

# Biodegradable Polyetheresteramides Synthesized from $\epsilon$ -Caprolactone, 6-Aminocaproic Acid, and Poly(ethylene glycol)

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Received 19 September 2006; accepted 4 June 2007

DOI 10.1002/app.27737

Published online 29 January 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Biodegradable aliphatic polyetheresteramides copolymers (PEEAs) were synthesized from  $\epsilon$ -caprolactone, 6-aminocaproic acid, and poly(ethylene glycol) (PEG) by melt-polycondensation method. FTIR, <sup>1</sup>H NMR, differential scanning calorimeter, wide-angle X-ray diffraction, and thermogravimetric analysis/differential thermogravimetry were used to characterize the PEEAs. The tensile testing, water absorption and hydrolytic degradation behavior were also studied. With the increase in PEG con-

tent, the water absorption increased. The rate of hydrolytic degradation depended on the copolymers' hydrophilicity and crystallinity. PEEAs with a relatively low content of PEG still retain good tensile properties. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1689–1695, 2008

**Key words:** biodegradable polyetheresteramides; thermal property; mechanical properties; hydrolytic degradation

## INTRODUCTION

Recently there has been growing interest in developing biodegradable polymers as a solution to the problems of plastics waste. Aliphatic polyesteramide copolymer is a new type of biodegradable polymer developed recently.<sup>1–9</sup> This copolymer combine characteristics of aliphatic polyamides such as mechanical properties and fiber/film forming with the hydrolytic degradability of the ester bonds.<sup>7,8</sup> Enhanced degradability of polyesteramide can be achieved by incorporating into the chain both hydrophilic and flexible segments consisting of  $-\text{CH}_2\text{CH}_2\text{O}-$  groups.<sup>10</sup> In our previous work, a new kind of aliphatic polyesteramide (PEA) copolymer based on  $\epsilon$ -caprolactone and 6-aminocaproic acid was synthesized by the melt polycondensation method, and the PEA fiber undergoes surface erosion in concentrated alkaline solutions.<sup>8</sup> This work is an extension of our previous, hydrophilic PEG was incorporated into the polyesteramide macromolecular main chain. The effects of the polyetheresteramide copolymer composition on water absorption,

hydrolytic degradation, thermal and mechanical properties were determined.

## EXPERIMENTAL

### Materials

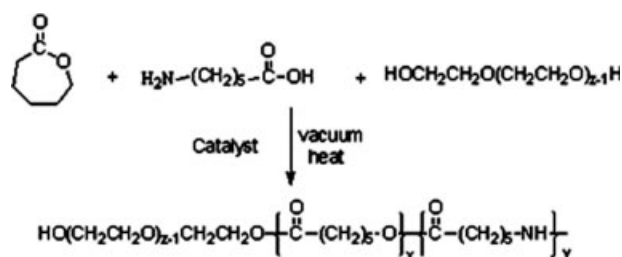
$\epsilon$ -Caprolactone ( $\epsilon$ -CL, purchased from Aldrich), 6-aminocaproic acid (AC, purchased from Aldrich) and others are all analytical reagent grade. All these materials were used as received without further purification.

### Synthesis of PEEA copolymers

In this article, the polyetheresteramide (PEEA) copolymers were synthesized from  $\epsilon$ -caprolactone ( $\epsilon$ -CL), 6-aminocaproic acid (AC), and PEG6000 ( $M_n = 6000$ ) by melt polycondensation method according to Scheme 1. The typical PEEA6-4 copolymer was prepared as follows:  $\epsilon$ -CL (0.357 mol, 41.20 g), AC (0.357 mol, 47.36 g), PEG6000 (0.00068 mol, 4.06 g), and tetrabutyl titanate (0.09 g) were added into the reaction vessel under a nitrogen atmosphere. The mixture was kept at 120–140°C for 1 h. It was then gradually raised to 160–180°C for 1 h. Then, the mixture was rapidly heated to 240–260°C under vacuum for about 1 h. At the end, the resultant hot melt was poured out onto a steel plate, thus PEEA6-4 copolymer was obtained. The copolymer chips were prepared by compressing at the temperature (melting +30°C), the thick of the chips is about 1.0 mm. The

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Contract grant sponsors: University of Electronic Science and Technology, China, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences.



**Scheme 1** Synthesis of polyetheresteramide copolymers by melt polycondensation method.

samples for WAXD, water absorption and hydrolytic degradation were cut from the chips. PEEA0 and PEEA6-8 copolymers were synthesized by the same method as for PEEA6-4 except the mass of PEG6000 was 0 and 7.37 g, respectively. All the samples prepared in this work were listed in Table I.

## EXPERIMENTAL METHODS

### Intrinsic viscosity measurement

Intrinsic viscosity  $[\eta]$  was measured at  $30^\circ\text{C} \pm 0.1^\circ\text{C}$  by using an Ubbelohde viscometer. All the copolymers were dissolved in *m*-cresol to prepare solutions at a concentration of ca. 0.5 g/dL  $[\eta]$  was calculated according to eq. (1):

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

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

### Differential scanning calorimetry

Nonisothermal crystallization behavior of PEEA copolymers was characterized on DuPont 2100. The specimens were heated from 35 to  $110^\circ\text{C}$  under nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ . The crystallinity of polyetheresteramide ( $X_c\%$ ) was determined by dividing the observed heat of fusion by the theoretical value for perfectly(100%) crystalline polymer according to eq. (2). The theoretical

$\Delta h_m^0$  value for polycaprolactone (PCL) and polyamide-6 (nylon 6 or PAC) are  $135.4 \text{ J/g}^{11}$  and  $230.0 \text{ J/g}$ ,<sup>12</sup> respectively. The theoretical  $\Delta H_m^0$  for the copolymers were calculated from heat of fusion of the homopolymers taking into account the composition of the polyetheresteramide according to eq. (3).<sup>13</sup>

$$X_c (\%) = \frac{\Delta h_m}{\Delta h_m^0} \times 100 \quad (2)$$

$$\Delta h_m^0 = 135.4 X_{\text{PCL}} + 230.0 X_{\text{PAC}} \quad (3)$$

where  $X_{\text{PCL}}$  and  $X_{\text{PAC}}$  are the mole fraction of CL and AC in the PEEA0 copolymer, respectively.

### Thermogravimetric analysis

Thermogravimetric measurement (TGA/DTA) was performed using thermogravimetric analyzer (DuPont 2100), the sample heat under a steady flow of nitrogen or air atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$  in the range of room temperature to  $600^\circ\text{C}$ .

### Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) (KBr) spectra of copolymers were taken in NICOLET-200SXV (Nicolet co. USA) Infrared Spectrophotometer.

### <sup>1</sup>H-nuclear magnetic resonance

<sup>1</sup>H-nuclear magnetic resonance (<sup>1</sup>H NMR) spectra (in CDCl<sub>3</sub>) were recorded on a Bruker AV-300 spectrometer (Bruker, Rheinstetten, Germany) at 300 MHz using tetramethylsilane (TMS) as an internal reference standard.

### Wide angle X-ray diffraction

Wide angle X-ray diffraction (WAXD) was performed at room temperature using a Rigaku DMAX1400 diffractometer (DMAX1400, Rigaku, Japan;  $\lambda = 0.15406 \text{ nm}$ ) operated at 40 kv and 100 mA with CuK $\alpha$  radiation. The specimens were fixed on the equipment and

**TABLE I**  
The PEEA Copolymers Obtained in This Work

PEEAs	PEG (% wt)		$\epsilon$ -CL (% wt)		$\epsilon$ -CL/AC/PEG (% mol)		$[\eta]^b$ (dL/g)
	Feed	Exp <sup>a</sup>	Feed	Exp <sup>a</sup>	In feed	Exp <sup>a</sup>	
PEEA0	0	0	50.21	52.29	50.00/50.00/0	52.08/47.92/0	1.02
PEEA6-4	3.42	4.22	48.49	50.38	49.95/49.95/0.10	52.32/47.55/0.12	1.06
PEEA6-8	7.37	8.59	46.50	48.22	49.89/49.89/0.21	52.42/47.33/0.25	0.98

<sup>a</sup> Determined by <sup>1</sup>H-NMR.

<sup>b</sup> Measured at  $30^\circ\text{C}$  in *m*-cresol.

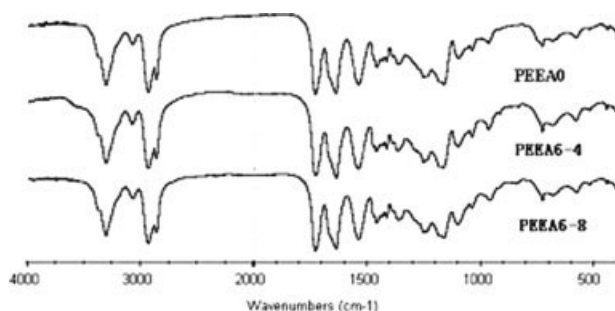


Figure 1 The FTIR diagram of PEEA copolymers.

data were collected with a step interval of  $0.02^\circ$  at a rate of  $4^\circ/\text{min}$ .

### Water absorption behavior

Water absorption testing was carried out as follows: the melt-pressed copolymer samples (ca  $10.0 \times 10.0 \times 1.0 \text{ mm}^3$ ) were immersed in distilled water at  $37^\circ\text{C}$  for different periods, then were taken out and the surplus surface water was removed by filter paper. The value was calculated, according to eq. (4):

$$\text{Water absorption \%} = \frac{W_{ht} - W_d}{W_d} \times 100 \quad (4)$$

where  $W_d$  is the weight of dry sample, and  $W_{ht}$  is the weight of humid sample at time  $t$ .

### Hydrolytic degradation

*In vitro* degradation experiments were carried out as follows: the melt-pressed copolymers sample (ca  $10.0 \times 10.0 \times 1.0 \text{ mm}^3$ ) were placed in a small bottle containing 10 mL of phosphate buffer solution (PBS) (pH = 7.2) or aqueous NaOH-KCl solution (pH = 12.0) containing 0.01 w/v% sodium azide as antibacterial agent at  $37^\circ\text{C}$ . The degradation medium was

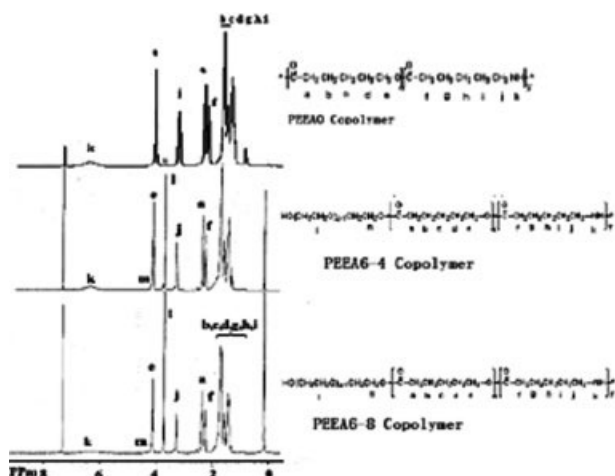


Figure 2  $^1\text{H}$  NMR spectra of PEEA copolymers (in  $\text{CDCl}_3$ ).

TABLE II  
Thermal Properties of PEEA Copolymers

Polymer	$T_m$ ( $^\circ\text{C}$ )	$\Delta H_m$ ( $\text{J g}^{-1}$ )	$\Delta H_m^0$ ( $\text{J g}^{-1}$ )	$X_c$ (%)
PEEA0	68.31	10.68	180.73	5.91
PEEA6-4	78.43	17.30	180.42	9.59
PEEA6-8	72.54	16.43	183.98	8.93

refreshed every week. The samples were removed from the bottles at predetermined times, rinsed thoroughly with distilled water and dried in vacuum at  $40^\circ\text{C}$  for 12 h. The degree of degradation was characterized by weight loss:

$$\text{Water loss \%} = \frac{W_0 - W_t}{W_0} \times 100 \quad (5)$$

where  $W_0$  is the dry weight before degradation,  $W_t$  is the dry weight at time  $t$ .

### The tensile property testing

The tensile properties of PEEAs films were measured at 200 mm/min on an Instron testing machine (model 4302) under  $15^\circ\text{C}$  and a humidity of 50%. The specimens were prepared by compressing at the temperature (melting +  $30^\circ\text{C}$ ). The size of specimens was about length 115 mm, wide 6.1 mm and 1.0 mm thickness.

## RESULTS AND DISCUSSION

### Polymer synthesis and characterization

FTIR and  $^1\text{H}$  NMR spectroscopies were used to characterize the chemical structure of the PEEA copolymers. Figure 1 shows the FTIR spectra of the PEEA copolymers. Because the weight fraction of PEG is lower, the absorption peak due to PEG could not be observed in FTIR.<sup>10</sup> As a result, there is no distinct

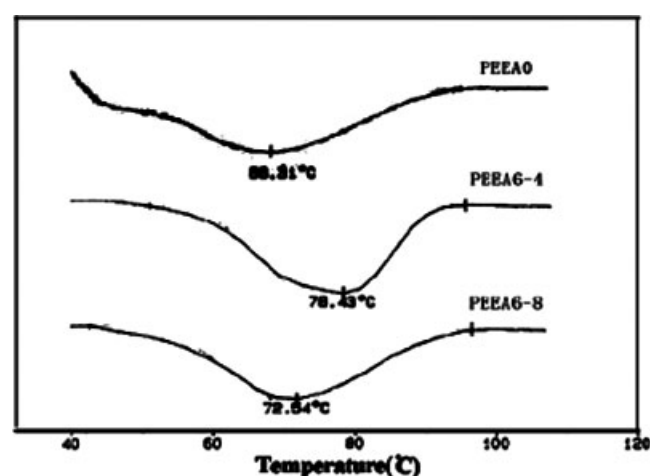


Figure 3 The DSC curves of PEEA copolymers under nitrogen atmosphere.

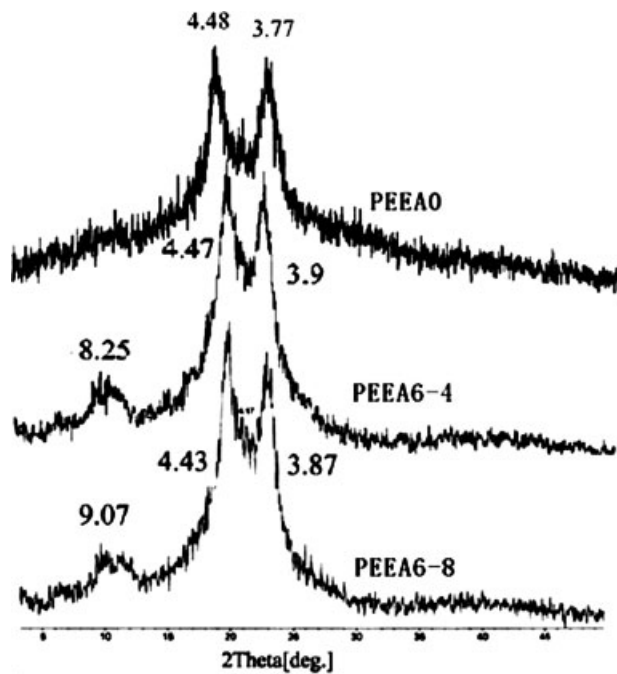


Figure 4 XRD patterns of PEEA copolymers.

difference in FTIR spectra of the three copolymers.  $^1\text{H}$  NMR analysis confirmed the chemical structure of the PEEA copolymers. The  $^1\text{H}$  NMR spectra exhibited all the expected resonances (see Fig. 2). The composition was determined by comparing the integral intensities of  $-\text{CH}_2-\text{O}-\text{CO}-$  resonances of PCL at 4.04–4.06 ppm with those of  $-\text{CH}_2-\text{NH}-$  of PAC at 3.20–3.22 ppm and those of  $-\text{CH}_2-\text{O}-$  of PEG at 3.60–3.70 ppm. With the increase in PEG content, the integral intensities of the peak at ca. 3.60 ~ 3.70 ppm increased accordingly. The compositions of the PEEA are in relatively good agreement with the starting compositions. The values of the intrinsic viscosity range from 0.98 to 1.06 dL/g. The chemical composition of the PEEA copolymers is showed in Table I.

#### Thermal properties and nonisothermal crystallization behavior

The results obtained from differential scanning calorimetry (DSC) analysis are summarized in Table II and Figure 3. The melting temperature ( $T_m$ ) was determined as the temperature of the main peak in the curve obtained

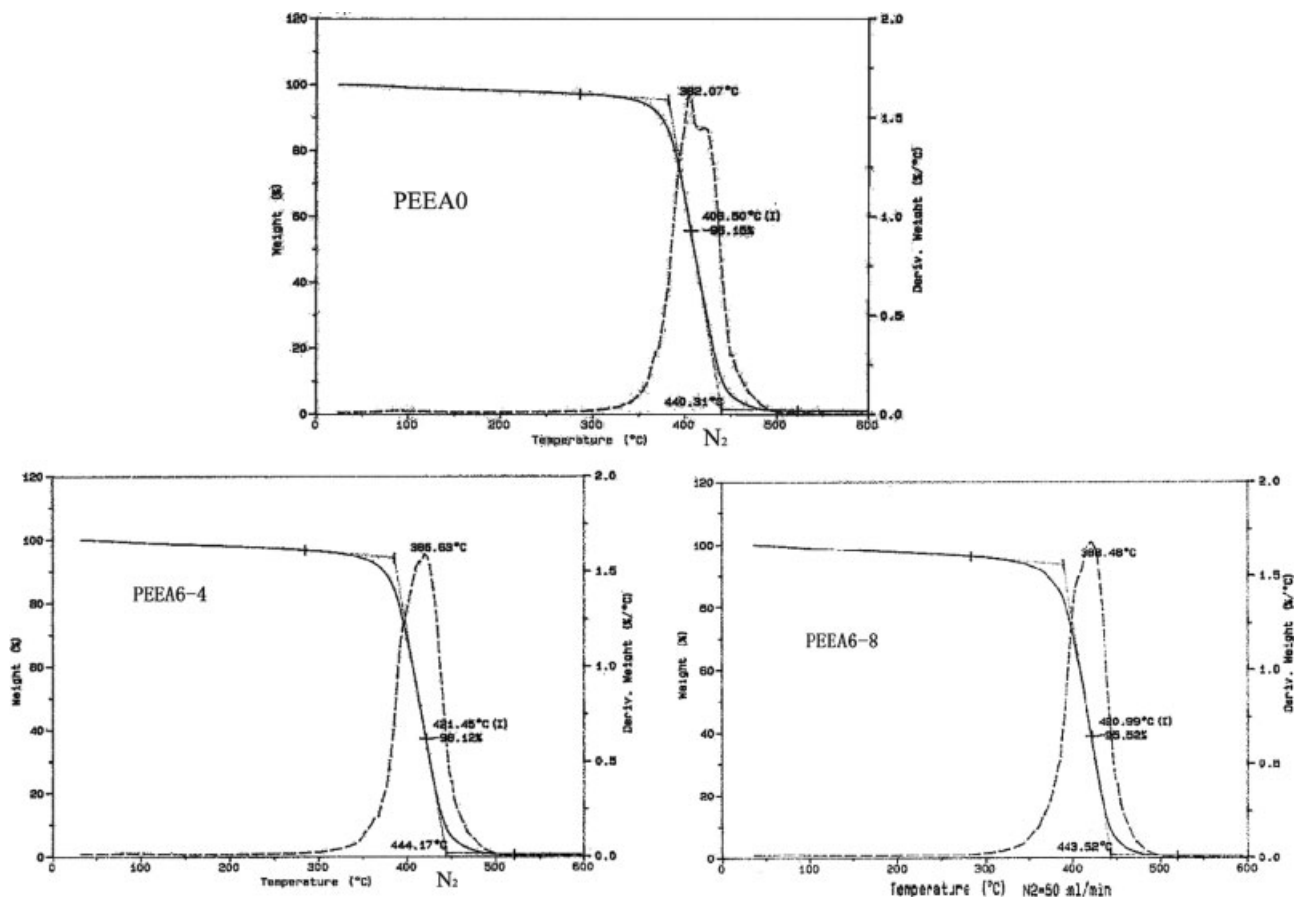


Figure 5 TGA/DTA traces of PEEA copolymers in nitrogen atmosphere.

TABLE III  
TGA Data of PEEA Copolymers at a Heating Rate of 10°C/min in Nitrogen

	Sample	PEEA0	PEEA6-4	PEEA6-8
	$\epsilon$ -CL (% wt) (Exp.)	52.29 <sup>c</sup>	50.38 <sup>c</sup>	48.22 <sup>c</sup>
Stage 1	$T_{d, 5\%}$ <sup>a</sup> (°C)	347.9	337.1	325.3
	$T_{d,1max}$ <sup>b</sup> (°C)	411.5	–	–
	Weight loss at stage 1 (%)	51.84	–	–
Stage 2	$T_{d,2max}$ <sup>b</sup> (°C)	433.6	–	–
	Weight loss at stage 2 (%)	47.21	–	–
	$T_{d, 10\%}$ <sup>a</sup> (°C)	373.3	372.9	370.6
	$T_{d, 15\%}$ <sup>a</sup> (°C)	382.9	383.9	383.9
	$T_{d, 30\%}$ <sup>a</sup> (°C)	397.0	399.1	401.1
	$T_{d, 50\%}$ <sup>a</sup> (°C)	410.2	413.3	414.2
	Residue at 590°C (%)	0.88	0.59	0.68

<sup>a</sup> Temperature where the weight loss is 5, 10, 15% and so on.

<sup>b</sup> Temperature of the largest decomposition rate during this stage.

<sup>c</sup> Theoretical value calculated from the molar ratio of CL/AC in experiment.

from the first scan. There is only one melting transition temperature in each polyetheresteramide. When PEG was incorporated into the polyesteramide main chain, both the melt temperature and crystallinity of PEEA were higher than polyesteramide, which might be due to the increase in flexibility of the macromolecular main chain when small amounts of PEG are present.<sup>10</sup> We also could see that the melt temperature and crystallinity of PEEA6-8 was lower than PEEA6-4's, and the melting peak of PEEA6-8 became wider than PEEA6-4's. A further increase in the PEG content results in a decrease of the crystallinity of the copolymers. This phenomenon is similar to thermal property of PEIT/PEG copolymers.<sup>14</sup>

Further information on the crystallization behavior of these polyetheresteramides was obtained by means of WAXD diffractometer. Figure 4 presents the WAXD patterns of PEEA copolymer crystallized from the melt. It can be seen that these samples exhibited two strong reflections at the diffraction angle  $2\theta$  (PEEA0: 19.85, 23.65; PEEA6-4: 19.90, 22.78; PEEA6-8: 20.05, 23.00). In fact, PEEAs diffraction patterns were very similar to the rhombic crystal of PCL<sup>15</sup> and  $\alpha$ -form (monoclinic) crystal of PAC (nylon 6) homopolymer.<sup>16</sup> There is no diffraction peak of PEG in the WAXD patterns. Crystallization of the PEG segment was not observed for PEEA copolymer with less than 40% PEG<sup>17</sup>; probably, the PEG content of these copolymers was too low to be able to form semi-crystalline domains.<sup>18</sup>

### Thermogravimetric analysis

The Thermogravimetric analysis curves of the polyetheresteramides under nitrogen atmospheres are shown in Figure 5 and Table III. PEEA6-4 and PEEA6-8 shows a one-stage degradation pattern in nitrogen. Combining the one melting transition tem-

perature in DSC curves of the PEEAs, the one-stage degradation pattern suggests that the structure of PEEA6-4 and PEEA6-8 polyetheresteramides could be random. With the increase in PEG content, we could see that  $T_{d,5\%}$  and  $T_{d,10\%}$  decrease.

### Water absorption

Depending on the composition, the water uptake of the PEEA copolymers ranges from 4.78 to 22.81 wt % (see Fig. 6). The water uptake increases obviously with the increase in PEG content. When 10% PEG 1000 was incorporated into the polyesteramide based on 11-aminoundecanoic acid, the water uptake increased to 9.0 wt %.<sup>10</sup> It can be seen that when the PEG macromonomer was incorporated into the polyesteramide main chain, the hydrophilicity of PEEAs increased. The results are in good agreement with water absorption behavior of PCL/PEG copolymer.<sup>19</sup>

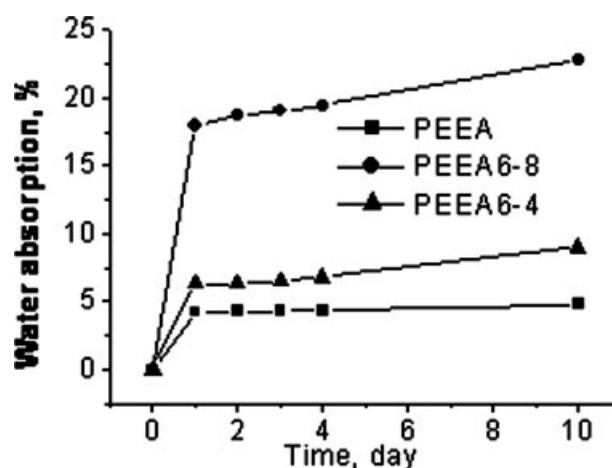


Figure 6 Water absorption behavior of PEEA copolymer chips in distilled water at 37°C.

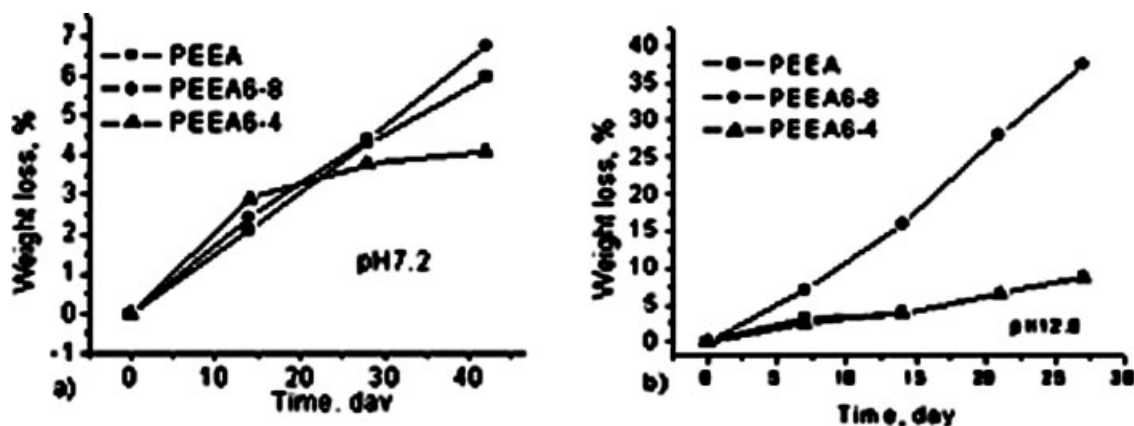


Figure 7 *In vitro* degradation behavior of PEEA copolymer chips.

### Hydrolytic degradation

The degradation of PEEA samples with a thickness of about 1.0 mm in PBS (pH = 7.2 and pH = 12.0) was examined at 37°C. The degradation results are shown in Figure 7. When the PEG macromonomer was incorporated into the polyesteramide main chain, the degradation rate of PEEA6-8 increased clearly; the PEEA6-4's degradation rate was not been improved although its water uptake was higher than PEEA0. The hydrolytic degradation behavior of semi-crystalline polymers is determined by the chemical composition, hydrophilicity, degree of crystallinity, molecular weight, etc.<sup>20–23</sup> The amorphous domains are the most susceptible to hydrolysis,<sup>24</sup> and the hydrophilicity is helpful to degradation. These amphiphilic PEEAs copolymers are semi-crystalline. With an increase in PEG content, the hydrophilicity and water absorption increase accordingly. Both the melt temperature and crystallinity of PEEA were higher than polyesteramide (PEEA0), the melt temperature and crystallinity of PEEA6-8 was lower

than PEEA6-4's. The hydrophilicity and crystallinity depended on the rate of Hydrolytic degradation of PEEAs.

### Tensile mechanical properties of PEEAs

The stress–strain curves of PEEAs are showed in Figure 8. The tensile behavior of PEEAs is typical of thermoplastic elastomers,<sup>18,25</sup> showing high extensions and relatively high modulus values. The values of the mechanical properties are given in Table IV. Young modulus and yield strength of these PEEAs copolymers decreased with the increase of PEG content, but the elongation at break increased. Tensile strength at break of PEEA6-8 did not decreased clearly. We can conclude that an increase in the PEG content induces a lower Young modulus and a higher elongation at break, the PEEAs with lower PEG content can retain proper mechanical characteristics.

### CONCLUSION

In this work, Biodegradable PEEAs copolymers were synthesized from  $\epsilon$ -caprolactone, 6-aminocaproic acid, and PEG by melt polycondensation. FTIR and <sup>1</sup>H NMR results suggest that the experimental value of CL/AC/PEG molar ratio is much closed to the theoretical value. DSC and WAXD results suggest that the crystallization behavior exists in polyetheresteramides. PEEA6-4 and PEEA6-8 shows a one-stage degradation pattern. With the increase in PEG content, water absorption was enhanced due to the increase in hydrophilicity of the copolymers. The hydrolytic degradation rate depended on the hydrophilicity and crystallinity of the PEEAs. The stress versus strain curves of PEEA copolymers show a typical ductile break behavior characteristic and high mechanical properties when the PEEAs contain small amounts of PEG.

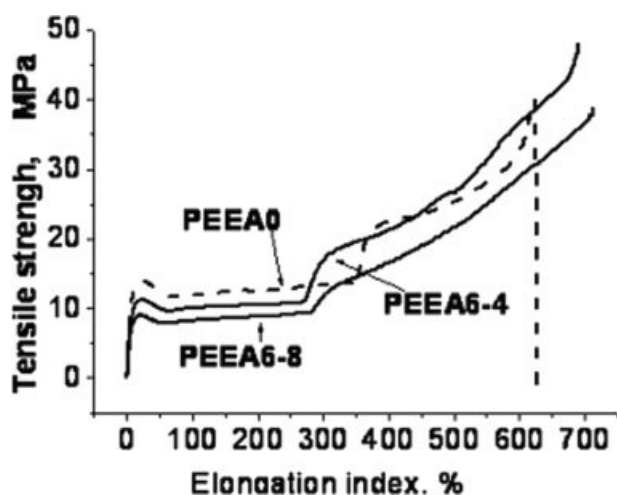


Figure 8 Stress versus strain curves of PEEA.

**TABLE IV**  
**Tensile Mechanical Properties of PEEA**

Sample	Thickness (mm)	Tensile strength at break (MPa)	Young modulus (MPa)	Yield point strength (MPa)	Elongation at break (%)
PEEA0	1.07	40.2	246.0	14.1	625.1
PEEA6-4	0.97	46.0	200.0	11.3	690.1
PEEA6-8	1.06	37.2	153.2	9.08	710.0

This project was sponsored by Outstanding Young Scientist Fund of Sichuan Province and the Import Excellent Talents Program of University of Electronic Science and Technology of China. The authors are grateful to the Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences for greatly supports.

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