

Polyester-Hydrophilic PEO Networks as Multifunctional Biomaterials

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Summary: In order to improve the hydrophilic and elastic properties of polyester networks, the amorphous polymer networks of hydrophobic polyester/hydrophilic poly(ethylene glycol) dimethacrylate (PEGDMA) were prepared by UV-photopolymerization of PEGDMA and poly[(D,L-lactide)-co-glycolide]tetraacrylate (PLGATA). The interpenetrating polymer networks (IPNs) based on polyesterurethane and PEGDMA were synthesized in situ by UV-photopolymerization of PEGDMA and thermal polymerization of oligo[(D,L-lactide)-co- ϵ -caprolactone]terao (PCLA) or poly[(D,L-lactide)-co-glycolide]terao (PLGA) with isophorone diisocyanate (IPDI). The polymer networks and IPNs are transparent soft materials, and show good shape-memory properties. They recovered their permanent shape in 12 seconds when the environment temperature was above glass transition temperature (T_g). The strain recovery rate (R_r) and the strain fixity rate (R_f) of the polymer networks and IPNs were above 90%. The wettability, degradation rate, mechanical properties, and T_g of the polymer networks and IPNs could be conveniently adjusted by changing PEGDMA content. The elastic networks are suitable for potential soft substrates with tailored mechanical properties for clinical or medical use.

Keywords: biodegradable; interpenetrating polymer networks; poly(ethylene glycol) dimethacrylate; polyurethane; shape-memory

Introduction

The multifunctional polymers with biodegradability and shape-memory capability enable insert spacious degradable implants through small incisions into the body or manipulate their shape upon demand during a minimally invasive procedure. When heated above a certain switching temperature, T_{trans} , the device changes back to its original shape.^[1] Shape-memory polymers have been

developed and investigated for decades as biocompatible materials for biomedical applications such as intelligent surgical suture.^[1,2] Biodegradable, biocompatible shape-memory polymers have been drawing scientists' interest as promising multifunctional materials with potential applications in minimally invasive surgery.^[1-9]

Degradable shape-memory polymer networks were prepared by photocrosslinking oligoester dimethacrylates. However, these materials are relatively brittle and therefore it is very difficult to be handled at room temperature, which seriously limits their applications. The incorporation of another amorphous phase with a low glass transition temperature (T_g) into these materials is an effective strategy to improve the elastic property of the networks. Many approaches have been investigated, such as using ϵ -caprolactone (CL) and glycolide

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(GA) as comonomers.^[10–13] Moreover, amorphous, elastic AB copolymer networks were prepared by the copolymerization of poly[(*L*-lactide)-*co*-glycolide]dimethacrylate with ethyl acrylate, *n*-butyl acrylate and hexyl acrylate as comonomers. Although the polyester blocks of these polymer networks are degradable, the high hydrophobicity and low degradation rate limit their application.

Poly(ethylene glycol) (PEG) is generally known as biocompatible material and most often used as a hydrophilic polymer. The hydrophilic PEG provides a biocompatible layer which reduces the absorption of plasma albumen and red blood cells. In this paper, we aimed to prepare elastic soft polymer networks as multifunctional biomaterials with shape-memory properties by introducing short PEG blocks into the polymer networks. The short PEG blocks form amorphous domains in the polymer networks to improve the elastic property. Moreover, PEG can also increase the hydrophilicity and degradability of the materials.

Here, we reported three series shape-memory networks prepared from hydrophobic poly[(*D,L*-lactide)-*co*-glycolide]tetraacrylate (PLGATA), oligo[(*D,L*-lactide)-*co*-glycolide]tetraol (PLGA), oligo[(*D,L*-lactide)-*co*- ϵ -caprolactone]tetraol (PCLA) and hydrophilic poly(ethylene glycol) dimethacrylate (PEGDMA). Differential scanning calorimetry (DSC) and X-ray diffraction pattern (XRD) were used to analyze the thermal properties and the crystallinity of polymer networks. PEG improved the hydrophilicity and in vitro degradation rate of the polymer networks. The biodegradable networks could quickly recover its original shape by thermal stimulus, but slowly when immersed in water. Polyester-PEG networks and polyesterurethane-PEG IPNs have high potential as smart implants or medical devices.

Experimental Part

Materials

D,L-lactide (LA), GA and CL were bought from Sigma-Aldrich. PEGDMA (number-average molecular weight (M_n) = 2000 and

10000) was synthesized by the literature method.^[14] Pentaerythritol and stannous octoate ($\text{Sn}(\text{Oct})_2$, 95%) were obtained from Sigma Chemical Co. All other used chemicals were analytical grade reagents from Tianjin Chemical Reagents Co. and used as received.

Synthesis of PCLA5K Tetraol Oligomer

5.000 g of LA, 5.000 g of CL, and 0.272 g of pentaerythritol were added to an exhaustively flamed dry reactor with machine stirring and nitrogen-purged set. After the pentaerythritol was completely dissolved, $\text{Sn}(\text{Oct})_2$ (0.2 wt%) was added and the polymerization was carried out in bulk at 130 °C for 2 d. Then the product was dissolved in dichloromethane, precipitated in *n*-hexane, washed with *n*-hexane three times, and finally dried under vacuum (4 mmHg) at room temperature to constant weight.

Synthesis of PLGA Tetraol Oligomers

PLGA5K and PLGA10K were designated to have M_n of 5000 and 10000, respectively, according to the ratio of monomers to initiator. The synthesis of PLGA was performed according to the analogical procedures as described in the synthesis of PCLA5K tetraol. GA was used to substitute CL in the synthesis.

Synthesis of Poly[(*D,L*-lactide)-*co*-glycolide]tetraacrylate (PLGATA)

The PLGA was dissolved in dry THF under a nitrogen atmosphere. Upon cooling in an ice bath, 8 equivalents of acryloyl chloride were added. To the mixture, 8 equivalents of dry triethylamine were added dropwise and the mixture was stirred at 0 °C for 12 h and kept at room temperature for another 12 h. The precipitated ammonium salt was separated by filtration and unreacted acryloyl chloride and excess triethylamine were removed by evaporation. The concentrated filtrate was precipitated in a *n*-hexane: diethylether: methanol mixture with the ratio of 18: 1: 1 to remove traces of salt and reprecipitated from a dichloromethane solution in *n*-hexane.

Preparation of Polyester/Poly(ethylene glycol) dimethacrylate Polymer Networks by UV-Photopolymerization

The PLGATA, PEGDMA and 2,2-dimethoxy-2-phenylacetophenone (0.05%) were dissolved in dichloromethane. The homogeneous solution was poured into a Teflon mold. After dichloromethane was evaporated under N₂ stream, a film with the thickness of 0.5 mm was formed. Consequently, the film was covered with quartz glass. Photocuring was performed on a heated plate of 50 °C for 30 min using a UV system equipped with a high-pressure mercury lamp (200 W). The wavelength range of the lamp was from 200 nm to 450 nm, and the full spectrum of the wavelength was used for experiments.

Preparation of IPNs of Polyesterurethane/Poly(ethylene glycol) dimethacrylate

Different compositions of PEGDMA and PCLA or PLGA were dissolved in dichloromethane 10 wt%/vol%, and then calculated amount of IPDI according to $-\text{NCO}/-\text{OH}=1.05$ was added with Sn(Oct)₂ (0.5 wt% based on PCLA or PLGA) as catalyst and 2,2-dimethoxy-2-phenylacetophenone (0.2 wt% based on PEGDMA) as photoinitiator. The solutions were transferred into Teflon molds, which were placed in phosphorus pentoxide desiccators to avoid moisture. The solvent dichloromethane was evaporated under N₂ stream. PEGDMA network formed by exposing the mixture under a 200 W high-pressure UV lamp at room temperature for 30 min. Polyurethane network was formed by completing reaction of IPDI and PCLA or PLGA in an oven at 80 °C for 2 d.

Characterization

DSC measurements were carried out on a Perkin-Elmer system with a heating or cooling rate of 10 °C/min in the temperature range of –60 °C – 100 °C under constant N₂ stream (30 mL/min). About 5 mg of samples was used for each measurement, and an empty aluminum pan was used as reference. The glass transition temperature (T_g) was determined according to the heating run.

XRD investigations were carried out on x'pert pro (Philips) diffractometer composed of a Co source and 2 theta scan ranged from 10° to 90° at 45 KV, 30 mA.

Swelling degree (Q) and Gel Content (G)

Polymer networks and IPNs were immersed in dichloromethane at room temperature for 24 h and the values of Q and G are calculated by the following formulae:

$$Q = \frac{m_s}{m_{dl}} \times 100\% \quad (1)$$

$$G = \frac{m_{dl}}{m_t} \times 100\% \quad (2)$$

where m_t , m_s and m_{dl} are weights of samples before immersion, swollen samples, and dried weight after swelling, respectively.^[15–18]

Water Uptake

Polymer networks and IPNs were immersed in 5 mL phosphate buffered saline (PBS, Na₂HPO₄, 0.100 mol · L^{–1} and NaH₂PO₄, 0.063 mol · L^{–1}, pH = 7.0) at 37 °C for 24 h. The values of water uptake are calculated using the following formula:

$$\text{Water uptake} = \frac{m_w}{m_{d2}} \times 100\% \quad (3)$$

where m_w , m_{d2} are weight of samples after immersion in water and dried weight after swelling, respectively.

Shape-Memory Test

The shape-memory properties of polymer networks and IPNs were performed on a tensile tester with thermo chamber and temperature controller set. They were cut into dumbbell-shaped specimen with dimension of 2.0 mm × 30.0 mm and were elongated at a stretching rate of 10 mm/min. Thermocyclic experiment included four steps: (1) heating up the specimen to 50 °C for 10 min, (2) stressing the sample to elongation of 50%, (3) cooling the specimen down in the extended state to suitable temperature at a rate of 5 °C/min and fixing the initial shape, (4) unloading the specimen and reheat to 50 °C at a rate of 5 °C/min in order to recover the permanent shape. The strain fixity rate (R_f) and strain

recovery rate (R_r) are calculated according to the following formulae:

$$R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m} \times 100\% \quad (4)$$

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)} \times 100\% \quad (5)$$

where ε_m , ε_p and ε_u are the maximum strain, the elongation of the sample after recovery, and under the stress-free state the elongation of the sample after retraction of the tensile stress, respectively.^[15–18]

In Vitro Degradation Experiments

The degradation experiments were carried out in 5.0 mL PBS, pH = 7.0 solution in a 25 mL glass vial and placed in a shaker bath ($37 \pm 0.5^\circ\text{C}$, 100 rpm). Periodically, the samples were removed from buffer solution, weighted and dried until constant weight was obtained. The measurements were repeated for 5 times to obtain an average value for each sample.

Results and Discussion

Synthesis of Polymer Networks and IPNs

The hydrophilic polymer networks were prepared by photopolymerization of PLGATA and PEGDMA (Figure 1). Besides the tetrafunctional netpoints resulting from initiator pentaerythritol in the oligomers, the new formed copoly(meth)acrylate chains acted as crosslink chains. The molecular weight of PLGATA and PEGDMA affected the crosslink density of the polymer networks. T_g and the hydrophilicity of the polymer networks were influenced by PEGDMA content in the polymer networks. The detailed effect of PEGDMA content and molecular weight on the hydrophilicity, thermal properties and crystallinity of polymer networks are discussed in the following parts.

Hydrophilicity of Polymer Networks and IPNs

The water uptake of polymer network films was determined in PBS for 24 h at 37°C and used to characterize the hydrophilicity.

The water uptake of PN5-2 series increased from 1.4% to 50.0% when PEGDMA2K content increased from 0 to 50 wt% (Table 1). The water uptake of PN10-2 series was higher than that of PN5-2 series with comparable PEGDMA content because the crosslinking density of PN10-2 series was lower. The same tendency of water uptake with PEGDMA content was also observed for IPNs. As expected, the introduction of hydrophilic PEGDMA blocks into polyester networks and IPNs increased significantly the hydrophilicity and biocompatibility of biomaterials.

Thermal Properties of Polymer Networks and IPNs

DSC and XRD measurements were performed to investigate the thermal properties and crystallinity of the polymer networks and IPNs. A single T_g was observed for all PN5-2 series polymer networks (Table 1), while no melting endotherm of PEG blocks was found, which was similar to IPNs, probably because of an increased compatibility of the short PEG chain with dominant PLGA blocks and insufficient phase separation. In addition, T_g was compositionally dependent and decreased with the increase of PEGDMA content. Figure 2 shows T_g determined from the DSC data and theoretical T_g calculated from both Fox and Gordon-Taylor equations ($k=0.5$). The experimental results were in good agreement with the values calculated by the Fox equation rather than by Gordon-Taylor equation. PEGDMA content in the polymer networks can be predicted from Figure 2 if a polymer network with a certain T_g is intended to prepare.

In contrast to PN5-2 series polymer networks, PN5-10 and PN10-10 series exhibited one T_m for the investigated compositions (Table 1), which indicated that polymer networks synthesized from PEGDMA10K were semicrystalline materials. Owing to the low crosslink density and long PLGA blocks, T_m of PEG blocks of PN10-10 was higher than that of PN5-10. When PEGDMA10K content was 20 wt%,

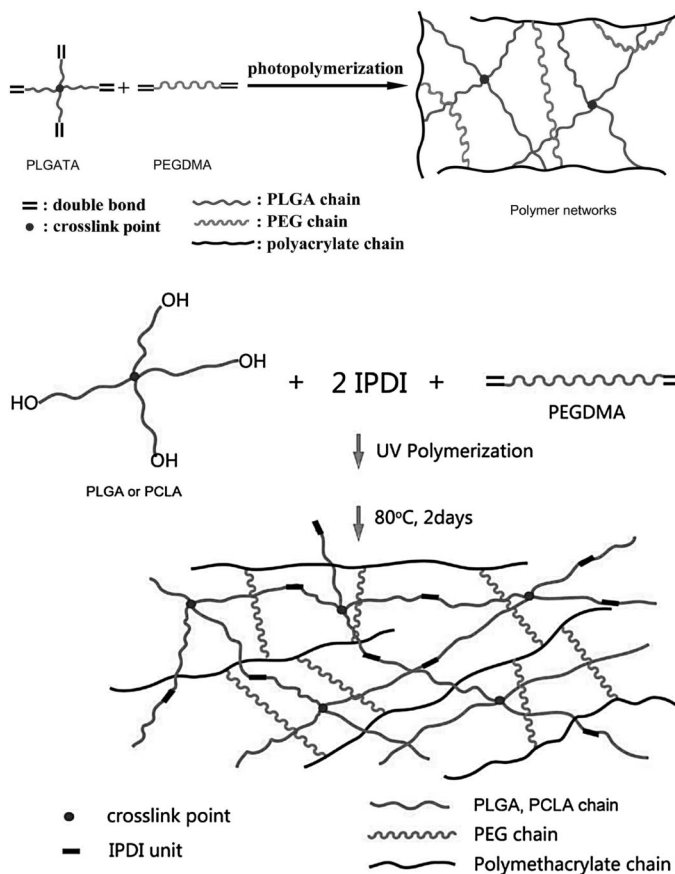


Figure 1.

Polymer network and IPN architecture. IPNs were synthesized from PCLA5K or PLGA5K and PEGDMA through UV polymerization and thermal polymerization of PCLA or PLGA with IPDI. Table 1 summarizes the influence of PEGDMA content on gel content (G) and the degree of swelling (Q) of IPNs and polymer networks. Except PN-10-10-20 and IPN-PCLA-5-10, the other networks had high G (> 90%), which confirmed that the IPNs and polymer networks were formed by the reactions as shown in Figure 1.

the PEG blocks formed semicrystalline domains with T_m of 45.5 °C and 53.0 °C for PN5-10-20 and PN10-10-20, respectively. The melting endotherm of PEG blocks increased with increasing PEGDMA10K content in the polymer networks.

XRD measurements were performed to investigate the crystallinity of PEG blocks in polymer networks and IPNs with different PEGDMA contents. For polymer networks of PEGDMA2K and 10K, the characteristic diffraction peaks of semicrystalline PEG domains appeared at 22.3° and 27.2° (Figure 3 A and B). These distinct diffraction peaks were not observed in PN5-2 and IPNs when PEGDMA contents

were in the range of 10 wt% to 50 wt%, which demonstrated that PEGDMA2K blocks formed amorphous domains (Figure 3). The network structure hindered the crystallibility of PEG blocks. However, the characteristic diffraction peaks with low intensity were observed for PN10-10-20 in Figure 3B. The long chain of PEG block and the low crosslinking density of the polymer network are favorable for PEG blocks to form semicrystalline phase. The results demonstrated that PEGDMA2K could not crystallize in the networks when PEGDMA content was below 50 wt%, however, PEG blocks formed semicrystalline domains when the molecular weight

Table 1.

Degree of swelling (Q), gel content (G) and thermal properties of polymer networks and IPNs with different PEGDMA content.

Sample ID ^{a)}	M _n of PEGDMA	PEGDMA (wt%)	Oligoester ^{b)}	Q (%)	G (%)	Water uptake in 24 h (%)	T _g (°C)	C _p (J/g · K)
PN5		0	PLGATA5K	260 ± 5	99.1 ± 0.5	1.4 ± 0.1	54.8	0.539
PN5-2-10	2000	10	PLGATA5K	360 ± 20	98.7 ± 0.9	10.7 ± 2.9	41.5	0.423
PN5-2-20	2000	20	PLGATA5K	350 ± 70	99.4 ± 0.1	11.3 ± 0.6	36.0	0.397
PN5-2-30	2000	30	PLGATA5K	470 ± 10	98.1 ± 1.4	18.8 ± 0.1	13.6	0.269
PN5-2-40	2000	40	PLGATA5K	410 ± 60	98.0 ± 0.2	38.8 ± 6.6	8.7	0.272
PN5-2-50	2000	50	PLGATA5K	460 ± 70	96.4 ± 2.3	50.0 ± 5.2	-21.8	0.634
PN10		0	PLGATA10K	310 ± 40	98.5 ± 1.4	3.0 ± 0.0	54.6	0.444
PN10-2-10	2000	10	PLGATA10K	400 ± 30	97.3 ± 0.4	16.6 ± 1.8	n.d. ^{c)}	n.d. ^{c)}
PN10-2-30	2000	30	PLGATA10K	410 ± 20	96.0 ± 0.8	32.8 ± 0.7	n.d. ^{c)}	n.d. ^{c)}
PN5-10-20	10000	10	PLGATA5K	540 ± 30	93.6 ± 4.3	25.9 ± 1.3	45.3 ^{d)}	2.53 ^{e)}
PN10-10-10	10000	10	PLGATA10K	430 ± 50	90.8 ± 6.7	19.0 ± 0.6	49.9 ^{d)}	7.5 ^{e)}
PN10-10-20	10000	20	PLGATA10K	440 ± 40	84.3 ± 7.1	36.3 ± 3.3	53.0 ^{d)}	17.0 ^{e)}
IPN-PCLA-5-0		0	PCLA5K	280 ± 30	95.2 ± 0.6	7.0 ± 0.5	35.5	0.552
IPN-PCLA-5-10	2000	10	PCLA5K	580 ± 70	87.4 ± 5.0	12.5 ± 0.6	11.9	0.425
IPN-PCLA-5-20	2000	20	PCLA5K	470 ± 70	90.4 ± 3.5	25.6 ± 1.2	7.1	0.450
IPN-PCLA-5-30	2000	30	PLGA5K	510 ± 80	91.2 ± 1.6	33.8 ± 1.5	2.9	0.322
IPN-PLGA-5-0		0	PLGA5K	935 ± 83	98.4 ± 0.6	3.4 ± 0.1	62.8	0.548
IPN-PLGA-5-10	2000	10	PLGA5K	619 ± 31	93.9 ± 1.8	7.9 ± 0.6	42.5	0.561
IPN-PLGA-5-20	2000	20	PLGA5K	740 ± 33	94.8 ± 1.8	29.6 ± 0.2	32.3	0.491
IPN-PLGA-5-30	2000	30	PLGA5K	751 ± 50	95.1 ± 1.7	48.8 ± 1.0	17.4	0.404

^{a)}PNX-Y-Z is polymer network of PLGATA-PEGDMA with X · 1000 = M_n of PLGATA blocks, Y · 1000 = M_n of PEGDMA and Z% = PEGDMA content. PN5 and PN10 are polymer networks of PLGATA5K and PLGATA10K, respectively. IPN-PCLA-X-Y or IPN-PLGA-X-Y is the ID of IPNs with X · 1000 = M_n of PCLA or PLGA oligomer, and Y% of PEGDMA2K content. ^{b)}Star-shaped oligomers, PLGATA5K, PLGATA10K, PCLA5K, PLGA5K. ^{c)}Not determined. ^{d)}T_m (°C). ^{e)}ΔH (J/g).

was 10000. This was also confirmed by DSC measurements (Table 1).

Mechanical Properties and Shape Memory Effect

One of the paper's purposes is to improve the elastic properties of polymer networks

of PN5 and PN10. At room temperature, PN5 and PN10 were brittle, hard materials with high Young's modulus (E) and low elongation at break. The introduction of additional amorphous PEG domains into the polymer networks is expected to improve significantly the elastic properties of the resulting polymer networks. The results showed that E of polymer networks and IPNs decreased significantly with increasing PEGDMA content. When the PEGDMA content increased above 30 wt%, the polymer networks were rubbery materials (Table 2). When the T_g of polymer networks was around room temperature, they exhibited the mechanical properties of soft materials as low σ_b and E.

The polymer networks exhibited macroscopic shape memory effect, and high strain fixity and strain recovery ability in thermocyclic tensile tests. The strain recovery rate (R_r) and the strain fixity rate (R_f) were above 90% by thermocyclic experiments. The T_{trans} of PN5-2 series could be easily adjusted in the range of 8.7 °C to 41.5 °C.

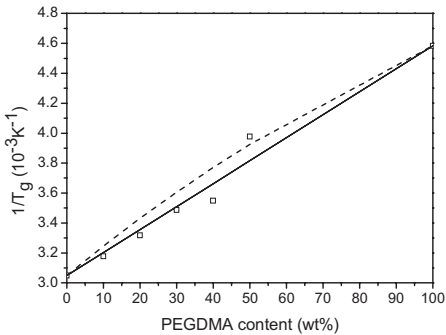


Figure 2. Relationship of 1/T_g of PN5-2 series with PEGDMA2K contents in the polymer networks. The experimental data from DSC were shown as square points, Fox equation calculation as solid line and Gordon-Taylor equation (k = 0.5) calculation as dash line.

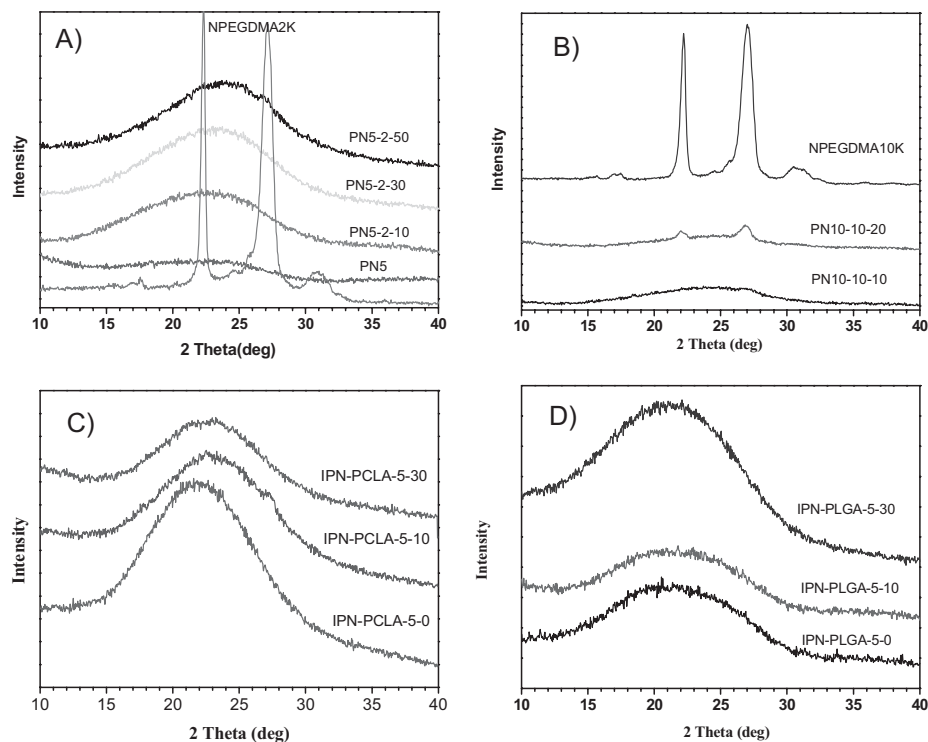


Figure 3.

XRD curves of PN5-2 (A), PN10-10 (B), IPN-PCLA (C), and IPN-PLGA (D) series polymer networks and IPNs with various PEGDMA content. NPEGDMA2K and NPEGDMA10K as references were also shown in the Figure.

By introducing 20 wt% of PEGDMA, the T_{trans} of the polymer network PN5-2-20 was around body temperature to match

Table 2.

Mechanical properties of polymer networks and IPN at room temperature.

Sample ID	E (MPa)	σ_b (MPa)	ε_b (%)
PN5	850 ± 80	31.0 ± 0.5	5.7 ± 1.2
PN5-2-10	520 ± 70	16.2 ± 2.4	20 ± 4
PN5-2-20	220 ± 2	16.3 ± 1.3	165 ± 8
PN5-2-30	50 ± 10	1.3 ± 0.2	260 ± 10
PN5-2-50	3.9 ± 0.7	3.7 ± 0.7	60 ± 8
PN10	970 ± 110	30.6 ± 2.7	6 ± 3
PN10-2-10	570 ± 50	15.6 ± 0.5	60 ± 8
PN10-2-30	12.6 ± 1.5	3.1 ± 0.7	120 ± 30
PN10-2-50	6.7 ± 2.4	1.8 ± 0.1	50 ± 10
PN5-10-10	440 ± 16	12.0 ± 0.4	6 ± 0.2
PN10-10-10	350 ± 20	3.3 ± 0.9	1.5 ± 0
IPN-PCLA-5-0	10.5 ± 1.2	15.5 ± 1.4	110 ± 20
IPN-PCLA-5-10	8.7 ± 0.4	7.2 ± 0.5	210 ± 30
IPN-PCLA-5-20	6.3 ± 0.8	12.5 ± 1.3	250 ± 50
IPN-PCLA-5-30	5.9 ± 0.8	12.3 ± 1.5	220 ± 50
IPN-PLGA-5-0	830 ± 3	7.2 ± 2.0	24 ± 7
IPN-PLGA-5-10	700 ± 104	20.0 ± 12.7	3.9 ± 1.2
IPN-PLGA-5-20	327 ± 40	12.5 ± 0.4	131 ± 10
IPN-PLGA-5-30	47.1 ± 6.8	16.5 ± 0.6	290 ± 16

the potential clinical applications. PN5-2-20 was used as an example to demonstrate the macroscopic shape-memory properties in Figure 4.

When polymer networks were immersed in water bath at room temperature, they recovered slowly their permanent shape along with hydration to some equilibrium value. Therefore, besides thermal stimulus, the recovery from the temporary shape to permanent shape could be initiated by another external stimulus: hydration of the materials. However, the recovery took very long time (ca. 6h) compared to thermal stimulus (12 s).

Degradation of IPNs

To evaluate the hydrolytic degradability of IPN films, the hydrolysis behavior was investigated in $\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ buffer (pH = 7.4) at 37 °C in a shaking water bath. The water uptake of the films increased gradually along with degradation time. The

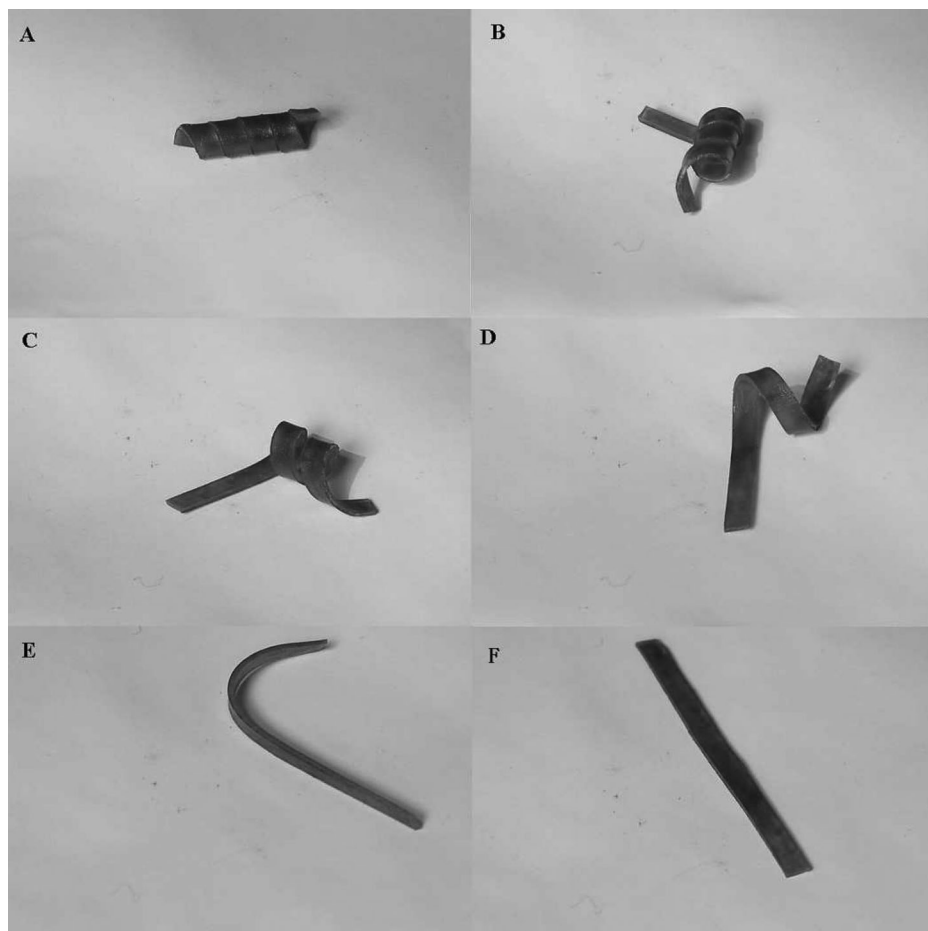


Figure 4.

Shape-memory photographs (A-F, 3 s interval) of PN5-2-20 showed the transition from temporary to permanent shape. The initial rod strip shaped film (F) was deformed into spiral shape in oven at 60 °C (A), cooled to 20 °C, withdrew the external force. Then the deformed sample was put into oven at 60 °C and recovered to its permanent shape (B-E).

high hydrophilicity of the film increased the diffusion ability of water molecules into polymer networks of IPN-PCLA-5-30 with 30 wt% PEGDMA content. The PEG block improved the hydrophilicity of the IPN and increased the degradation rate. The weight loss of the IPN-PCLA-5-30 film occurred mainly by the hydrolysis of ester bonds in the LA block, whereas the ester bonds of CL was relative hydrophobic and more stable in PBS than the PLA block. For IPN-PLGA-5-30, the hydrolysis rate of ester bonds in the glycolide block was higher than that in the LA block. IPN-

PLGA-5-30 showed higher degradation rate than IPN-PCLA-5-30.

Conclusion

Polyesterurethane-PEG interpenetrating polymer networks were synthesized via photopolymerization of PEGDMA and the crosslink of four armed oligomers PCLA or PLGA with IPDI. The amorphous polymer networks of polyester/PEGDMA were prepared by the photopolymerization of PEGDMA and poly[(D,L-lactide)-co-

glycolide]tetraacrylate. The wettability, mechanical properties, and T_g of the polymer networks could be conveniently adjusted by the variation of the compositions of hydrophobic PCLA or PLGA and hydrophilic PEGDMA. The materials could quickly recover its original shape when the environment temperature was above glass transition temperature, but slowly in water. The introduction of PEG networks improved the hydrophilicity of the IPNs and increased the degradation rate. Polyester-urethane-PEG networks and IPNs are highly potential for biomedical applications, such as smart implants or medical devices. They have a promising future for developing site-specific controlled drug delivery system or stent in the treatment of cardiovascular disease.

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