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ORIGINAL CONTRIBUTION

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Alkaline degradation behavior of polyesteramide fibers: surface erosion

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Abstract In this work, a new kind of aliphatic polyesteramide (PEA) copolymer based on ε-caprolactone and 6-aminocaproic acid was synthesized by the melt polycondensation method. Biodegradable PEA fibers were processed by the melt-spinning method. ^{1}H-NMR, FTIR, SEM, and tensile testing were used to characterize the degradation of PEA fibers in concentrated alkaline solution. The PEA fiber undergoes surface erosion in such concentrated alkaline solutions.

Keywords Polyesteramide · Degradation · Fiber · Surface erosion

Introduction

Aliphatic polyesters are an important class of biodegradable synthetic polymers [1, 2]. However, they are not easily substituted for generally used polymers because they have poor thermal and mechanical properties. Aliphatic polyamides (nylon 6 and nylon 66) have better thermal and mechanical properties than aliphatic polyesters, but they are nonbiodegradable, although some weight loss has been measured in enzyme degradation [3]. The large concentration of hydrogen bonds and high regularity of the polyamide structure are the possible reason for the inertness of these nylons to biodegradation. So, polyesteramides (PEA) composed of ester and amide backbones could potentially be a class of biodegradable polymers, which may have good degradability, thermal properties, and mechanical properties [4, 5, 6, 7].

PEA of similar $NH(CH_2)_5CO$ and $O(CH_2)_5CO$ co-unit contents was obtained (a) by the anionic copolymerization of ε-caprolactone and ε-caprolactam at 100–160 °C with sodiocaprolactam as catalyst [4, 5, 6], (b) by addition/condensation copolymerization of the hydroxyester $HO(CH_2)_5CONH(CH_2)_5COOCH_3$ at 180 °C with 1 wt% of $Ti(OBu)_4$ as catalyst [4], (c) by interchange reactions of nylon and polycaprolactone [7], and (d) by interfacial polymerization [8]. Several kinds of PEA copolymers have been prepared [9, 10, 11] in our laboratory. Gonsalves et al. [12, 13] have studied the hydrolytic degradation in buffer solution and the biodegradation by fungi of two types of nonalternating PEAs. They found that the random poly(ester-co-amide)s were readily degradable under the attack of the fungus *Cr. laurentii*. The biodegradation of this copolymer occurred via surface erosion, catalyzed by enzymes, while abiotic hydrolysis occurred not only on the surface, but also in the bulk of the copolymer.

Some investigators have reported that surface modifications of biodegradable polymers in alkaline solution could be used to generate a hydrophilic and rough surface for cell attachment [14, 15, 16].

In this paper, a new kind of PEA copolymer, P(CL/AC)50/50, based on ε-caprolactone and 6-aminocaproic acid was synthesized by the melt polycondensation method. Biodegradable [12] PEA fibers were produced by the melt-spinning method. To observe the detailed degradation and the surface modification of the PEA fiber in alkaline solution, this paper presents results on the surface

degradation of melt-spun PEA fibers in a concentrated NaOH solution at 37 °C. Characterization and discussions on the intrinsic viscosity, fiber diameter, fiber weight, fiber morphology, chemical structure, and tensile properties of the PEA fibers after degradation are presented.

Experimental

Synthesis of P(CL/AC)50/50 samples

P(CL/AC)50/50 copolymer was synthesized from ε-caprolactone and 6-aminocaproic acid by the melt polycondensation method. It was prepared as follows: 18.26 g (0.16 mol) of ε-caprolactone, 21.00 g (0.16 mol) of 6-aminocaproic acid, and 0.3 g of tetrabutyl titanate were added to the reaction vessel under nitrogen atmosphere. The mixture was kept at 120 °C for 1.5 h. The temperature was gradually raised to 200 °C in 40 min, then the mixture was rapidly heated to 260 °C under vacuum for 2 h. At the end, the resultant melt was poured out onto a steel plate. The P(CL/AC)50/50 copolymer obtained was cut into small particles with a diameter of ca. 4 mm using scissors, and dried to constant weight at 40 °C in a vacuum. The particles were used to produce PEA fibers.

Preparation of PEA fibers

Melt spinning of P(CL/AC)50/50 copolymers was carried out using a melt flow-rate instrument equipped with a single-nozzle circular spinnerette (0.9 mm diameter). PEA was extruded at 105 °C. The as-spun fibers were collected on a glass drum at ca. 4.5 m/min. The as-spun fibers were drawn to a 3.0 ratio at 45 °C to get the final hot-drawn fibers. The PEA fibers were stored in a desiccator for further use.

PEA fiber degradation

P(CL/AC)50/50 fibers were bundled into several groups, each group having ten fibers (each fiber was about 20 cm long). They were incubated in glass vessels with 40 ml of 1.0 M NaOH solution at 37 °C. At a predetermined time, one group of fibers was removed from the medium, washed with water thoroughly, and dried in vacuum at 40 °C for 2 h for further measurements. The diameter of the fibers was measured using an optical microscope.

Weight loss of PEA fibers

The weight loss of PEA fibers was calculated according to the dry weight of the fibers after degradation in alkaline medium according to Eq. 1:

$$\text{Weight loss } (\%) = \frac{W_0 - W_{dt}}{W_0} \times 100 \quad (1)$$

where W_0 is the dry weight before degradation and W_{dt} is the dry weight at time t.

Water uptake of PEA fibers

The wet weight of the PEA fibers after degradation was obtained by weighing the wet fibers after absorbing the surface water with a tissue. The water uptake of the fibers was calculated by rating the mass difference of the wet and the dried fibers as follows:

$$\text{Water uptake} = \frac{W_{wt} - W_{dt}}{W_{dt}} \times 100\% \quad (2)$$

where W_{wt} and W_{dt} are the wet and dried weight of PEA fibers at time t, respectively.

Intrinsic viscosity measurement

Intrinsic viscosity [η] was measured by using an Ubbelohde viscometer at 30 ± 0.1 °C. All the copolymers were dissolved in chloroform to prepare solutions of ca. 0.5 g/dL. [η] was calculated using Eq. 3 according to the Solomon–Ciuta method,

$$[\eta] = \frac{\sqrt{2\left(\frac{t}{t_0} - 1 - \ln\frac{t}{t_0}\right)}}{C} \quad (3)$$

where C is the concentration of the solution, t is the flow time of the solution, and t_0 is the flow time of pure solvent.

^{1}H-nuclear magnetic resonance (^{1}H-NMR)

^{1}H-NMR spectra (in $CDCl_3$) were recorded using a Bruker 300 spectrometer (Bruker, Germany) at 300 MHz using trimethylsilane as an internal reference standard.

Fourier-transform infrared spectroscopy (FTIR)

FTIR (KBr) spectra of the copolymers were taken with a Nicolet 200SXV spectrophotometer.

Surface morphology study

The morphology of PEA fibers was observed under an Amray scanning electron micrograph (SEM) (Amray, USA) at an electron voltage of 18 kV after gold coating.

Tensile properties of PEA fibers

The tensile properties of PEA fibers were measured by a tensile testing machine (PC/YG061F, Laizhou, Shangdong Province, China). A specimen gauge length of 10 mm was used. The tests were carried out at a crosshead speed of 300 mm/min at room temperature. The results obtained were averaged over four samples for each condition. The diameters of the fibers were measured with an optical microscope. The ultimate strength (σ) was calculated using Eq. 4:

$$\sigma = \frac{P}{A}(\text{MPa}) \quad (4)$$

where P is the absolute tensile breaking strength (N) of the PEA fiber and A is the fiber's transverse area (mm^2) before tensile testing.

Results and discussion

Synthesis of P(CL/AC)50/50 sample and preparation of PEA fibers

FTIR and ^{1}H-NMR were used to characterize the chemical structure of PEA copolymer. The ^{1}H-NMR spectrum is shown in Fig. 1. The characteristic absorption

peaks are also indicated in this figure. The chemical compositions were determined from ^{1}H-NMR spectra according to Eqs. 5 and 6:

$$X_{PCL} = I_e/(I_e+I_j) \quad (5)$$

$$X_{PAC} = I_j/(I_e+I_j) \quad (6)$$

where I_e and I_j are the integral intensities of the methylene hydrogen of PCL blocks at about 4.03 ppm, and the methylene hydrogen of PAC blocks at about 3.19 ppm, respectively. The sample CL/AC ratio (mol%) = 1.00/1.07, which is in accord with the feed ratio of CL/AC (mol%) = 1.00/1.00. The sample FTIR spectrum included bands at 3317 (N–H), 1737 (C = O), 1641, 1545 (amide I II), and 1170 cm^{-1} (C–O) consistent with an esteramide structure, as shown in Fig. 2.

The properties of the resultant PEA fibers are shown in Table 1.

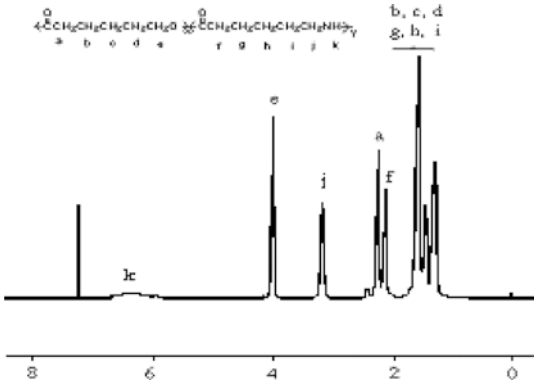

Fig. 1 ^{1}H-NMR spectrum of P(CL/AC)50/50 copolymer (in $CDCl_3$)

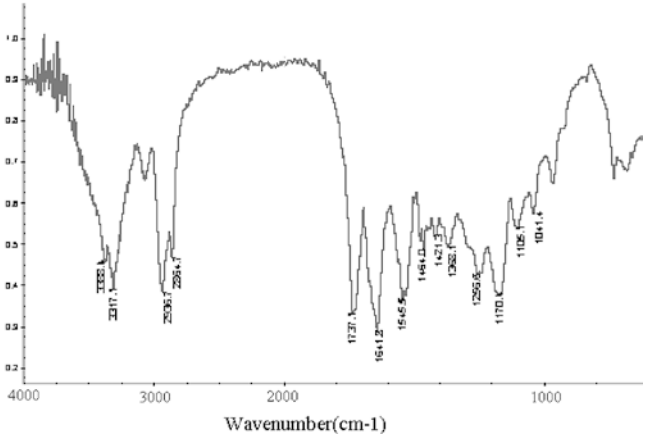

Fig. 2 FTIR spectrum of P(CL/AC)50/50 copolymer

Alkaline degradation behavior of PEA fibers

Water uptake

The water uptake of the PEA fibers during degradation was recorded and is illustrated in Fig. 3. The results showed that the maximum value of the water uptake was

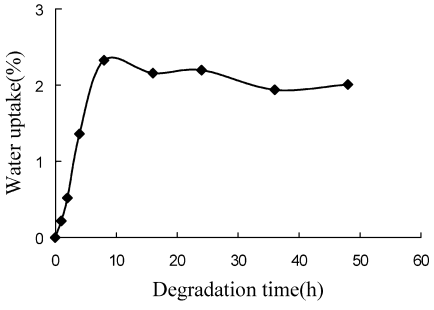

Fig. 3 Water uptake of the PEA fibers during degradation

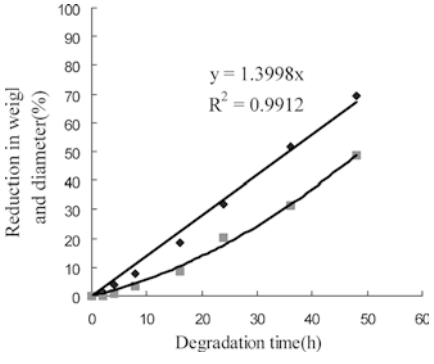

Fig. 4 Reduction in PEA fiber weight and diameter during degradation

Table 1 Properties of the hot-drawn PEA (CL/AC)50/50 fiber

Sample PEA (CL/AC)50/50	Spinning temperature	Draw ratio	Diameter (μm)	[η] (dl/g)[a]	CL/AC (mol%)[b]	Maximum elongation	Ultimate strength (MPa)
Hot drawn fiber	105 °C	3.00	142 ± 9	0.27	1.04/1.00	247 ± 13	125 ± 7

[a] Measured at 30 °C in chloroform at a concentration of 0.5 g/dl
[b] Determined by ^{1}H-NMR

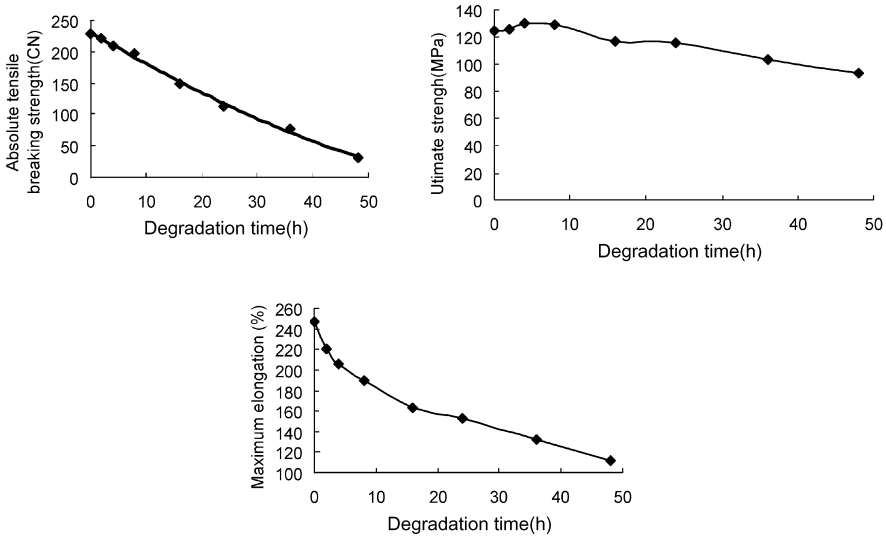

Fig. 5a–c Changes in the tensile properties of the PEA fibers during degradation in the concentrated alkaline solution. **a** Absolute tensile breaking strength. **b** Ultimate strength. **c** Maximum elongation

Table 2 Intrinsic viscosity and the ratio of ε-CL/AC (%mol%) of PEA fiber

Degradation time (h)	[η] (dl/g)[a]	CL/AC (%mol%)[b]
0	0.27	1.04/1.00
4	0.27	1.11/1.00
16	0.27	1.11/1.00
24	0.28	1.10/1.00
48	0.27	1.10/1.00

[a] Measured at 30 °C in chloroform at a concentration of 0.5 g/dl
[b] Determined by ^{1}H-NMR

obtained after 8 h of degradation. After that, the water uptake remained a constant value. The water was absorbed to a large extent by the macromolecules so that the water uptake appeared to be maximal after around 8 h.

Reduction of fiber weight and fiber diameter

When the PEA fibers were incubated in alkaline medium, they degraded, resulting in weight loss. Figure 4 shows the reduction of the weight and the diameter of the PEA fibers with degradation time. It could be seen that the weight and the diameter decreased significantly during degradation. After 48 h of degradation, the fiber mass decreased by 69.23% and the diameter changed from 142 ± 9 to 72 ± 5 μm. From the equations for the decrease in fiber weight ($y = 1.3398x$) with degradation time, it is possible that the PEA fibers could degrade completely and disappear in about 71.5 h under these experimental conditions. The fiber weight decreased in a linear way and exhibited a faster loss rate than did the fiber diameter. These P(CL/AC)50/50 fibers underwent a linear degradation profile, which was a typical characteristic of surface-eroding polymers [17].

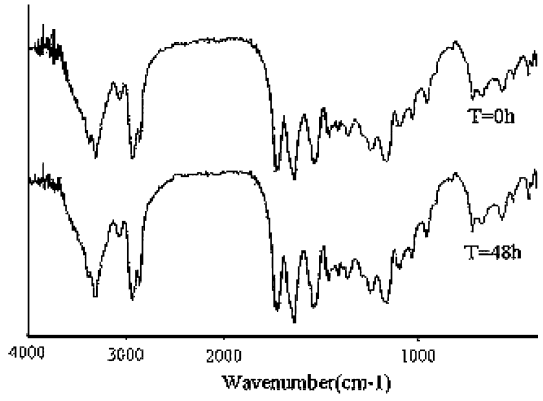

Fig. 6 FTIR spectra of P(CL/AC)50/50 fibers

Changes in tensile properties

Figure 5 presents the absolute tensile breaking strength (P), ultimate strength (σ), and maximum elongation curves of the PEA fibers after degradation in concentrated alkaline solution for different times. The results suggest that the ultimate strength of the PEA fibers did not show significant change during degradation. The absolute tensile breaking strength and the maximum elongation dropped noticeably with degradation time.

Changes in intrinsic viscosity and chemical composition

The intrinsic viscosity and the ratio of CL/AC (mol/mol) of the PEA fiber exhibited only slight change during degradation in the concentrated alkaline solution, as shown in Table 2. Figure 6 shows the FTIR spectra of PEA fibers during degradation. After degradation, there is no obvious change in these two curves, which indicated that the chemical structure was unchanged. The FTIR

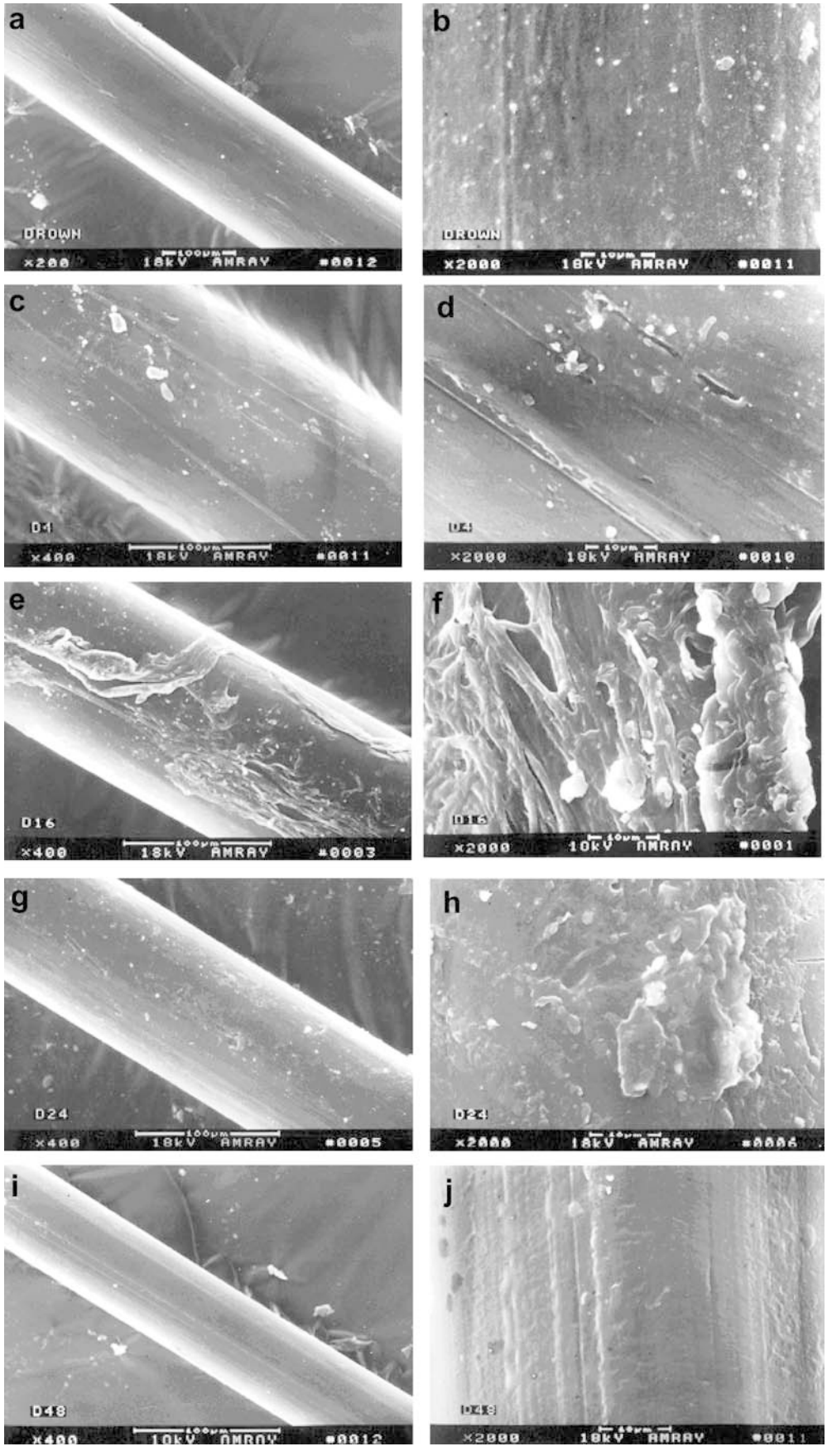

Fig. 7 SEM micrographs of the PEA fibers during degradation in concentrated alkaline solution

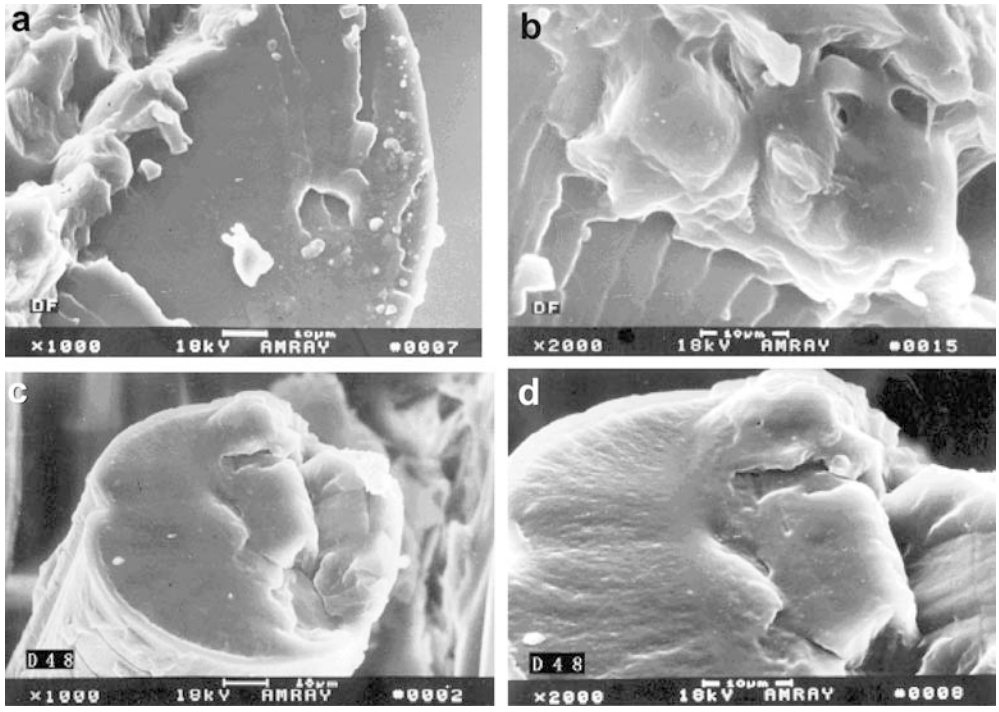

Fig. 8 The morphology of the PEA fibers broken in liquid nitrogen

spectra of PEA fibers at $t = 0$ h were consistent with those at t = 48 h. These results confirmed that the macromolecular weight and chemical structure didn't change significantly during degradation, which indicated that this degradation in concentrated alkaline solution had little effect on the inner part of the chemical structure of these PEA fibers.

Changes in surface morphology

During degradation, the surface morphology of PEA fibers would change. The results obtained by SEM analysis are shown in Fig. 7. The fiber had a relatively smooth surface before degradation (Fig. 7a, b). When the PEA fiber was degraded in alkaline solution for 4 h, small clefts along the fiber came into being (Fig. 7c). The micrograph at larger magnification (Fig. 7d) showed clefts that implied a desquamation from the fiber surface. The desquamation of the PEA fiber is clear after 16 h of degradation (Fig. 7e, f). The PEA fiber was desquamated in the concentrated alkaline solution, and some flakes had not dropped off. Desquamation phenomena are also obvious after fiber degradation for 24 and 48 h (Fig. 7g–j).

Figure 8 presents the SEM morphology of P(CL/AC)50/50 fibers broken in liquid nitrogen. The PEA fibers were tough before degradation, which could be confirmed from Figs. 6a and b. When the fibers were incubated in alkaline medium for 48 h they became thinner, but also had a toughness corresponding to that of the fiber before degradation, which could be seen from Figs. 6c and d. The cross section of the degraded fibers was the same as that of the fiber before degradation, which indicated that the degradation in concentrated alkaline solution did not affect the inner part of the fibers. From Fig. 7 and Fig. 8, a conclusion could be made that these PEA fibers underwent surface erosion when incubated in this concentrated alkaline solution.

Conclusion

In this paper, a new kind of biodegradable aliphatic PEA copolymer based on ε-caprolactone and 6-aminocaproic acid was synthesized by the melt polycondensation method. The PEA fibers were processed by the melt-spinning method. The P(CL/AC)50/50 fibers exhibited typical surface erosion in concentrated alkaline solution. During degradation, the water uptake of the fibers was very low, the weight and diameter of the PEA fibers decreased significantly, and the intrinsic viscosity and chemical composition changed slightly. There was a clear phenomenon of desquamation from the fiber surface during degradation; the ultimate strength of the fibers did not show significant changes during degradation. These results indicated that P(CL/AC)50/50 fibers exhibited typical surface erosion in the concentrated alkaline solution.

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