

Hydrogels of poly(ethylene glycol)-*co*-poly(lactones) diacrylate macromers and β -chitin

Young Moo Lee* and Seong Soo Kim

Department of Industrial Chemistry, College of Engineering, Hanyang University,
 Seoul 133-791, South Korea

(Received 5 February 1996; revised 29 July 1996)

Poly(ester-ether-ester) triblock copolymers composed of poly(ethylene glycol) (PEG) and lactones, D,L-lactide or ϵ -caprolactone, were crosslinked with β -chitin to prepare semi-interpenetrating polymer network (IPN) hydrogels by the u.v. irradiation method. Triblock copolymers were synthesized by bulk polymerization using low toxic stannous octoate as catalyst, or without catalyst. Photocrosslinked hydrogels exhibited an equilibrium water content in the range of 60–77%. From differential scanning calorimetry (d.s.c.) analysis, all the hydrogels revealed a drastic decrease in crystallinity after photocrosslinking. In the swollen state, tensile strengths of the semi-IPN hydrogels ranked above 1 MPa. In addition, in spite of their relatively high mechanical strength, elongation at break of swollen hydrogels ranged between 30 and 70%. © 1997 Elsevier Science Ltd.

(Keywords: hydrogel; poly(lactones); mechanical strength)

INTRODUCTION

The synthesis and properties of poly(ester-ether-ester) block copolymers based on various lactones and poly(ethylene glycol) (PEG) or poly(propylene glycol) have been reported in recent years^{1–5}. These polymers are generally used for biomedical materials, such as controlled release of drugs, bioabsorbable surgical sutures and wound covering materials. Among these polymers, copolymers of L-lactide, D,L-lactide, ϵ -caprolactone and PEG have been noted by many workers. Such types of block copolymers have been obtained in bulk by a ring opening polymerization mechanism.

Cerrai *et al.*³ reported the biocompatibility of block copolymers of L-lactide and PEG. Moreover, they synthesized triblock copolymers in bulk without any added catalysts in order not to leave toxic residues such as organometallic catalysts in the final product. These polymers are hydroxy terminated and can be used to prepare acrylates as end groups that undergo very rapid photopolymerization. Also, because of ester linkages in the polymer main chain, hydrolytic degradation is much enhanced. Sawhney *et al.*⁶ synthesized and characterized macromers having a PEG central block with terminal acrylate groups. The resulting macromer was photopolymerized in aqueous solution to bioerodible hydrogels.

Hydrogels are cross-linked three-dimensional hydrophilic polymer networks which retain large quantities of water without dissolution. Although these hydrogels are similar to natural tissues, they are subject to a decrease in mechanical strength. Much attention has been paid to hydrogels with a view to improving their mechanical properties in the swollen state. Various modifications to

achieve this include the introduction of interpenetrating polymer network (IPN) structures and of hydrophobic moiety. IPNs are defined as a combination of two or more polymers in network form that are synthesized in juxtaposition. If only one polymer is crosslinked, this type of network formation is called a semi-IPN. Hydrogels can be prepared in many different ways, including IPN formation.

In recent years Vyavahare *et al.*⁷ manufactured photocrosslinked hydrogels based on copolymers of PEG and lysine and investigated their semi-IPN properties. Ramaraj *et al.*⁸ synthesized interpenetrating hydrogel networks based on gelatin and polyacrylamide and studied the swelling behaviour with drug release analysis. According to Huang *et al.*'s work⁹, the incorporation of hydrophobic polycaprolactone improved the mechanical properties of the swollen networks. Corkhill *et al.*^{10,11} prepared semi-IPN hydrogels of *N*-vinyl pyrrolidone and *N,N*-dimethyl acrylamide with cellulose acetate (CA) and cellulose acetate butyrate (CAB) to develop articular cartilage materials. They reported that the more hydrophobic nature of CAB in comparison with CA led to a slightly lower equilibrium water content.

More recently, we reported that semi-IPNs composed of β -chitin and PEG diacrylate macromer showed a much improved tensile strength at high equilibrium water content^{12,13}. The incorporation of β -chitin improved the mechanical properties of the swollen networks and preserved their biocompatibility. Because of its good biocompatibility and mechanical property, β -chitin has been widely used as a biomedical material for several years^{14,15}. In our previous studies, β -chitin revealed even higher versatility than the more common α -chitin^{16–18}.

It has been known that aliphatic polyester is degraded

* To whom correspondence should be addressed

by hydrolysis and β -chitin by the lysozyme enzyme in the human body. Therefore, a combination of biodegradable β -chitin with poly(ester-ether-ester) block copolymers will make it possible to use as a new class of biomedical materials. In continuation of our efforts to prepare novel hydrogels, this paper intends to report on the synthesis and characterization of semi-IPN hydrogels composed of β -chitin and PEG-co-poly(lactones) diacrylate macromers obtained by reacting PEG with D,L-lactide or ϵ -caprolactone. In the present work D,L-lactide and ϵ -caprolactone with PEG were selected to obtain a poly(ester-ether-ester) triblock copolymer. β -Chitin was introduced to improve the mechanical properties and biocompatibility of semi-IPN hydrogels.

EXPERIMENTAL

Materials

D,L-Lactide (Tokyo Kasei Organic Chemicals, Japan) was recrystallized from ethyl acetate (Junsei Chemical Co. Ltd). ϵ -Caprolactone (Tokyo Kasei, Japan) was purified by vacuum distillation over CaH_2 . PEG ($M_n = 6000$) was purchased from Showa Chemicals Inc. and PEG ($M_n = 10\,000$ and $20\,000$) was obtained from Yakuri Pure Chemicals Co. Ltd. All PEGs were purified by azeotropic distillation with benzene (Junsei Chemical Co. Ltd). Acryloyl chloride and photoinitiator, 2,2-dimethoxy-2-phenylacetophenone, were purchased from Aldrich Chemical Co. and used without further purification. 1,2-Dichloromethane and anhydrous ethyl ether were purchased from Duksan Pharmaceutical Co. Ltd and J.T. Baker Inc., respectively. β -Chitin was prepared according to the literature procedure¹⁵. The degree of deacetylation of β -chitin was determined as 0.2 by the infra-red spectroscopic method.

Viscosity-average molecular weight of β -chitin, calculated by the viscometric method, was approximately 3×10^5 . All other chemicals were extra-pure reagent grade and used as received.

Synthesis of PEG-co-poly(lactones) copolymers

Prewighed amounts of PEG and D,L-lactide (5 mol D,L-lactide per mol of PEG) were placed in a 100 ml round-bottomed flask to prepare PEG-co-poly(D,L-lactide) (PEGL). 0.1 mol% of stannous octoate was added to the flask under a nitrogen atmosphere. The flask was connected to a vacuum line and the reaction mixtures were heated to 70°C . After 2 h, the flask was sealed off under reduced pressure and copolymerization was carried out in a thermostat oven at 180°C for 6 h. Copolymers from PEG and ϵ -caprolactone (10 mol ϵ -caprolactone per mol of PEG) (PEGC) were synthesized without catalyst for 48 h by the same method as for PEGL copolymers. All the resulting copolymers were dissolved in dichloromethane and precipitated in anhydrous ethyl ether, then filtered and dried *in vacuo*.

Synthesis of PEG-co-poly(lactones) diacrylate macromers (PEGLM or PEGCM)

10 g of copolymer was dissolved in 100 ml of dichloromethane in a 500 ml round-bottomed flask and cooled to 0°C . Triethylamine (4.38×10^{-3} mol) as a proton acceptor and acryloyl chloride (8.75×10^{-3} mol, three and half times the quantity of PEG) were carefully added to the flask. The mixture was stirred at room temperature for 24 h and the by-product triethanolamine hydrochloride

Table 1 Sample preparation and designation

Polymer code ^a	Molecular weight of PEG	PEG-co-poly(lactones) macromer (wt%)	β -chitin (wt%)
L-6-1, C-6-1	6000	50	50
L-6-2, C-6-2	6000	33	67
L-6-3, C-6-3	6000	25	75
L-10-1, C-10-1	10 000	50	50
L-10-2, C-10-2	10 000	33	67
L-10-3, C-10-3	10 000	25	75
L-20-1, C-20-2	20 000	50	50
L-20-2, C-20-2	20 000	33	67
L-20-3, C-20-3	20 000	25	75

^aL and C designate copolymer of PEG and D,L-lactide or ϵ -caprolactone, respectively. Polymer concentration in formic acid is 2.4 wt%

was removed through a glass filter. The filtrate was precipitated in an excess of anhydrous ethyl ether, and PEG macromer was then obtained by drying the precipitant at 40°C under vacuum for a day.

Preparation of semi-IPNs

2.4% (w/v) formic acid solutions with different compositions (1/1, 1/2 and 1/3 w/w) of PEG-co-poly(lactones) diacrylate macromers and β -chitin were prepared. Sample preparation and designations are listed in Table 1.

Characterization

Fourier transform infra-red (FTi.r.) spectra of block copolymers, PEGLM or PEGCM, and semi-IPNs were recorded on a Nicolet Model Magna IR 550 spectrometer. Molecular weights and molecular weight distributions of block copolymers were measured by gel permeation chromatography (g.p.c.) analysis, using a Millipore-Waters 401 apparatus. 0.1% (wt/v) tetrahydrofuran solution was injected into a series of Waters styragel columns (Millipore Co.). Swelling behaviour was studied by the general gravimetric method. Dry films were immersed in distilled water and the swollen weight was measured for each sample at a given time. Equilibrium water content (EWC) was calculated according to the following expression:

$$\text{EWC}(\%) = \frac{W_s - W_d}{W_s} \times 100 \quad (1)$$

where W_s and W_d denote the weight of swollen and dry hydrogels, respectively.

Thermal properties of semi-IPN hydrogels were investigated using a Du Pont Instruments 910 d.s.c. The measurements were carried out at a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen flow of 50 ml min^{-1} . Mechanical properties of semi-IPN hydrogels were measured on a universal testing machine (Hounsfield 10 KM) with a 50 kg load cell. Samples were held between the rubber jaws of the tensometer and the tests were carried out using a crosshead speed of 2 mm min^{-1} . From the computer program tensile strength and elongation at break were calculated and the load-extension curve was plotted. Reported values are the mean of at least five specimens and the deviation from the mean is within $\pm 5\%$.

RESULTS

Block copolymerization and synthesis of semi-IPNs

In general, cyclic ester compounds can be polymerized

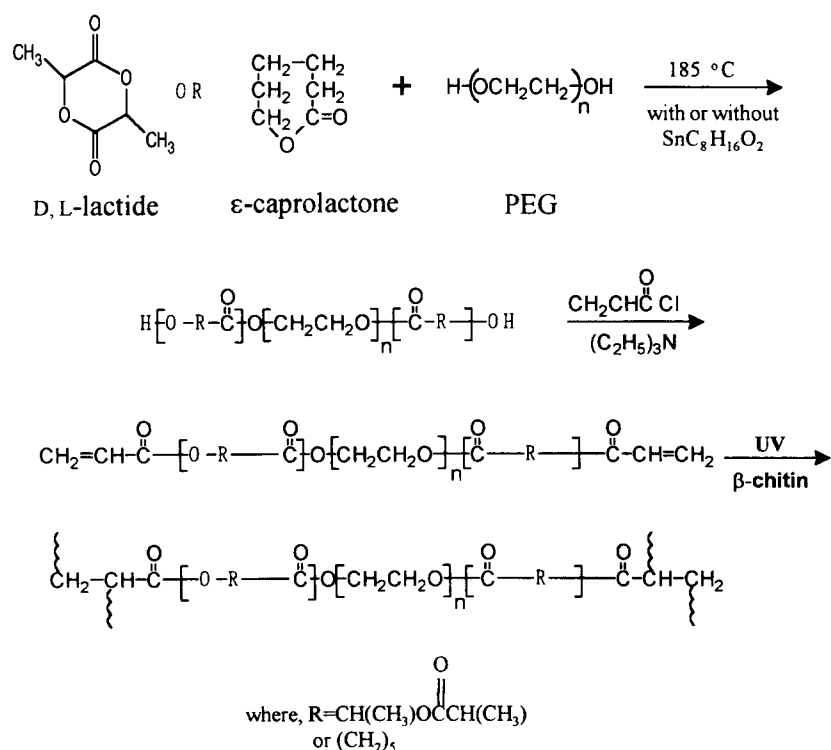


Figure 1 Synthetic scheme of PEGLM or PEGCM/ β -chitin semi-IPNs

by reacting with alcohol in the presence of an organometallic catalyst. As the majority of polylactones are used as biomedical material, such polymers should possess very low toxicity to ensure biocompatibility. Although many catalysts have been used in lactone polymerization, stannous octoate has been known to have much lower toxicity than most. Moreover, Cerrai *et al.*³ aimed to synthesize block copolymers of L-lactide or ϵ -caprolactone and PEG without catalysts so as not to leave residues of doubtful biocompatibility in the final product. In the present work D,L-lactide and ϵ -caprolactone with PEG were selected to obtain a poly(ester-ether-ester) triblock copolymer. β -Chitin was introduced to improve the mechanical properties and biocompatibility of semi-IPN hydrogels.

Figure 1 shows the synthetic route of semi-IPNs composed of PEGLM or PEGCM and β -chitin. Hydroxy-terminated triblock copolymers were prepared by reacting D,L-lactide and PEG in bulk, using stannous octoate as a ring-opening polymerization catalyst. Note that the PEGC block copolymer is obtained without catalyst by a simple ring-opening polymerization mechanism. As no transesterification catalyst is used, a longer reaction time (48 h) is required to polymerize ϵ -caprolactone initiated by PEG. Hydroxyl end groups are transformed into photocrosslinkable acrylate groups by reacting with acryloyl chloride. Finally, PEGLM or PEGCM and β -chitin are dissolved in formic acid and crosslinked with u.v. irradiation to prepare semi-IPNs.

Figure 2 shows the FTi.r. spectra of triblock copolymer (a), PEGCM (b) and semi-IPN (c). The FTi.r. spectrum of PEGLM is very similar to that of PEGCM and is not shown here. As shown in Figure 2a, a strong peak at 1735 cm^{-1} illustrates ester bond formation by the ring-opening reaction. A broad peak appears at around 3400 cm^{-1} and indicates that the block copolymers of lactone and PEG are $-\text{OH}$ terminated. The

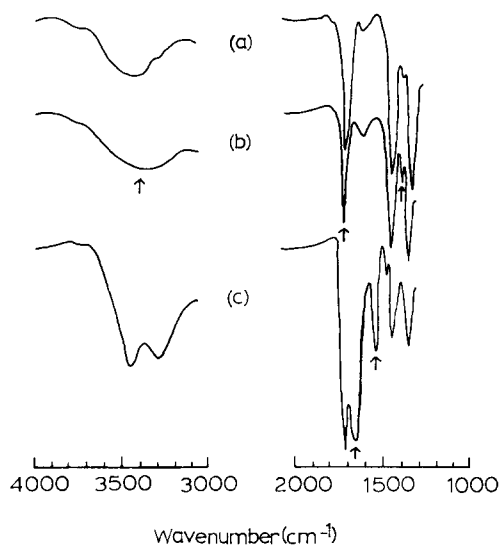


Figure 2 FTi.r. spectra of (a) PEGC, (b) PEGCM and (c) PEGCM/ β -chitin semi-IPNs

reaction between acryloyl chloride and hydroxyl groups in the block copolymers leads to a decrease of the $-\text{OH}$ stretching vibration peak appearing at around 3400 cm^{-1} . Furthermore, a new peak at 1409 cm^{-1} is thought to be due to the presence of conjugated carbon-carbon double bonds (Figure 2b). Three peaks at 1650 , 1560 and 1450 cm^{-1} in Figure 2c are assigned to the amide I, II and III bands of β -chitin in semi-IPNs. Since a photocrosslinking reaction was performed to prepare the semi-IPNs, the peak at 1409 cm^{-1} disappeared after u.v. irradiation.

G.p.c. analysis (not shown here) showed that lactone homopolymer and unreacted PEG were not present in all the copolymers obtained. The number average molecular

Table 2 Molecular weight of triblock copolymers estimated from g.p.c. diagram

Sample	M_n (calculated)	M_n (observed)	Polydispersity (M_w/M_n)
L-6	6.72×10^3	7.64×10^3	1.05
L-10	1.07×10^4	1.07×10^4	1.02
L-20	2.07×10^4	2.54×10^4	1.01
C-6	7.14×10^3	1.17×10^4	1.30
C-10	1.11×10^4	1.59×10^4	1.02
C-20	2.11×10^4	2.32×10^4	1.01

weight (M_n) of the block copolymers from g.p.c. diagrams nearly coincided with the theoretical values calculated from the feed composition. As listed in Table 2, M_n of samples ranges from 7000 to 23 000 g mol^{-1} , depending upon the sample. M_w/M_n ratios were in the range of 1.01 to 1.30, indicating that copolymers in this study were generally regarded as monodisperse polymers except for sample C-6.

Swelling behaviour and thermal properties

Equilibrium water contents (EWCs) of semi-IPN hydrogels are listed in Table 3. Photocrosslinked hydrogels swelled rapidly in water and reached an equilibrium within 20 min. These observations are almost in agreement with our previous studies of PEG/ β -chitin semi-IPNs^{12,13}. On the whole it has been known that hydrogels based on PEG tend to exhibit rapid swelling and high EWC^{6,7}. As shown in Table 3, all hydrogels have EWCs ranging from 60 to 77%. The EWC of semi-IPNs showed a tendency to increase with chain length of PEG and β -chitin content. As β -chitin content in the blends increases and crosslinkable end groups decrease in the macromer, the hydrogels seem

to possess a lower degree of crosslinking and higher EWC.

Recently, Corkhill *et al.*^{10,11} prepared semi-IPN hydrogels of *N*-vinyl pyrrolidone and *N,N*-dimethyl acrylamide with cellulose acetate (CA) and cellulose acetate butyrate (CAB) to develop articular cartilage materials. They reported that the more hydrophobic nature of CAB in comparison with CA led to a slightly lower EWC. Moreover, there is a clear difference in the freezing water content between IPNs because of steric hindrance. However, β -chitin in the semi-IPN hydrogels prepared in this study is hydrophilic in nature (ca. 48% EWC) and entangled with the crosslinked PEGM network. Therefore, water binding to the entangled β -chitin chain is effective in addition to interactions with water binding sites in the hydrophilic crosslinked PEGM network.

Table 3 also shows the free water and bound water contents in the hydrogels measured at equilibrium state. The results were evaluated from d.s.c. The free water melting thermograms appeared between 0 and 8°C. The endothermic peaks were used to determine the amount of free water in these hydrogels. The fraction of free water in total water was measured as the ratio of heat capacity of the observed endothermic area to that of distilled water. In addition, bound water is that which is hydrogen bonded to the PEG segments and is expressed as the difference between free water and EWC. The amount of free water in hydrogels is usually found to be more than half of the total water (EWC)¹³.

Melting temperatures, heat of fusion and crystallinities of PEG segments in PEG macromers and dry hydrogels are also listed in Table 3. While the PEG macromer before crosslinking showed a sharp melting transition at 56°C, the melting endothermic peak of hydrogels at

Table 3 Water contents, thermal properties and mechanical properties of semi-IPN hydrogels

Polymer code	EWC (%)	Free water (%)	Bound water (%)	T_m (°C)	ΔH_f (J g^{-1})	Crystallinity (%)	Tensile strength (MPa)		Initial modulus (MPa)	Elongation at break (%)	
							dry	wet		dry	wet
L-6-1	59	36	23	51	8	4	2.75	0.69	56.0	7.74	32.9
L-6-2	63	38	25	47	2	1	3.20	0.87	61.6	6.61	26.0
L-6-3	75	42	33	55	24	11	5.26	1.08	89.7	5.76	23.3
L-10-1	49	36	13	47	24	11	1.48	1.14	40.1	12.8	40.2
L-10-2	65	34	31	51	7	3	2.77	1.89	52.3	5.30	37.6
L-10-3	67	41	26	45	15	7	5.01	2.53	84.3	3.76	26.4
L-20-1	70	40	30	52	72	33	1.53	0.89	23.8	5.26	59.8
L-20-2	68	57	11	46	13	6	3.22	1.90	26.2	29.6	72.5
L-20-3	72	46	26	49	3	1	4.21	1.08	37.8	14.1	45.8
C-6-1	61	42	19	45	1	1	2.08	1.35	52.5	8.94	54.9
C-6-2	62	33	29	42	17	8	2.96	1.92	58.8	6.60	34.1
C-6-3	77	45	32	ND ^a	ND	ND	4.22	2.68	148.5	5.32	60.4
C-10-1	61	27	34	51	20	9	1.39	1.60	47.6	5.09	24.1
C-10-2	64	48	16	52	36	16	1.51	1.78	52.0	4.68	37.7
C-10-3	72	35	37	55	80	36	2.71	2.11	45.7	7.82	48.2
C-20-1	65	38	27	ND	ND	ND	2.18	0.95	16.1	3.68	30.0
C-20-2	70	43	27	49	74	34	3.01	0.95	32.0	6.12	32.0
C-20-3	74	40	34	51	23	11	3.20	1.28	32.2	5.61	35.4
PEGLM				56	154	70					
PEGCM				54	151	71					

^a ND = not detected

about 45–52°C became much broader after crosslinking. This demonstrates that the crosslinking reaction may prevent PEG segments from melting with a sharp transition. As might be expected, thermal transition of β -chitin was not detected at all¹⁸. Heat of fusion at T_m was calculated from the area of melting endothermic peaks and notably reduced during photocrosslinking. Crystallinities of PEG segments in semi-IPNs were estimated from the ratio of heat of fusion obtained from the d.s.c. analysis. Namely,

$$\text{crystallinity(\%)} = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \quad (2)$$

where ΔH_f^0 ($= 219.24 \text{ J g}^{-1}$)¹² and ΔH_f are the heat of fusion for 100% crystalline PEG and PEG segments in hydrogels, respectively. As listed in Table 3, all hydrogels revealed a drastic decrease in crystallinity even if the extent of diminishment was lower for some samples than for others. These observations are a typical phenomenon for many crosslinked polymers. While the photocrosslinking reaction was carried out in the solution, the reorientation of PEG segments during photocrosslinking was limited, resulting in a decrease of crystallinity. On the other hand, some samples may have photocrosslinked to a smaller extent.

Mechanical properties

Tensile strength of hydrogels is a very important factor in biomedical applications¹⁰. In particular, when the hydrogels are in contact with a tissue in the human body, they absorb a large quantity of water and suddenly lose their mechanical strength in the wet state. Many workers have attempted to improve the wet tensile strength. In the case of our present work, the incorporation of a semi-IPN structure containing β -chitin was expected to enhance the mechanical properties in the final product. Figure 3 shows the typical stress–strain curve of some samples.

Table 3 summarizes the tensile strengths of hydrogels in the dry and wet states. The tensile strength of semi-IPN hydrogels increases with β -chitin content. In general, crosslinking the polymer improves its mechanical

strength. Irrespective of decreasing crosslinking density, their mechanical strengths were still enhanced. The amount of β -chitin in blends plays a major role in improving the tensile strength compared with the effect of crosslinking. As can be seen in Table 3, wet tensile strengths of most hydrogels ranged above 1 MPa. Crosslinked polymers containing chitin do not usually show high elongation values because of the stiffness of the chitin chain, exhibiting a strong intramolecular hydrogen bonding. Initial moduli estimated from the stress–strain curve ranged between 16 and 148 MPa. In most of the semi-IPN hydrogels, it is interesting that their mechanical properties were not affected by changes in EWC. These results indicate that their mechanical properties are controlled by β -chitin as a reinforcing agent and not by changes in EWC. This coincides with Corkhill *et al.*'s work¹¹, which shows that the mechanical properties of semi-IPN hydrogels introducing cellulose acetate and cellulose acetate butyrate as well as vinyl copolymer hydrogels depend upon polymer structure and not upon changes in water content.

In addition, flexible PEG and amorphous poly(D,L-lactide) segments lower the rigidity of the β -chitin chain, resulting in small values of elongation at break in the dry state. As shown in Table 3, elongations at break in the wet state range between 30 and 70% along with relatively high tensile strength. Sample C-6-3 showed an elongation at break of 60.4% with a wet tensile strength of 2.68 MPa and an initial modulus in the dry state of ca. 149 MPa, and ranked as the hydrogel having the best mechanical properties among many samples. These values are higher than PEG/ β -chitin semi-IPN hydrogels¹³ (2.41 MPa).

CONCLUSIONS

Triblock copolymers from D,L-lactide or ϵ -caprolactone and PEG were synthesized with or without catalyst. Semi-IPN hydrogels based on their diacrylate macromers and β -chitin were prepared by the u.v. irradiation technique. FTi.r. confirmed the structure of triblock copolymers and semi-IPNs. Molecular weights observed

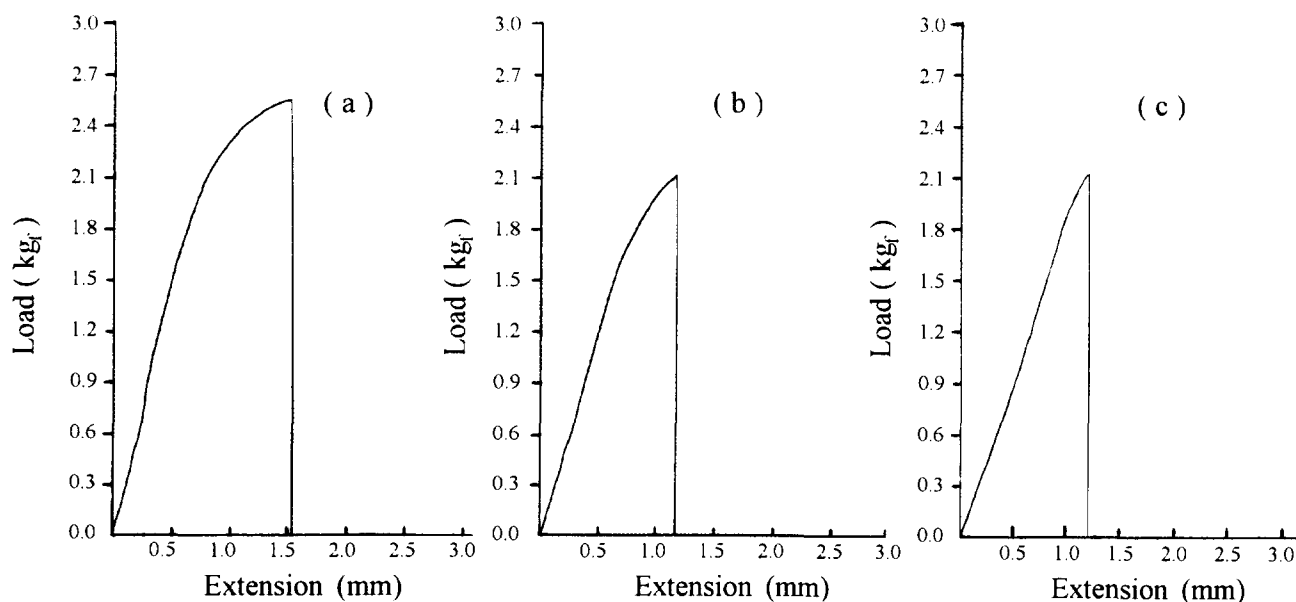


Figure 3 Typical load–extension curves of some semi-IPN hydrogels: (a) L-6-3; (b) L-10-3; (c) C-10-3

by g.p.c. analysis coincided with the theoretical values calculated from the feed composition. All hydrogels have EWCs ranging from 60 to 77%. With greater β -chitin content in blends and less degree of crosslinking, the hydrogels show higher EWC.

The amount of free water of hydrogels was usually found to be more than half of the total water. Melting endothermic peaks of hydrogels after photocrosslinking became much broader than before photocrosslinking. Upon crosslinking, crystallinities of PEG segments decreased remarkably, due to the restricted reorientation degree of PEG segments in semi-IPNs.

Tensile strength of the hydrogels in the swollen state ranked above 1 MPa and elongation at break between 30 and 70%. C-6-3 showed the best mechanical properties of elongation at break of 60.4%, with a tensile strength of 2.68 MPa in the wet state and an initial modulus in the dry state of ca. 149 MPa; this type is expected to be useful as a biomedical material^{7,11}.

ACKNOWLEDGEMENT

This work was supported from the 1996 Korean Ministry of Education Funds for Advanced Materials.

REFERENCES.

1. Zhang, X., Macdonald, D. A., Goosen, M. F. A. and Macauley, K.B., *J. Polym. Sci., Polym. Chem. Edn* 1994, **32**, 2965.
2. Cerrai, P., Guerra, G. D., Lelli, L., Tricoli, M., Guerra, R. S. D., Cascone, M. G. and Giusti, P., *J. Mater. Sci., Mater. Med.* 1994, **5**, 33.
3. Cerrai, P., Tricoli, M., Lelli, L., Guerra, G. D., Guerra, R. S. D., Cascone, M. G. and Giusti, P., *J. Mater. Sci., Mater. Med.* 1994, **5**, 308.
4. Zhu, K. J., Xiangzhou, L. and Shilin, Y., *J. Appl. Polym. Sci.* 1990, **39**, 1.
5. Kimura, Y., Matsuzaki, Y., Yamane, H. and Kitao, T., *Polymer* 1989, **30**, 1342.
6. Sawhney, A. S., Pathak, C. P. and Hubbell, J. A., *Macromolecules* 1993, **26**, 581.
7. Vyavahare, N. and Kohn, J., *J. Polym. Sci., Polym. Chem. Edn* 1994, **32**, 1271.
8. Ramaraj, B. and Radhakrishnan, G., *J. Appl. Polym. Sci.* 1994, **52**, 837.
9. Eschbach, F. O. and Huang, S. J., *Interpenetrating Polymer Networks*, Advances in Chemistry Series, 1994, p. 239.
10. Corkhill, P. H. and Tighe, B. J., *Polymer* 1990, **31**, 1526.
11. Corkhill, P. H., Fitton, J. H. and Tighe, B. J., *J. Biomater. Sci., Polym. Edn* 1993, **4**, 615.
12. Kim, S. S., Lee, Y. M. and Cho, C. S., *J. Polym. Sci., Polym. Chem. Edn* 1995, **33**, 2285.
13. Kim, S. S., Lee, Y. M. and Cho, C. S., *Polymer* 1995, **36**, 4497.
14. Kurita, K., Tomita, K., Tada, T., Ishii, S., Nishimura, S. and Shimoda, K., *J. Polym. Sci., Polym. Chem. Edn* 1991, **31**, 485.
15. Kurita, K., Ishii, S., Tomita, K., Nishimura, S. and Shimoda, K., *J. Polym. Sci., Polym. Chem. Edn* 1994, **32**, 1027.
16. Kim, S. S., Kim, S. J., Moon, Y. D. and Lee, Y. M., *Polymer* 1994, **35**, 3212.
17. Kim, S. J., Kim, S. S. and Lee, Y. M., *Macromol. Chem. Phys.* 1994, **195**, 1687.
18. Kim, S. S., Kim, S. H. and Lee, Y. M., *J. Polym. Sci., Polym. Phys. Edn* (accepted).
19. Horacek, I. and Kalisek, J., *J. Appl. Polym. Sci.* 1994, **54**, 1751.