Synthesis and Characterization of Gelatin-Polydimethylsiloxane Graft Copolymers

Meng Zhang,[1,2] Yuanjuan Wu,[3] Qingsi Zhang,[2] Yongmei Xia,[1] Tianduo Li[1,2]

[1]*School of Chemical and Materials Engineering, Jiangnan University, Wuxi 214122, People's Republic of China*
[2]*Shandong Provincial Key Laboratory of Fine Chemicals, Shandong Institute of Light Industry, Jinan 250353, People's Republic of China*
[3]*Central Laboratory, Shandong Academy of Agriculture Science, Jinan 250100, People's Republic of China*

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ABSTRACT: Gelatin-polydimethylsiloxane (PDMS) graft copolymers were prepared through the reaction between gelatin and α-[3-(2,3-epoxypropoxy)propyl]-ω-butyl-PDMSs. The copolymers were characterized by FTIR and ^{1}H-NMR spectra. As proved by wide angle X-ray analysis, a new characteristic crystalline peak appeared after the bonding of PDMS to gelatin chains. The microstructure and the elemental identification of gelatin and copolymers were followed through scanning electron microscope with energy dispersive spectrometer. The glass transition temperature of gelatin and copolymers were obtained by differential scanning calorimetry analysis. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2130–2137, 2011

Key words: gelatin; polydimethylsiloxane; graft copolymer; X-ray diffraction; glass transition temperature

INTRODUCTION

In respect of increasing global warming and pollution issues, much attention has been focused on the use of natural polymers. Among natural resources, proteins obtained from either animal or vegetable sources have been intensively studied because of their unique properties. For example, the use of proteins in cosmetic formulations to provide performance and conditioning benefits to skin and hair is well known.

Protein has reactive functional groups that allow further chemical modification, i.e., α-amino groups at one chain end or ε-amino groups of the lysine residues at the side chain as well as carboxyl groups at the other chain end, respectively. Graft and cross-linking copolymerization are well known methods for the modification of protein and represent convenient and effective ways for improving the physical and mechanical properties for practical uses. Various reagents have been used to modify protein, such as epoxy compounds,[1–3] glutaraldehyde,[4–6] diisocyanate,[7–9] carbodiimide,[10–13] and so on.

In recent years, proteins modified by siloxanes have drawn commercial attention. One major advantage is the possibility of combining film formation and moisture retention properties of proteins with lubricity and spreadability of silicones. Polydimethylsiloxane containing epoxy groups (PDMS-E) is one kind of functional silicone polymers and special epoxy compounds. Due to the existence of epoxy group, PDMS-E could be used to modify protein. Amino acids modified by PDMS-E are obtained by the reaction of an alkali salt of an amino acid and PDMS-E.[14] These new copolymers show promising potential for cosmetic applications. However, the reaction is not limited to amino acids, it can be extended to proteins in general. In the current study, four gelatin-PDMS graft copolymers were prepared by reacting monofunctional epoxy-terminated PDMS with gelatin.

EXPERIMENTAL

Materials

Gelatin, C.P. grade, was purchased from Sinopharm chemical reagent Co. Ltd. and was purified by freeze-drying to remove trace water before its use. Benzene (Shanghai General Factory of Chemicals) and tetrahydrofuran (THF, Tianjin Dahua Chemicals) were A.R. and were refluxed over potassium-sodium alloy. Dimethylchlorosilane (DMCS, Datian Chemical Auxiliaries Research Institute), allylglycidyl ether (AGE, Yudeheng Inc.), and hexamethylcyclotrisiloxane (D_3, ABCR, Karlsruhe, FRG) were used as received without further treatment. *n*-Butyllithium (Shanghai Shanglunhuayu Chemical Co. Ltd.) was used after titration.

Correspondence to: M. Zhang (wfzhangmeng@163.com), T. D. Li (litianduo@163.com).

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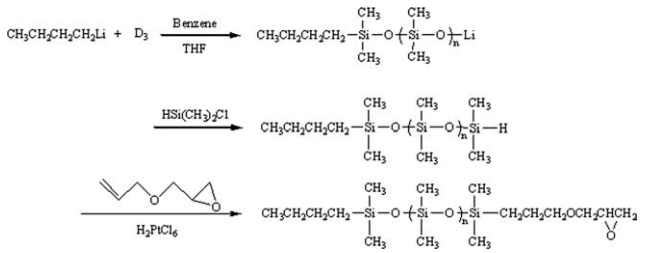


Scheme 1 Synthesis of PDMS-H and PDMS-E.

Characterization

Fourier transformed infrared spectra (FTIR) were obtained on a Nicolet 470 FTIR Spectrometer in dry air, at room temperature, on KBr pellets, in the range of 4000–400 cm^{-1}. ^{1}H-NMR spectra were recorded at 27°C on Bruker AVANCE 400 with $CDCl_3$ or D_2O as solvent and tetramethylsilane (TMS, $\delta = 0$ ppm) as internal standard. X-ray diffraction patterns were recorded on a Rigaku K max-r Ax diffractometer with scanning scope of 5°–40° and scanning speed of 4°/min using Cu Kα radiation. Gel permeation chromatography (GPC) was performed with Waters 1525 Binary HPLC Pump using Waters 2414 Refractive Index Detector, Styragel HT 2, 3, 4 as columns, THF as eluant, and polystyrene as the polymer standard. SEM analysis and elemental identification were provided on a FEI Quanta 200 Scanning Electron Microscope (SEM) equipped with energy dispersive. X-ray analysis system Sutw Sapphire detector under following experimental condition: accelerate voltage 20.00 kV, tilt angle 0.00°, take-off angle 45.00°, AmpT 100.0, resolution 128.90. Differential scanning calorimetry measurements are carried out using a Perkin–Elmer PYRIS Diamond DSC instrument. The samples (2.3 mg), sealed under aluminum pans are scanned in the temperature range of 0°–100°C. The heating rate is 10°C/min under the nitrogen atmosphere with a flow rate of 40 mL/min. The Si—H amount in PDMS with Si—H group at one end and epoxy group content in α-[3-(2,3-epoxypropoxy)propyl]-ω-butyl-PDMS was estimated by chemical titration, of which the details are available elsewhere.[15,16] The primary amino group content of gelatin was determined by Van Slyke amino nitrogen method.[17]

Synthesis of polydimethylsiloxanes with Si—H group at one end (PDMS-H)

According to reported procedures,[18,19] PDMS-H was prepared by the anionic ring-opening polymerization of D_3 using *n*-butyllithium as initiator and DMCS as terminating agent in a mixed solvent of benzene and THF. Four parallel equilibrium reactions were conducted with varying the ratio of D_3/initiator to achieve PDMS-H with different segment length consisting of dimethylsiloxane units.

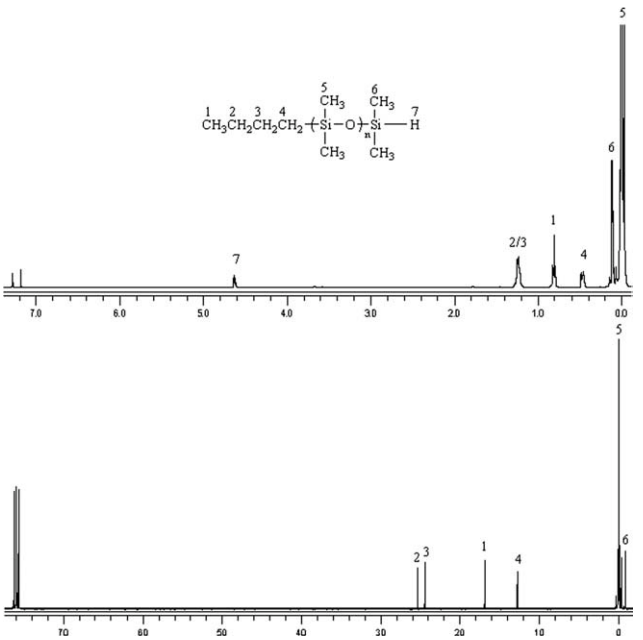


Figure 1 ^{1}H-NMR and ^{13}C-NMR spectra of PDMS-H.

Synthesis of α-[3-(2,3-epoxypropoxy)propyl] -ω-butyl-polydimethylsiloxanes (PDMS-E)

PDMS-E were synthesized by the hydrosilylation of AGE with PDMS-H in toluene, in the presence of

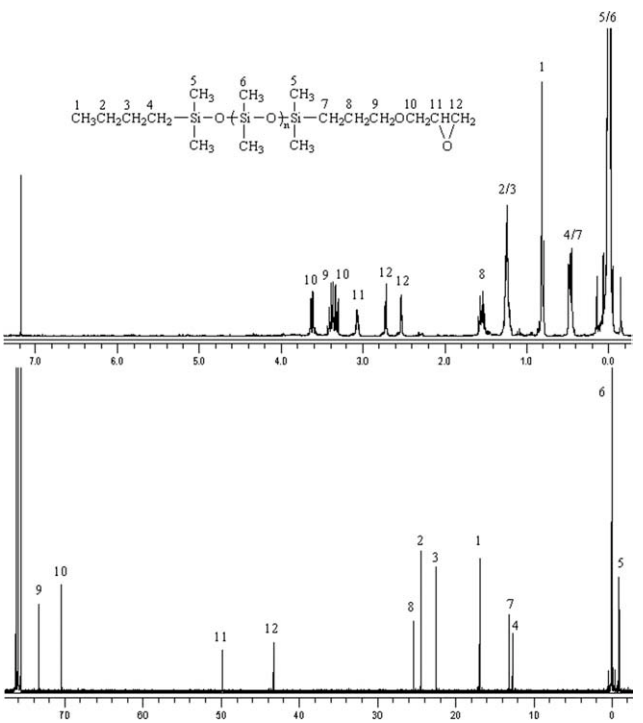


Figure 2 ^{1}H-NMR and ^{13}C-NMR spectra of PDMS-E.

TABLE I
Chemical Shifts δ of ^{1}H NMR and ^{13}C NMR of PDMS-H

Lable	1	2	3	4	5	6	7
δ (^{13}C ppm)	16.923	25.320	24.413	12.754	0.000	−0.864	
δ (^{1}H ppm)	0.80	1.24		0.46	0.00	0.11	4.62
Number of H	3	4		2	116	6	1
Peak split	t	m		t	s	s	s

TABLE II
Chemical Shifts δ of ^{1}H NMR and ^{13}C NMR of PDMS-E

Lable	1	2	3	4	7	5	6	8	9	10	11	12
δ (^{13}C ppm)	16.946	24.435	22.448	12.772	13.134	−0.842	0.000	25.337	73.345	70.415	49.858	43.352
δ (^{1}H ppm)	0.81	1.23		0.46		0.00		1.54	3.38	3.31/3.60	3.07	2.53/2.70
Number of H	3	4		4		122		2	2	2	1	2
Peak split	t	m		m		s		m	m	m	m	m

TABLE III
Molecular Weight of PDMS-H

Sample	M_n by theory	M_n by Si—H	M_n by ^{1}H NMR	M_n by GPC	PDI
PDMS-H_1	1000	1017	1004	1573	1.15
PDMS-H_2	1500	1460	1522	2003	1.17
PDMS-H_3	2000	1979	2137	2488	1.16
PDMS-H_4	2500	2436	2558	2955	1.17

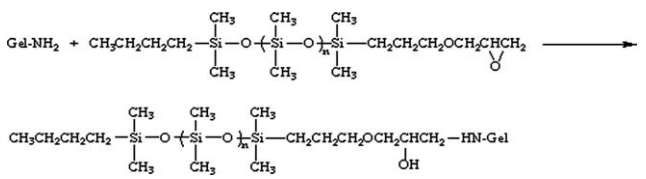
TABLE IV
Molecular Weight of PDMS-E

Sample	M_n by theory	M_n by epoxy	M_n by ^{1}H NMR	M_n by GPC	PDI
PDMS-E_1	1114	1246	1172	1762	1.16
PDMS-E_2	1614	1653	1585	2159	1.18
PDMS-E_3	2114	2097	2208	2678	1.19
PDMS-E_4	2614	2717	2726	3142	1.19

hexachloroplatinic acid 2% by weight solution in isopropanol in dry nitrogen, according to a procedure previously described.[20,21] The reaction mixture was heated to 110°C and kept at this temperature for 6 h. Toluene and excessive AGE were removed under vacuum.

Synthesis of gelatin–polydimethylsiloxane graft copolymers (Gel-PDMS)

Gel-PDMS copolymers were obtained by the addition reaction between primary amino groups of



Scheme 2 Synthesis of Gel-PDMS copolymers.

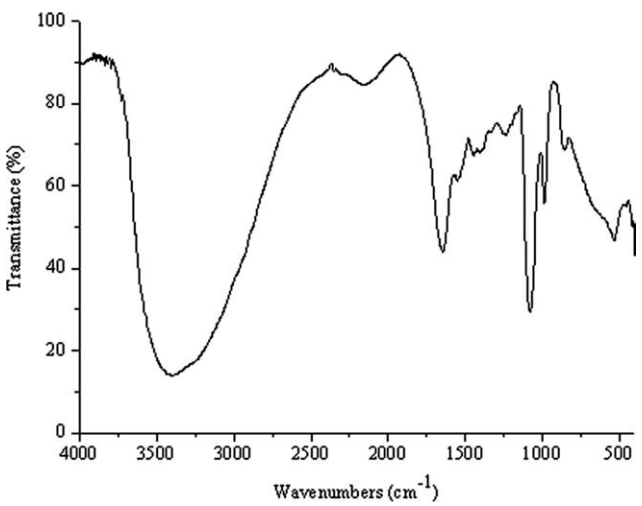


Figure 3 FTIR spectra of gelatin.

gelatin and epoxy groups of PDMS-E (epoxy/primary amino groups = 1.6*M* ratio). The method is outlined as following: about 2.000 g gelatin was dissolved in 25 mL water, and the pH value of the aqueous solution was adjusted to 10.5 by using 10% sodium carbonate aqueous solution. When the solution was heated to 50°C, PDMS-E in 10 mL THF was added dropwise. The reaction mixture was stirred for 24 h at 50°C. After removing THF under reduced pressure, the crude modified gelatin was obtained by freeze-drying from aqueous solution. Finally, the crude modified gelatin was put into Soxhlet extractor by using chloroform as extraction solvent and was extracted for 48 h to remove any unreacted PDMS-E.

Preparation of latex films of gelatin and Gel-PDMS copolymers

Gelatin and Gel-PDMS copolymers were dissolved in water and then were poured into a Teflon plate. Latex films were cast from a Teflon plate at room temperature.

RESULTS AND DISCUSSION

Synthesis and characterization of PDMS-H and PDMS-E

PDMS-H and PDMS-E, with different segment length consisting of dimethylsiloxane units, were obtained by anionic ring-opening polymerization and hydrosilylation reaction (Scheme 1), respectively. Infrared spectra of PDMS-H and PDMS-E are not given here because they are reported in our previous paper.[22] PDMS-H and PDMS-E were then subjected to ^{1}H and ^{13}C-NMR analysis, the corresponding spectra are shown in Figures 1 and 2. Corresponding peak assignments and characteristics

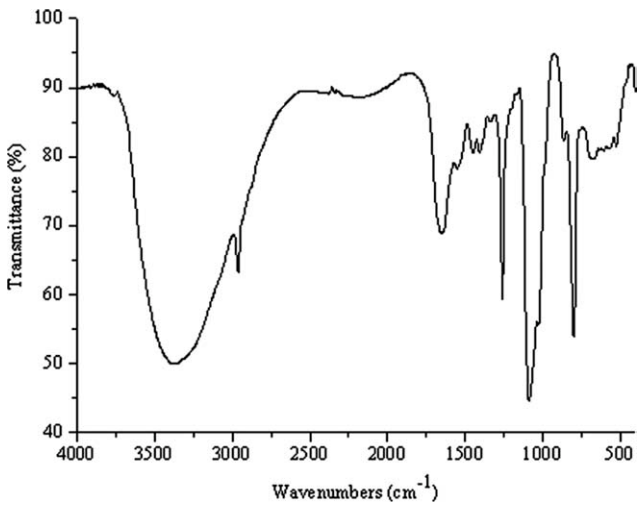


Figure 4 FTIR spectra of Gel-PDMS copolymers.

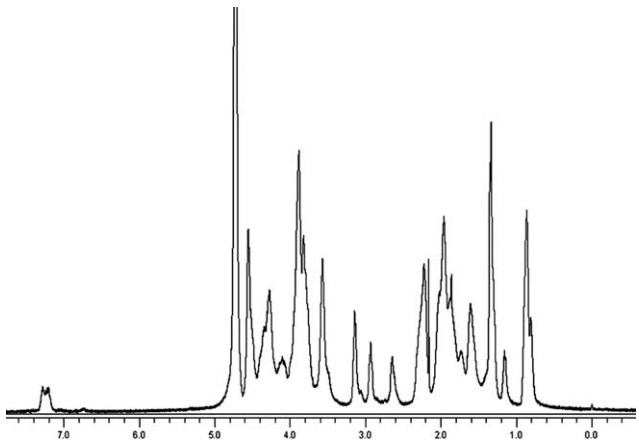


Figure 5 ^{1}H-NMR spectra of gelatin.

for ^{1}H-NMR are given in Tables I and II, which include also the data from their ^{13}C-NMR. From the chemical shifts, the peak area integrations and peak splits, all peaks were easily assigned. Based on the proton peak integration, the molecular weight of PDMS-H (Table III) and PDMS-E (Table IV) were estimated along with that obtained via GPC, functional group analysis (based on Si-H group or epoxy group), as well as the theoretical value. It is noteworthy that the theoretical molecular weight of PDMS-H and PDMS-E are in good agreement with the values measured from chemical titration or ^{1}H-NMR. However, the value from GPC is slightly larger than the theoretical value. This might be because of the fact that the polystyrene was used as the polymer standard in these test, which may lead to inaccurate result knowing that these two polymers were of very different natures.[20]

Synthesis and characterization of Gel-PDMS copolymers

Gel-PDMS copolymers were prepared according to Scheme 2 by reacting PDMS-E with gelatin. It is well

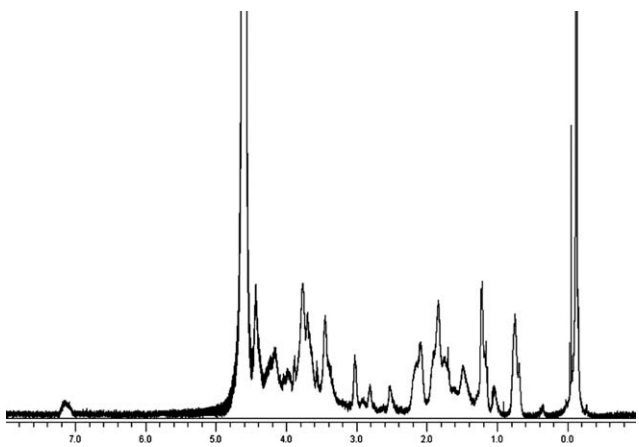


Figure 6 ^{1}H-NMR spectra of Gel-PDMS copolymers.

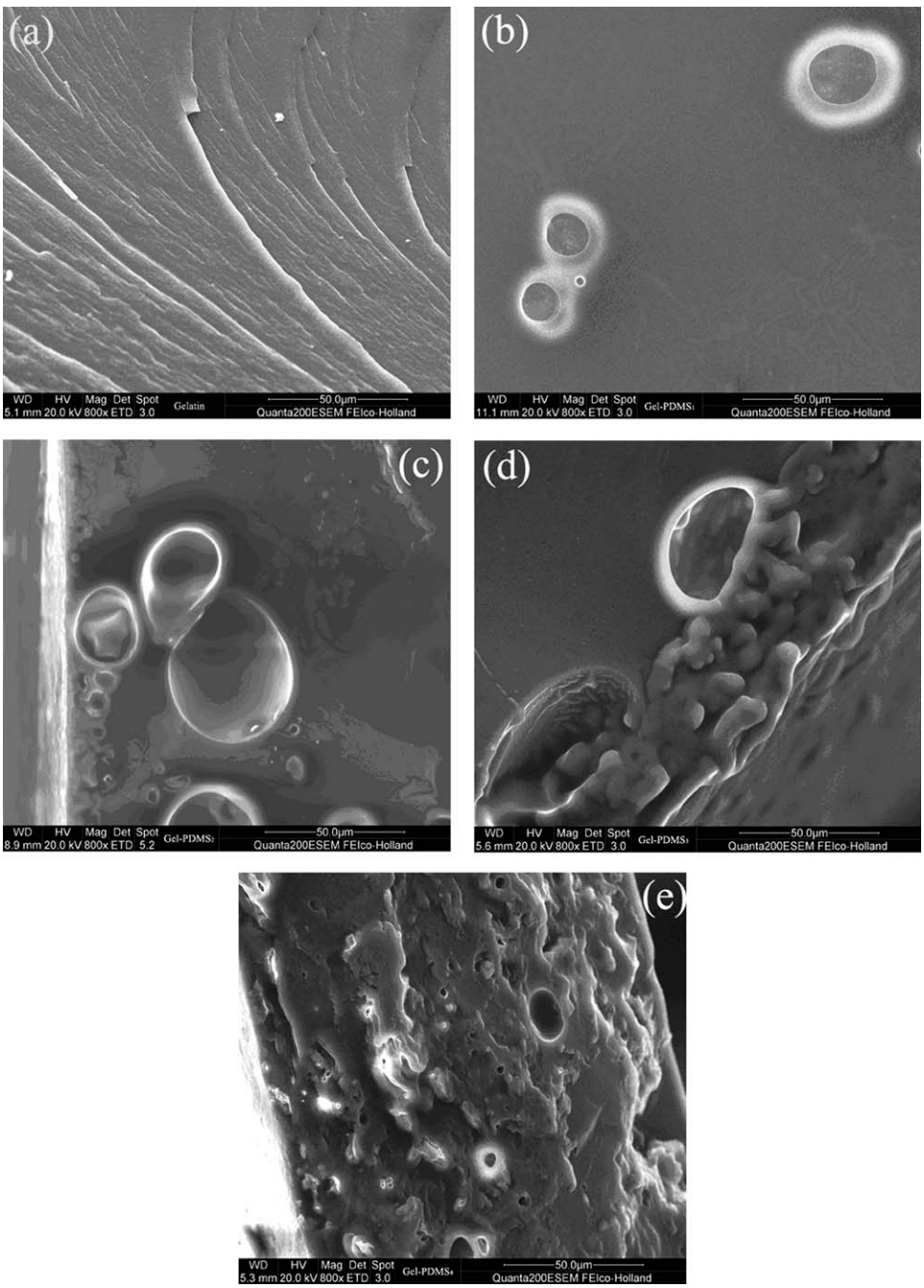


Figure 7 SEM pictures of gelatin and Gel-PDMS copolymers (a) gelatin, (b) Gel-PDMS$_1$, (c) Gel-PDMS$_2$, (d) Gel-PDMS$_3$, and (e) Gel-PDMS$_4$.

known that the primary amino groups quickly undergo nucleophilic substitution with epoxy rings. However, the reaction between amino groups of gelatin and epoxy rings linked to siloxane chains is quite difficult because the mentioned polymers have very different solubility parameters. In fact, the reaction takes place in a heterogeneous system, at the interface between gelatin aqueous solution and oil siloxane phase.

The structure of gelatin and Gel-PDMS copolymer were first studied by FTIR analysis (Figs. 3 and 4). The gelatin spectrum is characterized by a large band around 3450 cm^{-1} corresponding to NH stretching vibration, and bands between 1750 and 1500 cm^{-1} corresponding to amide vibrations. The amino and alkyl chains are identified in the band from 1200 to 1000 cm^{-1}. In Gel-PDMS spectra, attenuation of the characteristic bands of the biopolymer functional groups increases with segment length consisting of dimethylsiloxane units, whereas the typical bands of PDMS are clearly identified: vibration peak because of stretching of

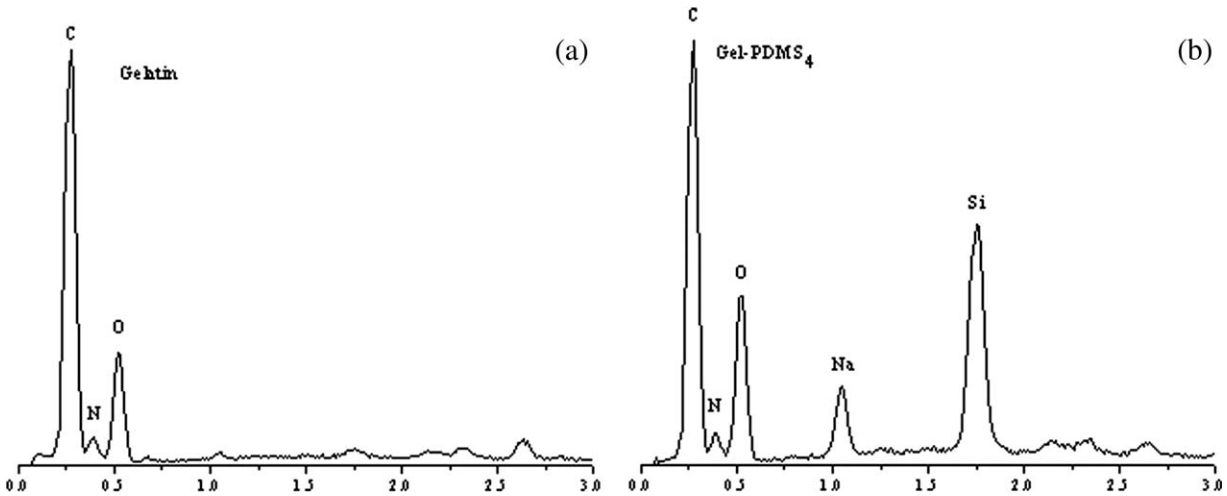


Figure 8 SEM-EDS spectra of gelatin and Gel-PDMS$_4$.

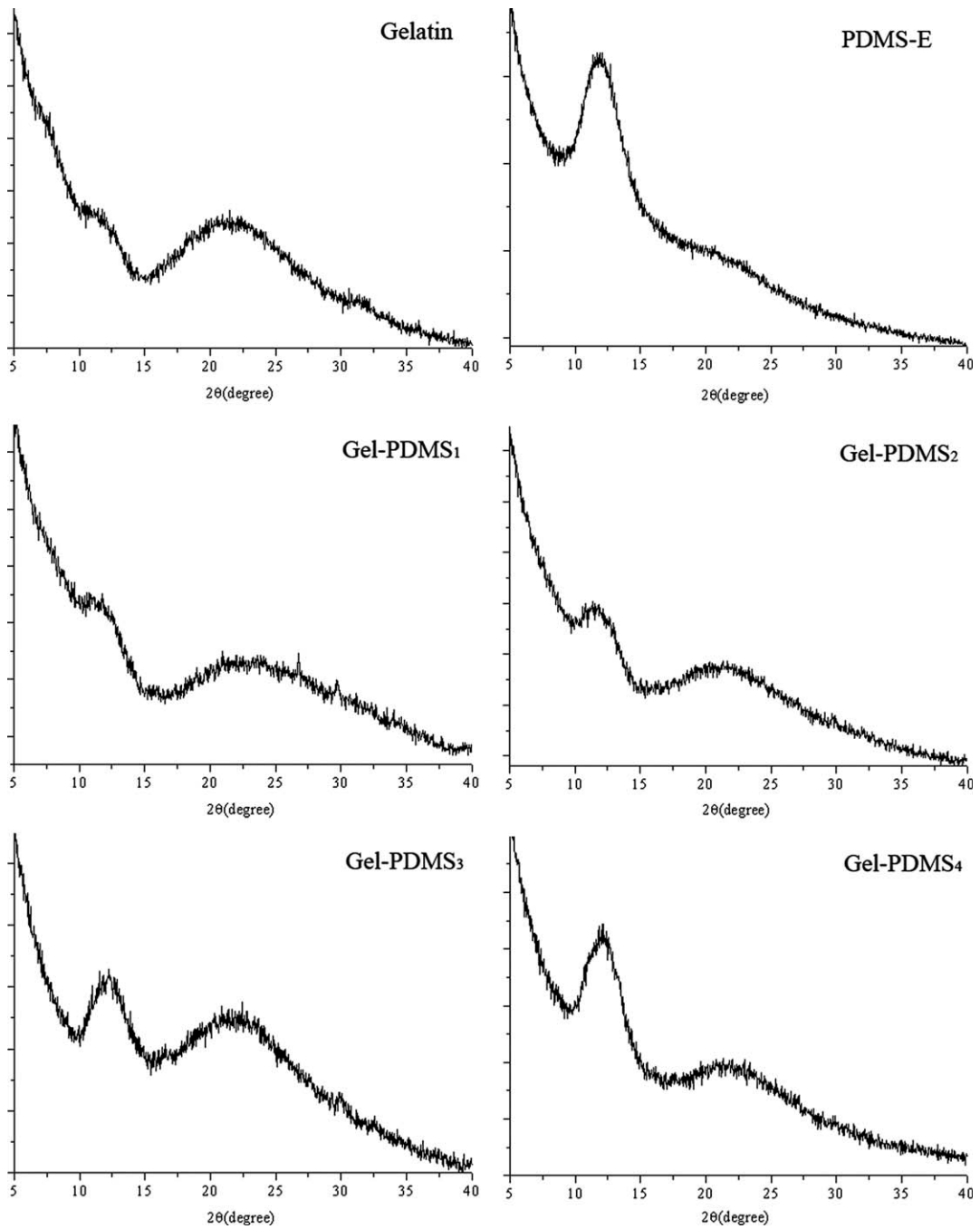


Figure 9 X-ray diffraction pattern of gelatin and Gel-PDMS copolymers.

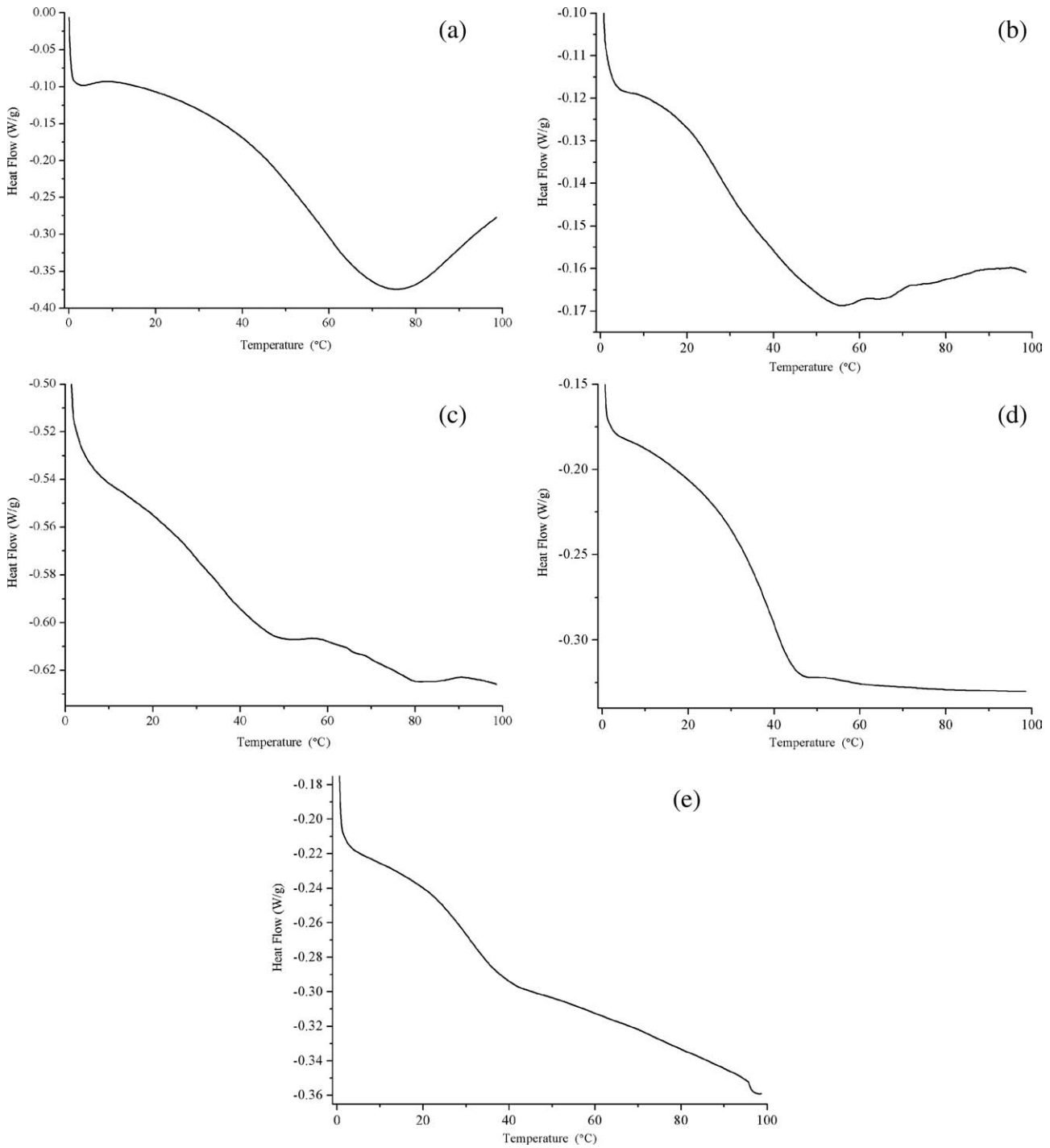


Figure 10 DSC curve of gelatin and Gel-PDMS copolymers (a) gelatin, (b) Gel-PDMS$_1$, (c) Gel-PDMS$_2$, (d) Gel-PDMS$_3$, (e) Gel-PDMS$_4$.

methylene and methyl situates at 2963 cm^{-1}, and two narrow bands corresponding to Si-CH_3, characteristic bands appear at 1261 cm^{-1} and 802 cm^{-1}. The FTIR analysis indicates that PDMS-E is linked to gelatin.

Comparison of ^{1}H-NMR spectra of gelatin (Fig. 5) and Gel-PDMS copolymer (Fig. 6) also confirms this result: the peak assigned to the Si-CH_3 proton is observed at $\delta = -0.12$ ppm in Figure 6 after PDMS-E linking to gelatin.

SEM-EDS analysis of Gel-PDMS copolymers

Latex films of gelatin and Gel-PDMS copolymers were processed by liquid nitrogen, and the morphology of the profiles were observed by SEM (Fig. 7).

SEM pictures show that the profile of gelatin exhibits a smooth surface. On the contrary, on the profile of Gel-PDMS copolymers appear a few irregular holes. It might be because of the reason that the phase separation generated at the interface between gelatin phase and PDMS phase during the formation of Gel-PDMS copolymer films. As we know, PDMS possess good water resistance and there are big different solubility parameters between gelatin and PDMS in water.

The elemental identification of latex films were measured by EDS analysis (Fig. 8). The EDS spectra indicate the presence of C, N, O, and Si atoms after PDMS-E linking to gelatin, and this result is in agreement with those obtained by FTIR and ^{1}H-NMR analysis.

X-ray analysis of Gel-PDMS copolymers

X-Ray diffraction pattern of PDMS-E, gelatin, and Gel-PDMS copolymers are shown in Figure 9. The XRD pattern of gelatin exhibits its characteristic crystalline peak at $2\theta = 22^\circ$, but Gel-PDMS copolymers present different X-ray patterns as compared to gelatin. Two diffraction peaks were observed after the bonding of PDMS to gelatin chains. One was at $2\theta = 22^\circ$, indicating the modification of the interplanar distances for the phases similar to gelatin. The other was at $2\theta = 12.5^\circ$ and similar to the characteristic crystalline peak of PDMS-E, indicating the formation of a new crystalline phase.

DSC analysis of Gel-PDMS copolymers

The glass transition temperature (T_g) of gelatin and Gel-PDMS copolymers were obtained by differential scanning calorimetry analysis. As seen from Figure 10, the T_g of Gel-PDMS copolymers decreases after PDMS bonding to gelatin. The T_g of gelatin, Gel-PDMS$_1$, Gel-PDMS$_2$, Gel-PDMS$_3$, and Gel-PDMS$_4$ are 75, 56, 52, 49, and 43°C, respectively. It is well known that the T_g of PDMS is around −120°C, when gelatin was bonded with different segment length consisting of DMS units, the T_g changes of Gel-PDMS copolymers are evident from 20 to 32°C compared with that of gelatin. However, the T_g change among Gel-PDMS copolymers are not evident. The reason might be the molecular weight of PDMS-E adjacent to each other is a little different.

CONCLUSIONS

Gel-PDMS copolymers were successfully obtained by the ring opening reaction of epoxy group linked to siloxane chain with primary amino groups of gelatin. Because of the large difference between solubility parameters of gelatin and PDMS, the reaction occurred in heterogeneous conditions. The FTIR, ^{1}H-NMR, and EDS analysis indicated that PDMS-E was linked to gelatin successfully. The Gel-PDMS copolymers presented a new crystalline peak at $2\theta = 12.5^\circ$ as compared to gelatin. When PDMS was bonded to gelatin chain, the glass transition temperature of the copolymers decreased evidently.

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