Biomedical Property Modifications of Poly(vinyl chloride) with Methoxylated Poly(ethylene glycol)-Poly(ε-caprolactone) Diblock Copolymer

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ABSTRACT: Manufacturing biomedical flexible Poly (vinyl chloride) (PVC) products requires the nontoxic plasticizers and the biocompatibility. In this study, a series of methoxylated poly(ethylene glycol)-poly(ε-caprolactone) diblock copolymer (MPEG-PCL) with variety molecule weight were synthesized by ring-opening polymerization of ε-caprolactone with methoxylated poly(ethylene glycol) (MPEG) as macroinitiator. The structure of the block copolymers was characterized utilizing FTIR, NMR, SEC, and DSC. Because the compatibility between PVC and PCL, a series of MPEG-PCL/PVC blends were prepared. The results of DSC and mechanical properties of blends show that PVC could be plasticized with MPEG-PCL and the diblock copolymer is probably to be used as a polymeric plasticizer for PVC. Moreover, the water contact angle results indicated that MPEG-PCL also provided PVC the hydrophilic properties. At the same time, it was found that the blends showed favorable anticoagulation property which can probably exploit the potential application of the blends in the biomedical areas. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 107–115, 2009

Key words: Poly(vinyl chloride); methoxylated poly(ethylene glycol)-poly(ε-caprolactone) diblock copolymer; blends; modification; biocompatibility

INTRODUCTION

Poly(vinyl chloride) (PVC) has been manufactured and commercialized for many years because of its excellent mechanical properties, flame retardant properties, corrosion resistance properties, and cheap price. However, its poor thermo-stability makes the thermoplastic process almost impossible without plasticizer, especially in flexible PVC products which are widely used for the production of biomedical and baby-care commodities. In the flexible PVC processing, phthalates is a kind of the most widely used plasticizer. Unfortunately, a large number of toxic effects because of the leaching of phthalates from the PVC products have been described either in animals or in human tissues.[1–3] During the last years great attentions were given to find alternative materials to phthalates in PVC applications.[4] The possible approaches includes the utilizing of nontoxic small molecule plasticizers such as azelates, citrates, and sebacates; surface treatment; and cross-linking to inhibit plasticizer's migrations etc. Using polymeric plasticizer is another important route.[5–7] By choosing the "soft" polymer with lower glass transition temperature to blend with PVC, the flexible polymer alloy could be obtained. Here the soft polymers take effects as a plasticizer. Moreover, because of the entangle effect between the soft polymer chains and PVC chains, the migration of plasticizer could be avoided.

One of the most important application fields of flexible PVC is the biomedical area, for example, used as the blood bag, endocardiac vessel, and oxygenation bag etc. The biomedical application of PVC requires not only the security but also the biocompatibility, especially the blood compatibility including the anticoagulant and nonhemolytic properties which usually profit from the surface hydrophilic modifications of PVC as the first step. To achieve this purpose, the methods including temporarily surface coating or permanently surface grafting with blood-compatible or hydrophilic materials were used.[8–10] Then, whether we could solve both the plasticization and hydrophilic modification in one step?

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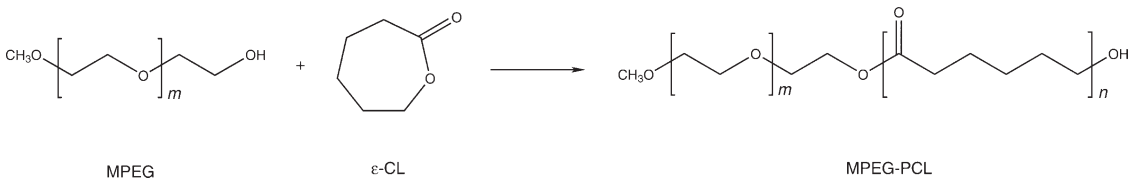

Scheme 1 Synthesis of MPEG-PCL.

Here, we reported a multifunctional polymeric plasticizer for PVC as an alternative to phthalates, methoxylated poly(ethylene glycol)-poly(ε-caprolactone) diblock copolymer (MPEG-PCL), which plasticized PVC and also provide PVC the hydrophilic properties. As a kind of biocompatible, biodegradable linear polyester, poly(ε-caprolactone) (PCL),[11] a polymer based on the ring-opening polymerization of ε-caprolactone (CL), has received great attention over the last two decades, and has been used in medical applications as homo- and co-polymers, for example, as suture in bone fracture fixation, as tissue-engineering scaffold and as drug-release carrier. Block copolymers containing a PCL segment have attracted more attention because of the properties that they are nontoxicity and biodegradable and miscible with a wide range of polymers.[12] These characters made the copolymers can be potentially applied in surface modification of common polymers, construction of drug-delivery vehicles, etc. Poly(ethylene glycol) (PEG) is one of the most important segments used in PCL copolymers for its excellent properties: nontoxicity, biocompatibility, anticoagulation, and nonimmunogenicity. Using PEG as macroinitiator, PCL-PEG copolymers[13,14] have been synthesized and studied by many researchers and the PCL-PEG multiblock copolymers blended with PVC have also been studied by Penco[15] focusing on the miscibility of copolymers with PVC, and Ferruti[16] paying more attentions on the possibility of using the copolymers as the substitutes for di(ethylhexyl) phthalate in flexible PVC formulations. They all used the tri-block copolymers and did not investigate the surface properties, especially the bio-properties of such blends.

In this study, utilizing methoxylated poly(ethylene glycol) (MPEG) as macroinitiator, a series of MPEG-PCL diblock copolymers were synthesized with ring-opening polymerization of CL. By solvent blending, flexible MPEG-PCL/PVC alloys containing different amount of MPEG-PCL were prepared and the plasticization effect of copolymers was found. Because of the enrichment of MPEG segment on the blends surface, the copolymers also provide PVC the hydrophilic and anticoagulation properties. With biocompatible MPEG-PCL copolymer as nontoxic polymeric plasticizer, the plasticization and hydrophilication were resolved in one step.

EXPERIMENTAL

Materials

MPEG with number average molecule weight of 700 g/mol (with PDI 1.12), a gift from Nanjing Teva Chemical Industry Co., (Nanjing, China) was dried by refluxed with benzene (which was previously dried by refluxed with Na for few hours and distilled off) for at least 2 hrs and benzene was distilled off at normal pressure, the residual MPEG was vacuum dried for 48 hrs in P_2O_5 desiccators before use. ε-Caprolactone (CL) (Acros) was dried with CaH_2 over 2 days and then distilled under reduced pressure in a nitrogen atmosphere before use. PVC for packing solid medicine with polymerization degree of 800 obtained from Qionghua Group (Jiangsu, China) was used as received. Tetrahydrofuran (THF), stannous octanoate, chloroform ($CHCl_3$), and anhydrous ether (All AR grade) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China) and used without further purification.

Synthesis of MPEG-PCL diblock copolymers

Scheme 1 shows the synthesis route of MPEG-PCL diblock copolymers. According to the blueprints of the copolymers, different amount of dried MPEG and fresh distilled ε-CL were charged into a 10 mL glass tube, then a drop of stannous octanoate was added and the glass tube was sealed under vacuum, and placed in a thermostat at 140°C to polymerize for 72 h. After been cooled to room temperature, the crude products were dissolved in 20 mL $CHCl_3$ and the solution was added dropwise to 200 mL cold (−5°C) anhydrous ether to precipitate the products, repeat twice, filtered out and vacuum dried to give MPEG-PCL diblock copolymers. Based on the designed molecule weight of 5000, 8000, and 10,000 g/mol, the samples were recorded as MPEG-PCL 5K, MPEG-PCL 8K, and MPEG-PCL 10K, respectively.

Preparation of MPEG-PCL/PVC blend samples

PVC and MPEG-PCL diblock copolymer were separately dissolved in THF with the concentration of 5 g per 100 mL solvent, and then the two solutions were mixed according the different contents of

MPEG-PCL in PVC and casted in glass dishes. THF was evaporated at room temperature to provide the blend films. In the blended samples, the mass fraction for each MPEG-PCL is 5%, 10%, 20%, and 30% and assigned as 5K5%, 5K10%, 5K20%, respectively, and the rest may be deduced by analogy.

Instrumentation

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet Nexus 870 FTIR spectrometer (Thermo Nicolet, USA) from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} at room temperature on a KBr pellet with approximately 1% sample concentration.

^{1}H-NMR spectra were taken on a Bruker ARX500 NMR spectrometer (Bruker, German) with $CDCl_3$ as solvent and TMS as internal standard.

Size Exclusion Chromatography (SEC) of MPEG-PCL samples was performed at 25°C on a SEC system composed of a Waters 515 HPLC pump (Waters, US), a Wyatt DAWN EOS Multi-Angle Laser Light Scattering (MALLS) detector (Wyatt, US), and a Wyatt Optilab rEX refractive index detector (Wyatt, US). The columns were Styragel HR3, HR4, and HR5 (300 × 7.8 mm) in series from Waters. HPLC grade THF was used as eluent at a flow rate of 1 mL/min under 600 psi pressures. THF and samples were filtered with pore size of 0.45 μm (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, US). The columns were calibrated using polystyrene standards with molecular weights ranged from 900 to 1.74 × 10^6 g/mol (with NMD 1.02-1.11). ASTRA software (Version 5.3.1.4) was utilized for data acquisition and analysis. The sample concentration was 5 mg/mL.

The differential scanning calorimetry (DSC) thermograms were recorded at heating rate of 20°C/min in N_2 atmosphere ranged from 0°C to 100°C for MPEG-PCL copolymer and −50°C to 120°C for blend samples with a Perkin-Elmer Pyris 1 thermal analysis system (PerkinElmer Life. Sciences, Boston, MA). Each sample was scanned twice without controlling the cool rate.

The scanning electron microscope (SEM) photographs were taken on Philips XL30 ESEM operated at an acceleration voltage of 5 kV.

The water contact angles of blend samples were recorded with a KSV CAM200 optical contact angle and surface tension meter system (KSV Instruments, Helsinki, Finland) at 20°C with relative humidity at 85%. Every data point was the average of 10 determinations. Before the determining of water contact angle, the blend films were immersed in distilled water at 70°C for 4 h to anneal and allow the migration of PEG segment to the surface of polymer blends and then vacuum dried for 24 h.

According to ASTM 1708, the mechanical properties of MPEG-PCL/PVC blends were recorded on an Instron 3366 Universal Testing Machine (Instron Engineering Corporation, Canton, USA) with crosshead speed of 5 mm/min at room temperature with relative humidity at 60%. Before the test, all the samples was annealed at 70°C for 1 h and slowly cooled with the oven.

Plasma recalcification time (PRT) determination

A series of dried tubes was coated with mixed solutions in section 2.3 of MPEG-PCL 5K and 8k copolymers blend with PVC, dried and kept in refrigerator at 4°C for 24 hr. Fresh rabbit blood (0.1 mL) containing sodium citrate and 0.1 mL solution of $CaCl_2$ (0.025 mol/L) were added into each tube. The time of the emergence of a milky white flocculate was recorded. The results were compared with those of blank tubes, the tubes coated with silicon oil and bare PVC, respectively. Five tubes were coated and determined for every sample and the 5 point average value was adopted as the result.

RESULTS AND DISCUSSION

Synthesis and characterizations of MPEG-PCL

Synthesis of MPEG-PCL diblock copolymers

Ring-opening polymerization is a typical process to prepare PEG and PCL. In this study, using certain content of MPEG as macroinitiator, different amount of CL monomer were polymerized to provide the MPEG-PCL diblock copolymer with different average molecular weight. Table I show the polymerization compositions and result polymers.

FTIR spectra of MPEG and MPEG-PCL diblock copolymers

FTIR spectra of samples were recorded to prove the successful synthesis. Figure 1 shows the typical spectrum of MPEG and MPEG-PCL 8K. On the spectrum of MPEG, the characteristic peaks assigned to groups on polyether are clearly observed, including the A-OH group at wavenumber of 3450 cm^{-1}, A-CH_2 group at 2880 cm^{-1}, C-O-C group at 1110 cm^{-1} and so on. On the spectrum of MPEG-PCL diblock copolymer, the peak correlated to A-OH group at about 3450 cm^{-1} is decreased obviously for the consumption in ring-opening polymerization of CL. At 1730 cm^{-1}, the strong absorption is a characteristic peak correlated to the ester bond in PCL segment, which provide the evidence of the successful synthesis of target diblock copolymer composed with PEG and PCL segments.

TABLE I
Synthesis and Compositions of MPEG-PCL

Samples	MPEG in feed (mol % in EO + CL)	Average molecule weight[a]		PDI[a]	MPEG in copolymers (mol % in EO + CL)[b]
		M_n	M_w		
MPEG-PCL 5K	28.3	5970	11400	1.91	24.6
MPEG-PCL 8K	19.0	8930	16600	1.85	17.2
MPEG-PCL 10K	15.5	9570	17900	1.87	14.1

[a] Determined by SEC.
[b] Evaluated from ^{1}H-NMR spectrum, where EO means ethylene oxide.

NMR spectra of MPEG and MPEG-PCL diblock copolymer

^{1}H-NMR spectrum of MPEG-PCL 8K was shown in Figure 2. The resonance peak at 3.65 ppm is corresponds to the PEG segment while the other peaks are the typical resonance for PCL segment. The different relative intensities between MPEG and PCL resonance peaks give the promotion of different ratio between MPEG and PCL segments among the copolymers. From the integral results, the mole fractions of MPEG in MPEG-PCL copolymers calculated as the EO and CL constitutional units are evaluated and listed in Table I.

Molecule weight determining of MPEG-PCL diblock copolymers

Figure 3 shows the SEC trace of MPEG-PCL copolymers with 1mL/min THF as eluent at 25°C on a Waters model 515 gel permeation chromatograph. The average molecule weight and polydispersity index calculated from the curves are listed in Table I. The block copolymers composed by MPEG and PCL segments, the unimodal distribution indicate that the copolymerization has been completed successfully and no homopolymer exist.

DSC analysis of MPEG and MPEG-PCL diblock copolymers

Figure 4 shows the DCS results of MPEG-PCL with different molecular weight. As shown in Figure 4(A), all the first scanning curves show monomodal melting peak and the melting point increase following the molecule weight, as 57.8, 61.4, and 62.7°C for MPEG-PCL 5K, 8K, and 10K samples, respectively. However, when the samples were scanned for the second time, the bimodal peaks were observed and the detail data were labeled on Figure 4(B). The peak at lower temperature was assigned to MPEG segment while the higher one should be attributed to PCL segment. Following the molecule weight of MPEG-PCL increasing, the two peaks are closing and trend to amalgamate. The bimodal phenomena indicated the microphase separation in the MPEG-PCL diblock copolymer system at our MPEG/PCL ratio system. The same phenomenon was also found in the Ref [14] and was proved carefully by WAXD

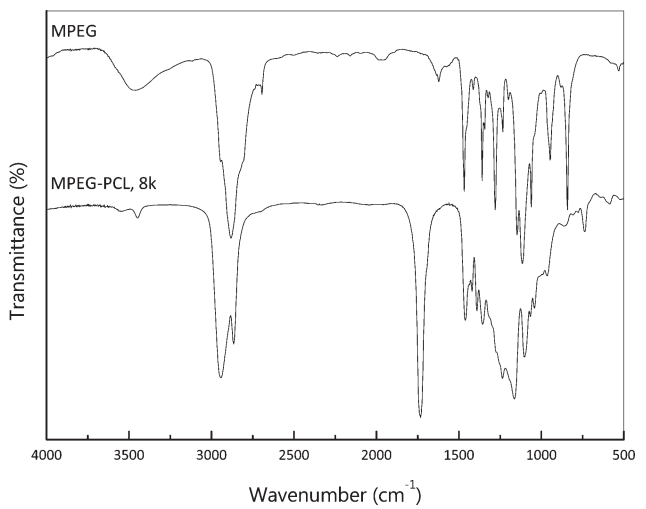

Figure 1 FTIR spectrum of MPEG and MPEG-PCL 8K.

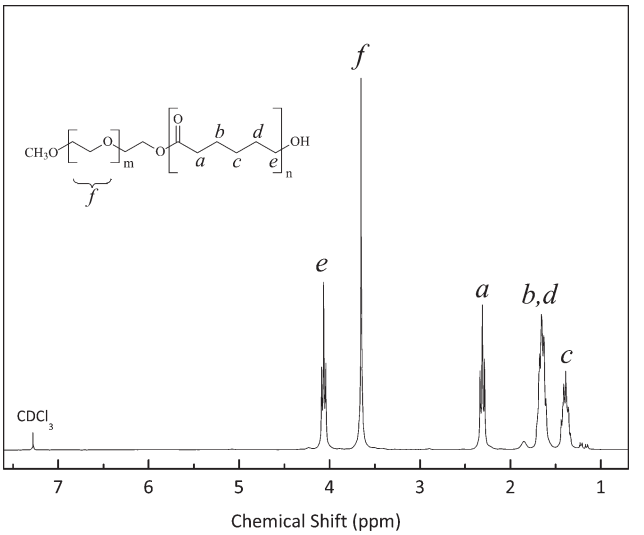

Figure 2 ^{1}H-NMR spectra of MPEG-PCL 8K.

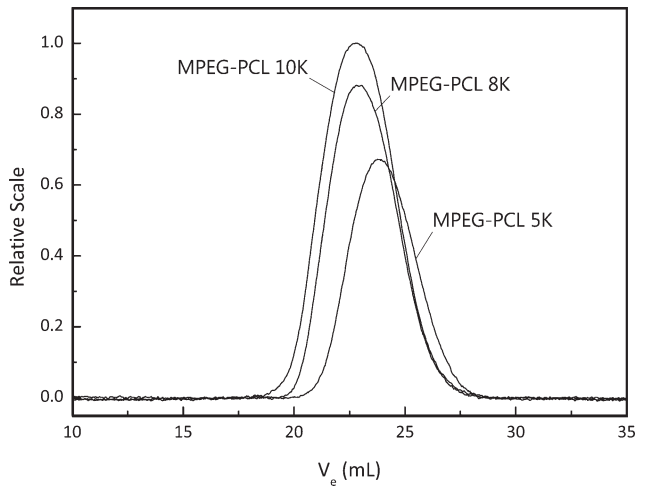

Figure 3 SEC traces of MPEG-PCL diblock copolymers.

and polarized optical microscopy. For our aim, hydrophilic modifying PVC utilizing MPEG-PCL with self-assembling process, the phase separation is favorable which should promote the migration of MPEG segment to the surface of materials and decrease the water contact angle of blends.

Plasticization of PVC with MPEG-PCL diblock copolymers

Glass transition temperature (T_g) of MPEG-PCL/PVC blends

It is well known that both the melting point and T_g of MPEG and PCL are lower than that of PVC. When MPEG-PCL copolymer was introduced and homogenously dissolved in the matrix, the copolymer is able to hinder the interactions between the PVC chains. That predicates the decreasing of T_g and the PVC is probably to show flexible properties. By means of DSC, PVC blended with MPEG-PCL block copolymers at variety content was studied. As an example, Figure 5 shows the traces of MPEG-PCL 5K/PVC blends with copolymer concentration ranged from 5% to 30%. During the first heat scanning [Fig. 5(A)], a slight endothermic transition at about 47°C was observed in lower copolymer concentration samples (5% and 10%, respectively), which can be attributed to the melting processes of MPEG-PCL copolymer, thus indicating at least a partial phase separation between MPEG-PCL and PVC. However, at relatively higher concentration, no enthalpic peak was observed in the corresponding blends, thus suggesting the miscibility of MPEG-PCL with PVC at higher concentrations. Moreover, when the samples were heat scanned at the second time, the enthalpic peak disappeared [Fig. 5(B)] which indicated that the MPEG-PCL diblock copolymer is miscible with PVC after been annealed. For other MPEG-PCL samples with higher molecule weight, the similar result was concluded. Summarized the measured T_g of blends at the second heat scanning, the shifts following concentration were illustrated in Figure 6.

From Figure 6, when the MPEG-PCL copolymer was introduced into PVC, the T_g of blends was reduced without any exception. Only 5% copolymer was added, the T_g decreased to about half of the original ones and more MPEG-PCL introduced, more decrease observed. Moreover, comparing the influence of the copolymer's molecule weight to T_g, it could be found that the copolymer with lower molecule weight shows more effect on the T_g decreasing. At the higher concentration, the effect is much regular. When more than 20% MPEG-PCL was feed, especially for those which have low molecule weight (5K and 8K), the T_g of PVC blends is lower than ambient temperature and the blends exhibit the properties of flexible PVC products. Moreover, comparing the plasticization effect of

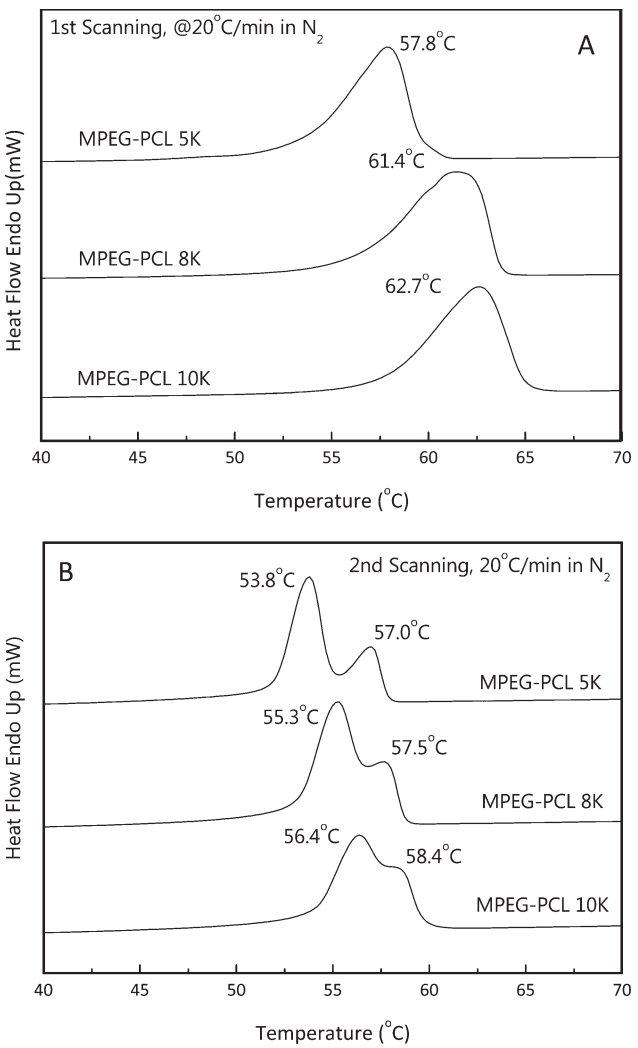

Figure 4 DSC curves of MPEG-PCL copolymers: (A) the first scan; (B) the second scan.

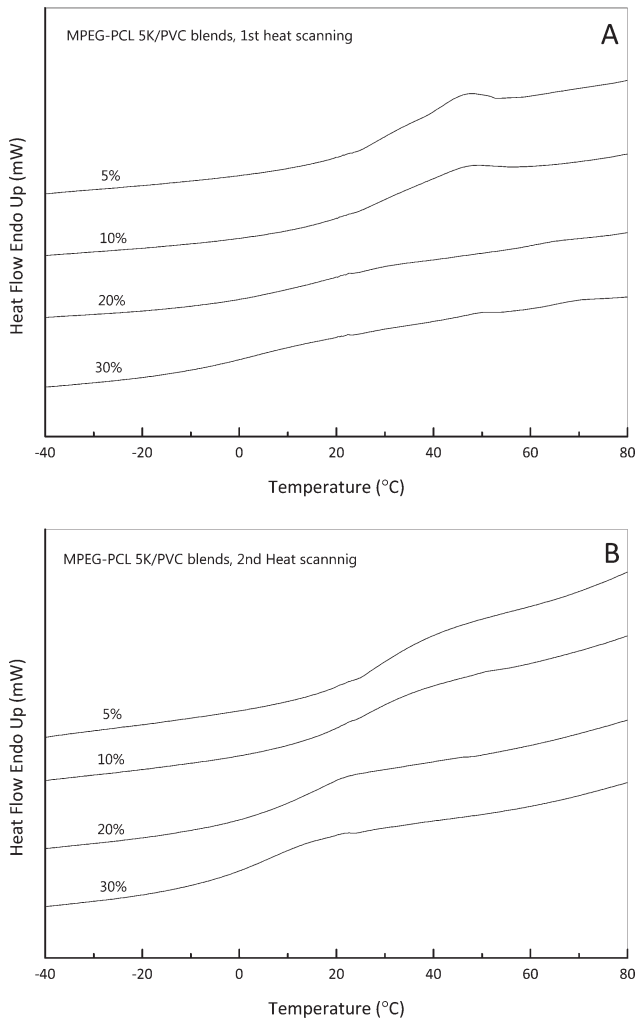

Figure 5 DSC curves of MPEG-PCL 5K/PVC blends: (A) the first scan; (B) the second scan.

MPEG-PCL and commercial dioctylphthalate (DOP),[17] MPEG-PCL shows higher effective than that of DOP at low concentration. With the concentration increasing of plasticizer, the T_g decreasing of PVC/MPEG-PCL blends act as the exponential function rather than the linear function of PVC/DOP blends.

Mechanical properties

According to the method described in ASTM 1708, the mechanical properties of MPEG-PCL/PVC blends were determined. Figure 7 shows the typical strain-stress curves of MPEG-PCL 5K/PVC blends. The other samples show the similar results and the major mechanical properties of all blend samples are listed in Table II.

From the mechanical properties, the plasticization effect of PVC with MPEG-PCL diblock copolymers was observed clearly. As a comparison, the bare PVC sample shows evident yield point on strain-

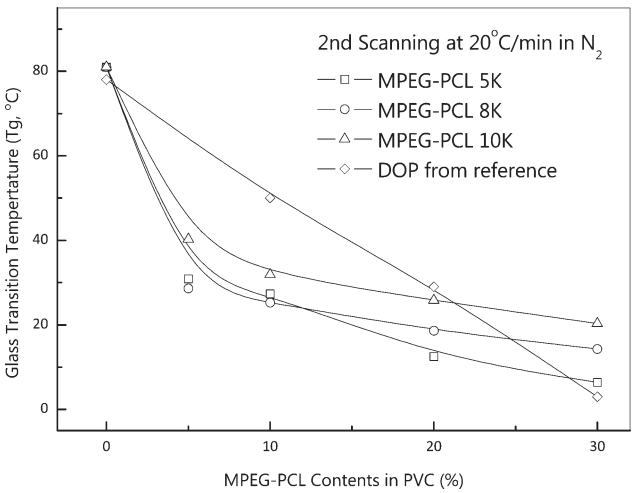

Figure 6 T_g shift of MPEG-PCL/PVC blends following MPEG-PCL content.

stress curve and exhibit highest yield strength, tensile strength and Young's modulus but low yield strain and tensile stain. After been plasticized with MPEG-PCL, under the lower additions, the blend samples still show the typical strain-stress curves as a plastic: the yield point is still existent but the yield strength, tensile strength and Young's modulus decreased while yield strain and tensile strain are increased. However, when the content of MPEG-PCL with lower molecule weight exceed 20% or reached 30% (for those with higher molecule weight), the yield point on strain-stress curves is disappeared, the whole curve looks like a typical strain-stress curve of a rubber or strictly as leather. At this condition, the tensile strain is as high as 7 times to bare PVC. Moreover, the MPEG-PCL copolymer with lower molecule weight, e.g. 5K, shows highest plasticizer efficiency. That is accordant to the regular pattern of those familiar plasticizers.

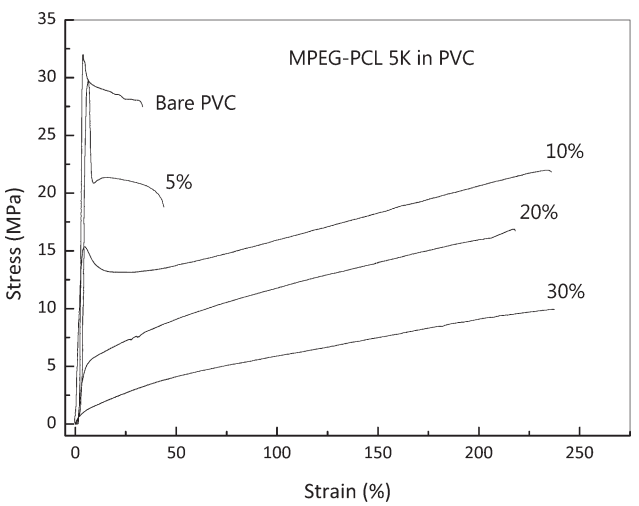

Figure 7 Typical strain-stress curves of MPEG-PCL 5K/PVC blends.

TABLE II
Mechanical Properties of MPEG-PCL/PVC Blends

Samples	Yield strength σ_y, MPa	Yield strain ε_y, %	Tensile strength σ_s, MPa	Tensile strain ε_s, %	Young's modulus E, MPa
Bare PVC	32 ± 2	3.8 ± 0.2	27 ± 1.4	33 ± 4	12 ± 0.6
5K5%	30 ± 1.5	6.3 ± 0.3	19 ± 1	44 ± 5	9 ± 0.5
5K10%	15 ± 1	4.6 ± 0.2	22 ± 1	235 ± 20	3.3 ± 0.17
5K20%	–	–	17 ± 0.8	218 ± 21	1.4 ± 0.2
5K30%	–	–	10 ± 0.5	237 ± 24	0.4 ± 0.1
8K5%	23 ± 1.1	3.8 ± 0.2	16 ± 0.8	47 ± 5	11 ± 0.5
8K10%	15 ± 1	11.8 ± 0.6	20 ± 1	224 ± 24	5 ± 0.2
8K20%	–	–	13 ± 0.6	196 ± 20	0.5 ± 0.1
8K30%	–	–	10 ± 0.5	212 ± 20	0.4 ± 0.08
10K10%	30 ± 1.5	3.7 ± 0.2	25 ± 1.3	196 ± 20	15 ± 1
10K20%	20 ± 1	5.9 ± 0.3	25 ± 1.3	223 ± 23	4.7 ± 0.3
10K30%	–	–	18 ± 0.8	248 ± 25	0.6 ± 0.1

Certainly the significant changes in mechanical properties will influence the applications of the blends: for those fields need the rigid PVC, these property changes will limit their applications whereas for those fields need the flexible PVC products, such as catheter, blood bag etc., the softening are appropriate.

Hydrophilic modification of PVC with MPEG-PCL diblock copolymers

When the MPEG-PCL diblock copolymers were introduced into the PVC matrix, the hydrophilic MPEG segments were tended to migrate to and enrich on the surface of PVC. Especially when the blends were immersed to anneal in the water, the migration was enhanced and led to the PVC's surface PEGylated. It looks like the surface was coated with a layer of PEG and the water soluble properties of PEG would decrease the surface water contact angle. However, the PCL segment in diblock copolymers is compatible with PVC, which makes the PCL segment act as an anchor to fix the PEG segment on the PVC surface and reduce the loss of PEG when contact with water. This effect could be expressed as the model shown in Figure 8 and a direct result according to this model is that the blends sample will become more hydrophilic and the surface water contact angle will decrease.

Figure 9 shows the test results of surface water contact angle of MPEG-PCL/PVC blends with bare PVC membrane as control. In the figure, the error bars denote the average result of 10 parallel determinations. From Figure 9, the water contact angle decreased in generally with the increasing of MPEG-PCL concentration. For MPEG-PCL 5K and 8K, the decreasing is almost linear. For the sample 5K 30% content, the water contact angle decreased to 57°C. But for MPEG-PCL 10K, the deceasing trend shows a little abnormality, which can probably be attributed to the influence of higher molecule weight. In our system, the higher the molecule weight of MPEG-PCL, the higher the PCL/PEG segment ratio and the lower the PEG content in diblock copolymers were presented. For the MPEG-PCL with higher molecule weight, the migration of PEG segment is more difficult because of the augmentation

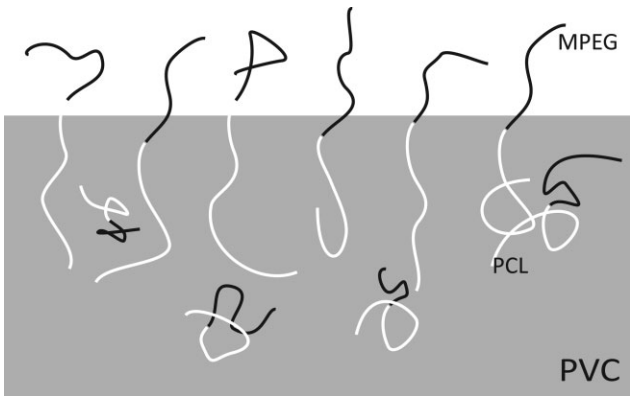

Figure 8 The model of surface modified PVC with MPEG-PCL.

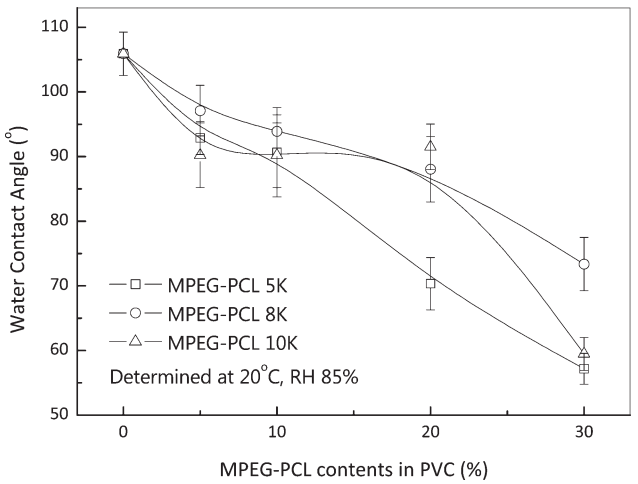

Figure 9 The water contact angle transformations of blend samples.

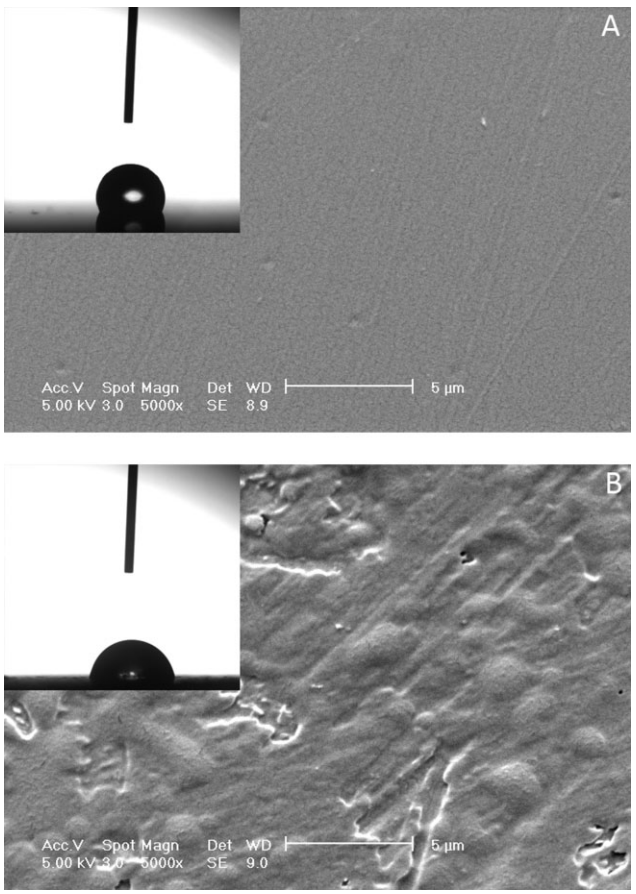

Figure 10 SEM photographs of (A) the Bare PVC and (B) the 5K 20% sample surface with inserts of a 5 μL water drop dripped on the surfaces, respectively.

of the molecule size and the weakening of the microphase separation of the PCL/PEG segments in diblock copolymers, as shown in the DSC determination [Fig. 4(B)].

Figure 10 shows the SEM photographs of bare PVC and the 5K 20% blend sample with magnification 5000 times while the inserts show the actual photograph of a 5 μL water drop dripped on the bare PVC surface [Fig. 10(A)] and on the 5K 20% blend sample surface [Fig. 10(B)] respectively. The SEM photographs approved the expectation in Figure 8: when 20% MPEG-PCL diblock copolymer was incorporated into PVC, the surface of PVC was coated with PEG segments and the original smooth surface become undulant for the swelling of PEG segments.

Anticoagulation properties of MPEG-PCL/PVC blends

The introduction of MPEG-PCL into PVC matrix result in the plasticization effect, and the hydrophilic modification was also be observed. The surface hydrophilication of MPEG-PCL/PVC blends promoted the possible application in biomedical devices. Thus, we determined the plasma recalcification time (PRT) to study the compatibility of MPEG-PCL/PVC blend. Figure 11 shows the result of the copolymer sample with molecule weight of 5K and 8K with blank, silicon oil and bare PVC as control. While Table III shows the PRT ratios of tube coated with blends to blank tube, to tubes coated with silicon oil and bare PVC.

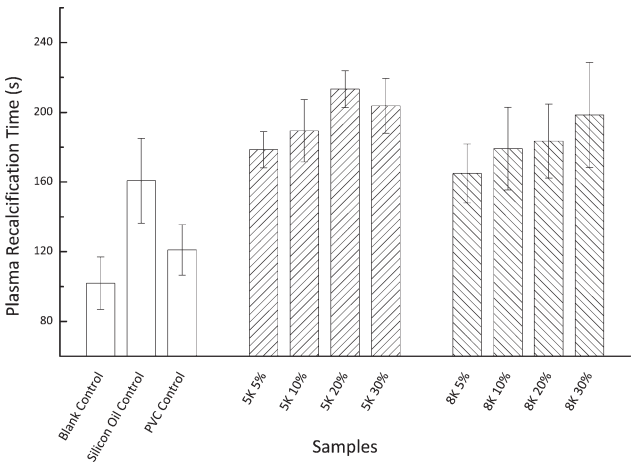

Figure 11 Plasma recalcification time of MPEG-PCL 5K and 8K/PVC blends.

The results show that the PRT of black tube, of the tube coated with silicon oil and coated with bare PVC is 102, 161 and 121 s, respectively. By applying Student's *t*-test, it was found that all the MPEG-PCL/PVC blend samples shows significantly different to blank and the anticoagulation character is obviously. The best one in MPEG-PCL 5K group is the 5K 20%, while in 8K group the best one is 8K 30%. Relative to silicon oil, Student's *t*-test indicated that only the sample 5K 20% shows significantly different and whose anticoagulation is better than that of silicon oil, while the others are correspond to silicon oil. To inspect the effect of MPEG-PCL diblock copolymer, the bare PVC was also adopted as control. The Student's *t*-test presents the result that every sample containing MPEG-PCL copolymer has

TABLE III
PRT Ratios of Tube Coated with PVC Blends to the Blank Tube, to the Tube Coated with Silicon Oil and Bare PVC

Samples	Blend/blank	Blend/silicon oil	Blend/bare PVC
5K5%	1.75	1.11	1.48
5K10%	1.86	1.18	1.57
5K20%	2.09	1.33	1.76
5K30%	2.00	1.27	1.68
8K5%	1.62	1.03	1.36
8K10%	1.76	1.11	1.48
8K20%	1.80	1.14	1.52
8K30%	1.95	1.24	1.64

significantly different to bare PVC: it was that the MPEG-PCL copolymer offers PVC the anticoagulation properties. In general, the more MPEG-PCL introduced, the higher anticoagulation were observed. This property prompts that the modified PVC by MPEG-PCL diblock copolymer is probably potentially applied in biomedical area, such as the blood bag, endocardiac vessel, and other occasions directly contact with blood.

CONCLUSIONS

By ring-opening polymerization of CL with MPEG as macroinitiator, the MPEG-PCL diblock copolymers with series molecule weight were synthesized successfully. Utilizing solvent blend method, series composites of MPEG-PCL/PVC were prepared and found that MPEG-PCL offered PVC the plasticization effects: the diblock copolymer is probably be used as a polymeric plasticizer to manufacture the flexible PVC products. At the same time, MPEG-PCL also provided PVC the hydrophilic and anticoagulation properties which exploit the potential application in biomedical areas.

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