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Studies On Uniaxial Tensile Behaviour Of Poly(Ester-Ester) Thermoplastic Elastomers

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ABSTRACT

Tensile properties of poly(ester ester) elastomers with different content of hard segments were investigated. The tensile tests were performed in the temperature range of 313 to 453 K. The elastomers having a higher content of the hard segments show a higher Young's modulus because the hard segments are crystallized to form a hard domain which acts as crosslinks. The number density of the crystalline domains decreased with increasing temperature. There is no marked difference in the activation energy to form the crystalline domains between samples with different contents of hard segments.

KEYWORDS

Poly(ether ether) thermoplastic elastomer;
Uniaxial tensile properties;
Elastic modulus;
Yield behaviour;
Plastic flow

INTRODUCTION

Most thermoplastic elastomers (TPEs) have been produced as multi-block copolymers consisting of repeated hard and soft segments. Hard segments of the TPEs form crystalline domains with a melting temperature higher than room temperature while the soft segments are amorphous. The TPEs are expected to behave as rubbers at room temperature. The crystalline domains act as cross-links and restrict the mobility of the soft segments. At a higher temperature than the melting temperature of the hard segment domains, the hard segment domains cannot act as cross-links, and thus in that temperature range the TPEs behave as viscous liquids.

Poly(ether ester) elastomers consisting of aromatic ester units as hard segments and aliphatic polyether glycol units as soft segments have attracted much attention in industry because of their high thermal stability and high tensile toughness[1,2]. There are many studies on structures[3-6] and mechanical properties[7-9] of the poly(ether ester) elastomers that aim to reveal the origin of the high mechanical performance of the elastomers.

In this work, we investigated the tensile properties of TPEs consisting of aromatic and aliphatic polyesters [poly(ester ester) elastomers] which have recently been developed to improve thermal stability. The temperature and strain-rate dependence of tensile properties of the novel poly(ester ester) elastomers was investigated.

EXPERIMENTAL

Materials

Two kinds of poly(ester ester) elastomers (PELPRENE S-1002 and S-2002) were provided from Toyobo Co., Ltd., Japan. The hard and soft segments of the PELPRENE consist of poly(butane-1,4-diyl terephthalate) (PBT) and poly(6-hydroxyhexanoic acid) (PCL), respectively. The number average and weight average molar masses (M_n and M_w, respectively) are 63.4 kg/mole and 131.4 kg/mole for S-1002, and M_n = 60.3 kg/mole and M_w = 123.0 kg/mole for S-2002. The average sequence length of PCL units is about 12 units for both samples, while that of PBT units is different; 9.1 units for S-1002 and 15.2 units for S-2002. The pellets of the elastomers were press-molded at 493 K for S-1002 and at 533 K for S-2002 for 5 minutes to obtain sheet samples.

Measurements

Plots of tensile engineering stress (σ_E) against elongational ratio (λ) of S-1002 and S-2002 were measured with a Tensilon AGS-1kNG (Shimadzu Co., Japan) at two initial strain rates ($\dot{\varepsilon}_0$; $\dot{\varepsilon} = \nu/l_0$, where ν is the cross-head speed and l_0 is the initial length) 2.8 × 10^{-3} s^{-1} and 2.8 × 10^{-2} s^{-1}. The elongational ratio was calculated by l/l_0, with l being the length. The stress σ_E was evaluated from the load divided by the initial cross-sectional area. The width and thickness of the samples were 5.0 mm and 0.80 mm, respectively. The initial length between clumps was ca. 30 mm. The tensile tests were performed in the temperature range of 313 to 453 K.

RESULTS AND DISCUSSION

Stress-strain curves obtained from experiments

Figure 1 shows the σ_E-λ curves of S-1002 measured at $\dot{\varepsilon}_0$ = 2.8 × 10^{-3} s^{-1}. At small strains, the σ_E values increase linearly with λ. The stress σ_E at large strains also increases with increasing λ but the slope of the curves is much smaller than that of the curves at small strains. The overall stress level increases with decreasing temperature (T). An inflection point appears at about λ = 1.1 on the σ_E-λ curve at T = 393 K while yielding behavior becomes complicated for the curves at T > 393 K.

Figure 1: The elongational ratio (λ) dependence of engineering stress (σ_E) for S-1002 at $\dot{\varepsilon}_0$ = 2.8 × 10^{-3} s^{-1}. The symbols stand for the experimental temperature as ◊ : 453 K, □: 433 K, Δ : 413 K, x : 393 K, * : 353 K, ○: 313K

Figure 2 shows the σ_E-λ curves of S-1002 at $\dot{\varepsilon}_0$ = 2.8 × 10^{-2} s^{-1}. The shape of the curves is almost similar to that of the curves at $\dot{\varepsilon}_0$ = 2.8 × 10^{-3} s^{-1} (Figure 1). The overall stress level is also lowered as T is elevated.

As shown in figures 3 and 4, the stress-elongation curves measured at different elongation rate are almost similar at the same T. The σ_E-λ curves of S-2002 at λ < 5 are almost similar in shape to those of S-1002, but the large enhancement of σ_E in the σ_E-λ curves of S-2002 is observed at λ > 5.

Mechanical properties at small strains

The Young's modulus (E_0) of S-1002 decreases

Figure 2: The elongational ratio (λ) dependence of engineering stress (σ_E) for S-1002 at $\dot{\varepsilon}_0 = 2.8 \times 10^{-2}$ s^{-1}. The symbols are the same as in figure 1

Figure 3: The elongational ratio (λ) dependence of engineering stress (σ_E) for S-2002 at $\dot{\varepsilon}_0 = 2.8 \times 10^{-3}$ s^{-1}. The symbols are the same as in figure 1

Figure 4: The elongational ratio (λ) dependence of engineering stress (σ_E) for S-2002 at $\dot{\varepsilon}_0 = 2.8 \times 10^{-2}$ s^{-1}. The symbols are the same as in figure 1

with increasing T (see TABLE 1). The comparison at the same T shows that the values of E_0 measured at a higher strain rate are slightly larger than those at a lower strain rate. The E_0 of S-2002 is almost twice as high as that of S-1002 at the same T. The hard segments aggregate to form the crystalline domains because the melting temperature (T_m) of the elastomers used in this study is reported to be 473 K for S-1002 and 479 K for S-2002, according to the data sheets prepared by the manufacturer. The crystalline domains must be harder than the amorphous matrix consisting of the soft segments; hence, E_0 is expected to increase by a filler reinforcement effect. The increase of E_0 is assumed to be described by the following equation[10]

$$E_0 = E_{00}(1 + 2.5\varphi + 14.1\varphi^2) \qquad (1)$$

Here, E_{00} is the modulus without filler particles (crystalline domains), φ being the volume fraction of the domains. The E_0 can be determined by the two factors: one is the contribution from the increase of the number density of the elastically effective chain (namely, E_{00}) and the other is the contribution originating from the mixing the fillers with the higher modulus than matrix. The values of φ are necessary to discuss the details of the latter contribution, but

TABLE 1: Initial Young's modulus (E), Elongational ratio at yield (λ_Y) and Yield Stress (σ_Y) for the sample at initial strain rate ($\dot{\varepsilon}_0$) at various temperatures (T)

Sample	$10^3\dot{\varepsilon}_0$ / s	T / K	E / MPa	λ_Y	σ_Y / MPa
S-1002	2.8	313	88	1.1	8.3
		353	61	1.1	5.0
		393	41	1.1	3.8
		413	36	1.1	3.3
		433	25	1.1	1.9
		453	12	1.1	1.0
	28	313	86	1.1	9.1
		353	65	1.2	6.5
		393	39	1.1	4.1
		413	33	1.1	3.3
		433	24	1.2	2.6
		453	11	1.1	1.1
S-2002	2.8	313	160	1.1	11
		353	120	1.1	8.7
		393	83	1.1	6.3
		413	61	1.1	4.7
		433	52	1.1	3.6
		453	38	1.1	2.5
	28	313	130	1.1	11
		353	110	1.1	8.8
		393	76	1.1	6.6
		413	66	1.1	5.3
		433	50	1.1	3.9
		453	38	1.1	2.6

the content of the hard segments is unknown at present. It has been reported for poly(ether ester) elastomers containing PBT units that T_m decreases as the content of hard segments decreases[2]. If this is also applicable to our systems, a little difference in T_m between S-1002 and S-2002 suggests that only a little difference exists in the content of the hard segments, or equivalently, only a little difference in the contribution originating purely from the reinforcement effect exists for S-1002 and S-2002. This indicates that the large difference in E_0 must be attributed to the difference in E_{00} rather than in the reinforcement effect.

According to the classical theory of rubber elasticity[11], the modulus E_0 of incompressible materials is related to the number density of cross-links (ν) and T in K as

$$\mathbf{E_0 = 3\nu RT,} \tag{2}$$

where R is the gas constant. Assuming that ν is the number density of crystalline domains, this equation leads to the conclusion that the values of ν of S-2002 becomes almost twice as high as those of S-1002 at the same T because the ratio of E_0 of S-2002 to that of S-1002 at the same T lies around 2, as stated previously. The hard domains melt at T_m; namely, ν vanishes at $T = T_m$. The quantity, ν, is a decreasing function of T. These imply that ν can be written by a following form.

$$\boldsymbol{\nu = \nu_0 \exp(-\Delta E_m/R\Delta T)} \tag{3}$$

where $\Delta T = T_m - T$ and ΔE_m might be a kind of activation energy, ν_0 being ν at $\Delta T \rightarrow \infty$. Although in an actual case, the value of n must level off with decreasing temperature, this cannot be reflected in equation 3.

Figure 5 shows the semi-logarithmic plots of ν against$(\Delta T)^{-1}$ for S-1002 and S-2002. Although the values of log n do not change linearly with $(\Delta T)^{-1}$, the log ν-$(\Delta T)^{-1}$ curve is approximated by a straight line at $(\Delta T)^{-1} > 0.01$. At $(T)^{-1} < 0.01$, the data points deviate upward from the line. There is no marked difference in the curves between the different strain rates for both samples. The curve of S-2002 exhibit a similar behavior to that of S-1002 but the values of n is higher than those of S-1002 over the entire range of $(\Delta T)^{-1}$. The soft segments will be crystallized at 323-333 K because the melting points of the crystalline domains of poly(6-hydroxyhexanoic acid) is reported around 328 K[12]. This is the major reason for the upward deviation of ν from the straight line. The values of ΔE_m and ν_0 can be estimated from the best-fit line of the log ν-$(\Delta T)^{-1}$ curves at $(\Delta T)^{-1} > 0.01$ on the basis of equation 3. The values obtained for both samples are tabulated in TABLE 2. The ΔE_m value of S-1002 is close to that of S-2002, implying that the size of the crystalline domains in S-1002 is similar to that in S-2002.

Mechanical properties at large strains

The permanent residual strain, not observed at the applied strains smaller than the strain at the inflection point ($\lambda \approx 1.1$), occurred at all temperatures examined when the sample was stretched to the strains beyond the inflection point. The inflection point appearing at $\lambda \approx 1.1$ corresponds to the onset of the plastic deformation. The permanent residual strain reflects a structural change caused by the ap-

Figure 5: The semi-logarithmic plots of ν against $(\Delta T)^{-1}$. The triangles and circles represent for ν for S-1002 and S-2002, respectively. The white and black symbols represent the samples at $\dot{\varepsilon}_0 = 2.8 \times 10^{-3}$ s^{-1} and at $\dot{\varepsilon}_0 = 2.8 \times 10^{-2}$ s^{-1}, respectively. The best-fit lines for the data at$(\Delta T)^{-1} > 0.01$ are also shown

TABLE 2: Estimated ΔE_m and ν_0 in equation 3

Sample	ΔE_m / J·mol^{-1}	$10^3\ \nu_0$ / mol·m^{-3}
S-1002	290	5.8
S-2002	270	10

plication of the large strain. It has been reported for poly(ether ester) elastomers containing PBT units that the hard segment PBT domains are fractured when the applied strain is larger than the yield strain[6]. This strongly suggests that the PBT hard domains in the elastomers used in this study are also fractured at the strains beyond the yield strain.

The stretch ratio at yield point (l_Y) is defined as the stretch ratio at the inflection point. The point with the smallest values was regarded as the λ_Y when several inflection points occurred. The yield stress (σ_Y) is defined as the stress at λ_Y; namely, $\sigma_Y = E_0\lambda_Y$. The estimated values of λ_Y and σ_Y are listed in TABLE 1. The values of λ_Y of S-1002 are almost the same at any T while σ_Y of S-1002 decreases with increasing T. No marked differences in σ_Y and λ_Y between the samples elongated at the different strain rate are observed. The values of σ_Y and λ_Y of S-2002 show a similar behavior to that of S-1002, but the higher values of σ_Y in S-2002 as compared with S-1002 are observed at all T examined. Because $\sigma_Y = E_0\lambda_Y$, σ_Y increases with increasing E_0 if λ_Y remains constant; hence, the decrease of σ_Y with increasing T is due to the decrease of E_0 since λ_Y remained around 1.1 for all T. The higher σ_Y for S-2002 than S-1002 is attributed to the higher E_0 since no marked difference in λ_Y was observed between S-1002 and S-2002. Because E_0 is in proportion to ν, according to equation , the difference in λ_Y is caused only by the difference in ν.

The deformation of the crystalline domains at the strains beyond the yield point ($\lambda > \lambda_Y$) can be phenomenologically regarded as the uniaxial plastic flow. Assuming that the samples behave as the Bingham fluid, the relationship between σ_E and the extensional strain rate ($\dot{\varepsilon}_p$) can be expressed by the following equation[13].

$$\sigma_e = \sigma_Y + \eta_p \dot{\varepsilon} \tag{4}$$

with η_p being the plastic viscosity. The samples would become difficult to flow as the number density of the crystalline domains increases, that is, η_p would increase with increasing ν; hence, we assume that η_p can be written as a similar function of T to ν. Thus, (η_p) can be written by using ΔT as

$$\eta = \eta_0 \exp(-\Delta E_p / R\Delta T) \tag{5}$$

Here, ΔE_p is the activation energy of the plastic flow. The quantity η_{p0} is the plastic viscosity at $\Delta T \rightarrow \infty$.

Figure 6 shows the $(\Delta T)^{-1}$ dependence of η_p drawn on semi-logarithmic plots for S-1002 and S-2002 at $\lambda = 3.0$. Although log η_p is not a linear function of $(\Delta T)^{-1}$, the log η_p-$(\Delta T)^{-1}$ curve at $(\Delta T)^{-1} > 0.01$ can be approximated by a straight line, as in the case of ν-$(\Delta T)^{-1}$ plots. The value of ΔE_p can be estimated from the best-fit line of the log η_p-$(T)^{-1}$ curves at $(\Delta T)^{-1} > 0.01$ on the basis of equation 5.

Figure 7 shows the λ dependence of ΔE_p. The quantity ΔE_p is almost constant around 2.8×10^2 J·mol^{-1}. The estimated ΔE_p represents the activation energy of the plastic flow. The flow requires the breakdown of the crystalline domains, of course. As mentioned previously for DE_m, no large difference in size of the crystalline domains existed between S-1002 and S-2002. As a result, no marked difference in estimated ΔE_p was observed for the samples. It is

Figure 6: The semi-logarithmic plots of η_p at $\lambda = 3$ against $(\Delta T)^{-1}$. The symbols are the same as figure 5. The best-fit lines for the data at $(\Delta T)^{-1} > 0.01$ are also shown

Figure 7: The λ dependence of ΔE_p. The white and black symbols represent the samples at $\dot{\varepsilon}_0 = 2.8 \times 10^{-3}$ s^{-1} and at $\dot{\varepsilon}_0 = 2.8 \times 10^{-2}$ s^{-1}, respectively

natural that ΔE_m and ΔE_p are close to each other.

CONCLUSION

Tensile properties of poly(ester ester) elastomers with different content of hard segments at various temperature were investigated. The elastomers having a higher content of the hard segments show a higher Young's modulus because the hard segments are crystallized to form a hard domain which acts as cross-links. The number density of the crystalline domains decreased with increasing temperature. There is no marked difference in the activation energy to form the crystalline domains between samples with different contents of hard segments.

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