ELSEVIER

Thermochimica Acta 391 (2002) 271–277

thermochimica acta

www.elsevier.com/locate/tca

Melting of polyether block amide (Pebax): the effect of stretching

E.V. Konyukhova[a,*], A.I. Buzin[b], Yu.K. Godovsky[a]

[a]Karpov Institute of Physical Chemistry, Vorontzovo Pole 10, 103064 Moscow, Russia
[b]Enikolopov Institute of Synthetic Polymer Materials, ul. Profsoyuznaya 70, 117393 Moscow, Russia

Received 13 September 2001; received in revised form 12 November 2001; accepted 14 November 2001

Abstract

We report results of a DSC study of the influence of stretching on the processes of melting of blocks in copolyetheramide based on polytetramethyleneoxyde and polyamide-12 (PA-12). It has been found that uniaxial stretching of the film brings significant changes to the PTMO block and has almost no influence on the thermal characteristics of PA-12. The melting of PTMO acquires multiplet character. The melting peaks are shifted to the region of higher temperatures and their areas are redistributed with an increase in the degree of deformation. It has been found the degree of crystallinity of PTMO increases under stress.

Keywords: Thermoplastic elastomers; Polytetramethyleneoxide; Polyamide-12; Melting; Stretching

1. Introduction

Pebax polyether block amides are a new family of engineering thermoplastic elastomers [1–3]. Their general structure is $(A–B)_n$. They consist of linear and regular chains of hard polyamide segments having molecular weight between 600 and 4000, and soft polyether segments of molecular weight between 600 and 2000. The soft and hard segments are relatively short blocks. In the temperature region of exploitation, the soft segment component is viscous or rubbery while the hard segment is glassy or semicrystalline. The ratio of the polyamide and polyether blocks controls the hardness. The length of the polyamide block influences the melting point of the polymer. Since polyamide and polyether segments are not miscible, the polyether block amides have a biphase structure [1,4–6]. Factors that control the degree of microphase separation include copolymer composition, block length and crystallizability of either segment. The Pebax with long PA block ($M_w > 2000$) has a more disordered amorphous PA phase than the Pebax with short PA block ($M_w < 2000$).

Several articles were published describing the structure of these materials [4,7,8]. However, the most of the literature has paid not enough attention to the interesting property of these materials [9–11]. The unique properties of this copolymer are directly related to its two-phase microstructure with the hard domain acting as a reinforcing filler and as a thermally reversible cross-link [9,12,13]. The presence of three-dimensional hydrogen bonding within the hard domain usually leads to a strong hard-domain cohesion.

It is a matter of special interest to study the changes in microphase structure that occur in the elastomeric material during mechanical deformation. The knowledge of the microphase behavior and strain-induced chain alignment is essential for better understanding

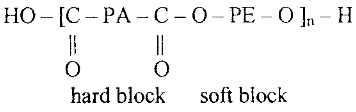
---

[*] Corresponding author.
E-mail address: kon@cc.nifhi.ac.ru (E.V. Konyukhova).

of the macroscopic properties of these materials. It is well known that stretched rubber networks can crystallize when a suitable chain microstructure is present [14–19]. Crystallization of a stretched polymer network may be initiated by two different mechanisms: strain-induced crystallization and temperature-induced crystallization. The present work reports results of the study of the induced crystallization phenomenon in polyether block amide copolymer. Various DSC experiments have been performed to investigate the changes of the thermal characteristics of PA–PTMO elastomer upon stretching.

2. Experimental

The copolyetheramide used in this study was a commercial film Pebax™ 2533 based on polyamide-12 (PA-12) ($M_w = 530$, 22 wt.%) and polytetramethyleneoxide (PTMO) ($M_w = 2000$, 78 wt.%), a product of Elf Atochem (Philadelphia, PA). The general formula of this copolymer is [1]:



$$\mathrm{HO-[\underset{\overset{\|}{O}}{C}-PA-\underset{\overset{\|}{O}}{C}-O-PE-O]_n-H}$$

The thermal characterization of the material was carried out in a Mettler TA 3000 DSC in a flow of He. All the heating scans were done from −140 to 250 °C at 20 °C/min. Sample weights were 10–30 mg. The temperature and the heat-flow rate were initially calibrated using the onset of the melting peak and the heat of fusion of indium (156.6 °C and 28.45 J/g).

To study the effect of mechanical deformation the experiments were performed on the three kinds of the samples: as-received films (mode 1); stretched films allowed to relax prior to DSC experiments (mode 2); stretched films under tension with constant strain (mode 3). The samples are characterized in Table 1.

The films first were stretched to a certain strain using Instron tensile testing apparatus at room temperature, with a speed of 10 mm/min (Fig. 1). Then they were taken out of the machine and relaxed to a stress of zero. Since the films deform plastically in the range of loads studied, incomplete elastic recovery was observed.

Table 1
Stretching characteristics of the samples

Films	Mode	Tensile strain (%)	Residual strain (%)
As-received (**P_0**)	1	0	0
Stretched (**P_1**)	2	100	5
Stretched (**P_2**)	2	200	20
Stretched (**P_3**)	2	300	100
Stretched (**P_4**)	2	400	110
Stretched (**P_5**)	2	500	230
Stretched (**P_6**)	2	600	370
Stretched (**P_7**)	3	600	600

3. Results

3.1. As-received film $\mathbf{P_0}$ (mode 1)

Fig. 2 shows DSC traces for heating of as-received and quenched samples. The transition temperatures and other thermal characteristics are summarized in Table 2. The heat of fusion of PTMO and PA blocks was normalized on their content in a block copolymer. The extent of the microphase separation was evaluated by comparison of the transition temperatures and the heat of fusion in the samples studied and in the corresponding homopolymers.

Heating of the as-received sample **P_0** reveals the following transitions:

1. the glass transition (T_g) in the low temperature region,
2. three endothermic melting peaks: T_{m1} in the range −50 to 10 °C with a maximum at about 0 °C, T_{m2} in the range 10–80 °C with a maximum at about 50 °C and T_{m3} in the range 80–150 °C with maximum at about 135 °C.

The traces of the quenched samples differ from the initial samples only by the absence of the peak T_{m2}. Two exothermic peaks resulting from the crystallization of PA-12 ($T = 64$ °C, $Q = 21.3$ J/g) and PTMO ($T = -17$ °C, $Q = 20.0$ J/g) are observed during cooling of the samples heated to 250 °C.

The glass transition temperature ($T_{g\ \mathrm{PTMO}}$) is not changed with the rate of cooling, appearing at −86 to −83 °C. It is in good agreement with the value of pure PTMO (−84 °C [20]). The absence of the glass transition of PA block in our traces may be attributed to it low content in the sample.

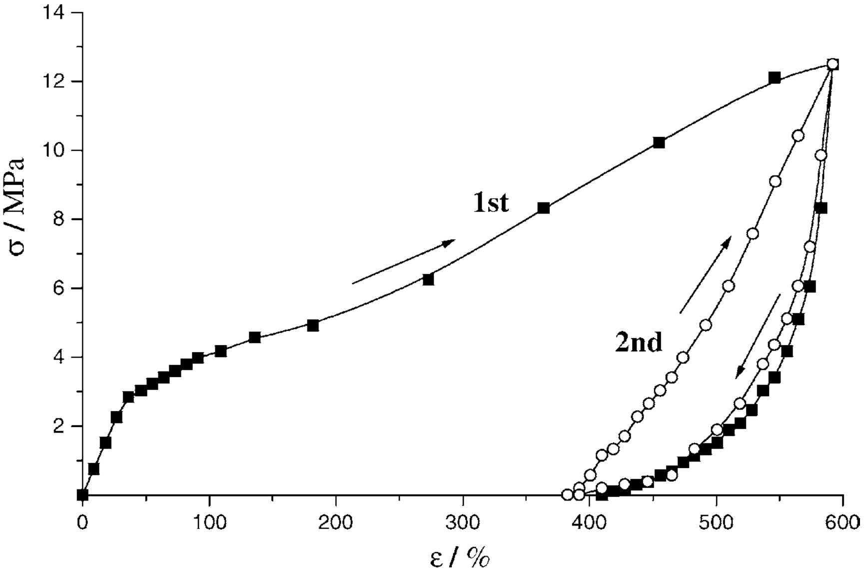


Fig. 1. The stress–strain curves of as-received (1st) and stretched (2nd) samples.

Equality of T_g of PTMO blocks to T_g of the homopolymer can be used as a proof of incompatibility of the components in the melt. Moreover, biphase structure of Pebax^{TM} 2533 was confirmed by the studies of other authors [1,4,5,10,12].

Let us consider now a melting range. It is obvious that the peak T_{m1} corresponds to the melting of PTMO. It should be noted the absence of the cold crystallization of PTMO, which is observed on heating traces of partly compatible microheterogeneous systems PBT–PTMO ($M_{w\,PTMO} = 2000$, 60 wt.%) [19] and polyurethane elastomers ($M_{w\,PTMO} = 2000$, 80 wt.%) [16]. This fact can be considered as indirect proof of incompatibility of the blocks in Pebax^{TM}. The

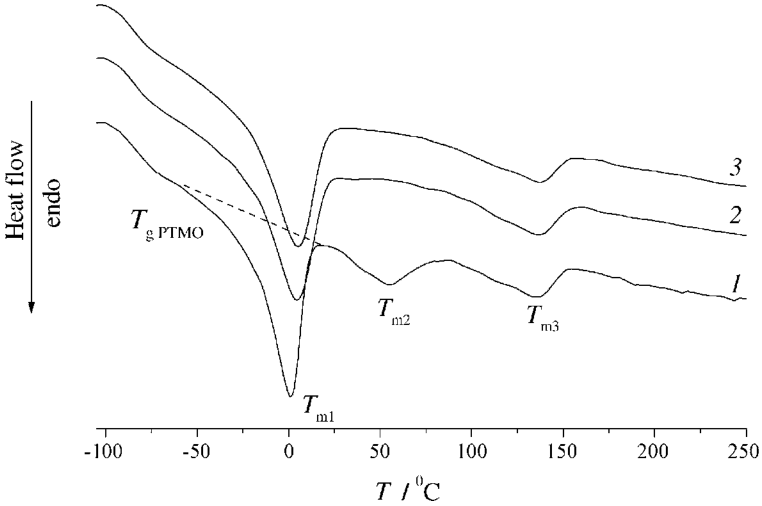


Fig. 2. DSC traces of as-received film: 1—first heating, 2—heating of the quenched sample, 3—heating after cooling with 10 °C/min. The dashed line marked the baseline for determination of the heat of fusion (as example).

Table 2
Thermal characterization of as-received sample $\mathbf{P}_0$ and homopolymers

Sample	T_g (°C)	$T_{m\,PTMO}$ (°C), T_{m1}	$Q_{m\,PTMO}$ (J/g), Q_{m1}	$T_{m\,PA}$ (°C)		$Q_{m\,PA}$ (J/g)	
				T_{m2}	T_{m3}	Q_{m2}	Q_{m3}
$\mathbf{P}_0$	−83	0	20.1	53	136	10.5	19.5
$\mathbf{P}_0$ quenched	−86	3	21.0	–	136	–	20.4
$\mathbf{P}_0$ after cooling with 10 °C/min	−85	3	23.1	–	135	–	18.0
PTMO-2000	−87	36	51.6	–	–		
PA-12	37	–	–	179	179		43.0

temperature, heat and temperature range of melting of PTMO block is independent of cooling rate.

Identification of the peak T_{m2} is not so easy. It can be attributed both to the melting of PTMO, and the melting of PA, because $T_{g\,PA} = 41$ °C, and the peak is observed at 53 °C. However, we do not have enough reasons to attribute it to the melting of PTMO. Consecutive annealing during 30 min at peak maximum temperature shifts it by about 10 °C to the higher temperatures, which is much higher than equilibrium melting temperature of PTMO ($T_m^\circ = 57$ °C [20]). Quenched samples do not exhibit this peak at all. It is known [19,21], that similar transitions were observed in many segmented systems: polyurethanes, polyether polyurethaneureas, elastomers based on polyethers and polyesters. Typically they are linked with processes occurring in the hard blocks. The most probable reason for such endotherms is destruction or reorganization of the ordered structures formed by hard segments in the course of annealing. Therefore, from our viewpoint, it is more correct to attribute this peak to the melting of PA.

Peak T_{m3} corresponds to the melting of the hard PA block. The temperature, heat and temperature range of melting of PA block is independent of the cooling rate.

Melting temperatures and heats of fusion of PTMO and PA blocks are lower than corresponding homopolymers. This is probably connected with formation of more defect crystalline structures than in homopolymers because of low MW of the blocks.

Only two melting peaks T_{m1} and T_{m3} are observed on the heating trace after quenching of the melt or its slow cooling independent of how much times this procedure was repeated. Thus, on heating of as-received film, the melting of PTMO block is observed as one peak T_{m1}, and melting of PA block as two peaks T_{m2} and T_{m3}.

3.2. *Stretched films* $\mathbf{P}_{1-6}$ *(mode 2)*

Fig. 3 shows heating traces for the samples $\mathbf{P}_{1-6}$. Characteristics of their transitions are summarized in Tables 3 and 4. It can be seen that even at low deformations of the films (sample $\mathbf{P}_1$: $\varepsilon = 100\%$, $\varepsilon_{res} = 5\%$) in addition to transitions observed in $\mathbf{P}_0$ (T_g in the low temperature region, the melting peak of PTMO T_{m1} and two peaks resulting from the melting of PA-12 (T_{m2} and T_{m3})), one more endothermic peak T_{m4} occur in the region of 30 °C.

Glass transition temperatures of PTMO blocks (Table 3) are independent of the degree of stretching and are the same as in the sample $\mathbf{P}_0$. The same can be noted about temperature, heat and temperature range of melting of PA block (peak T_{m3}) (Table 4). The peak T_{m2} is noticeable only in the samples $\mathbf{P}_{1-2}$, and its parameters stay constant. This peak is observed as a shoulder of the peak T_{m4} in the samples $\mathbf{P}_{3-4}$. It is impossible to determine its maximum temperature and area.

Melting temperature of PTMO block (peak T_{m1}) does not change with an increase in the degree of deformation, but its heat decreases by a factor of 2.5. The temperature of the peak T_{m4} is virtually independent on the degree of stretching of the original film, but its heat increases significantly.

The analysis of the dynamics of changes observed in the peaks T_{m1} and T_{m4} allows to conclude that they both correspond to melting of PTMO crystallites. At the same time, the total heat of fusion of both peaks of the samples $\mathbf{P}_{1-6}$ does not exceed the heat of fusion of PTMO block in the sample $\mathbf{P}_0$ and is almost unchanged with increasing deformation. It can be supposed that these peaks correspond to melting of PTMO crystals with different morphology.

Thus, uniaxial stretching of the as-received film makes almost no any changes in the region of glass

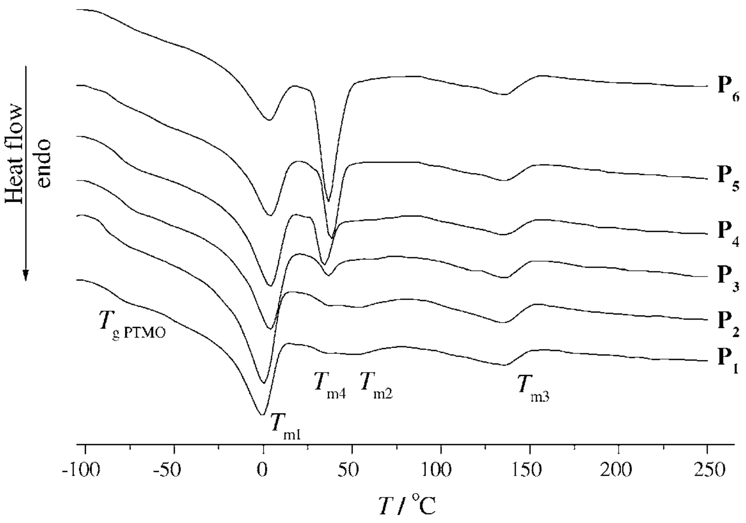


Fig. 3. DSC traces of heating of the stretched samples $\mathbf{P_{1-6}}$.

Table 3
Thermal characterization of PTMO block in as-received and stretched samples

Sample	$T_{g\ PTMO}$ (°C)	$T_{m\ PTMO}$ (°C)			$Q_{m\ PTMO}$ (J/g)			Q_{Σ} (J/g)
		T_{m1}	T_{m4}	T_{m5}	Q_{m1}	Q_{m4}	Q_{m5}	
$\mathbf{P_0}$	−83	0	–	–	20.1	–	–	20.1
$\mathbf{P_1}$	−85	1.0	33.8	–	19.7	1.5	–	21.2
$\mathbf{P_2}$	−84	1.9	35.8	–	19.2	1.7	–	20.9
$\mathbf{P_3}$	−85	2.4	35.8	–	16.9	2.7	–	19.6
$\mathbf{P_4}$	−85	3.0	36.1	–	15.5	5.1	–	20.6
$\mathbf{P_5}$	−84	3.1	37.4	–	12.1	7.1	–	19.2
$\mathbf{P_6}$	−82	3.6	34.6	–	8.2	11.2	–	19.4
$\mathbf{P_7}$	−69	8.8	58.1	83.8	7.4	12.8	2.6	22.6

transition of PTMO and melting of PA, but influences significantly region of PTMO melting.

3.3. Stretched sample $\boldsymbol{P_7}$ (mode 3)

The heating trace of the sample $\mathbf{P_7}$ is shown in Fig. 4. This sample was uniaxially stretched to 600%, fixed at this deformation, and placed in DSC pan for analysis. It can be seen from Fig. 4 that the glass transition temperature of PTMO block in the sample $\mathbf{P_7}$ is by 15 °C higher than in the samples $\mathbf{P_{0-6}}$ (Table 3). The melting of PTMO block occurs as three peaks (Fig. 4):

Table 4
Thermal characterization of PA block in as-received and stretched samples

Sample	T_{m2} (°C)	T_{m3} (°C)	Q_{m2} (J/g)	Q_{m3} (J/g)
$\mathbf{P_0}$	53	136	10.5	19.5
$\mathbf{P_1}$	53	132	5.4	20.0
$\mathbf{P_2}$	53	134	5.4	19.1
P_3	+	135	+	16.8
$\mathbf{P_4}$	+	134	+	16.8
$\mathbf{P_5}$	−	134	−	18.2
$\mathbf{P_6}$	−	134	−	17.3
$\mathbf{P_7}$	−	136	−	14.1

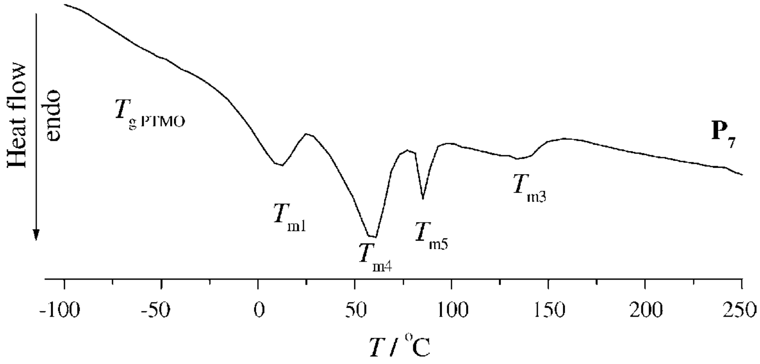


Fig. 4. DSC traces of heating of the sample $\mathbf{P_7}$.

1. the temperature of the first peak (T_{m1}) is higher, and its heat (Q_{m1}) is lower, than in the samples $\mathbf{P_{0-6}}$,
2. the temperature of the second peak (T_{m4}) and its heat (Q_{m4}) is higher than in the samples $\mathbf{P_{0-6}}$,
3. the temperature of the third peak (T_{m5}) is by 30 °C higher than T_{m4},
4. the total degree of crystallinity of PTMO is higher than in the samples $\mathbf{P_{0-6}}$.

Thus, with an increase in the degree of stretching the melting peak of PTMO block has undergone transformation from the single peak at 0 °C to the three peaks at 9, 60 and 84 °C. Seemingly, the peak T_{m5} corresponds to the melting of extended chain crystals of PTMO. Somewhat questionable in such interpretation can be the fact that the temperature of the fifth peak is much higher than the equilibrium melting temperature of PTMO. However, similar excess was observed for example in highly oriented PE [22,23]. Moreover, since the total degree of crystallinity of PTMO has increased, it can be supposed that uniaxial stretching of the as-received film up to the deformations close to breaking is accompanied by an additional stress-induced crystallization of PTMO. However, additional studies by another methods should be done to make such a conclusion.

4. Conclusions

Our calorimetric studies show that uniaxial deformation of the film Pebax^{TM} 2533 results in significant changes in the region of melting of PTMO and has almost no any influence on the melting of PA. The melting of PTMO in unstretched sample occurs as a single peak. As the degree of stretching increases the melting endotherm of PTMO acquires doublet character. The position of the low temperature peak does not change, but the second peak moves to higher temperatures. At the same time, intensity of the first peak decreases, while the second one increases. The melting isotherm of PTMO becomes a triplet, when highly oriented sample is melted in isometric conditions. An increase in the total degree of crystallinity of PTMO in this sample allows to suggest additional crystallization of PTMO under tension. However, to confirm such a conclusion and for clarification of the nature of the peaks observed additional X-ray studies are necessary.

Acknowledgements

The research described in this publication was made possible by support of the Russian Foundation for Basic Research (Grant 00-03-33123).

References

[1] N.R. Legge, G. Holden, H.E. Schroeder, Thermoplastic Elastomers, 2nd Edition, Hanser Publishers, 1996.
[2] G. Deleens, P. Foy, E. Marechal, Eur. Polym. J. 13 (1977) 343.
[3] G. Deleens, Kunstst-Ger. Plast. 73 (1983) 264.
[4] H.S. Faruque, C. Lacabanne, Polymer 27 (1986) 527.
[5] G.H. Hatfield, Y. Guo, W.E. Killinger, R.A. Andrejak, P.M. Roubicek, Macromolecules 26 (1993) 6350.
[6] M.L. Di Lorenzo, M. Pyda, B. Wunderlich, J. Polym. Sci. B 39 (2001) 1594.

[7] H.S. Faruque, J. Mater. Sci. 5 (1995) 5210.
[8] R.S. McLean, B.B. Sauer, Macromolecules 30 (1997) 8314.
[9] P. Gauvin, J.-L. Philippart, J. Lemaire, Makromol. Chem. 186 (1985) 1167.
[10] H.S. Faruque, C. Lacabanne, J. Mater. Sci. 22 (1987) 67.
[11] R.S. McLean, B.B. Sauer, J. Polym. Sci. B 37 (1999) 889.
[12] M.E. Rezac, T. John, P.H. Pfromm, J. Appl. Polym. Sci. 11 (1997) 1983.
[13] S. Warner, J. Elast. Plast. 22 (1990) 166.
[14] P.J. Flory, J. Chem. Phys. 15 (1947) 397.
[15] A. Schmidt, W.S. Veeman, V.M. Litvinov, W. Gabrielse, Macromolecules 31 (1998) 1652.
[16] W. Dexi, R.E. Lyon, R.J. Farris, Chin. J. Polym. Sci. 3 (1987) 262.
[17] C.B. Wang, S.L. Cooper, Macromolecules 16 (1983) 775.
[18] R.E. Lyon, R.J. Farris, W. MacKhight, J. Polym. Sci. Polym. Lett. Ed. 21 (1983) 323.
[19] E.V. Konyukhova, Y.K. Godovsky, V.M. Neverov, S.N. Chvalun, M. Soliman, Polymerwerkstoffe, Halle/Saale (2000) 435.
[20] B. Wunderlich, Thermal Analysis, Academic Press, Boston, 1990.
[21] J.W.C. Van Bogart, D.A. Bluemke, S.L. Cooper, Polymer 22 (1981) 142.
[22] S.N. Chvalun, N.P. Bessonova, M.B. Konstantinopolskaya, Y.A. Zubov, N.F. Bakeev, Dokl. Acad. Nauk 294 (1987) 1417.
[23] A.S. Vaughan, G. Ungar, D.C. Bassett, A. Keller, Polymer 26 (1985) 726.