The effects of pressure on drawing polyoxymethylene: 3. Effects of voids on the chemical resistance of polyoxymethylene drawn fibres

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Assessment was made of the chemical resistance of superdrawn polyoxymethylene fibres produced by pressurized drawing. The fibres were found to have good properties such as alkali, acid, thermal and weather resistance. The relation between these properties and fibre structure is discussed.

(Keywords: chemical resistance; void; drawn fibre; polyoxymethylene)

INTRODUCTION

Polyoxymethylene (POM) is a thermoplastic resin, known as polyacetal, and has comparatively good hardness, stiffness, strength and also thermal, chemical, solvent and dimensional stability. It is thus widely used as an engineering plastic. The theoretical crystalline modulus of POM is estimated as 90–150 GPa[1,2]. Hitherto, superdrawn POM has been found to be quite useful owing to its superior mechanical properties such as with respect to tensile strength[3–5], modulus[4–7], heat shrinkage[8], creep[9], flexural characteristics[4] and coefficient of thermal expansion[10]. Little is known, however, about its chemical resistance. In part 2, superdrawn POM fibres were shown to be produced by pressurized drawing and to have a dense and fully oriented structure. In the following we discuss the chemical resistance of superdrawn POM fibres in relation to structure.

EXPERIMENTAL

POM drawn fibres were prepared by pressurized and conventional drawing using undrawn tube with an outer diameter of 3.2 mm and inner diameter of 1.0 mm from the acetal homopolymer 'Tenac 3010' (Asahi Chemical Ind. Co. Ltd). These preparations and measurements of mechanical properties were conducted as in parts 1 and 2. Silicone oil on the drawn fibres was completely removed by fresh Freon-113. The details for this are presented in part 2.

Measurement of chemical resistance

Alkali resistance was determined from retention of tensile modulus, tenacity and weight of sample dipped in 4% aqueous sodium hydroxide at 60°C. Acid resistance was determined in the same way except that 4% aqueous hydrochloric acid was used at 60°C.

Thermal ageing was assessed according to JIS K7212 (1977) as follows. The sample was exposed to heated air in an oven for a certain time, and taken out. The retention of tenacity was measured at room temperature.

Weather resistance was determined at 63°C using a sunshine weathermeter (Suga-Shikenki Co.) and a sunshine super-long-life weathermeter (WEL-SUN-HC). A sunshine carbon arc lamp served as the light source. After removing the weathered sample from the weathermeter, retention of tenacity was measured at room temperature.

The cross-sectional areas of the samples before and after chemical treatments were determined from sample diameters. Sample structure was observed with a scanning electron microscope (Hitachi-Seisakusho Co., S-430).

RESULTS AND DISCUSSION

Table 1 shows the physical properties of samples used for subsequent experiments. Pressurized drawn fibres of $\lambda = 18$, 20 and 22 were all transparent. The conventional drawn fibres and undrawn filament were white.

Alkali resistance

Table 2 shows the retention of tenacity, tensile modulus and weight of the samples in 4% aqueous sodium hydroxide at 60°C. The pressurized fibres showed 100% resistance. The tenacity of the conventional fibres and undrawn filament rapidly decreased. The retention of the conventional fibres was more improved than that of the undrawn filament. The fibre eventually became so brittle that the tensile modulus and tenacity could not be measured. The loss of tenacity was greater for conventional fibres with a large void ratio. The weight loss of the conventional fibres was slight (several per cent) in spite of remarkable tenacity loss. Loss of tensile modulus was little observed. Thus, fibrils along the fibre axis were not damaged.

The alkali resistance test of the pressurized fibres under more severe conditions was carried out in 4% aqueous sodium hydroxide at 160°C in an autoclave. The fibres

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Table 1 Physical properties[a] of the drawn POM fibres

	σ (kg)	E (GPa)	W ($g\,m^{-1}$)	D (mm)	x_c (%)	ρ_{cal} ($g\,cm^{-3}$)	ρ_{app} ($g\,cm^{-3}$)	f_v (%)
Pressurized drawn fibre								
$\lambda=18$	68.5	38	0.572	0.709	77	1.43	1.45	0
$\lambda=20$	68.9	43	0.515	0.673	81	1.44	1.45	0
$\lambda=22$	65.9	46	0.468	0.641	83	1.44	1.45	0
Conventional drawn fibre								
$\lambda=18$	59.3	32	0.572	0.727	77	1.43	1.38	3
$\lambda=20$	55.6	37	0.515	0.692	81	1.44	1.37	5
$\lambda=22$	50.3	40	0.468	0.670	83	1.44	1.33	8
Undrawn filament	7.4	2	1.488	1.155	50	1.42	–	–

[a] λ = draw ratio, σ = tenacity, E = apparent tensile modulus, W = weight, D = diameter, x_c = crystallinity, ρ_{cal} = calculated density, ρ_{app} = apparent density, f_v = void ratio

Table 2 Alkali resistance of the drawn POM fibres

	Tenacity (%)				Modulus (%)				Weight (%)			
	100 h	200 h	300 h	500 h	100 h	200 h	300 h	500 h	100 h	200 h	300 h	500 h
Pressurized drawn fibre												
$\lambda=18$	100	102	102	100	103	103	103	103	100	100	100	100
$\lambda=20$	100	102	102	100	103	103	103	103	100	100	100	100
$\lambda=22$	100	103	95	98	103	104	103	104	100	100	100	100
Conventional drawn fibre												
$\lambda=18$	100	102	100	96	102	103	102	100	100	100	100	100
$\lambda=20$	100	100	94	66	102	102	100	99	100	100	100	98
$\lambda=22$	68	53	5	0	100	100	–	–	98	97	97	96
Undrawn filament	0	–	–	–	–	–	–	–	97	–	–	–

completely decomposed in 6 h. The pressurized fibres showed better alkali resistance than the conventional fibres and an undrawn filament under the limited conditions in this work. The good resistance of the pressurized fibres was due to the highly oriented structure, but this is difficult to explain only as due to rapid decrease in the tenacity of the highly oriented conventional fibres.

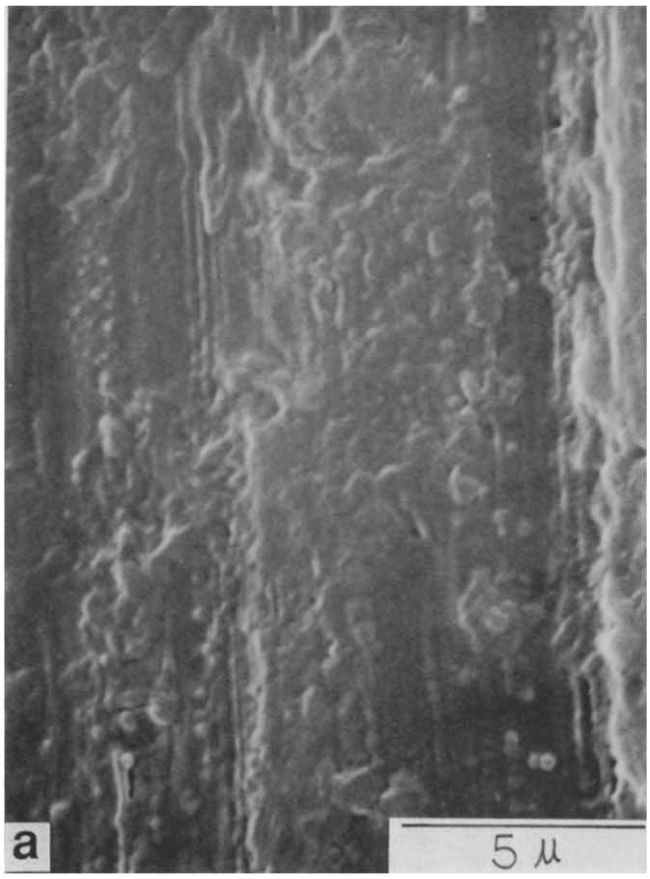
Figures 1a and *1b* show SEM micrographs of the original sample surface. The pressurized fibre showed a dense structure free of voids. The conventional fibre showed a void structure of a ladder connecting fibrils transversely to the fibre axis. *Figures 2a* and *2b* show SEM micrographs of the sample surface after being dipped in 4% aqueous sodium hydroxide at 60°C for 500 h. The pressurized fibres retained the dense structure, while conventional fibres became more fibrous and bundles of fibrils split. This occurred without lateral bonding, thus permitting the fibrils to slip easily even with a small applied mechanical force. The remarkable decrease in tenacity in the conventional fibres may possibly have been due to rupture of the lateral bonding between bundles of fibrils by alkali solution, since the tensile modulus showed virtually no decrease. The good alkali resistance of the pressurized fibres was due to the dense structure, which did not permit penetration of the alkali solution.

Acid resistance

Table 3 shows the retention of tenacity, tensile modulus and weight of the samples in 4% aqueous hydrochloric acid at 60°C. These parameters decreased rapidly for all samples compared with the case of alkali resistance. The pressurized fibres were more durable than the conventional fibres and undrawn filament. Loss in tenacity of the pressurized fibres was nearly the same as weight loss. The tenacity of the conventional fibres decreased more rapidly than weight. It thus follows that pressurized fibres decomposed from the surface exposed to the acid and conventional fibres decomposed on the surface and inside due to penetration of the acid. The conventional fibres became less stable with increase in the void ratio.

Fibre decomposition was also examined in 4% aqueous hydrochloric acid at 80°C. The pressurized fibres and conventional fibres completely decomposed in 48 and 8 h, respectively

Figures 3a and *3b* show SEM micrographs of the drawn samples ($\lambda=22$) dipped in 4% aqueous hydrochloric acid at 60°C for 100 h. The pressurized fibres decomposed on the surface but maintained their dense structure. The



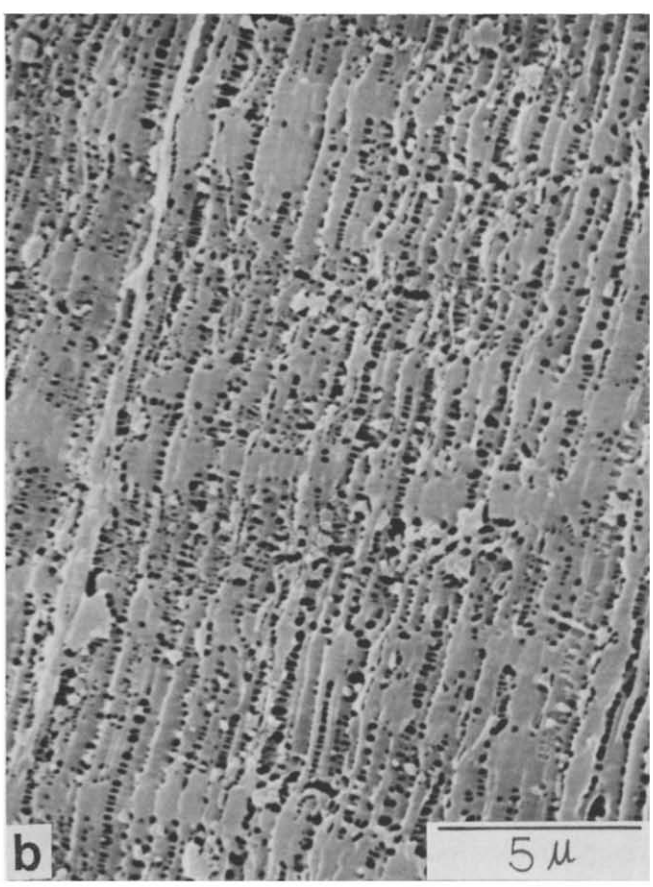
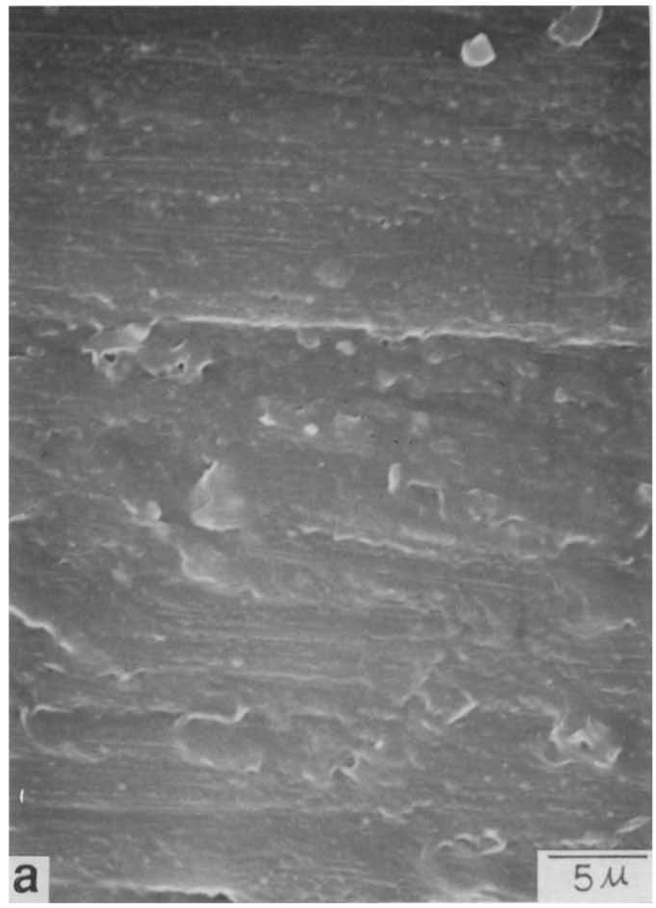


Figure 1 SEM micrographs of the original sample surfaces: (a) pressurized drawn fibre ($\lambda = 22$); (b) conventional drawn fibre ($\lambda = 22$)



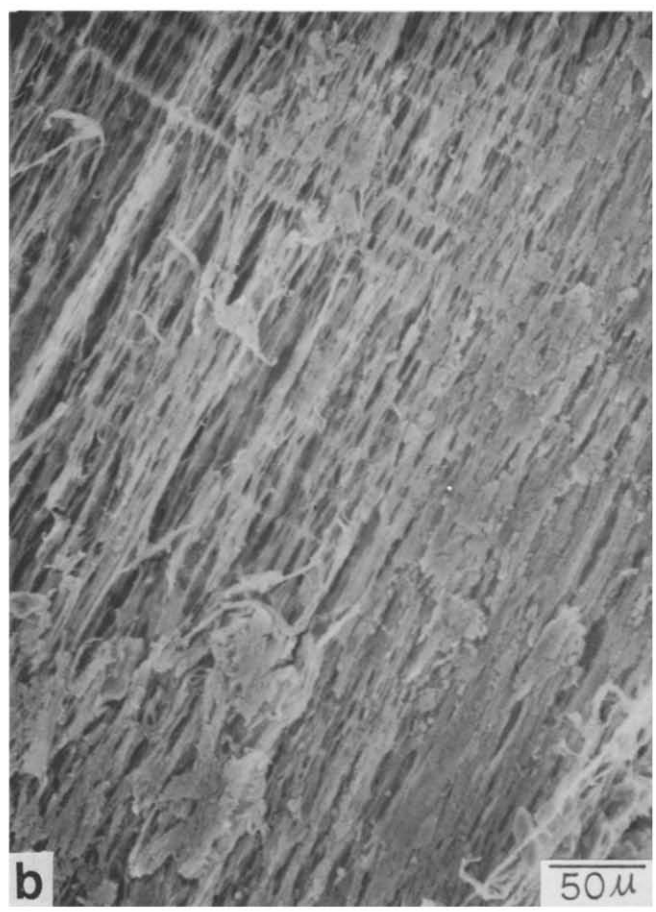


Figure 2 SEM micrographs of the sample surfaces of drawn fibres ($\lambda = 22$) after being dipped in 4% aqueous sodium hydroxide at 60°C for 500 h: (a) pressurized drawn fibre; (b) conventional drawn fibre

Table 3 Acid resistance of the drawn POM fibres

	Tenacity (%)			Modulus (%)			Weight (%)		
	20 h	60 h	100 h	20 h	60 h	100 h	20 h	60 h	100 h
Pressurized drawn fibre									
$\lambda = 18$	93	88	82	100	100	100	96	91	84
$\lambda = 20$	94	88	82	100	100	100	96	91	84
$\lambda = 22$	95	89	82	100	100	100	97	92	85
Conventional drawn fibre									
$\lambda = 18$	80	62	42	100	100	96	90	75	65
$\lambda = 20$	60	42	28	100	96	88	72	65	54
$\lambda = 22$	43	24	19	96	85	76	66	50	40
Undrawn filament	50	0	0	–	–	–	60	24	0

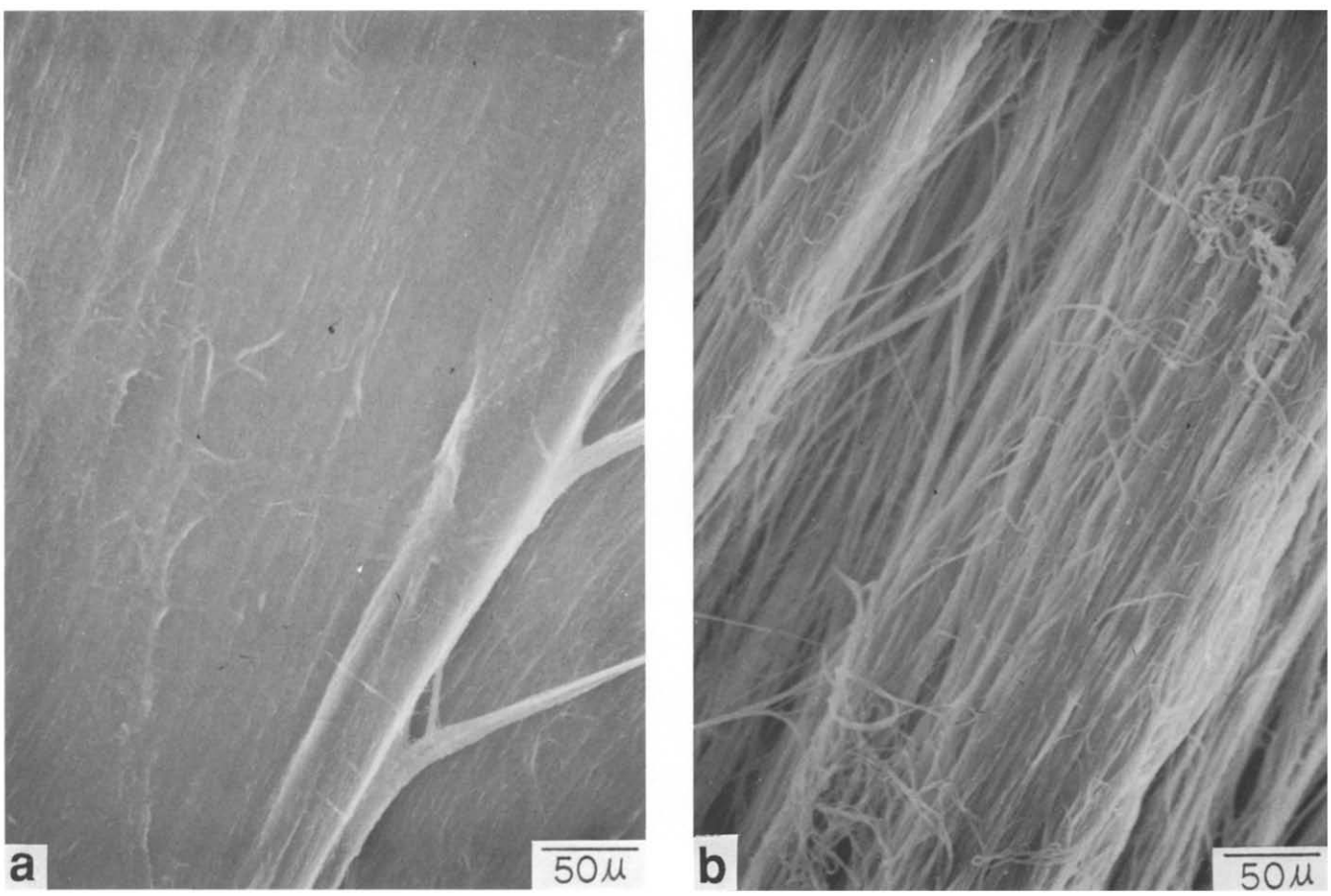


Figure 3 SEM micrographs of drawn fibres ($\lambda = 22$) dipped in 4% aqueous hydrochloric acid at 60°C for 250 h: (a) pressurized drawn fibre; (b) conventional drawn fibre

conventional fibres decomposed on the surface and inside, and the ladder structure noted prior to dipping vanished completely. Improvement of the pressurized fibres was for the same reason as for alkali resistance.

Resistance to weather

Table 4 shows the resistance of the drawn fibres to weather. For pressurized and conventional fibres, this parameter was higher than for the undrawn filament. The pressurized fibres kept 95% their tenacity at 1000 h (equivalent to 4 years under natural conditions) and were of good quality compared with the conventional fibres and undrawn filament. The tenacity subsequently became 78% at 1500 h, nearly the same as that of the conventional fibres at 1000 h. The tenacity of the conventional fibres decreased with greater void ratio. The tensile modulus and weight of both drawn fibres decreased little during 1500 h.

Thermal resistance

Figure 4 shows the thermal ageing properties of drawn fibres with $\lambda = 22$. For pressurized fibres, it was higher

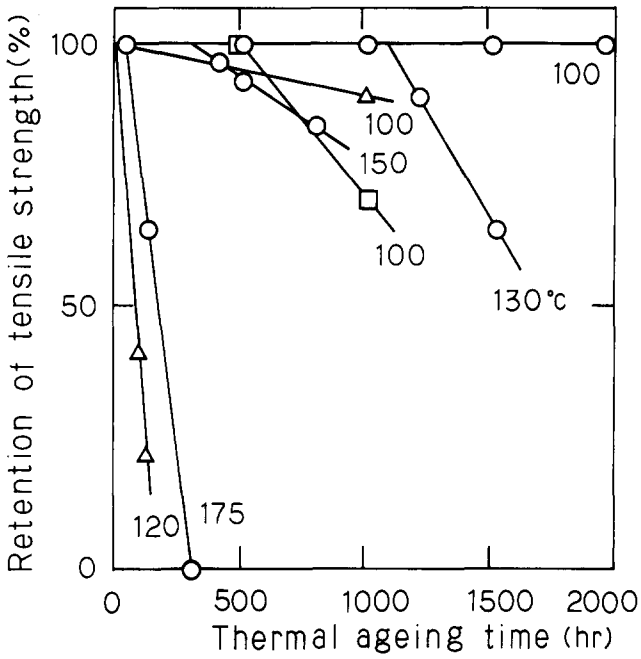


Figure 4 Retention of the tenacity of drawn fibres aged in hot air at several temperatures: (○) pressurized drawn fibre; (△) conventional drawn fibre; (□) undrawn filament

than that for conventional fibres and undrawn filament. The tenacity of the pressurized fibres was maintained for a certain period and subsequently decreased linearly with weathering time. This decrease occurred more rapidly with rise in temperature. *Figures 5a* and *5b* show SEM micrographs of the surfaces of thermally aged drawn fibres. The pressurized fibres kept their transparency and external appearance. The conventional fibres aged so much as to peel off like scales. The thermal ageing of the conventional fibres may have given rise to the porous structure of the surface, and may have been caused by oxidation, because it was not observed in an atmosphere of nitrogen.

CONCLUSIONS

Resistance to chemical factors such as alkali, acid, weather and heat on the part of the pressurized and conventional fibres was assessed and its relationship to fibre structure was examined. The pressurized fibres were found to be superior to the conventional ones. The structure of the pressurized fibres was dense and free of voids, while conventional fibres showed a porous structure containing many voids. The structure means less resistance since it permits chemical substances to penetrate the inside of fibres and surface area exposure is large. The good chemical resistance of pressurized fibres is due to their dense structure and high degree of molecular orientation.

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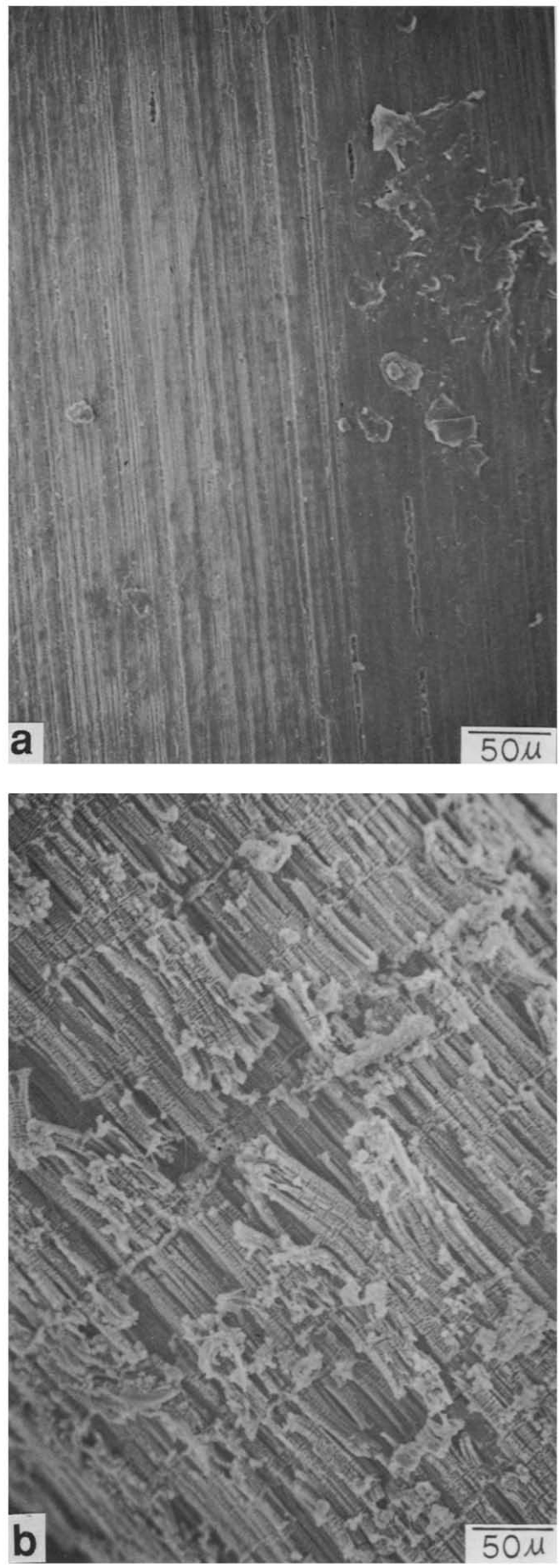

Figure 5 SEM micrographs of the surface of drawn fibres aged in hot air: (a) pressurized drawn fibre after 2300 h at 100°C; (b) conventional drawn fibre after 1500 h at 100°C

Table 4 Weather resistance of the drawn POM fibres

	Tenacity (%)			Modulus (%)			Weight (%)		
	500 h	1000 h	1500 h	500 h	1000 h	1500 h	500 h	1000 h	1500 h
Pressurized drawn fibre									
$\lambda = 18$	100	95	78	100	100	99	100	100	98
$\lambda = 20$	100	95	78	100	100	99	100	100	98
$\lambda = 22$	100	95	78	100	100	99	100	100	98
Conventional drawn fibre									
$\lambda = 18$	100	92	75	100	100	99	100	100	97
$\lambda = 20$	100	85	75	100	100	99	100	100	97
$\lambda = 22$	87	80	74	100	99	98	100	98	97
Undrawn filament	34	0	–	–	–	–	–	–	–

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