JOURNAL OF MATERIALS SCIENCE 22 (1987) 675–678

A thermally stimulated current technique for measuring the molecular parameters of Pebax, a polyether–block amide copolymer

HAFIZ S. FARUQUE*, C. LACABANNE
Laboratoire de Physique des Solides, Groupe Polymère, Université Paul Sabatier, 118 Route de Narbonne, Toulouse, France

---

The primary relaxation peaks of Pebax copolymer having a soft segment, poly(tetramethylene glycol) (PTMG) ($\bar{M}_n = 2032$) and a hard segment, polyamide 12 (PA12) ($\bar{M}_n = 615$) are located at −69.5 and 18° C for a raw sample and at −71.5 and 4° C when the sample is recrystallized after fusion using the thermally stimulated current (t.s.c.) method. A comparison is made of rapid and slow cooling t.s.c. on hard-segment molecules. Applying the fractional polarization method, the modes β_{PTMG} and β_{PA} have been analysed. The parameters (such as activation energy and relaxation time) associated with the dipolar relaxation process of Pebax have been calculated. The maximum energy observed for modes β_{PTMG} and β_{PA} is 1.47 eV at −66° C and 1.34 eV at 1° C, respectively. The elementary processes that constitute the modes β_{PTMG} and β_{PA} obey a compensation law with compensation temperature $T_c = -43°$ C and compensation relaxation time $\tau_c = 3.4 \times 10^{-2}$ sec for mode β_{PTMG}, and $T_c = 66°$ C and $\tau_c = 2.8 \times 10^{-4}$ sec for mode β_{PA}.

---

1. Introduction

The thermally stimulated current (t.s.c.) technique is essentially a d.c. measurement with continuously varying temperature. It is applicable in ranges of equivalent frequencies of 10^{-2} to 10^{-4} Hz [1, 2]. The study of t.s.c. can provide insight into molecular motion in polymers. The parameters associated with each dipolar relaxation process (such as activation energy, relaxation time and the relaxation strength) can also be calculated [3]. The sample is mounted between an electrode system in a vacuum cryostat kept at a pressure of 10^{-6} mm Hg. Surface conductance is not a problem so long as the cryostat is kept free of vapour. This can be achieved by an initial vacuum bake-out and then filling with helium which improves heat transfer and minimizes temperature gradients [4]. The specimen is heated to a certain temperature depending on the sample in order to eliminate the initial charges [5]. The sample is then polarized by an external electric field (10 to 30 kV cm^{-1}) at a temperature T_p for t_p (2 min) to allow complete alignment of any dipole and drift of the free charges [6]. The polarization is frozen in by cooling the sample under the applied field down to liquid nitrogen temperature. The applied voltage is turned off for 2 min to remove stray surface charges. The sample is then connected to an electrometer (lowest detectable current range 10^{-15} A). The resistance of the shunt resistor in the electrometer is kept at least two orders of magnitude less than the sample resistance so that the charge in the specimen is freely discharged. The specimen is heated at a controlled linear rate of 7.5 °C min^{-1} and the relaxation of dipoles is followed by monitoring the current arising from their thermally stimulated discharge. The depolarization current density is recorded as a function of temperature by using an $X-Y$ plotter. If the material contains several traps of different energy, the corresponding number of current density peaks should be observed during heating.

The current density can be defined by

$$J(T) = -\frac{\mathrm{d}P(T)}{\mathrm{d}t} = \frac{P(T)}{\tau(T)} \qquad (1)$$

Here, $\tau(T)$ = relaxation time and $P(T)$ = polarization. The values of $P(T)$ are affected by the temperature dependence of relaxation time. Moreover, if the depolarization heating velocity is constant, i.e.

$$T = T_0 + bt$$

then

$$J(T) = \frac{P_0}{\tau} \exp\left[-\frac{1}{b}\int_{T_0}^{T} \frac{\mathrm{d}T}{\tau}\right] \qquad (2)$$

Provided τ obeys the Arrhenius equation

$$\tau(T) = \tau_0 \, \mathrm{e}^{\Delta H/kT} \qquad (3)$$

Equation 2 takes the form

$$J(T) = \frac{P_0}{\tau_0} \exp\left[-\frac{\Delta H}{kT} - \frac{1}{b\tau_0}\int_{T_0}^{T} \mathrm{e}^{-\Delta H/kT}\, \mathrm{d}T\right] \qquad (4)$$

---

* *Present address*: Electrical and Electronic Engineering Department, Bright Star University of Technology, Post Box 58158, Ajdabia, Libya.

0022–2461/87 $03.00 + .12

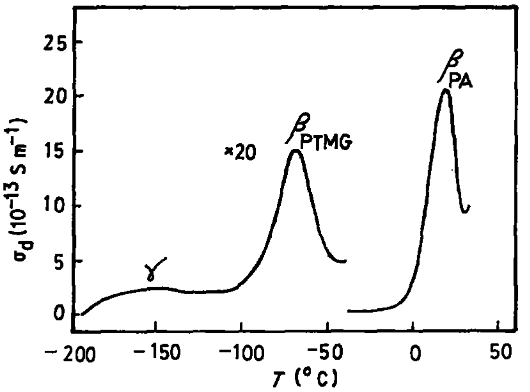

Figure 1 T.s.c. spectrum of Pebax (PA12-615 block PTMG 2032). $T_p = 70°C$.

2. Materials

Pebax copolymers are thermoplastic elastomers formed by joining blocks of two dissimilar homopolymers along the chain backbone. The general structure is $(A-B)_n$, where B (the soft segment) is usually formed from a polyether of molecular weight between 600 and 2000 and the hard segment is a polyamide having molecular weight between 600 and 4000. The soft and hard segments are relatively short blocks which alternate n times to give a polymer of high molecular weight [7]. At the service temperature, the soft segment component is viscous or rubbery while the hard segment is glassy or semicrystalline. Most segmented copolymers exhibit a two-phase microstructure with the hard domain acting as physical crosslinks. The extent of hard segment/soft segment mixing will depend on the overall hard segment content, both segment lengths and the affinity of one segment for the other [8]. Hard domains are reasonably pure but soft domains consist of soft segments plus some trapped hard segments since $-NH_2$ groups of hard segment form hydrogen bonds with oxygen of the ether linkage. Upon heating, the extended soft segments contract or relax, causing additional hard segments to be pulled out of the hard domain and phase mixing to occur. Rapid cooling creates a thermodynamic driving force for the phase to separate again [9, 10]. The thermally stimulated depolarization technique is well suited to the study of the relaxation behaviour of Pebax and is a useful means for characterizing the nature of phase separation.

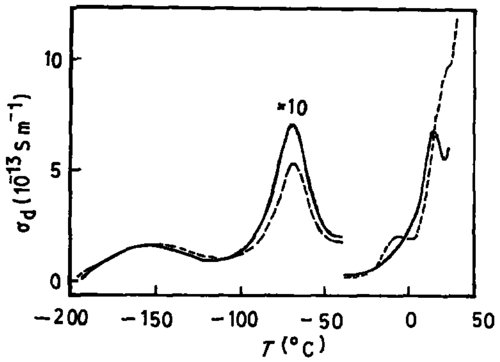

Figure 3 T.s.c. spectra of Pebax (PA12-615 block PTMG 2032) indicating the effect of cooling. $T_p = 80°C$. (——) Spectrum obtained due to rapid cooling (40°C min^{-1}); (– – –) spectrum obtained due to slow cooling (80 to −50°C at a speed of 2°C min^{-1}).

3. Results and discussion

The glass transitions of PA12 ($\bar{M}_n = 615$) and PTMG ($\bar{M}_n = 2000$) are observed at 41°C and −74°C, respectively. A raw sample (area = $64 \times 10^{-6}\,m^2$, thickness = 2.5 mm) and a sample recrystallized after fusion (area = $1.33 \times 10^{-4}\,m^2$, thickness = 1.25 mm) of Pebax copolymer having hard segment PA12 ($\bar{M}_n = 615$) and soft segment PTMG ($\bar{M}_n = 2032$) have been studied by t.s.c. applying $0.2\,MV\,m^{-1}$ and $0.32\,MV\,m^{-1}$, respectively. Fig. 1 shows the t.s.c. spectrum of a raw sample of Pebax (PA12-615 block PTMG 2032). The phases β_{PTMG} and β_{PA} are separated at −69.5 and 18°C, respectively. When the sample is recrystallized after fusion (Fig. 2), the phase β_{PA} has been displaced to lower temperature at 4°C but the phase β_{PTMG} remains in the same region (−71.5°C). A sample is heated to 120°C and kept in vacuum for 16 h. Fig. 3 represents t.s.c. spectra indicating the effect of rapid and slow cooling after polarization. The glass transition of the hard segment PA12 has been observed to split into two parts when the temperature is decreased at a speed of 2°C min^{-1} after polarization. Due to slow cooling, the chain takes a

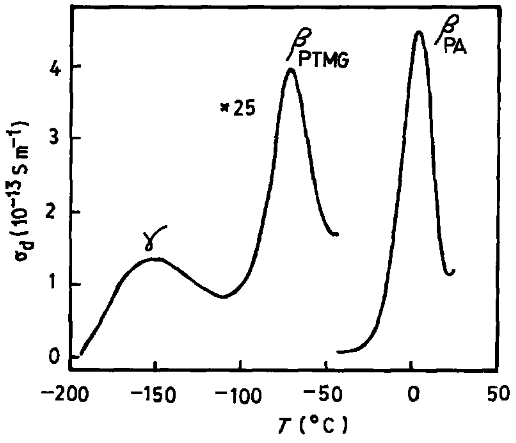

Figure 2 T.s.c. spectrum of Pebax (PA12-615 block PTMG 2032) indicating the effect of recrystallization. $T_p = 70°C$.

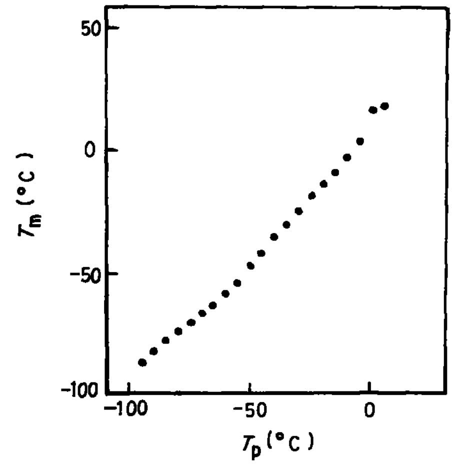

Figure 4 The variation of T_m of elementary peaks as a function of T_p for Pebax (PA12-615 block PTMG 2032).

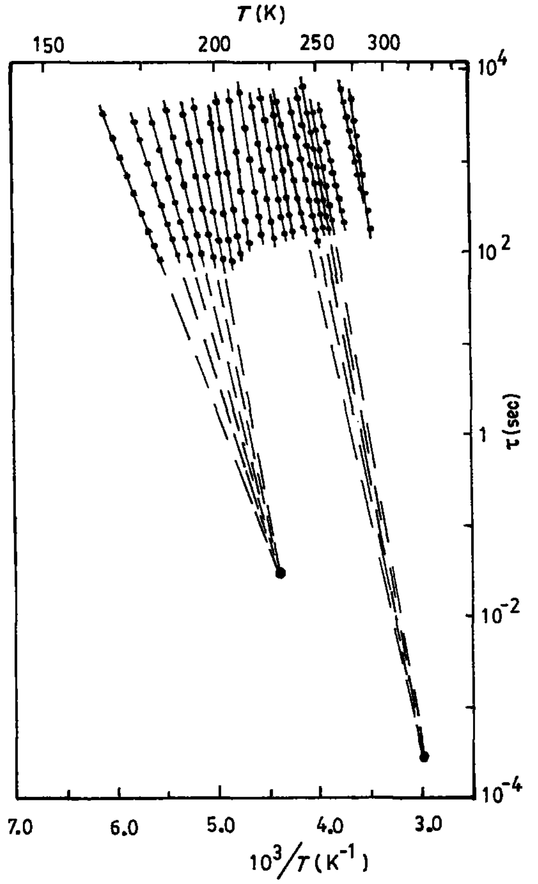

Figure 5 Arrhenius diagram of relaxation time isolated in Pebax (PA12-615 block PTMG 2032). $T_{c1} = 230$ K, $\tau_{c1} = 3.4 \times 10^{-2}$ sec; $T_{c2} = 339$ K, $\tau_{c2} = 2.8 \times 10^{-4}$ sec.

more probable conformation and the material becomes stable. To obtain the values of activation energy and relaxation time at different temperatures, the raw sample has been studied by the fractional polarization method [11].

The variation of T_m as a function of T_p in Fig. 4 represents the existence of two modes of relaxation in Pebax. Fig. 5 shows an Arrhenius plot indicating the presence of two modes β_{PTMG} and β_{PA} characterized by the compensation law. All the parameters have been listed in Table I and the points associated with elementary peaks have been verified by the plot of ln τ_0 against ΔH (Fig. 6).

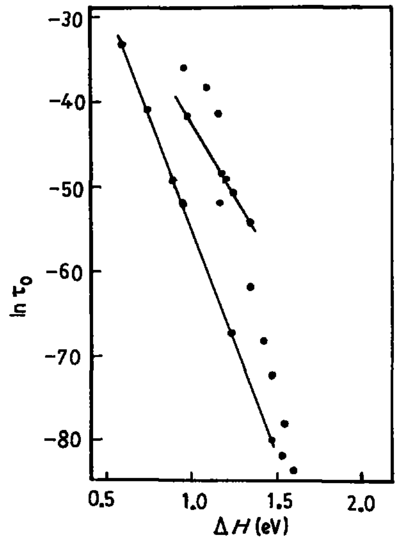

Figure 6 The variation of ln τ_0 as a function of ΔH for the relaxation times isolated in Pebax (PA12-615 block PTMG 2032). $T_{c1} = 230$ K, $\tau_{c1} = 3.4 \times 10^{-2}$ sec; $T_{c2} = 339$ K, $\tau_{c2} = 2.8 \times 10^{-4}$ sec.

TABLE I The parameters ΔH and τ_0 of Arrhenius peaks isolated at T_m in copolymer Pebax (PA12-615 block PTMG 2032)

Peak	T_p (°C)	T_m (°C)	ΔH (eV)	τ_0 (sec)	Remarks
1	−95	−88	0.59	4.0×10^{-15}	$C\beta_{PTMG}$
2	−90	−82	0.73	1.7×10^{-18}	$C\beta_{PTMG}$
3	−85	−78	0.88	4.7×10^{-22}	$C\beta_{PTMG}$
4	−80	−74	0.95	2.9×10^{-23}	$C\beta_{PTMG}$
5	−75	−70	1.23	6.5×10^{-30}	$C\beta_{PTMG}$
6	−70	−66	1.47	2.0×10^{-35}	$C\beta_{PTMG}$
7	−65	−63	1.53	2.5×10^{-36}	
8	−60	−58	1.60	4.3×10^{-37}	
9	−55	−53	1.54	1.3×10^{-34}	
10	−50	−45	1.47	3.4×10^{-31}	
11	−45	−41	1.42	2.5×10^{-30}	
12	−40	−34	1.34	1.7×10^{-27}	
13	−35	−30	1.16	3.4×10^{-23}	
14	−30	−23	0.98	8.2×10^{-19}	$C\beta_{PA}$
15	−25	−16	1.17	9.3×10^{-22}	$C\beta_{PA}$
16	−20	−12	1.19	5.5×10^{-22}	$C\beta_{PA}$
17	−15	−8	1.24	1.2×10^{-22}	$C\beta_{PA}$
18	−10	1	1.34	3.4×10^{-24}	$C\beta_{PA}$
19	−5	5	0.95	3.3×10^{-16}	
20	0	19	1.08	2.3×10^{-17}	
21	5	20	1.15	1.2×10^{-18}	

4. Conclusion

The secondary relaxation γ is the motion of CH_2 sequences. Both the hard and soft segments contain CH_2 sequences, but the major contribution to γ relaxation comes from the soft segment. The β_{PTMG} phase has the same characteristics as that of the homopolymer PTMG (Fig. 7). The amorphous phase of PTMG has not been disturbed by PA but the amorphous phase of PA has been plasticized, i.e. some hard segments are dissolved in the soft segment matrix phase. Long sequences of PA reduce the molecular mass of PTMG and a new glass transition appears because of melting of the crystalline phase of PTMG [12], but for short sequences of PA the molecular mass of PTMG is not reduced much and the melting of the

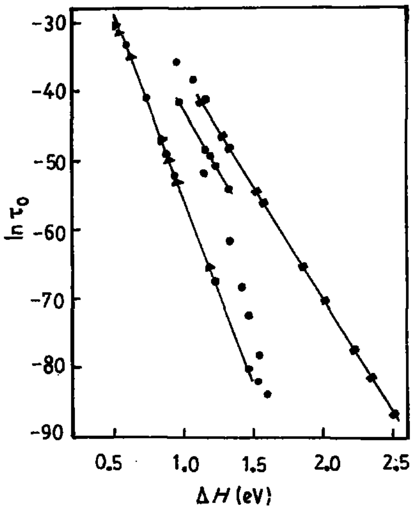

Figure 7 Comparison between homopolymers and copolymers representing the variation of ln τ_0 as a function of ΔH. (●) Pebax, (▲) PTMG 2000, (■) PA12000.

crystalline phase has been blocked by the formation of chain entanglements associated with more molecular mass. As a result, no new glass transition is observed.

Acknowledgements

This work was sponsored by French Government and ATOCHEM Industry of France. The authors are grateful to Drs D. Chatain and P. Demond for useful consultations.

References

1. J. Van TURNHOUT, "Thermally Stimulated Discharge of Polymer Electrets" (Elsevier, Amsterdam, 1975) p. 92.
2. J. VANDERSCHUEREN and J. GASIOT, *J. Appl. Phys.* **37** (1979) in *Topics* 135–223.
3. C. BUCCI, R. FIESCHI and G. GUIDI, *Phys. Rev.* **148** (1966) 816.
4. CHI-MING HONG and D. E. DAY, *J. Appl. Phys.* **50**(8) (1979) 5352P.
5. K. OHARA and G. REHAGE, *Colloid Polym. Sci.* **259** (1981) 318P.
6. Sk. SHRIVASTAVA, J. D. RANADE and A. P. SHRIVASTAVA, *Thin Solid Films* **67** (1980) 201P.
7. H. N. Ng. A. E. ALLEGREZZA, R. W. SEYMOUR and S. L. COOPER, *Polymer* **14** (1973) 255P.
8. T. R. HESKETH, J. W. C. VAN BOGART and S. L. COOPER, *Polym. Eng. Sci.* **20**(3) (1980) 190P.
9. G. L. WILKES, S. BAGRODIA, W. HUMPHRIES and R. WILDNAUER, *J. Polym. Lett.* **13** (1975) 321P.
10. G. L. WILKES and R. WILDNAUER, *J. Appl. Phys.* **46** (1975) 4148.
11. FARUQUE SHARIF, thesis, D. Ing., Toulouse (1984).
12. P. DEMONT, F. SHARIF, D. CHATAIN and C. LACABANNE, in Proceedings of OTS meeting on Pebax, Strasbourg, June 1984.

Received 27 March
and accepted 8 May 1986