Shape-Memory Behaviors of Sensitizing Radiation-Crosslinked Polycaprolactone with Polyfunctional Poly(ester acrylate)

G. M. Zhu,[1] Q. Y. Xu,[2] G. Z. Liang,[1] H. F. Zhou[1]

[1]Department of Applied Chemistry, Northwestern Polytechnical University, 127 West Friendship Road, Xi'an, 710072, People's Republic of China
[2]Northwest Institute of Nuclear Technology, Post Box 69, Xi'an, 710024, People's Republic of China

ABSTRACT: The sensitizing effects of polyfunctional poly(ester acrylate) on the radiation crosslinking of polycaprolactone (PCL) were studied. The influences of the use of the polyfunctional material, the number of functional groups, and the radiation dose on the radiation crosslinking, dynamic mechanical properties, and shape-memory behaviors of PCL, respectively, were investigated. The radiation crosslinking of PCL, under the conditions in which the polyfunctional material was applied, did not follow the classic Charlesby–Pinner equation but instead followed the Chen–Liu–Tang relation. The efficiency of the radiation crosslinking of PCL was distinctly improved with the polyfunctional material. The greater the usage and functional group number were, the greater gel content and the more distinctive the radiation-crosslinking effects were. This also indicated that the polyfunctional material directly participated in the crosslinking reaction. Dynamic mechanical analysis indicated that enhanced radiation crosslinking better raised the heat deformation temperature of PCL and presented a higher and wider rubbery-state plateau; it also produced greater strength at temperatures higher than the melting temperature and provided greater force for recovering the deformation than pure PCL. The shape-memory results revealed that sensitizing crosslinked PCL presented 100% recoverable deformation and a quicker recovery rate. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 634–639, 2005

**Key words:** crosslinking; polyesters; radiation

INTRODUCTION

Polycaprolactone (PCL) is a novel biodegradable polymer. It has been promoted as soil-degraded agricultural films, packing materials, and so forth, and it is one of the most likely biodegradable materials for large-scale mass production.[1] PCL also has good biocompatibility and security for living organisms and has been shown to undergo degradation and absorption *in vivo*; it has been exploited for drug-delivery systems, bioabsorbable sutures, orthopedic fixing materials, and tissue-engineering scaffolding.[2–4] However, its terrible heat deformation, which comes from the lower melting temperature (T_m) of PCL (only 60°C or so), limits the extent of its applications. High-energy irradiation of the polymer not only can raise its strength, heat resistance, and size stability but also can bestow novel properties upon the polymer, such as shape-memory behavior after radiation crosslinking. In our work,[5] radiation-crosslinked PCL exhibited shape-memory effects at lower temperatures, and this shape-memory functional PCL could be used as bioabsorbable sutures, orthopedic fixing materials, and so forth. However, the radiation-crosslinking efficiency of pure PCL was lower. At the time of crosslinking, radiation caused the scission of molecular chains and the deterioration of mechanical properties; this is undesirable. In this work, we blended PCL with several kinds of polyfunctional poly(ester acrylate)s (PEAs) to improve the radiation-crosslinking efficiency of PCL and reduce the radiation damage; meanwhile, the shape-memory behaviors of sensitizing radiation-crosslinked PCL were also investigated.

EXPERIMENTAL

Materials

PCL–H5 was purchased from Nippon Daicel Co. (Osaka, Japan); its weight-average molecular weight was 50,000. Polyfunctional PEA was bought from Tianjin Tianjiao Chemical Industry, Ltd. (Tianjin, China), and was blended with PCL to improve the degree of radiation crosslinking of PCL. Its typical structure was as follows:

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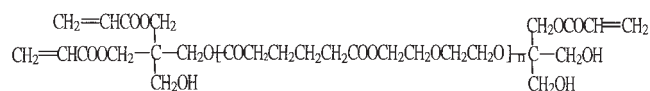
n was 2–5, and the molecular weight was between 700 and 1200. PEA was selected as a crosslinking agent because, besides the double bond in the molecule, its structure was similar to that of PCL and perhaps it had better compatibility with PCL.

Preparation of the samples

The polyfunctional material was added gradually to PCL in a blender at 70°C and roll-milled for 15 min to ensure complete mixing. Then, the blend was compression-molded in a press at 60–70°C for 5 min to produce 2-mm-thick sheets. The composition of the blend was 98/2 (mol/mol) PCL/PEA. The blend was marked T2, T indicating a trifunctional material and 2 meaning 2 mol of PEA per 100 blends of PCL and PEA.

Specimens for strain recovery measurements were prepared in the following order. The compression-molded sheet was cut into 50 mm × 5 mm × 2 mm strips. Each strip was heated 10°C above T_m of the PCL crystals (actual temperature = 65°C) and kept there for 3 min. As it became transparent, the strip was stretched at this temperature to double its original length (deformation ε_0) and then cooled immediately to a setting temperature under constrained conditions of constant length. In our work, room temperature was chosen as the setting temperature. At room temperature, with the external forces withdrawn, the deformation of the samples could be maintained for a long time because the hardened crystal phase resisted elastic recovery effectively. The deformed specimens were then used for studying the deformation recovery behavior during a process of a constant heating rate.
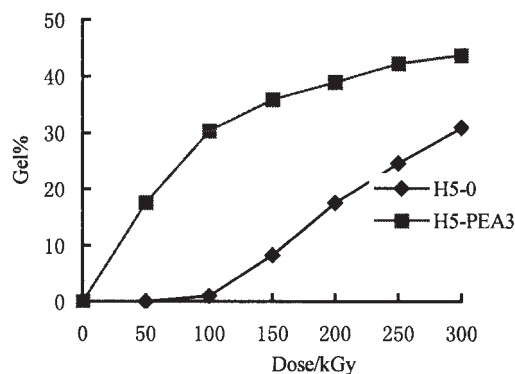
Radiation

The samples, enclosed in a PE bag with limited air, were irradiated with a cobalt-60 plate resource, which was supplied by the Xi'an Radiation Research Center (Xian, China); the dosage rate was 4 kGy/h. The radiation dose (*D*) was 0, 50, 100, and 300 kGy, respectively. Sample T2, irradiated at 100 kGy, was marked T2-100; the others were labeled in the same manner.

Measurement of the gel content (*G*%)

G% was determined by Soxhlet extractor with toluene (refluxing for 30–40 h). The ratio of the remaining mass of insoluble material (dried to a constant weight in a vacuum oven) to the original mass was defined as *G*% as follows:

$$G\% = \frac{\text{Mass of residue (g)}}{\text{Original mass (g)}} \times 100\%$$

Figure 1 Relationship between the gel fraction and radiation dose for H5/PEA3.

Dynamic mechanical analysis (DMA)

The temperature dependence of the elastic modulus [i.e., Young's modulus (*E*)] of the sensitizing radiation-crosslinked PCLs was measured with a dynamic mechanical thermal analyzer (model 2980, TA Instrument, New Castle, DE). The sample size was 20 mm × 8 mm × 2 mm; DMA was carried out at 10 Hz and at a 20°C/min heating rate.

Shape-memory behavior

The shape-memory behavior was examined with a heat-shrinking test.[6] The size of the specimen was 50 mm × 5 mm × 2 mm. The heating rate was approximately 2°C/min. The recovery process was expressed as the temperature dependence of the strain [$\varepsilon(T)$] or the recovery rate [$R(T)$], the percentage of the recovery strain at temperature *T* in the total fixed strain: $R(T) = [\varepsilon_0 - \varepsilon(T)]/\varepsilon_0$. Through the measurement of the length of the samples at different temperatures, the relation curves between the strain recovery ratio and temperature could be drawn. Some important parameters were obtained from these measurements to characterize the shape-memory behavior of the samples. The final recovery rate (R_f) showed the recovery ability of the sample. On the recovery-ratio/temperature curves, the temperature related to 50% R_f was defined as the shape-memory response temperature (T_r) of the deformed samples.

RESULTS AND DISCUSSION

Sensitizing effects of PEA on the radiation crosslinking of PCL

The relationship between *G*% and *D* for pure PCL–H5 and the H5/PEA3 blend are shown in Figure 1. *G*% of the PCL/PEA3 blends increased greatly in comparison with pure PCL. This shows that PEA had a distinct promoting function for the radiation crosslinking of PCL.
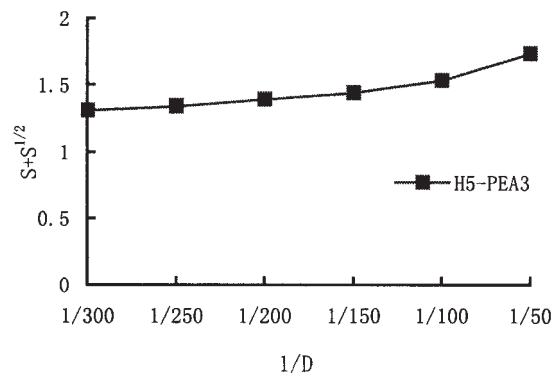
Figure 2 Relationship between $S + S^{1/2}$ and $1/D$ for PCL–H5 and the H5/PEA3 blend.

According to the classical Charlesby–Pinner equation[7]

$$S + S^{1/2} = p_0/q_0 + 1/(q_0\mu_1 D)$$

where S is the sol fraction and p_0 and q_0 are constants indicating the sensitivity of dissociation and crosslinking to radiation, respectively. The experimental results were analyzed with a plot of $S + S^{1/2}$ versus $1/D$, as shown in Figure 2. When PEA was applied, the radiation crosslinking of PCL deviated much from the Charlesby–Pinner equation. That is, in the presence of PEA, the radiation crosslinking of PCL did not follow random crosslinking. This was because the Charlesby–Pinner equation was deduced under the assumption that the polymer molecular weight distribution (MWD) could agree with a normal distribution.[7] After PEA was applied, the initial MWD of the polymer blend system became wider and deviated from a normal distribution, and this resulted in the deviation from the Charlesby–Pinner equation. However, the fact that the curve of $S + S^{1/2}$ versus $1/D$ bent to $1/D$ revealed that (1) in comparison with pure PCL, the blend was less likely to split and more likely to crosslink, and (2) the crosslinking efficiency decreased as D increased.

A better linear plot was obtained with the Chen–Liu–Tang[8] relation $D(S + S^{1/2}) = 1/q_0'\mu_1 + (\alpha_0/q_0)D^{1/2}$, as shown in Figure 3. q_0' is a constant reflecting the crosslinking efficiency; it also refers to the contribution of a unitary dose to the crosslinking density. μ_1 is the number-average degree of polymerization, and α_0 is a constant. As the Chen–Liu–Tang relation was valid for describing crystal polymers with flexible chains, PCL blended with PEA just as PCL was plasticized and made its chain more flexible to fit the relation better.

The $G\%$ data for pure PCL was plotted with the Charlesby–Pinner equation, and the value of $1/q_0\mu_1$ could be estimated from the intercept.[5] The value of
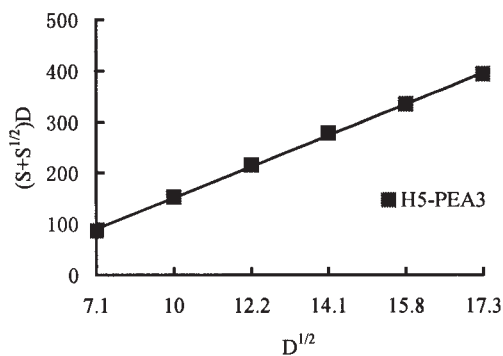
Figure 3 Relationship between $(S + S^{1/2})D$ and $1/D$ for the PCL/PEA blends.

$1/q_0'\mu_1$ could be obtained from Figure 3. If PEA did not affect the polymerization degree of PCL, q_0'/q_0 could be obtained from the ratio of $1/q_0\mu_1$ to $1/q_0'\mu_1$; it equaled 4.94 (Table I). As q_0 refers to the probability of a crosslinking unit induced by a unitary dosage, the q_0'/q_0 ratio can reveal the sensitizing crosslinking efficiency after the addition of PEA. From q_0'/q_0, we concluded that the polyfunctional materials distinctly improved the crosslinking efficiency of PCL. With the addition of 2 mol of PEA to 98 mol of PCL, the sensitizing crosslinking efficiency increased nearly 5 times over that of pure PCL–H5.

Effects of PEA with different functional group numbers on the radiation crosslinking of PCL

The effects of 2 mol % PEA with two, three, or four double-bond functional groups on the radiation crosslinking of PCL–H5 were investigated, as shown in Figure 4. The greater the functional group number is, the greater $G\%$ and the more distinctive the radiation-crosslinking sensitizing effects were with the same D value. On the other hand, all the $G\%$ values increased greatly and quickly at a lower dose and then gently over 300 kGy; perhaps the reaction of PEA was quicker in the beginning; when it had been depleted, the crosslinking speed slowed down. This also indicated that the polyfunctional material directly participated in the crosslinking chemical reactions.

Effect of the PEA usage on the radiation crosslinking of PCL

We also studied the effects of PEA usage on the radiation crosslinking of PCL, as shown in Figure 5. With

TABLE I
Sensitizing Effect of Polyfunctional PEA on Radiation Crosslinking

Sample	$1/(q_0'\mu_1)$	$1/(q_0'\mu_1)$	q_0'/q_0
H5–PEA	—	29.53	4.94
H5	145.86	—	

the same D value, the higher the PEA proportion was, the greater $G\%$ was. This also indicated that the more double bonds there were, the more distinctly the crosslinking efficiency improved. This was ascribed to there being more double bonds to join the crosslinking reaction.

The IR spectra of PCL samples irradiated with different dosages are shown in Figure 6. When D was greater than 100 kGy, the characteristic absorption band of the elastic vibration of the double bond at 1663 cm^{-1} almost disappeared; that is, the double bonds were depleted. From the effects of PEA with different functional group numbers and different dosages on the radiation crosslinking of PCL, we concluded that PEA had a clearly promoting function for the crosslinking of PCL. The reason was that the double bonds of the polyfunctional material were easily unlocked by rays and participated in the crosslinking chemical reactions,[9] as shown in the following:

R—(CH=CH$_2$)$_n$ represents the polyfunctional material.
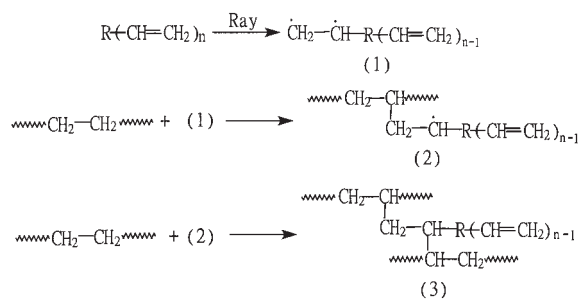
Other unsaturated function groups in (2) and (3) could also be unlocked and induce crosslinking reactions as follows:
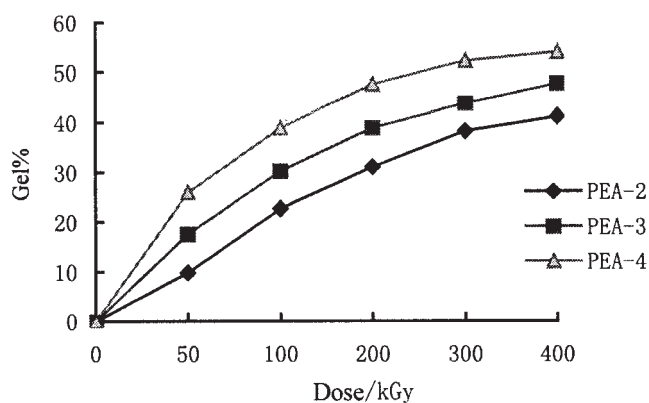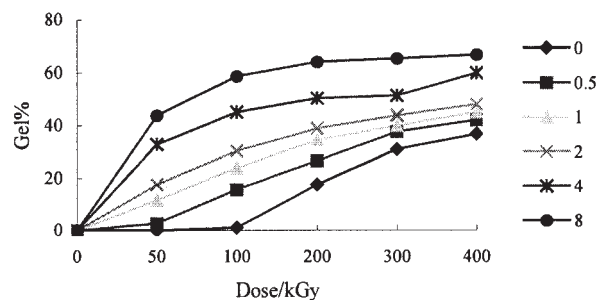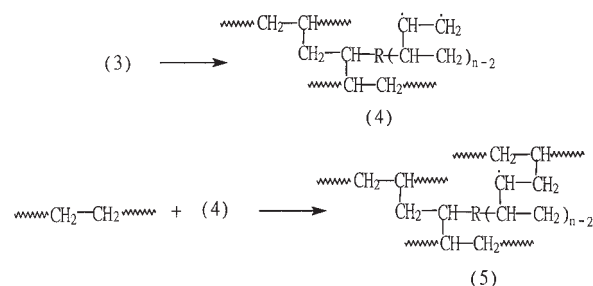

Figure 5 Effects of PEA3 (mol %) on the radiation crosslinking of PCL–H5.

This reaction mechanism was also proved with the IR spectra of PCL/PEA during the process of radiation crosslinking (shown in Fig. 6). With D increasing, the characteristic absorption band of the double bond at 1663 cm^{-1} became weak. That is, the double bonds were sensitive to the rays and were easily unlocked to join in the reactions, so the double bonds were expended quickly. This was in agreement with the law of $G\%$ changing with D; in the beginning, $G\%$ increased rapidly, and then it increased gently.

Dynamic mechanical properties of enhancing radiation-crosslinked PCL

The temperature dependence of E for several samples was measured to investigate the effects of sensitizing radiation crosslinking on the heat resistance of PCL–
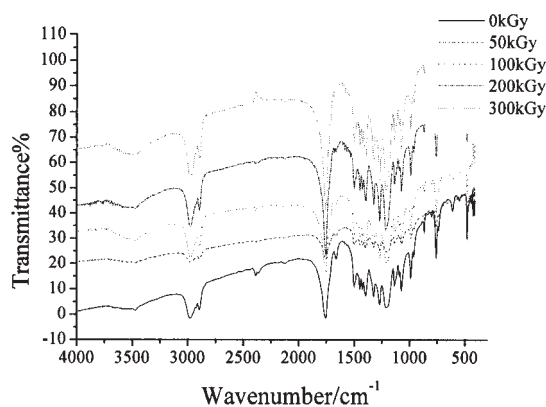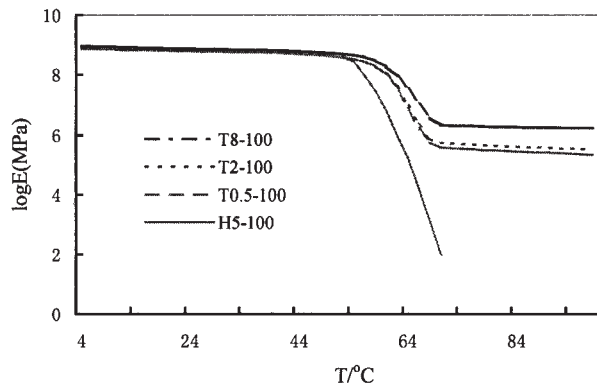

Figure 4 Effects of different PEAs on the radiation crosslinking of PCL.

Figure 6 IR spectrum of 2 mol % PEA3/PCL blends.

Figure 7 Relationship between E and the temperature for PCL–H5.

H5. The results are shown in Figure 7. In T8-100, T represents the function group number of PEA (3), 8 indicates the PEA usage (8 mol %), and −100 indicates D (100 kGy). The others were labeled in the same manner.

E of PCL increased with the PEA usage. This was mainly ascribed to the crosslinking degree increasing with the PEA usage at the same D value. According to the elastic theory of rubber,[10] E can be determined as follows:

$$E = 3\rho RT/M_C \qquad (1)$$

where R is the gas content, T is the absolute temperature, ρ is the polymer density, and M_c is the molecular weight between the crosslink points. The larger the crosslinking degree was, the smaller M_c and the bigger E became. Besides, E changed gently with the temperature before T_m, and then it decreased rapidly by three-to-four orders of magnitude near T_m. This was mainly attributed to the collapse of crystalline PCL. The uncrosslinked H5 samples lost their tensile strength around 53°C, but the crosslinked samples still
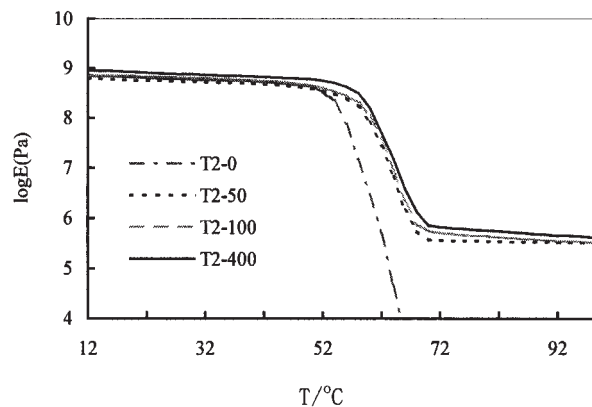
Figure 8 Effect of the radiation dose on E of enhancing crosslinked PCL.
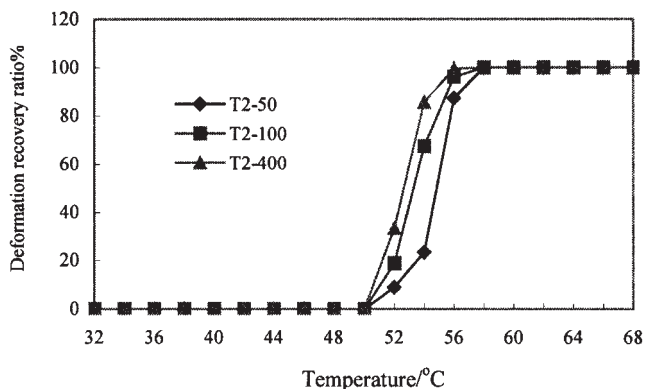
Figure 9 Effect of the radiation dose on the deformation recovery ratio of sensitizing crosslinked PCL.

maintained a certain tensile strength above T_m. The effect of D on E of enhancing crosslinked PCL is shown in Figure 8. The crosslinking degree increased as D (kGy) increased, and so did E. Because[11]

$$M_c = W/q = W/q_0 D = 0.48 \times 10^7/G_c D \qquad (2)$$

where W is the molecular weight of the main-chain unit, q is the crosslinking probability induced by a unitary dose, and G_c is the output of the crosslinking reaction, combining eqs. (1) and (2), we can obtain

$$E = 6.25 \times 10^{-7}\rho RTG_c D \qquad (3)$$

Because G_c is basically determined by the chemical constitution of the polymers, we could see that E was proportional to D: the bigger the dose, the higher E.

Shape-memory behaviors

We carried out the deformation recovery tests of several samples to study the relationship between the shape-memory behaviors and the degree of crosslinking. The experimental results for blends of H5 and 2 mol % PEA with different D values are shown in Figure 9, and the corresponding shape-memory parameters are summarized in Table II. The shape recovery was measured at different temperatures. The sensitizing crosslinked sample, which was irradiated with more than 50 kGy, was heated above its T_m, deformed,

TABLE II
Effects of D on the Shape-Memory Parameters of Sensitizing Crosslinked PCL

Sample	G (%)	T_r (°C)		R_f (%)
T2-0	0	—	58.3	0
T2-50	17.6	55	58.0	100
T2-100	30.3	54	55.4	100
T2-400	47.9	52.5	54.6	100

and cooled quickly to a temperature below T_m; the deformed shape became frozen. When it was warmed again above T_m, the strain recovered its original shape and exhibited a typical shape-memory effect. The response temperature was closely related to the crystal melting temperature. The response temperature of samples irradiated with 100 and 400 kGy was lower than that of the samples irradiated with 50 kGy. This was because a higher D value could cause crystal damage and make the crystal melting temperature lower. Moreover, the deformation recovery curve of the samples radiated at higher doses was steep. This indicated that the bigger the degree of crosslinking, the faster the velocity of the deformation recovery.

The effects of PEA usage on the shape-memory behaviors of sensitizing crosslinked PCL are displayed in Figure 10, and the corresponding shape-memory parameters are listed in Table III. The results were similar to the effects of D on shape-memory behaviors. At the same dose, with an increase in PEA usage, the degree of crosslinking increased, and the velocity of the deformation recovery grew quickly. When some specimens were added with more than 2 mol % PEA3 and were irradiated with 100 kGy, the degree of crosslinking was over 20%, and the deformation could recover completely.

CONCLUSIONS

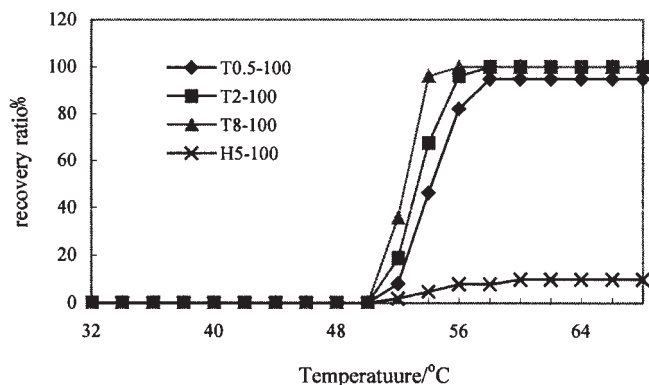PEA with polyfunctional double bonds had a distinct promoting function for the radiation crosslinking of

TABLE III
Effects of PEA on the Shape-Memory Behaviors of Sensitizing Crosslinked PCL

Sample	G (%)	T_r (°C)	T_m (°C)	R_f (%)
H5-100	1	54	56.0	8
T0.5-100	15.7	54	55.7	95
T2-100	30.3	54	55.4	100
T8-100	58.7	52.5	54.7	100

PCL. The greater the double-bond number and the usage of the polyfunctional material were, the greater G% was. The crosslinking of the PCL/PEA blends did not follow the classical Charlesby–Pinner equation, but with the Chen–Liu–Tang relation, a better linear fit was obtained. From the q_0'/q_0 ratio, we found that the crosslinking efficiency of PCL was greatly improved with the polyfunctional material. The sensitizing crosslinking effect was mainly attributed to the bridge reaction of the double bonds. DMA indicated that enhanced radiation crosslinking better raised the heat deformation temperature of PCL and presented a higher and wider rubbery-state plateau; it produce greater strength at temperatures higher than T_m and provided enough force to recover the deformation. The shape-memory results revealed that enhanced crosslinked PCL presented 100% recoverable deformation and a quicker recovery rate than pure PCL.

References

1. Yavuz, H.; Babac, C. J Polym Environ 2003, 11, 107.
2. Pitt, C. G. Biodegradable Polymers as Drug Delivery Systems; Marcel Dekker: New York, 1990; p 71.
3. Barralet, J. E.; Wallace, L. L.; Strain, A. J. Tissue Eng 2003, 9, 1037.
4. Kweon, H.; Yoo, M. K.; Park, I. K.; Kim, T. H.; Lee, H. C.; Lee, H. S.; Oh, J. S.; Akaike, T.; Cho, C. S. Biomaterials 2003, 24, 801.
5. Zhu, G.; Liang, G.; Xu, Q.; Yu, Q. J Appl Polym Sci 2003, 90, 1589.
6. Li, F. K.; Zhang, X.; Xu, M. J Appl Polym Sci 1999, 71, 1063.
7. Charlesby, A. Atomic Radiation and Polymers; Pergamon: London, 1960; p 134.
8. Chen, X.; Liu, K.; Tang, A. J Jilin Univ 1977, 4, 39.
9. Bowmer, T. N.; Davis, D. D.; Kwei, T. K.; Vroom, W. I. J Appl Polym Sci 1981, 26, 3669.
10. Cowie, J. M. G. Polymers: Chemistry and Physics of Modern Materials, 2nd ed.; Chapman & Hall: New York, 1991; p 314.
11. Ha, H.; Wu, J. Radiation Chemistry of Polymers; Peking University Press: Beijing, 2002; p 88.

Figure 10 Effects of PEA3 on the strain recovery ratio.