table 1.

Table 1. Soft and hard segments contents and some characteristic temperatures of the samples (W_s , W_h – soft and hard segments contents, in wt.%; T_{g1} – glass transition temperature of the soft phase; T_{m1} and T_{m2} – melting temperatures of the soft and hard phases, respectively; T_{c1} and T_{c2} – temperatures of crystallization (if appear).

Polymer symbol	W_s [%]	W_h [%]	T_{g1} [°C]	T_{m1} [°C]	T_{c1} [°C]	T_{m2} [°C]	T_{c2} [°C]
PBT	0	100	-	-	-	225	193
PAE _{HMDA}	20	80	-1	-	-	214	180
	40	60	-14	-	-	190	158
	50	50	-21	47	29	179	131
	60	40	-21	54	30	172	124
	80	20	-29	57	21	130	53
PAE _{CHMDA}	20	80	~0	-	-	218	182
	40	60	-7,5	-	-	203	159
	50	50	-14	-	-	193	137
	60	40	-15	-	-	174	150
	80	20	-32	~130	~109	152	149
PAE _{EA750}	20	80	-48	-	-	219	187
	40	60	-41	-	-	208	171
	50	50	-45	-	-	195	158
	60	40	-47	-	-	183	142
	80	20	-54	-	-	130	52
PAE _{EA2100}	20	80	-81	15	-20	222	190
	40	60	-76	14	-25	219	186
	50	50	-73	11	-31	215	178
	60	40	-73	11	-30	214	175
	80	20	-74	13	-42	160	109

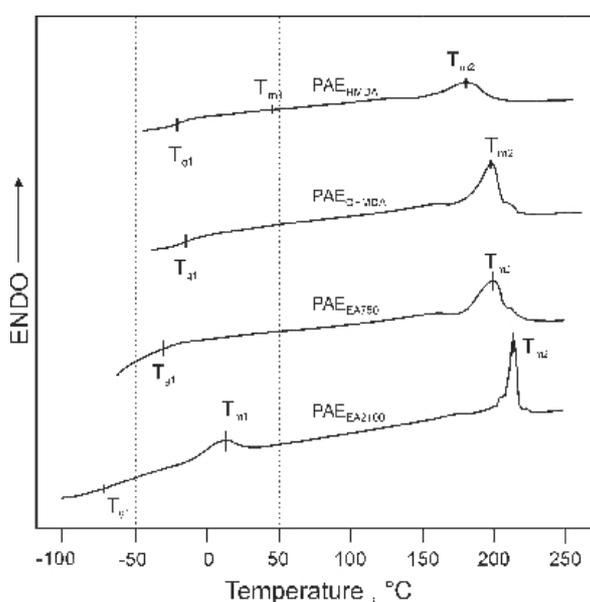


Fig. 1. Selected DSC-plots for different PAE with the soft segment content $W_s = 50$ wt.%.

3.2. Results of DMTA study

The results of the mechanical thermoanalysis are shown in Figs. 2a-2d. Generally, the elastic properties of these PAE change with temperature in a way typical for thermoplastic elastomers [6]. The storage elastic modulus E' vs. temperature T exhibit a bending point at the glass transition. At almost the same temperature, $\tan\delta$ reach maximal value and the peak became more sharp for higher soft phase content W_s . The last fact means that the amorphous phase is more homogeneous one [2].

For two of PAEs : PAE_(CHMDA) and PAE_(EA2100), a second peak of $\tan\delta$ appears in higher temperatures (Fig. 2b and 2d); such a result suggests a new phase appearance in these materials.

3.3. Results of DETA study

The dielectric spectroscopy method used in this work consists in the measurements of the com-

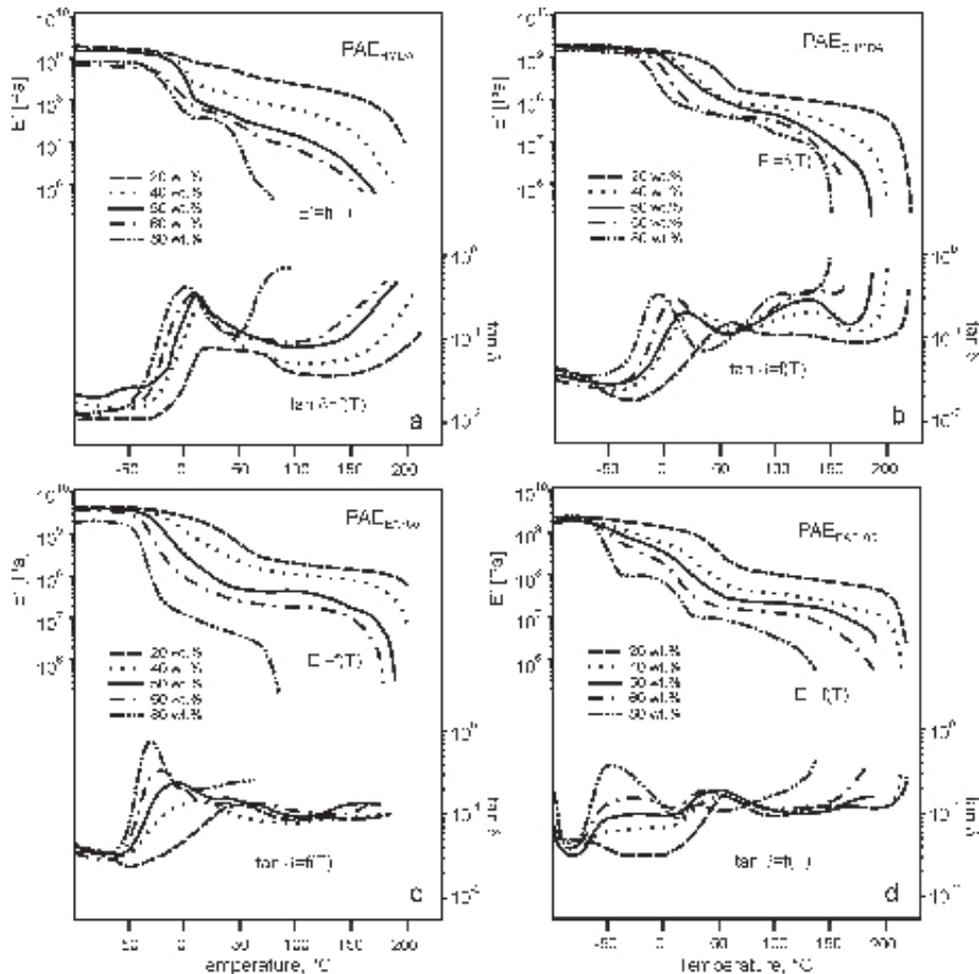


Fig. 2. DMTA- plots: storage elastic modul E' and tangent of loss $\tan\delta = E''/E'$ at 1 Hz of frequency for all groups of the PAE; sample symbols as in Table 1.

plex dielectric permittivity $\epsilon^* = \epsilon' - j\epsilon''$ as a function of frequency and temperature. A selected plots of dielectric loss ϵ'' versus temperature for the PAE_(EA750) with different W_s - contents are presented in Figs. 3a, 3b, and 3c. A strong influence of the W_s -value on maximal values of ϵ'' can be observed here, but temperature shift of the peaks is rather small. The last fact corresponds with the glass transition temperature changes for this kind of copolymer, see Table 1. Figs. 4a and 4b demonstrate dielectric spectra of the PAE_(EA750) with $W_s = 50$ wt.%; the peak shift at different frequencies can be described by a Vogel-Fulcher equation [7].

3.4. Discussion

To consider the results obtained, let us subdivide the PAEs into two pairs: 1) PAE_{HMDA} and PAE_{CHMDA}, 2) PAE_{EA750} and PAE_{EA2100}.

The first two copolymers contain hexamethylenediamines with the same number of carbon atoms, but in different conformation: one – aliphatic and other – cyclic. The aliphatic block gives more soft and flexible material having lower T_{g1} and T_{m2} values. The cyclic – in contrast – more rigid in room temperature and with higher T_{g1} and T_{m2} . The presence of hydrogen bonds in the CHMDA leads to a cross-linking of the soft blocks providing phase separation and, in as a consequence, stiff of the material. A presence of the T_{m1} and a second peak in DMTA- plots (Fig. 2a) indicates that a third phase (inter-phase) appears here at higher temperature. Dielectric spectra (an example in Fig. 5.) of these two PAEs are similar and show two relaxation processes: the $\tilde{\alpha}$ one at about +20 °C assigned to the glass transition T_{g1} and the β process in the temperature range within -100 and -50 °C, which is associated with local motion attached to both the soft and the hard segments. The temperature region of

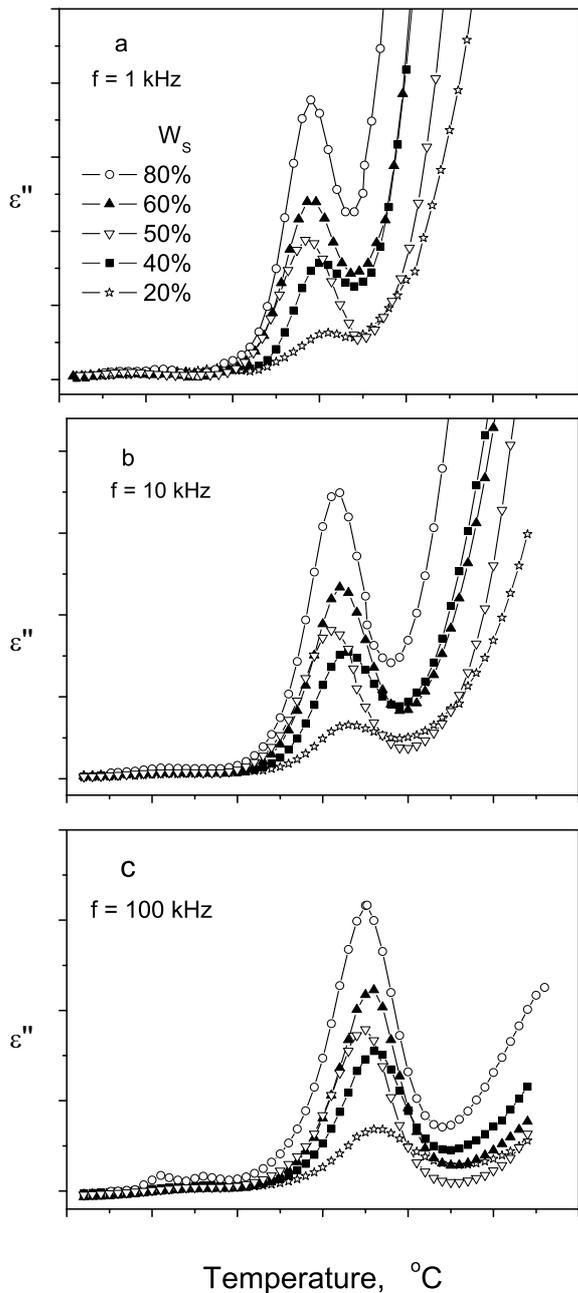


Fig. 3. Dielectric loss ϵ'' as a function of temperature at selected frequencies for the PAE_(EA750) copolymers with different soft phase contents W_s as printed in the Figure (in wt.%).

the $\tilde{\alpha}$ process shifts down with W_s increase, while the temperature of the $\tilde{\beta}$ process is weak dependent on W_s .

The second pair of the copolymers contains the same etheroamides, but with different molecular mass (i.e. the soft blocks' length). This fact is very

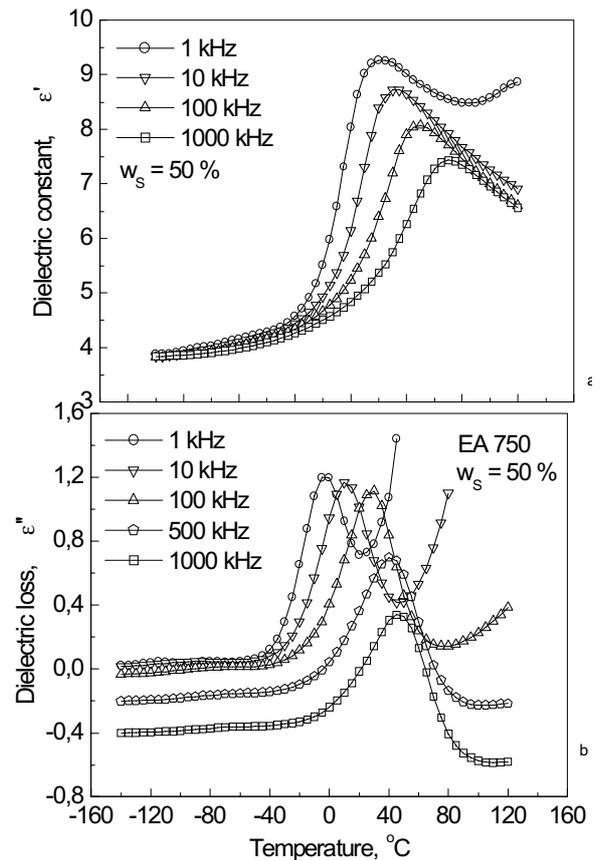


Fig. 4. Dielectric spectra of the PAE_(EA750) sample with $W_s = 50$ wt%.

essential for physical properties of these two copolymers. As one can see in Fig.1, the T_{g1} of PAE_{EA2100} lies very low, T_{m2} is very high, and T_{m1} is clearly marked for $W_s > 50$ wt.%. At the same time, the DMTA $\tan\delta$ plot (Fig. 2d) exhibits a second peak at $T = 50$ °C, while the E' vs. T –dependence is the two-step-like for high W_s values. These phenomena can be caused by crystallization process in the soft phase which contains very long blocks of etheroamide 2100. In contrast to this, all spectra for the PAE_{EA750} are simple and typical for many block copolymers [3]. The $\tilde{\beta}$ relaxation is well expressed in the PAE_{EA2100} and very poor, difficult to observe in PAE_{EA750}.

For a better illustration, one representative curve of the ϵ'' vs. T for each PAE (with the same $W_s = 50$ wt.% and the same frequency of 10 kHz) is presented in Fig. 5. The region of abnormal increasing of the ϵ'' -value, signed as MWS (Maxwell-Wagner-Sillars polarization) is caused by relaxation of charge carriers which are collected at the phase borders.

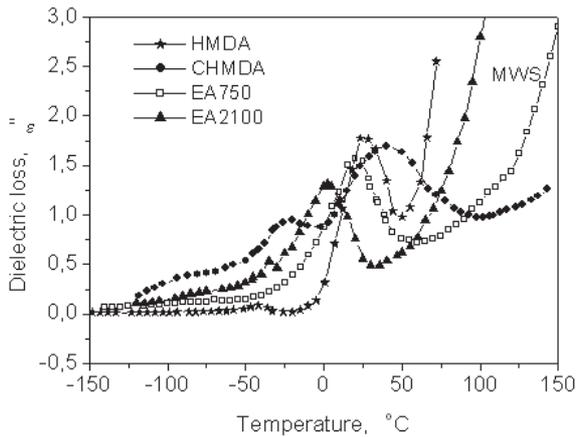


Fig. 5. Fig. 5. The $\epsilon''(T)$ - plots for the representative PAEs with the W_s - value of 50 wt.%. The MWS sign a region of the Maxwell-Wagner-Sillars polarization.

A presence of such an effect indicates the multi-phase structure of the polymer [8].

4. CONCLUSIONS

All the investigated multiblock copolymers exhibit properties of thermoplastic elastomers: a multi-phase structure and a long plateau of the elastic modulus E' within glass-to-melting temperatures.

There is a deep influence of the oligoamide type and its quantity (W_s) onto physical properties of the materials. This ability allows to design special materials for particular application, e.g. typical elastomeric details.

A new phase formation at high temperature and W_s observed in some samples can be explained as the result of the mutual solvation of the soft and hard blocks. Such phenomena were previously observed in poly(ether-ester) copolymers [3].

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