

Fiber Formation from Semi-Interpenetrating Polymer Networks Consisting of Polycaprolactone and a Poly(ethylene glycol) Macromer

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ABSTRACT: Semi-interpenetrating polymer networks (SIPNs) consisting of polycaprolactone (PCL) and poly(ethyleneglycol) (PEG) macromer was prepared to improve tensile property in developing biodegradable sutures. When the PEG macromer formed SIPNs with PCL, biodegradability, mechanical strength, and hydrophilicity were improved. The SIPNs fibers formed from the dry spinning process showed an increase of not only tensile strength but also water content with an increase of PEG content. These results represent an increase of the crosslinking density of the PEG network with hydrophobic property. The drawing of SIPNs fibers also further enhanced the tensile strength and the crystallinity of the SIPNs fibers. Unimelting temperature of the SIPNs fiber was observed as an indication of the polymer network without phase separation. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 835–841, 2002; DOI 10.1002/app.10351

Key words: semi-interpenetrating polymer networks (SIPNs); polycaprolactone (PCL); poly(ethylene glycol) (PEG) macromer; biodegradable sutures

INTRODUCTION

Materials used for sutures are normally classified into biodegradable and nonbiodegradable categories. One major advantage of a biodegradable suture is the elimination of the necessity for surgical removal.^{1,2} The most thoroughly investigated and used biodegradable polymers are the poly(hydroxy esters) such as poly(lactic acid) (PLA), poly(glycolic acid) (PGA), and poly(LA-co-GA).³ However, the disadvantage of using biodegradable materials is that the suture has weak mechanical properties; that is, low tenacity and modulus. This disadvantage has been extensively

studied to overcome it. Messier et al.⁴ reported that sutures coated with polycaprolactone (PCL) provided good knot slip-down, a smooth surface, and three-throw knot security. Also, Bezwada et al.⁵ reported that the suture coated with a copolymer of ϵ -caprolactone and glycolide exhibited improved pliability and knotting characteristics while sustaining absorbancy and having good physical properties.

Another approach for enhancing the desirable characteristics of sutures is to produce composite sutures. The catgut/polymer composite sutures exhibited excellent surface properties, such as smoothness, knottability, and resistance to knot slippage.⁶ Shalaby et al.⁷ also reported that silk and thermoplastic elastomers with hydrophobicity improved strength retention, reduced tissue reaction, and lowered the amount of tissue grown

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when compared with the natural silk braided sutures.

Physical properties for the polymer blend system were improved by independently crosslinking a hydrophobic network within the cross-linked hydrophilic network.⁸ The mixture of two independently cross-linked polymers that cannot be physically separated is an interpenetrating polymer networks (IPN). If only one of the two polymers is crosslinked, the product is called a semi-interpenetrating polymer networks (SIPNs). It is usually prepared by polymerizing or crosslinking one component in the presence of the other.

In this study, we aim to prepare biodegradable suture based on SIPNs composed of PCL and the poly(ethylene glycol) (PEG) macromer.

PCL is one of the biodegradable nontoxic polyesters. But the PCL homopolymer itself is degraded very slowly because of its hydrophobic property. The biodegradability can be improved by copolymerization⁹ or by blending it with various hydrophilic polymers¹⁰ such as PEG and poloxamer. PEG, a widely used biomaterial, is water soluble, nontoxic and nonimmunogenic.¹¹

The PEG macromer having an acrylate-terminated PEG derivative has been chosen by many researchers as a synthetic polymer for network formation.^{12–16} The water-soluble PEG macromer was used as matrix for the incorporation of other polymers such as poly(hydroxyethyl methacrylate),¹³ β -chitin,¹⁴ PLA,¹⁵ and PCL,¹⁶ forming a crosslinked three-dimensional hydrogels.¹⁷

We prepared a PEG macromer terminated with acrylate groups, and then SIPNs were prepared from PCL and the PEG macromer. The PEG with the hydrophilic segment could be used for improving both the biodegradable property of PCL and its mechanical properties. In a previous study,¹⁸ the degradation rate of the PCL/PEG SIPNs increased with increasing PEG weight fraction. The solution of PCL and the PEG macromer in the presence of the initiator was dry-spun to obtain biodegradable sutures.

EXPERIMENTAL

Materials

PEGs with molecular weight (M_n) of 1000, 2000, and 8000 were obtained from Wako Chemical, Co. (Tokyo, Japan). PEG with molecular weight of 20,000 was purchased from Sigma Chemical Co. (St. Louis, MO). PCL (molecular weight M_n

= 40,000) acryloyl chloride and benzoyl peroxide were obtained from Aldrich Chemical Co. (Milwaukee, WI). All other chemicals used were of reagent grade and were used without further purification.

Acrylation of PEG

Purified PEGs (1.6 mM) with variable molecular weights (molecular weight M_n = 1000, 2000, 8000, and 20,000) were dissolved in 150 mL of benzene in a 500-mL round-bottomed flask. A total of 3.2 mM of triethylamine and 7.5 mM of acryloyl chloride were added into the flask, and the reaction mixture was stirred for 3 h at 80°C. The acrylated PEG macromer (AcPEG) was recovered from the reaction mixture by precipitating the filtrate into n-hexane after removing the triethylamine hydrochloride through filtration. The PEG macromer recovered was washed in n-hexane and then dried at 40°C under reduced pressure for 24 h.

Synthesis of PCL/PEG SIPNs

One weight % of benzoyl peroxide as an initiator was added into the PCL/AcPEG macromer (0, 5, 10, and 20 wt %) mixture dissolved in methylene chloride. The reaction mixture was stirred for 3 h at 80°C under nitrogen atmosphere in temperature-controllable oil bath.

Measurement of FTIR

IR spectra were measured using an FTIR spectrometer (Midac Co., Shelton, CT).

Measurement of Water Content

Water content was calculated from the weight differences of dry and wet samples swollen in distilled water. The free water on the surface of the sample was removed with filter paper. The weight of the swollen samples was measured with a time interval and determined as the weight at equilibrium state. The water contents were calculated as $(W_s - W_d)/W_s \times 100\%$, where W_s is the weight of the swollen sample and W_d is the weight of the dry sample.

Dry-Spinning of PCL/PEG SIPNs Fiber

The PCL/PEG SIPNs solution was dry-spun, taking advantage of the low boiling point (40°C) of methylene chloride, through a circular nozzle (Φ = 0.5 mm, L/D = 1, where L is length and D is

diameter) at room temperature and 3 kg/cm^2 by using pressurized nitrogen. The molecular weight of PEG used for fiber formation was 8000.

Tensile Properties of SIPNs Fibers

The tenacity and elongation of SIPNs fibers at break was measured by using a tensile tester (Rheometric Scientific, USA) with samples of 20 mm at an extension rate of 10 mm/min.

Thermal Property of SIPNs Fibers

The melting temperature (T_m) of the SIPNs fibers was measured by a differential scanning calorimeter (DSC 2910, TA Instruments Co., USA) under nitrogen atmosphere at heating rate of $10^\circ\text{C}/\text{min}$.

Scanning Electron Microscope

Fracture surface of the fibers coated with gold/palladium was observed by using a scanning electron microphotograph (SEM, Hitachi S-4700, Japan).

RESULTS AND DISCUSSION

The FTIR spectrum of the PEG showed an absorption band at 3447 cm^{-1} caused by the termi-

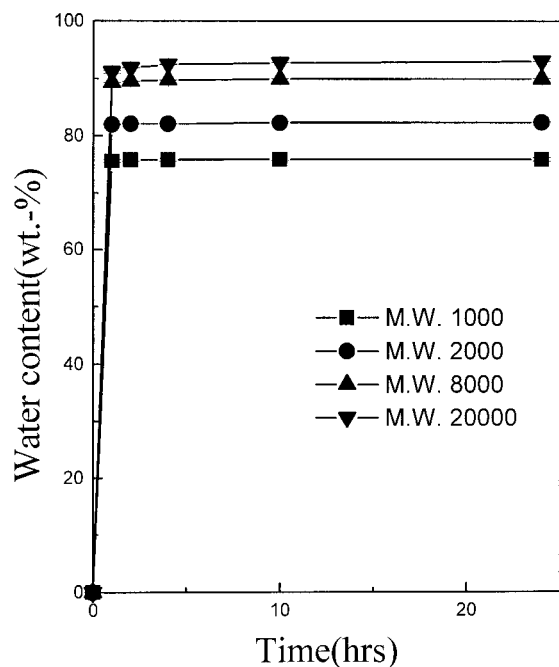


Figure 1 Water content of poly(ethylene glycol) (PEG) network against the molecular weight of PEG.

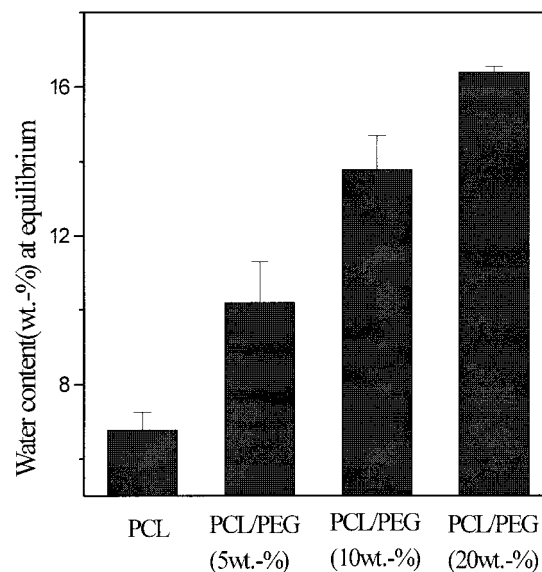


Figure 2 Equilibrium water content of polycaprolactone/poly(ethylene glycol) (PEG) semi-interpenetrating polymer networks against weight fraction of PEG (molecular weight = 8000).

nal hydroxyl group¹⁹ (not shown in the data). This band became weaker in the PEG macromer because of the acrylation of PEG.²⁰ The band at 2872 cm^{-1} attributable to the C-H stretching²¹ was present in both polymers. The results indi-

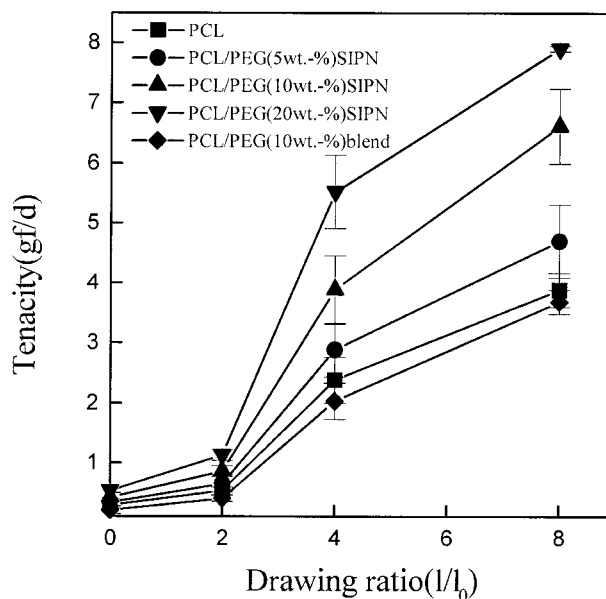


Figure 3 Tenacity of polycaprolactone/poly(ethylene glycol) (PEG) semi-interpenetrating polymer networks fiber against the drawing ratio (molecular weight of PEG = 8000).

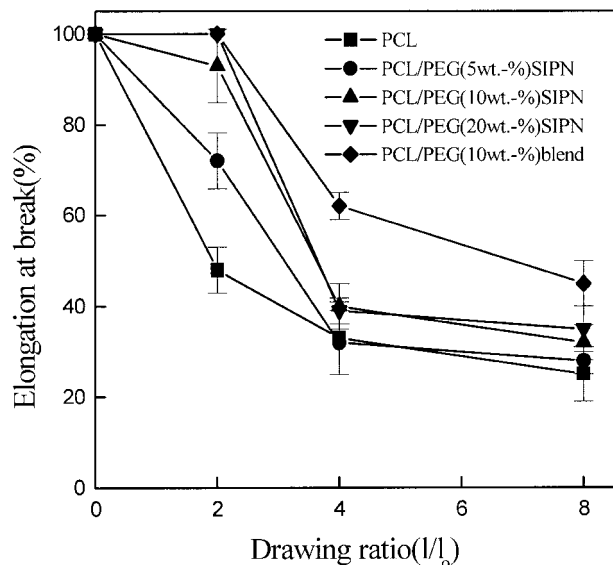


Figure 4 Elongation at break of polycaprolactone/poly(ethylene glycol) (PEG) semi-interpenetrating polymer networks fiber against drawing ratio (molecular weight of PEG = 8000).

cate that the terminal hydroxyl groups in the PEG precursor were converted to acrylate groups by a reaction with acryloyl chloride.

Hygroscopic property of the AcPEG network was determined with the water content, as shown

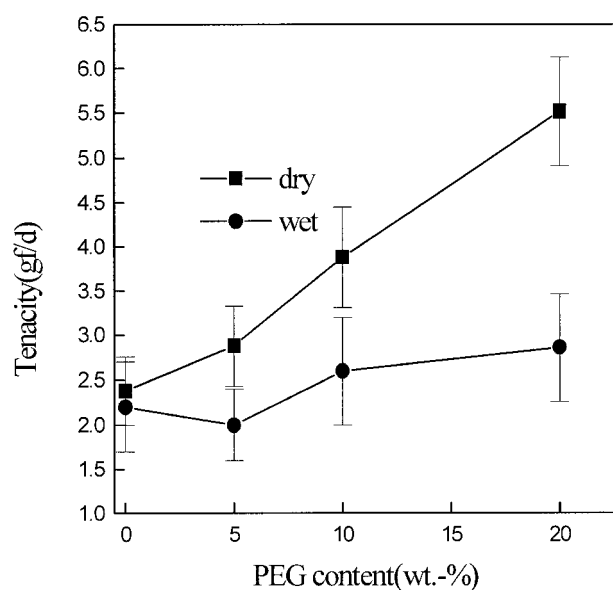


Figure 5 Tenacity of polycaprolactone/poly(ethylene glycol) (PEG) semi-interpenetrating polymer networks fiber against PEG content at a drawing ratio of 4 (molecular weight of PEG = 8000).

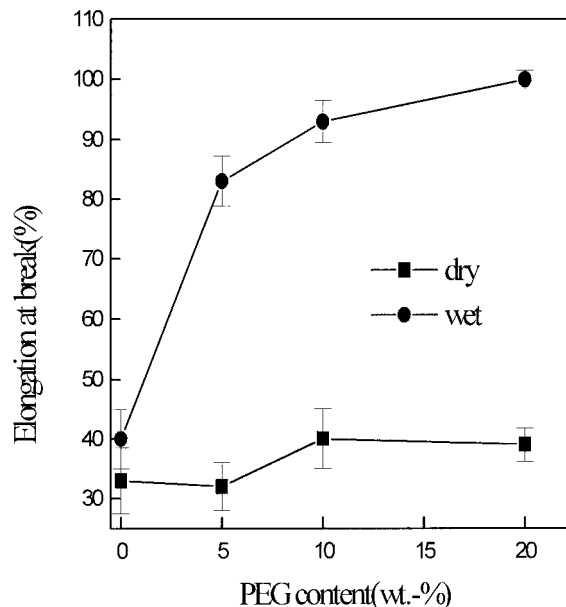


Figure 6 Elongation at break of polycaprolactone/poly(ethylene glycol) (PEG) semi-interpenetrating polymer networks fiber against PEG content at a drawing ratio of 4 (molecular weight of PEG = 8000).

in Figure 1. The figure showed that the PEG networks were swollen rapidly and reached equilibrium within 1 h because of the strong hydro-

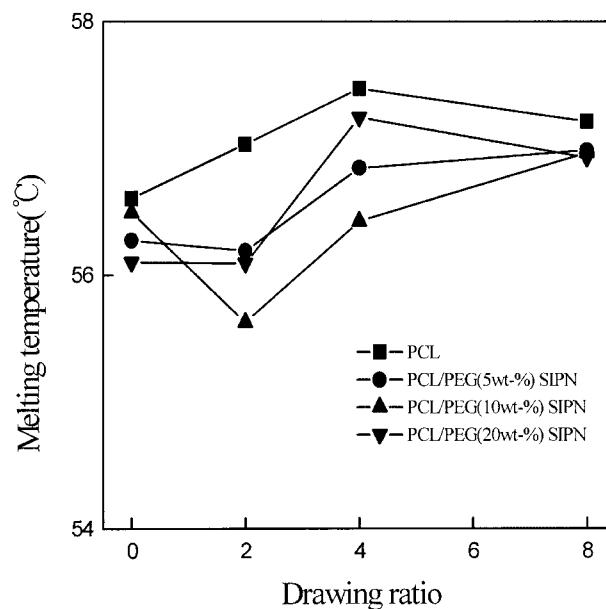


Figure 7 Melting temperature of polycaprolactone/poly(ethylene glycol) (PEG) semi-interpenetrating polymer networks fiber against drawing ratio (molecular weight of PEG = 8000).

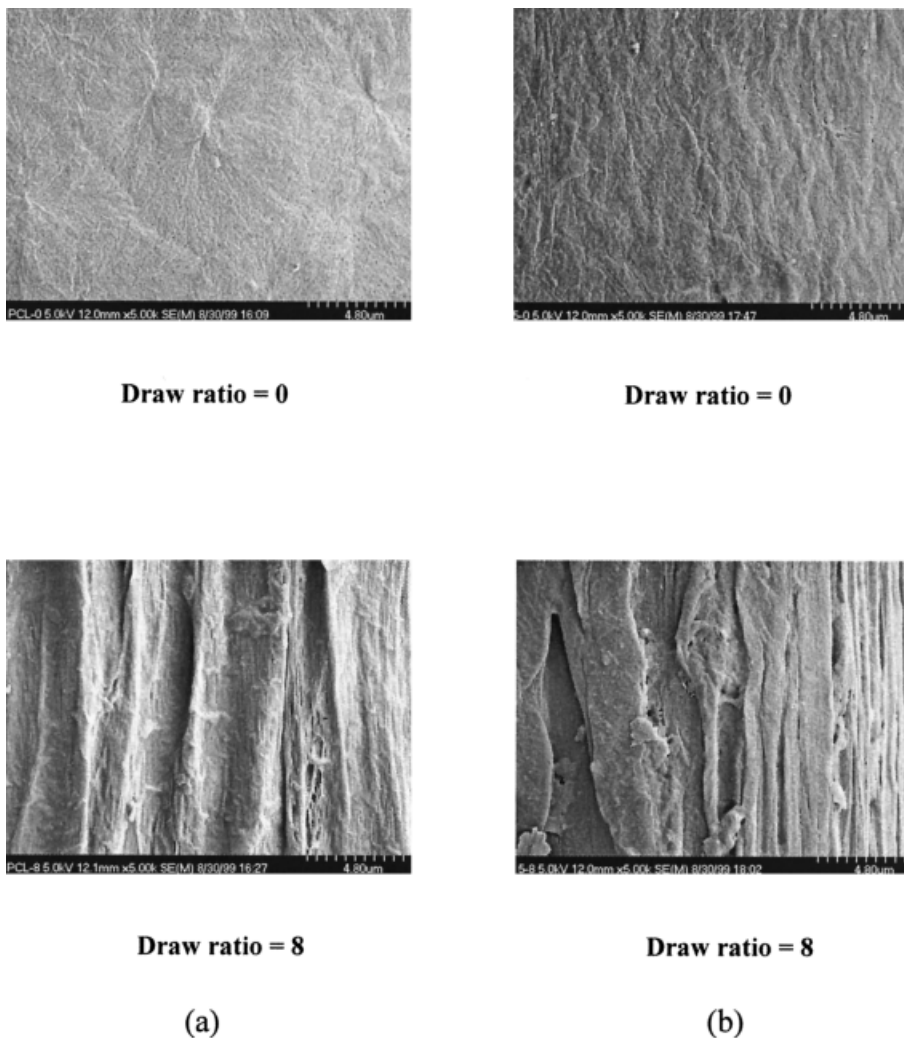


Figure 8 Scanning electron microscope photographs of fiber surfaces: polycaprolactone (PCL) (a) and PCL/poly(ethylene glycol) semi-interpenetrating polymer networks (b).

philic property of the PEG. The water content of PEG networks increased from approximately 75 to 93 wt % with an increase in molecular weight of PEG from 1000 to 20,000. The results suggest that the AcPEG of higher molecular weight forms longer segments in the network, creating larger rooms for the water to reside.

The AcPEG weight fraction effect in PCL/PEG SIPNs on water content is shown in Figure 2. More water was contained with an increase of AcPEG weight fraction as a result of its hydrophilic property. It may be also a result of the increased PEG network with an increase of PEG fraction in the SIPNs.

Tenacity dependence of PCL/PEG SIPNs fibers on the draw ratio of the dry fiber is shown in Figure 3. The tensile strength of the PCL/PEG

SIPNs (20 wt % of AcPEG) fiber increased two times more than that of PCL fiber itself or of the PCL/PEG blend fiber at a draw ratio of 8. It is suggested that the increased crosslinking density of PEG improved the tenacity of the SIPNs fiber. The tenacity increased with an increase of draw ratio as a result of the inducing of crystallization through the orientation of the fiber.

Elongations at the break of the SIPNs fiber against the draw ratio in the dry fiber are shown in Figure 4. The results suggest that elongation at the break decreased with an increase of draw ratio and increased with PEG content. Thus, the higher the concentration of PEG, the larger the resulting value of elongation at the break. The PEG network would contribute to be less crystallized resulting more elongation.

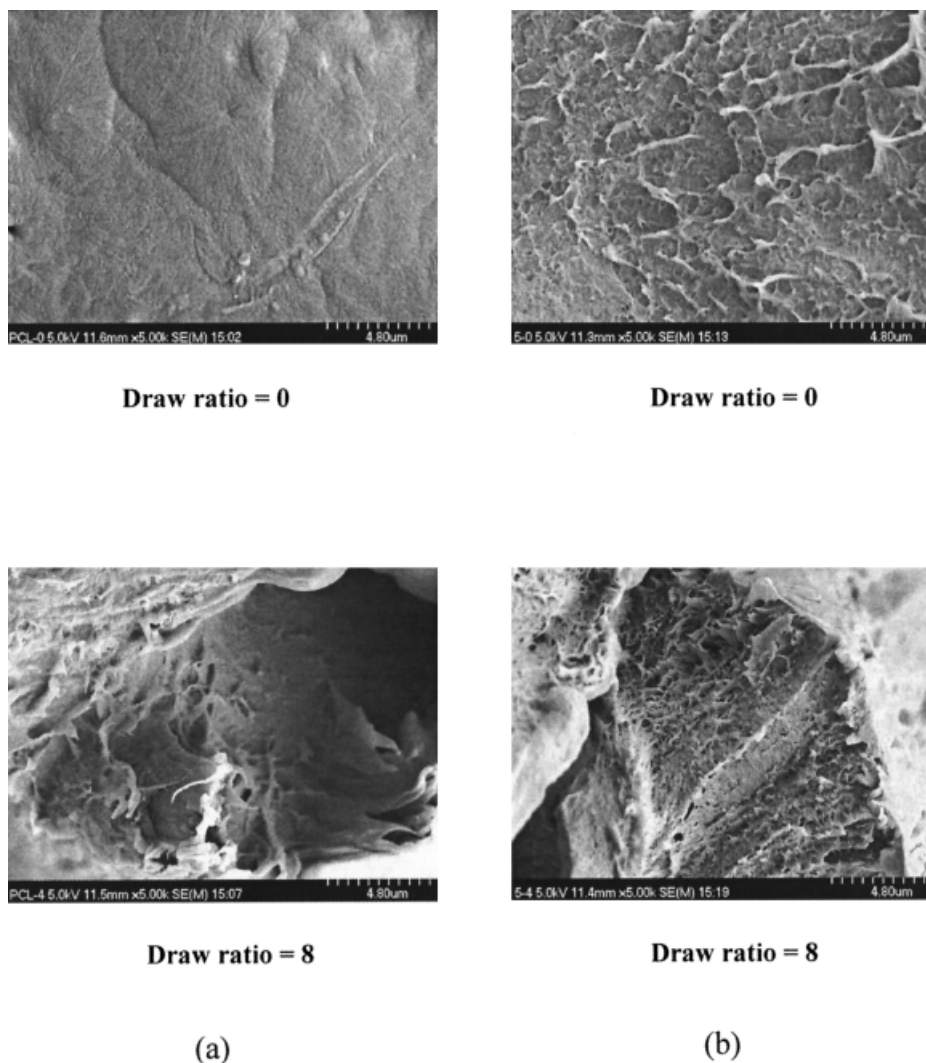


Figure 9 Scanning electron microscope photographs of a cross section of fibers: polycapralone (PCL) (a) and semi-interpenetrating polymer networks (b).

The concentration effects of AcPEG in SIPNs fibers at a draw ratio of 4 on the tenacity and elongation at the break are shown in Figures 5 and 6. The tenacity of the SIPNs dry fiber was two times stronger than that of wet fiber because the water in the network would destroy the crystalline structure and/or weaken the crosslinks in the network. However, elongation at the break of the SIPNs of wet fiber was higher than that of dry fiber. The result would come from the plasticizer function of the water in the networks.

As shown in Figure 7, the melting point of the SIPNs fiber was reduced from PCL fiber itself. It is probable that a structure less crystalline than PCL would result from the interpenetrating network of the SIPNs. The melting point increased

with an increase in draw ratio as a result of the increased crystallinity induced by drawing.

SEM photographs of a PCL fiber (a) and a PCL/PEG SIPNs fiber (b) are shown in Figure 8. The surface of the SIPNs fiber is rougher than that of the PCL fiber, although the aligned morphology was developed through a drawing of eight times. The heterogeneity from the interpenetrating network is considered to introduce the rough surface.

SEM photographs of cross sections in PCL and PCL/PEG SIPNs are shown in Figure 9. More porous structure was observed in the SIPNs fiber than in the PCL fiber, which would be a result of the rather porous network structure originally formed from the interpenetration between PCL and AcPEG in the solution.

CONCLUSIONS

SIPNs between PCL and AcPEG were formed and the fiber from the SIPNs showed the more desirable properties for sutures, such as tensile property and water content. The tensile strength of the SIPNs was 8 gr · force/denier which doubled that of the PCL itself. The water content for the SIPNs containing 20 wt % PEG of molecular weight 20,000 was maximum at 93 wt %. The behaviors would result by the introduction of hydrophilic PEG and network formation among the consisting polymers. The morphology of the SIPNs was dependent on the network introduced by interpenetration between the PCL and AcPEG.

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