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Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

INSTANTANEOUS STRAIN RECOVERY ELASTICITY AND ENDOTHERMIC HEAT CHANGE IN NYLON-6 MONOFILAMENTS AND SILICONE RUBBERS

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Abstract

The instantaneous elastic moduli for a nylon-6 monofilament were derived on strain recoveries right after creep, stress relaxation, and rapid elongation, E_c, E_s and E_e, respectively. It was found that during strain recovery $E_s(>E_e)$ and E_e increase monotonically with increasing load, m_l, on the sample. The extrapolated value of E_s at $m_l=0$ g is almost equal to Young's modulus, 4.06 GPa. The value of E_c also increased with increasing m_l, and at $m_l=600$ g (1.93 t cm^{-2}) reached about 14 GPa. The endothermic heat change right after creep, stress relaxation or rapid elongation, Q, was negligibly small. For comparison, E_s, E_c and Q were also investigated for silicone rubber. It was found that E_s (53.8 MPa at the draw ratio $D=1.2$) decreased abruptly at $D=1.3$. In the range of $D=1.4$–1.9, E_s was only 22.6 MPa. In the case of stress relaxation, Q increased with increasing D from 4 J mol^{-1} (at $D=1.2$) to 56 J mol^{-1} (at $D=1.9$). Furthermore E_c (5.58 MPa at $m_l=133.8$ g (429.4 kg cm^{-2})) increased gradually with increasing m_l and attained 16.6 MPa at $m_l=548.4$ g (1.76 t cm^{-2}). In the case of creep, Q was in the range of 0–11.5 J mol^{-1} and larger when larger loads, m_2, were removed during the later stages of creep.

Keywords: instantaneous strain recovery elasticity, nylon-6 monofilament, silicone rubber

Introduction

For highly oriented monofilaments [1, 2] of nylon-6 and polyvinylidenechloride and polypropylene films [3], the energetics of the strain recovery [4] has been observed by rapid removal of part or all of the load on a sample during creeping. The initial velocity of shrinkage was linked to the elastic modulus, E, of the instantaneous strain recovery [1–3]. In this study the behavior of instantaneous strain recovery of nylon-6 monofilaments right after creep, stress relaxation, or rapid elongation was observed. From the initial velocity of shrinkage, the elastic moduli of instantaneous strain recovery for the cases of creep, stress relaxation and rapid elongation were derived, E_c, E_s and E_e, respectively. The endothermic heat, Q, right after rapid removal of a load on a

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sample was negligible, indicating energy elasticity. For comparison, Q, E_s and E_c were investigated for silicone rubber with entropy elasticity [5]. The rubber is exothermic when stretched rapidly and endothermic when the stress is released [6].

Theoretical treatment

Elastic modulus of instantaneous strain recovery

The behavior of instantaneous strain recovery is observed by rapid removal of part or all of the load on a sample during creep, stress relaxation, or rapid elongation. According to Newton's law, the kinetic equation of the initial behavior is given by:

$$m_1 x'' = -C(x_o - x) + m_1 G - T\left(\frac{\mathrm{d}S}{\mathrm{d}x}\right)_{P,T} \quad (1)$$

where x and x_o are the shrinkage and the final shrinkage after the rapid removal of a load from the sample, respectively; m_1 is the load left on the sample; C is Hooke's constant; G is the gravitational acceleration; $T\mathrm{d}S/\mathrm{d}x$ is a force due to the entropy elasticity [5] (here $\mathrm{d}x=-\mathrm{d}L$, L is the sample length, S is the entropy); $-T\mathrm{d}S$ is related to the endothermic heat change caused by the instantaneous strain recovery. The third term on the right hand side of Eq. (1), which was negligibly small for a highly oriented nylon-6 monofilament, is predominant for rubbers and should be negligible for ideal energy elasticity. The solution, x, of Eq. (1) without the third term is given by [1, 3]:

$$x = \alpha_1 \exp\left\{\left(\frac{C}{m_1}\right)^{1/2} t\right\} + \alpha_2 \exp\left\{-\left(\frac{C}{m_1}\right)^{1/2} t\right\} + \frac{m_2 G}{C} \quad (2)$$

According to the conditions of $x=0$ at $t=0$ and $x=m_2G/C$ at $t=\infty$, α_1 and α_2 should be 0 and $-m_2G/C$, respectively; where t is the time and m_2 is the load on a sample removed during creep, stress relaxation, or rapid elongation. Accordingly, Eq. (2) is rewritten as:

$$x = \left(\frac{m_2 G}{C}\right)\{1 - \exp(-qt)\}, \quad q = \left(\frac{C}{m_1}\right)^{1/2} \quad (3)$$

From Eq. (3), E is derived [1, 3]:

$$E = \left(\frac{CL}{\sigma}\right) = \left(\frac{L}{\sigma}\right)\left(\frac{1}{m_1}\right)\left(\frac{Gm_2}{V}\right)^2 \quad (4)$$

where V is the initial velocity of strain recovery and σ is the cross section of the sample. In the case of silicone rubber, the shrinkage velocity increased gradually and then attained a top velocity reflecting the entropy elasticity. If it is hypothesized that the top velocity is attributed to only energy elasticity, the top velocity corresponds to a simple harmonic motion, and C can be derived from Eq. (4) by choosing V at the top velocity. One can then calculate Q by:

$$Q = \frac{\int_0^{t_1} m_1 x'' x' \mathrm{d}t + (Cx_o - m_1 G)x_1 - \frac{1}{2}Cx_1^2}{M} \qquad (5)$$

where t_1 is the time when the top velocity is attained, x_1 is x at $t = t_1$ and M is the molecular weight of the sample.

Experimental

Sample

A nylon-6 monofilament (320 D) with the density 1.141 g cm^{-3} at 25°C, a crystallinity 30.0% and a degree of crystalline orientation of 0.94 was used. The second sample was a commercial silicone rubber in form of strips (thickness: 0.1 cm and 0.05 cm) with the width 0.3 cm.

Young's modulus

The measurement of load-elongation curves was carried out at room temperature of about 20°C and 35–45%RH. Young's moduli of 4.06 GPa for a nylon-6 monofilament (sample length: 2.5 cm), 2.81 MPa for a silicone rubber (sample length: 1.0 cm and thickness: 0.1 cm), and 3.17 MPa for another silicone rubber (sample length: 2.0 cm and thickness: 0.05 cm) were obtained from the initial slope of a load-elongation curve. The elongation rate was 10 cm min^{-1}. The dependence of Young's modulus on the elongation rate was not reproducible. Figure 1 shows the representative load-elongation curves for the nylon-6 monofilament and the silicone rubber.

Instantaneous strain recovery right after rapid elongation

Figures 2 and 3 show the apparatus and a representative behavior at $m_1 = 18.5$ g for a nylon-6 monofilament. In this measurement there is no load B in Fig. 2. All measurements of strain recovery were carried out at atmospheric pressure, about 20°C and 35–45%RH. The procedure of measurement was as follows: First a weight (a) is attached to the electromagnet (b) and the sample (c) is held by the grips (d) under tension of weight A. Then the weight (a) is dropped by switching off the electromagnetic. After the weight (a) reaches the

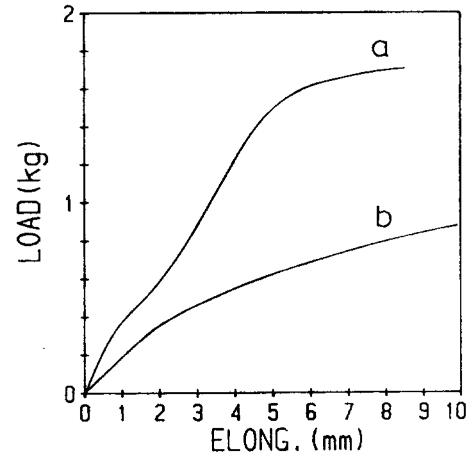

Fig. 1 The load-elongation curves for a nylon-6 monofilament (a) (sample length: 2.5 cm) and a silicone rubber (b) (sample length: 1.0 cm, thickness: 0.1 cm). Elongation rate: 10 cm min^{-1}

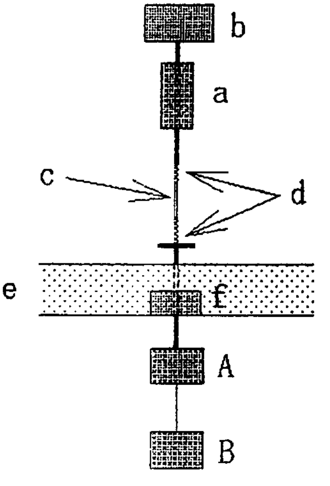

Fig. 2 Apparatus for measuring the strain recovery behavior. a: weight to be dropped, b: electromagnetic, c: sample, d: grips, e: iron plate, f: displacement meter, A and B: loads

lower grip (d), the combination of the weight (a) and the lower grip (d) collides with the iron plate (e) and stretches the sample. The weight (a) rebounds upward after pressing the lower grip (d) against the iron plate (e) and the load forced on the sample is removed, except for the prior load A contained in the weight of the lower grip parts. At this time the shrinkage of the sample towards the initial extension is started. The initial shrinkage behaviors detected by the displacement meter (f) are drawn on the display by a computer and E_e beyond point P is given by:

$$E_e = \left(\frac{CL}{\sigma}\right) = \left(\frac{Lm_1}{\sigma}\right)\left(\frac{V}{x_o}\right)^2 \tag{6}$$

with $x_o = Gm_2/C$.

The initial elongation velocity of a nylon-6 monofilament by the weight (a) was at an average of 106.7 cm s^{-1}.

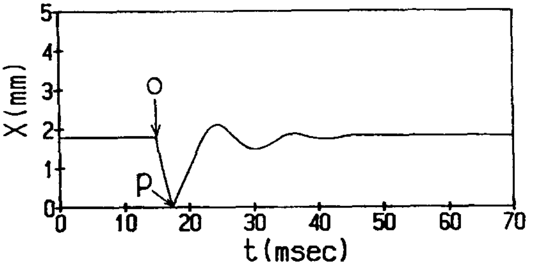

Fig. 3 Strain recovery behavior after rapid elongation for a nylon-6 monofilament. $m_1 = 18.5$ g. X: shrinkage and t: time. O and P: beginning points of elongation and shrinkage

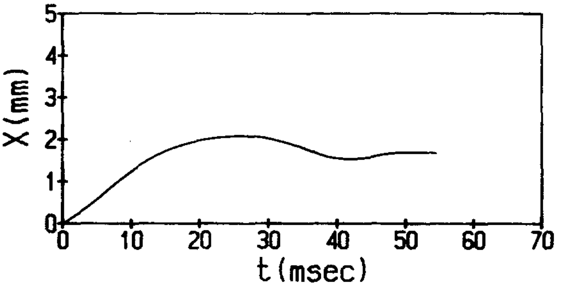

Fig. 4 Strain recovery behavior after creep for a nylon-6 monofilament. $m_1 = 45.5$ g and $m_2 = 498.6$ g. X: shrinkage and t: time

Instantaneous strain recovery right after creep

The apparatus in Fig. 2 was used for nylon-6 monofilament and silicone rubber. First two loads A ($=m_1$) and B ($=m_2$) are suspended on a sample (c). After about 20 min, B was removed by cutting a thread connecting A and B. The initial behavior of a sample was detected by the displacement meter (f) and then was drawn on the display by a computer or recorded by a photocorder. Figures 4 and 5 show the initial behavior right after the rapid removal of B for a nylon-6 monofilament and a silicone rubber (thickness: 0.05 cm). As shown in Figs 4 and 5, for a nylon-6 monofilament an abrupt initial shrinkage was observed right after the rapid removal of m_2, and for a silicone rubber the shrinkage velocity increased gradually and then attained a top velocity.

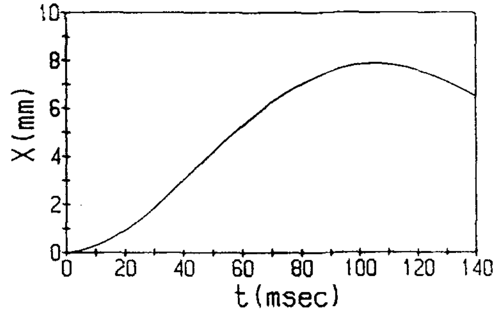

Fig. 5 Strain recovery behaviour after creep for a silicone rubber (thickness: 0.05 cm). $m_1=133.8$ g and $m_2=88.9$ g. X: shrinkage and t: time

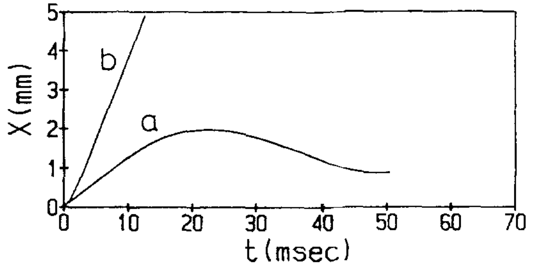

Fig. 6 Strain recovery behaviour after stress relaxation for a nylon-6 monofilament. a: $m_1=135.9$ g and $m_2=700$ g, b: $m_1=45.5$ g and $m_2=900$ g. X: shrinkage and t: time

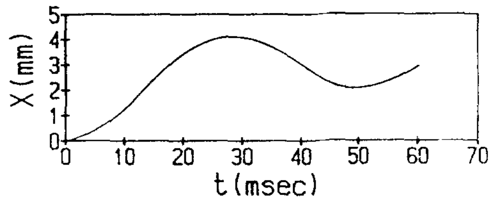

Fig. 7 Strain recovery behaviour after stress relaxation for a silicone rubber (thickness: 0.1 cm) at $D=1.40$. $m_1=45.5$ g and $m_2=175$ g. X: shrinkage and t: time

Instantaneous strain recovery right after stress relaxation

In this measurement, a load cell was installed instead of an electromagnet (b). First by two loads A ($=m_1$) and B, a sample (c) is elongated to a constant length; the lower grip (d) is attached to the iron plate (e) by the load B of a heavy weight. Next when the relaxation load arrived at an appointed load, the thread connecting A and B is cut with scissors. The initial behavior under a load A right after the removal of B is drawn on the display by a computer and E_s was calculated from Eq. (4), where m_2 is the relaxation load detected by the load cell just before the removal of B. Figures 6 and 7 show the initial behaviors right after the rapid removal of B during the stress relaxation for a nylon-6 monofilament and a silicone rubber (thickness: 0.1 cm), respectively. The initial behaviors in these samples are similar to the cases of instantaneous strain recovery after creep.

Results and discussion

Nylon-6 monofilament

E_e and E_s

Figure 8 shows the relationships between E (E_e, E_s and E_c (described in the next section)) and m_1 for a nylon-6 monofilament. As shown in Fig. 8, E_e and E_s ($>E_e$) increase with increasing m_1, reflecting the change of the chain cohesive state. The dependence of E_s on m_2 (=700 g, 800 g and 900 g) was not found to be reproducible. The extrapolated value of E_s at m_1=0 g was almost equal to Young's modulus (4.06 GPa). The result of $E_s > E_e$ may be attributed to the difference of relaxation times related to the relative cohesive state.

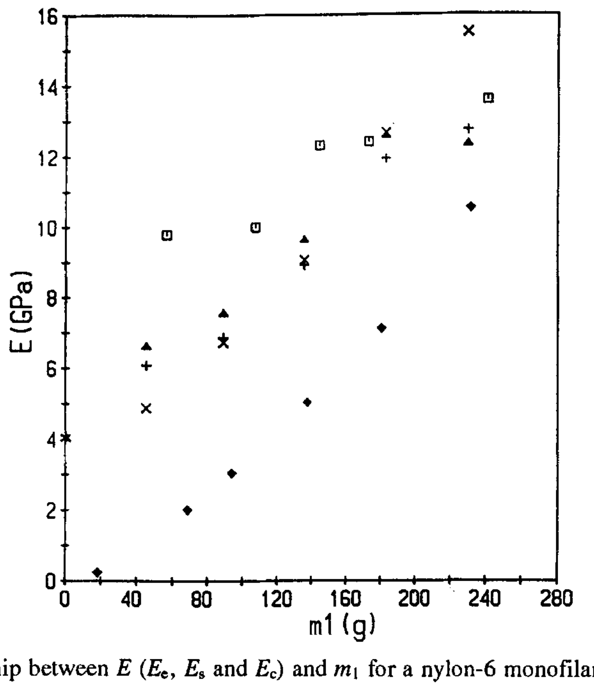

Fig. 8 Relationship between E (E_e, E_s and E_c) and m_1 for a nylon-6 monofilament. E_e: ♦; E_s: × (m_2=700 g), + (m_2=800 g), ▲ (m_2=900 g); E_c: ⊡; Young's modulus: *

E_c

Figure 9 shows the relationship between V and m_2 in the case of creep for a nylon-6 monofilament. When m_1 is 56.9 g, 107.7 g or 240.5 g, the values of V

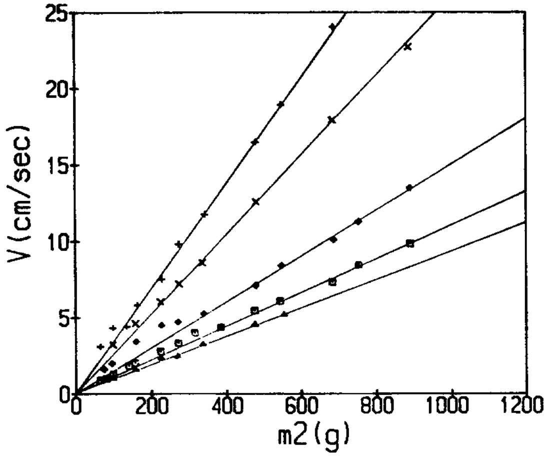

Fig. 9 Relationship between V and m_2 for a nylon-6 monofilament. m_1 (+:56.9 g, ×: 107.7 g, ♦: 240.5 g, ▣: 423.5 g, ▲: 605.2 g)

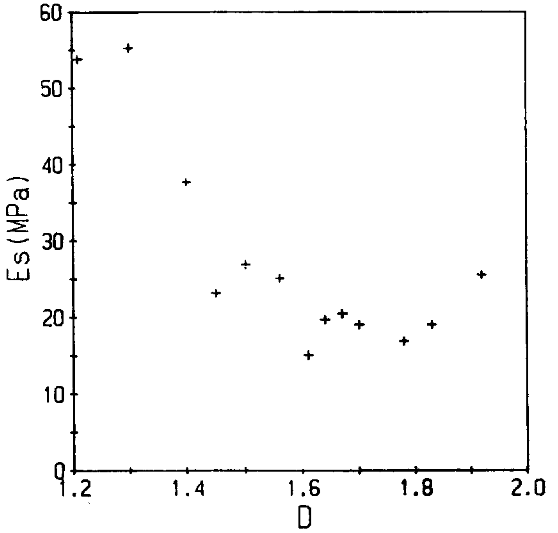

Fig. 10 Relationship between E_s and D for a silicone rubber (thickness: 0.1 cm)

in the lower range of m_2 are a little larger than the straight solid line of extrapolation. The sum of m_1 and the minimum value of m_2 in the experimental straight line was in the yield load range of 200–500 g on the load – elongation curve. From the slope of each straight line, E_c was calculated using Eq. (4). The relationship between E_c and m_1 is shown in Fig. 8. E_c increased with increasing m_1 and reached about 14 GPa at m_1=600 g (omitted in Fig. 8). Also in this case it is expected that a dense cohesive state could be introduced with increasing m_1. The value of E_c at m_1=173 g is close to E_s.

Silicone rubber

E_s and Q

Figure 10 shows the relationship between E_s and the draw ratio, D, for a silicone rubber (thickness: 0.1 cm). The value of E_s (53.8 MPa at D=1.2) decreased abruptly over D=1.3. In the range of D =1.4–1.9, E_s was an average of 22.6 MPa. Figure 11 shows the relationship between Q and D for a silicone rubber (thickness: 0.1 cm). Q was 4–56 J mol^{-1} in the range of D=1.2–1.9, and larger as D increased.

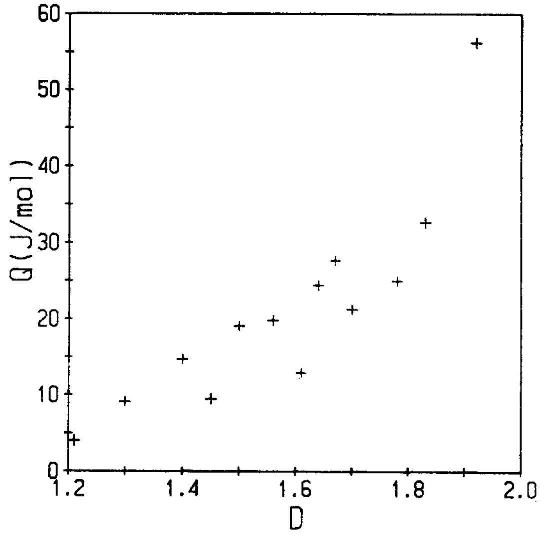

Fig. 11 Relationship between Q and D for a silicone rubber (thickness: 0.1 cm)

E_c and Q

Figure 12 shows the relationship between V and m_2 in the case of creep for a silicone rubber (thickness: 0.05 cm). For each m_1 (133.8 g, 238.2 g and 337.1 g) a straight line was obtained. From the slope of each straight line, E_c was calculated using Eq. (4). Figure 13 shows the relationship between E_c and m_1. The modulus E_c increased with increasing m_1, corresponding to the irreversible change of the cohesive state; the decrease of the recovery ratio to the initial length by increasing m_1+m_2. The recovery ratio was 80.0% at m_1+m_2=600 g, 90.7% at m_1+m_2=450 g, 96.3% at m_1+m_2=300 g and 99.3% at m_1+m_2=150 g. Figure 14 shows the relationship between Q and m_2 at each m_1 (238.2 g and 337.1 g). The value of Q was in the range of 0–11.5 J mol^{-1} and larger for larger m_2. Here let's hypothesize that the highly stretched state of a silicone rubber is equivalent to its frozen (glassy) state in the entropy change [5]. The heat capacity difference ΔC_p between a liquid and a glass at the glass

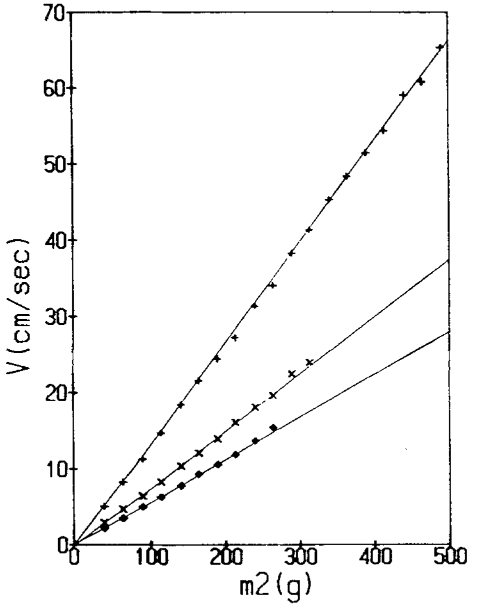

Fig. 12 Relationship between V and m_2 for a silicone rubber (thickness: 0.05 cm) m_1 (+: 133.8 g, × : 238.2 g and ♦: 337.1 g)

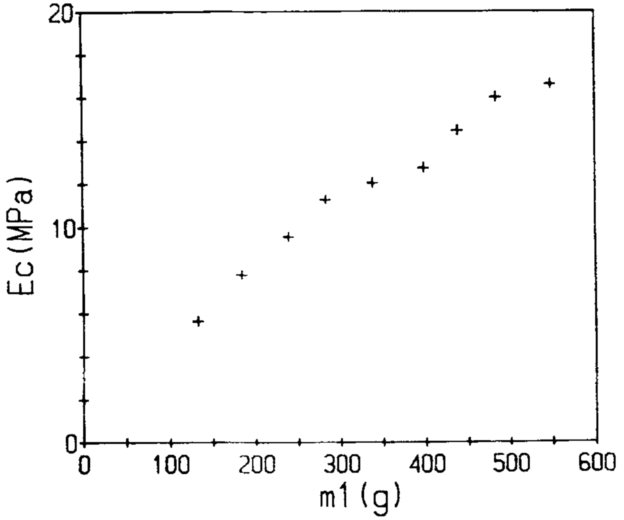

Fig. 13 Relationship between E_c and m_1 for a silicone rubber (thickness: 0.05 cm)

transition temperature, T_g, is 27.7 J $(K\ mol)^{-1}$ for polydimethyl-siloxane (T_g=146 K) [7]. Therefore, when the stretched state is released, a rise in temperature, ΔT=0.42 K ($=Q/\Delta C_p$, Q=11.5 J mol^{-1}) at m_1=238.2 g and

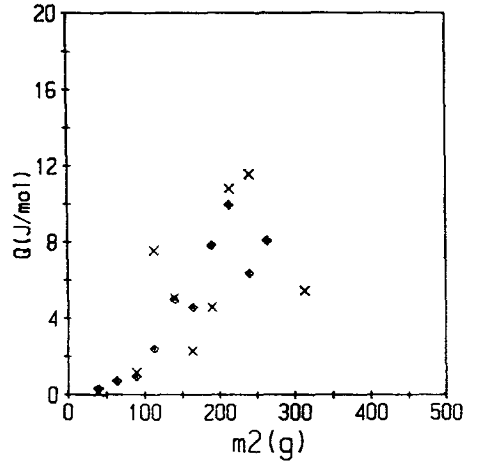

Fig. 14 Relationship between Q and m_2 at each m_1 (238.2 g (×), and 337.1 g (♦)) for a silicone rubber (thickness: 0.05 cm)

m_2=239.9 g in the case of creep (Fig. 14) and ΔT=2.03 K (=$Q/\Delta C_p$, Q=56.3 J mol^{-1}) in the case of stress relaxation at D=1.92 (Fig. 11), is expected. These values of ΔT are reasonable comparing with 2.06 K for Neoprene at D=2.0 and 0.42 K for Latex at D=2.0 [6].

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