Effect of pressure on drawing poly(oxymethylene) fibres: 4. Heat shrinkage of annealed superdrawn fibres

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The heat shrinkage of annealed transparent superdrawn poly(oxymethylene) fibres was quite small (even less than that of white fibres). This parameter is discussed in relation to fibre structural parameters such as void ratio, crystallinity, crystallite orientation and crystal size.

(Keywords: poly(oxymethylene); drawing; pressure effects)

INTRODUCTION

Highly oriented thermoplastic fibres having extremely high tensile modulus and strength are usually produced by drawing. However, intact fibres after drawing exhibit natural shrinkage even at ambient temperature, and at elevated temperature the heat shrinkage is considerably promoted. Thus, the fibres are generally annealed after drawing to prevent shrinkage. The relationship between mechanical properties and fibre structure, such as crystallinity and crystallite orientation, has been studied for various superdrawn fibres including polypropylene (PP), polyethylene (PE) and poly(oxymethylene) (POM).

Wyckoff[1] and Compostella *et al.*[2] studied the annealing of superdrawn PP fibres and found increased tenacity to result from greater crystallite orientation, crystallinity or both. Sheehan and Cole[3], however, considered that this could not necessarily be explained by these factors. Taylor and Clark[4] noted that superdrawn PP fibres exhibited only a small amount of shrinkage accompanied by 16% less modulus and 10% less tensile strength when held for 1 h at 155°C. Egorov[5] produced drawn POM filaments having a draw ratio of 7–13 by hot drawing and annealing at 150–170°C to prevent heat shrinkage. He found that filaments with larger draw ratios showed less shrinkage and reduction in tensile strength on annealing. Nakagawa *et al.*[6] obtained large diameter superdrawn POM fibres, whose tensile modulus was as much as 60 GPa, by microwave heating/drawing to produce POM fibres which could be used in optical fibres. After annealing, the fibres showed a linear expansion coefficient as small as $10^{-6}\,°C^{-1}$; the same as that for quartz optical fibres. They also estimated the crystal modulus of POM from the relationship between dynamic moduli corrected for void ratios and heat shrinkage on annealing[7].

The heat shrinkage of annealed superdrawn fibres is an important factor when considering fibre applications. The authors recently developed a new superdrawing technique under high pressure and found the resultant fibres possessed excellent mechanical properties and chemical resistance by virtue of their dense structure[8,9]. The present study was conducted to examine heat shrinkage of annealed superdrawn POM fibres as well as effects of fibre structure on heat shrinkage.

EXPERIMENTAL

Sample preparation

The POM drawn fibres were prepared by pressurized drawing and conventional drawing from an undrawn tube (outer diameter 4.6 mm, inner diameter 1.5 mm) using the acetal homopolymer Tenac 3010 (Asahi Chemical Industry Co. Ltd), according to the procedure described elsewhere[10]. Silicone oil on the drawn fibres was removed with fresh freon-113.

Measurements

Tensile modulus in the direction of the fibre axis was determined from the slope of the stress–strain curve obtained with an Instron tensile testing machine. The cross-sectional area for calculating this parameter was determined from the diameter of the sample. The value obtained was taken as the bulk modulus (E). The modulus E', corrected for void ratios (f_v), was determined from $E' = E/(1 - f_v)$. The value of f_v was estimated from the apparent density (ρ_{app}) and true density (ρ), as follows:

$$f_v = 1 - (\rho_{app}/\rho) \qquad (1)$$

The value of ρ_{app} was obtained from the weight per unit length and cross-sectional area and ρ was obtained from the crystallinity (X_c) according to reference 8. The crystallinity was based on differential scanning calorimetry (d.s.c.) measurements. The sample was cut into small pieces (0.1 mm thick). The sample (5.0 mg) was then subjected to d.s.c. at a heating rate of 8°C min^{-1}. The draw ratio (λ) was determined from that of the sample weight per unit length before and after drawing. Crystal orientation (f_c) was calculated from the half-width of the (1 0 0) reflection. The size of crystals perpendicular to the (1 0 0) plane was determined as

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Table 1 Physical properties of drawn POM fibres

λ	W (g m^{-1})	E (GPa)	E' (GPa)	Diameter (mm)	ρ_{app} (g cm^{-3})	ρ (g cm^{-3})	f_v (%)	Appearance
Pressurized drawn fibre								
20	1.054	43	43	0.96	1.45	1.44	0	t
21	1.004	45	45	0.94	1.45	1.44	0	t
22	0.958	46	46	0.92	1.45	1.44	0	t
23	0.916	47	47	0.90	1.45	1.45	0	tl
24	0.878	45	48	0.91	1.36	1.45	6.0	w
26	0.811	45	50	0.89	1.31	1.46	10.0	w
Conventional drawn fibre								
21	1.004	36	38	0.97	1.35	1.44	6.6	w
22	0.958	36	40	0.97	1.29	1.44	10.4	w
26	0.787	34	44	0.94	1.14	1.46	21.9	w

Abbreviations: t, transparent; tl, translucent; w, white; W, weight per metre; E, bulk tensile modulus; E', modulus corrected for void ratios; ρ_{app}, apparent density; ρ, true density; f_v, void ratio; λ, draw ratio

Table 2 Heat shrinkage of drawn POM fibres

λ	E' (GPa)	First heat shrinkage (%)	Second heat shrinkage (%)
21	45	1.54	0.01
24	48	1.39	0.02
26	50	1.31	0.08

First annealing was at 130°C for 20 h; second annealing was at 100°C for 2300 h

follows. The diffraction profile of an equatorial reflection was deconvoluted by the standard Stokes technique. The instrumental profile was obtained for an aluminium sample, using the same geometry. Crystal size (L) was deduced from the half-width (B) of the profile using the Scherrer equation[11]:

$$L = K\lambda / B(\text{true}) \cos\theta \qquad (2)$$

$$B(\text{true}) = B(\text{obs}) - B(\text{inst}) \qquad (3)$$

where K was put[11] at 0.9 and B(true), B(obs) and B(inst) are the true, observed and instrumental half-widths, respectively.

Heat shrinkage

The original drawn fibres were annealed in two steps, and the heat shrinkage at each step was measured. Annealing was first conducted by the following two procedures: (1) the original fibres were left without tension in heated air at 120 or 130°C for 20 h in an oven; and (2) the fibres were passed through heated silicone oil at 170°C for 2 min. The latter operation was carried out at a feed speed 4% faster than the take-up speed, and the resultant fibres were left again in air heated at 120°C for 2 h. Heat shrinkage in the first annealing (first shrinkage) was measured before the second annealing. The second annealing was carried out as follows: the samples were left without tension for a certain period of time in air at temperatures maintained at 100, 110 and 120°C. The first and second heat shrinkages were measured under a tension of 50 g so as to eliminate the influence of sample curvature and bending. The original sample length was 2000 mm.

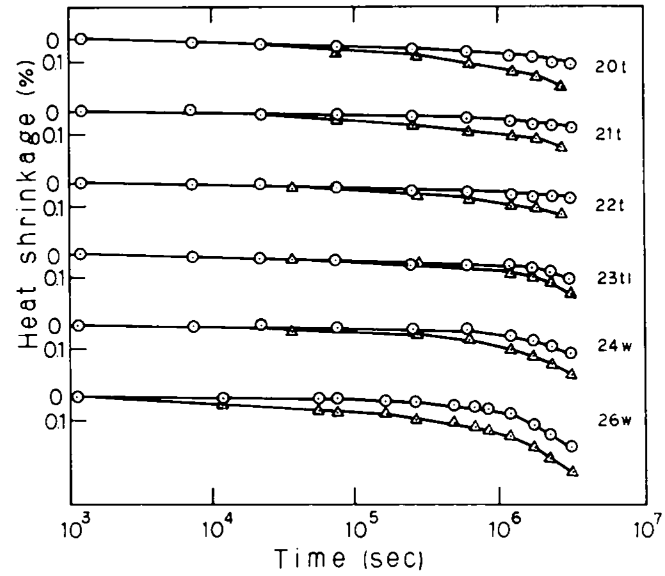

Figure 1 Second heat shrinkage of the pressurized drawn fibres with various draw ratios which were annealed at 170°C for 2 min followed by 120°C for 2 h. Second annealing temperature: (○) 100°C; (△) 120°C

RESULTS AND DISCUSSION

Table 1 presents the physical properties of the original drawn samples and *Table 2* gives the shrinkage of the first and second annealed samples with various tensile moduli (E'). The first shrinkage decreased with increase in modulus, as also noted by Takeuchi *et al.*[7]. That is, the shrinkage was inversely proportional to the modulus. The second shrinkage was much less than the first and showed no definite relationship to the modulus. *Figure 1* shows the second shrinkage *versus* time curves at 100 and 120°C for drawn samples having various draw ratios. The samples had been annealed at 120°C for 20 h. Samples with $\lambda = 20, 21, 22$ and 23 shrunk less than those with $\lambda = 24$ and 26. Shrinkage was essentially the same for samples with $20 \leqslant \lambda \leqslant 23$, but increased for $\lambda = 24$ and 26. The samples were transparent for $20 \leqslant \lambda \leqslant 22$, translucent for $\lambda = 23$ and white for $24 \leqslant \lambda \leqslant 26$. *Figure 2* shows the second shrinkage *versus* time curves for both transparent samples with $\lambda = 21$ and 22 (pressurized drawing) and white samples with $\lambda = 26$ (pressurized

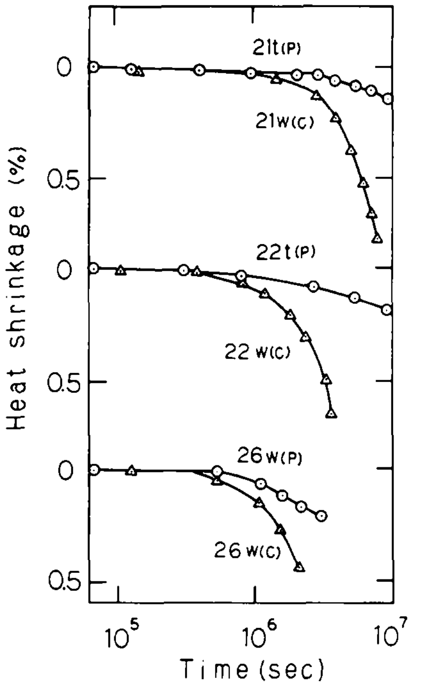

Figure 2 Second heat shrinkage at 100°C of the transparent fibres and white fibres which were annealed at 120°C for 20 h: (○) transparent fibres (pressurized drawing); (△) white fibres (conventional drawing)

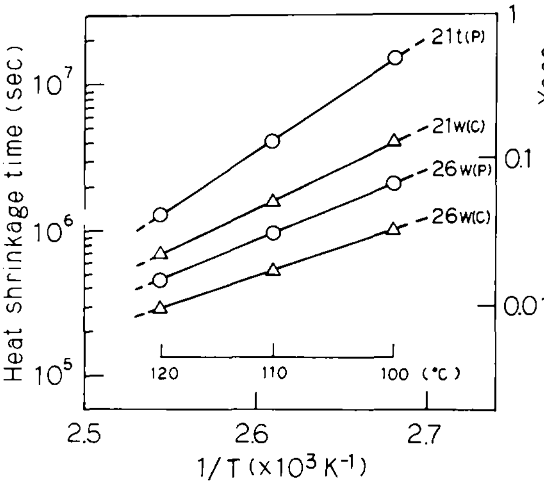

Figure 3 Relationship between the reciprocal of temperature and the logarithm of time required for 0.1% heat shrinkage. First annealing was at 130°C for 20 h

drawing) and $\lambda = 21$, 22 and 26 (conventional drawing). The transparent samples shrank far less than the white samples.

Figure 3 shows log(time required for 0.1% shrinkage) *versus* reciprocal temperature plots for the transparent drawn sample with $\lambda = 21$ (pressurized drawing) and white samples with $\lambda = 26$ (pressurized drawing) and $\lambda = 21$ and 26 (conventional drawing). In all cases, an Arrhenius type linear relationship is evident. The transparent sample had a larger slope than the white samples, and thus was more capable of resisting shrinkage. In *Figure 3*, the velocity of shrinkage for the transparent and white samples with the same draw ratio (21) are 1.5×10^{-8} and $4 \times 10^{-7}\,s^{-1}$ at 100°C, respectively. The fact that the transparent fibres are smaller than the white fibres in the second shrinkage is indicated here for the first time. Void ratios, crystallinity, crystallite orientation and crystal size were measured before and after the first and second annealings and the results are shown in *Table 3*. Based on the results obtained, the following statements can be made: (1) the second shrinkage is larger for samples with larger void ratios; (2) the magnitudes of crystal orientation, crystallinity and crystal size did not affect the second shrinkage; (3) crystal orientation, crystallinity and crystal size increase slightly after annealing. It would thus appear that the second shrinkage of superdrawn POM fibres is affected by voids but not by crystalline parameters such as crystallinity, orientation and crystal size. Shrinkage was accompanied by a slight increase in these parameters and consequently semicrystalline cohesion and reorientation may occur during the second shrinkage. Also, crystal movement may be easier for samples having many voids, since they facilitate the thermal movement in semicrystallites.

Table 3 Change in the fibre structure parameters on annealing

	λ	Original	First annealing	Second annealing
f_v (%)	21t(p)	0.0	0.0	0.0
	21w(c)	6.6	5.6	4.5
	26w(p)	10.0	9.4	8.2
	26w(c)	21.9	20.6	19.4
f_c (%)	21t(p)	97.6	97.7	97.7
	21w(c)	97.3	97.5	97.5
	26w(p)	97.3	97.5	97.5
	26w(c)	97.0	97.3	97.3
L_c (%)	21t(p)	135	158	170
	21w(c)	122	144	159
	26w(p)	110	135	152
	26w(c)	102	125	143
X_c (%)	21t(p)	73	73	73
	21w(c)	73	73	73
	26w(p)	78	79	79
	26w(c)	78	79	79

Abbreviations: λ, draw ratio: t, transparent; w, white; (p) pressurized drawn fibre; (c), conventional drawn fibre; f_v, void ratio; f_c, crystal orientation; L_c, crystal size; X_c, crystallinity.
First annealing was at 130°C for 20 h; second annealing was at 100°C for 2300 h

CONCLUSIONS

Annealed superdrawn POM fibres exhibit quite a small second heat shrinkage with a velocity as small as 10^{-8}–$10^{-7}\,s^{-1}$ at 100°C. The second heat shrinkage of transparent fibres is somewhat less than that of white fibres. This may be related to the void ratio but not to the magnitude of crystal orientation, crystallinity or crystal size.

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