

Synthesis and Properties of Segmented Poly(urethane-urea)s Containing Phosphorylcholine Moiety in the Side-Chain

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In order to improve the biocompatibility of segmented polyurethane which has been widely used as a biomedical material, the synthesis of segmented poly(urethane-urea) containing phosphorylcholine (PC) moiety was carried out by using aromatic diamine monomer with PC unit. The obtained poly(urethane-urea)s were soluble in aprotic polar solvents such as NMP, DMSO and DMF, but insoluble in water, alcohol and acetone. In addition, it was confirmed from the results of blood contacting experiments that the polymer exhibited the excellent biocompatibility, even though the PC content was around 15 wt.%, which would be due to the surface structure derived from PC side chain. From the results of stress-strain measurements, poly(urethane-urea) films exhibited the elastic properties, which were almost as same as those of segmented polyurethane. On the other hand, the gas permeability of the poly(urethane-urea) film, which consisted of the high permeable siloxane soft segment, slightly increased as compared with polyurethane film consisting the similar backbone component.

KEY WORDS: Segmented Poly(urethane-urea) / Phosphorylcholine / Diamine Monomer / Polyaddition / Biocompatibility / Mechanical Property /

Segmented polyurethanes (SPU) have been widely used in the practical medical devices^{1,2} as elastomers because of their suitable mechanical properties and biocompatibility, which consisted of short alternating blocks of soft and hard segments. The soft segment is typically a low glass transition temperature (T_g) polyether, polyester or polyalkylenediol, the molecular weights of which are 400–5000. The hard segment is usually a high glass transition temperature component, such as semi-crystalline aromatic diisocyanate linked with a low molecular weight chain extender. The biocompatibility of SPU is thought to be derived from the micro phase separation of soft and hard segments. However, the blood compatibility of SPU is not enough to be applied for long-term implantation. It has been suggested that the biodegradation and cracking of the SPU occurred *in vivo* due to the adsorption of proteins, the adhesion of macrophages and the peroxide formation,^{3–5} which resulted in the reduction of the mechanical strength of SPU. Moreover, it was reported that the soft segment of SPU was degraded by the oxygen radicals produced from adherent macrophages.⁶ Therefore, several studies of the surface or chemical modification of SPU have been conducted to improve the blood compatibility through reducing the adhesion of cells and proteins.^{7–11}

On the other hand, 2-methacryloyloxyethyl phosphorylcholine (MPC) polymer has been developed as an excellent blood compatible material, which efficiently reduces the adhesion of cells and proteins on the polymer surface.^{12,13} The MPC polymer was designed based on the inspiration from the chemical structure of phospholipids polar group in biomembrane. Considerable attention has been given to biomedical

polymers containing phospholipids functionality, and particularly to those with the phosphatidylcholine moiety,^{14,15} which is a major component of the extracellular surface of the phospholipids bilayer. Ishihara and his coworkers have demonstrated a great decrease in protein adsorption and platelet adhesion on MPC polymer containing phosphorylcholine groups, therefore, in these years, MPC polymer has been now widely applied in the biological and medical fields.^{16–22} They have also investigated the polymer composite consisting of SPU and MPC polymer, in order to reduce the protein adsorption on the polymer surface and to improve the biocompatibility of SPU.^{23–26}

In this study, as another approach to improve the biocompatibility of SPU which has been widely used as a biomedical material, the synthesis of segmented poly(urethane-urea) chemically bonded to phosphorylcholine (PC) moiety was carried out by using aromatic diamine compound containing PC unit as a comonomer. We have been developing the synthesis of a novel aromatic diamine monomer with PC group, 2-(3,5-diaminophenylcarbonyloxy)ethyl phosphorylcholine, to prepare novel aromatic polyamides containing PC group in the side chain, the backbone component of which was durable as compared with that of MPC polymers.²⁷ Then, it was revealed that PC group was also effective to improve the biocompatibility to such rigid polymer compounds, which would be due to the surface property covered with polar PC units. Therefore, in this paper, we attempted to prepare segmented poly(urethane-urea) containing PC group by using the diamine monomer with PC unit as a coupling reagent in the polyaddition of diols with diisocyanate, which would lead to new

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IR, ν (KBr, cm^{-1}): 3315 (N-H), 2961, 2860 (C-H), 1708 (C=O), 1590, 1541, 1508, 1261 (Si-C), 1240 (P=O), 1025 (Si-O-Si), 798, 740.

SPUU-2b was prepared by the similar procedure of the preparation of **SPUU-2a** with changing the molar ratio of BD, HO-PDMS and DAPC as shown in Table I.

Preparations of Segmented Polyurethane (SPU-1)

Under an argon atmosphere, BD (0.48 g, 5.33 mmol) and DBTDL (0.20 g, 0.32 mmol) were dissolved in a flask with 5.0 mL of NMP, and a solution containing MDI (2.00 g, 7.99 mmol) in 5.0 mL of NMP was gradually added to the mixture at room temperature. After the mixture was stirred at 50 °C for 2 h, a solution of HO-PTMG (2.66 g, 2.66 mmol) dissolved in 3.0 mL of NMP was added dropwise at 0 °C. Then, after the mixture was stirred at 50 °C for 1 h, the reaction mixture was poured into excess methanol/diethyl ether (1/1 vol.) mixed solvents to provide a white precipitate, which was collected by filtration and purified by reprecipitation from its NMP solution to excess methanol/diethyl ether (1/1 vol.) mixed solvents. Finally, the product was dried *in vacuo* to give **SPU-1** as a white powder. Yield: 4.95 g (96.3%).

$^1\text{H NMR}$, δ (400 MHz, DMSO- d_6 , ppm): 1.53 (m, -CH₂-), 1.73 (m, -CH₂-), 3.28 (m, -CH₂-), 3.78 (s, -PhCH₂Ph-), 4.30 (m, -CH₂-), 7.04 (d, $J = 8.30$ Hz, -Ph-), 7.35 (d, $J = 7.80$ Hz, -Ph-), 9.40 (s, -NH-).

IR, ν (KBr, cm^{-1}): 3319 (N-H), 3033, 2957, 2899 (C-H), 1701 (C=O), 1597, 1526, 1414, 1310, 1225 (C-O-C), 1065, 1016, 914, 814, 770.

Preparations of Segmented Polyurethane (SPU-2)

In the above polymerization reaction for **SPU-1**, HO-PDMS (2.66 g, 2.66 mmol) was used instead of HO-PTMG, and the similar reactions and reprecipitation were carried out to afford **SPU-2** as a white powder. Yield: 5.00 g (97.3%).

$^1\text{H NMR}$, δ (400 MHz, DMSO- d_6 , ppm): 0.01 (s, -Si(CH₃)₂), 0.52 (m, -SiCH₂-), 1.53 (m, -CH₂-), 1.73 (m, -CH₂-), 3.32 (m, -CH₂-), 3.40 (m, -CH₂-), 3.81 (s, -PhCH₂Ph-), 4.28 (m, -CH₂-), 4.38 (m, -CH₂-), 7.11 (d, $J = 7.30$ Hz, -Ph-), 7.38 (d, $J = 7.80$ Hz, -Ph-), 9.55 (s, -NH-).

IR, ν (KBr, cm^{-1}): 3315 (N-H), 2961, 2860 (C-H), 1708 (C=O), 1590, 1541, 1508, 1261 (Si-C), 1025 (Si-O-Si), 798, 740.

Characterizations

$^1\text{H NMR}$ spectra were conducted with a JEOL NM-TH5SK 400 MHz FT NMR spectrometer, and the chemical shifts were estimated in ppm units with tetramethylsilane (TMS) as an internal standard. Infrared (IR) spectra were recorded with a Shimadzu FT/IR-8400 spectrometer. The molecular weights of polymers were estimated by Tosoh gel permeation chromatography (GPC) system equipped with a pump of CCPD, three columns of TSK gels Multipore HXL-M, a column oven of CO-8010 and RI detector of RI-8010 in DMF eluent at 40 °C. Average molecular weights were calibrated based on polystyrene standards. Differential scanning calorimetry (DSC) was

carried out on a Seiko Instruments DSC-6200 under a nitrogen flow rate of 30 mL/min and a heating rate of 10 °C/min.

Preparations of Polymer Films

The obtained polymers were dissolved in dimethylformamide (DMF) at about 10 wt. %. Then, the solution was cast on the poly(ethylene terephthalate) sheet, and the solvent was evaporated at 60 °C over a period of 24 h to form polymer films. The obtained films were dried for 2 h at 80 °C *in vacuo*.

Surface Characterizations of Polymers

The polymer films were cut into circular pieces with a diameter of 14 mm and a thickness of 0.1–0.2 mm. Contact angles of water on the surfaces of the polymer films were measured using an Erma contact-angle microscope at room temperature. On the other hand, X-ray photoelectron spectroscopy (XPS) was conducted on the surface of polymer films by using ULVAC-PHI Quantum 2000 XPS apparatus. The take-off angle of the photoelectron was 45 degree.

Evaluation of Blood Compatibility

Whole blood was collected from healthy donors. In a polyethylene disposable syringe containing 3 mL of a 3.8 wt. % aqueous sodium citrate solution, 30 mL of fresh blood was collected. The citrated whole blood was immediately centrifuged for 15 min at 1200 rpm to obtain citrated platelet-rich plasma (PRP).

The circular pieces of polymer films were contacted with phosphate-buffered solution (PBS, pH = 7.4) at r.t. for overnight to equilibrate the surface, then the human whole blood or PRP was poured onto the films and incubated at 37 °C for 60 min. After the incubation, the whole blood and PRP were removed with an aspirator, and the films were rinsed three times with PBS, and then 0.7 mL of 2.5 vol. % glutaraldehyde in PBS was poured onto each film, and the materials were maintained at room temperature for 2 h in order to fix the blood components on the plates. After the fixation, it had been rinsed five times with distilled water, and then the plate was freeze-dried. The surfaces of the polymer films were observed with a scanning electron microscope (SEM) by using JEOL JSM-5200 after a gold-sputtering treatment.

Measurement of the Amount of Platelets Adsorbed on the Polymer Surface

After incubating the polymer films in the above procedure, PRP was removed and the films were washed 3 times with PBS and transferred into 0.5 wt. % aqueous solution of polyethylene glycol mono-*p*-isooctylphenyl ether (Triton X100) to elute the adsorbed platelets. The concentration of platelets in the Triton X100 solution was counted by a lactate dehydrogenase (LDH) assay using an LDH-Cytotoxic Test Kit (Wako Chemicals, Osaka, Japan). The concentration of platelets in PRP was determined with a Coulter counter (MULTISIZER II, Beckman Coulter, CA) and the number of platelets that adhered on the polymer films was estimated based on the absorbance of the PRP-diluted system.

Table I. Results of polymerizations

Code	Molar ratio of monomers MDI:BD:HO-X-OH:DAPC	Yield (%)	PC content ^{a)}		$M_n^{b)} \times 10^{-3}$	$M_w/M_n^{b)}$
			(mol %)	(wt. %)		
SPU-1	6:4:2:0	96.3	0	0	104	2.11
SPUU-1a	6:3:2:1	91.3	12.7	6.37	88.9	1.79
SPUU-1b	6:2:2:2	85.7	27.6	12.5	77.4	1.56
SPUU-1c	6:1:2:3	83.5	41.5	16.5	38.7	1.59
SPU-2	6:4:2:0	97.3	0	0	53.1	1.91
SPUU-2a	6:3:2:1	92.7	12.5	6.23	44.4	2.23
SPUU-2b	6:2:2:2	87.1	26.4	11.8	44.0	2.32

^aPC content was calculated from the ratio of peak intensities of ¹H NMR spectra. ^bNumber-average and weight-average molecular weight (M_n and M_w) were determined by GPC based on polystyrene standards.

Measurements of Mechanical Strength

The polymer films were cut into rectangular strips with a length of 70 mm, a width of 15 mm and a thickness of 0.1–0.2 mm. Stress-strain curves were obtained on a JT Torsi LSC-01/30, where the gauge length was 50 mm and the crosshead speed was 12 mm/min.

Measurements of Gas Permeability Coefficients

Sample films were cut into circular pieces with a diameter of 36 mm and a thickness of 0.1–0.2 mm. Gas permeabilities of the membranes were measured using the ordinary vacuum method at 30 °C with the apparatus, Tsukuba-Rikaseiki K-315N-01, where the permeation area was 7.07 cm². The gas permeability coefficients (P , cm³(STP)·cm·cm⁻²·s⁻¹·cmHg⁻¹) were calculated from the slope of the time-pressure curve, dp/dt , in the steady state.

RESULTS AND DISCUSSION

Synthesis of Segmented Poly(urethane-urea) Containing PC Unit

At first, two kinds of segmented oligourethanes were prepared by polyaddition of 4,4'-diphenylmethane diisocyanate (MDI) with 1,4-butanediol (BD) in NMP, followed by the addition of hydroxyl-terminated poly(tetramethylene glycol) (HO-PTMG) or hydroxyethoxypropyl-terminated polydimethylsiloxane (HO-PDMS) as the soft segment. In the polymerization vessels, 2-(3,5-diaminophenylcarbonyloxy)ethyl phosphorylcholine (DAPC) was finally added to couple the oligourethanes to obtain segmented poly(urethane-urea)s containing PC unit (SPUU-1a,b,c and SPUU-2a,b), as shown in Scheme 1. The similar segmented polyurethanes without PC unit (SPU-1 and SPU-2) were prepared from MDI and BD with HO-PTMG or HO-PDMS as reference samples. These polymerization reactions proceeded smoothly by using dibutyltin dilaurate (DBTDL) as a catalyst, whereas the low molecular weight polymers were obtained in very low yields without using DBTDL. In addition, the catalyst could be efficiently removed by the reprecipitation of polymer solutions into methanol/diethyl ether mixed solvents.

Table I summarizes the results of polymerizations. Several poly(urethane-urea)s with different contents of PC unit were prepared by changing the amount of DAPC in the polyaddition.

In the case of SPUU-2 series, the higher PC content more than 26 mol % could not be achieved, because the polymer was not precipitated when DAPC was used higher than the equimolar amount of BD or HO-PDMS. The chemical structures of these polymers were confirmed by their ¹H NMR and IR spectra, as described in the experimental section. The compositions of PC unit in SPUU-1 and SPUU-2 series were determined from the ratio of the peak intensities of the ammonium proton (3.10–3.15 ppm) of PC unit and methylene proton (3.78–3.80 ppm) of *p,p'*-diphenylmethane unit, where the *p,p'*-diphenylmethane unit was exist in every monomer components. The observed PC content in mol % was a little lower than the molar ratio of DAPC against all of the diol monomers, and the yields were decreased as the PC content increased. Probably, the highly hygroscopic property of DAPC would disturb the polyaddition using a moisture-sensitive MDI. In IR spectra, the absorption peaks of the urethane and urea groups were observed at 3315 cm⁻¹ and 1710 cm⁻¹, and the PC group was identified from the peak at 1240 cm⁻¹. The number-average molecular weights (M_n) of the obtained polymers were over 10⁴, and tough films were prepared from these SPU and SPUU by a solvent casting method.

The SPUU-1 series containing PTMG segment exhibited a good solubility in aprotic polar solvents such as NMP, DMF and DMSO at room temperature, whereas it was insoluble in methanol, ethanol, acetone, tetrahydrofuran (THF) and water. By the way, the SPUU-2 series containing PDMS segment was soluble in NMP, DMF, DMSO and THF, but insoluble in methanol, ethanol, acetone and water. Therefore, the solubility of SPUU-1 series was slightly different from that of SPUU-2 series due to their difference of soft segment. Such a solubility in the specific solvents is advantageous in the processing for medical devices, and the insolubility in other solvents enables the material durable to these solvents. From the results of DSC measurements, SPUU-1 and SPUU-2 series were glassy polymers, the glass transition (T_g) of which was not observed in the range of –50 °C –250 °C, although SPU-1 showed the melting point (T_m) at 215 °C. Such a thermal stability of these polymers would be sufficient for the applications to biomaterials and medical devices, especially in the sterilization process.

Therefore, as compared with MPC polymer, it was found that the physical characteristics of SPUU-1 and SPUU-2 series

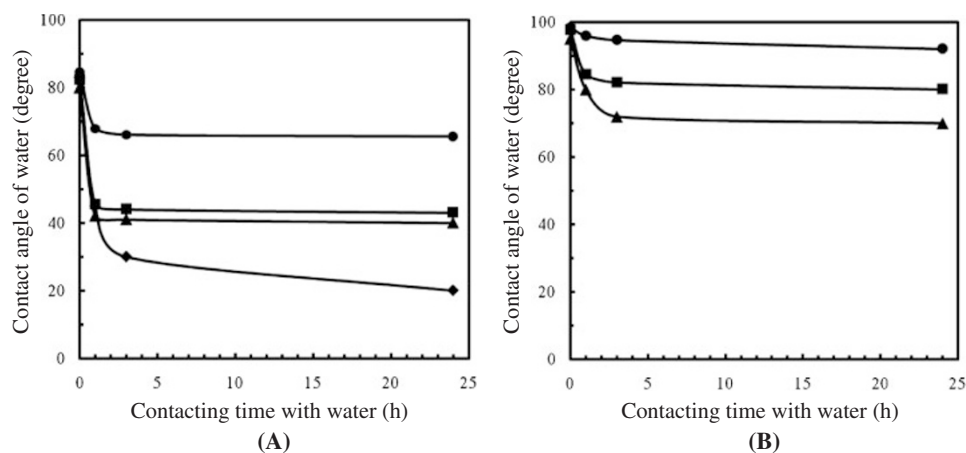


Figure 1. The time course of contact angle of water on the polymer films after treatment with water. (A) ●: SPU-1, ■: SPUU-1a, ▲: SPUU-1b, ◆: SPUU-1c. (B) ●: SPU-2, ■: SPUU-2a, ▲: SPUU-2b.

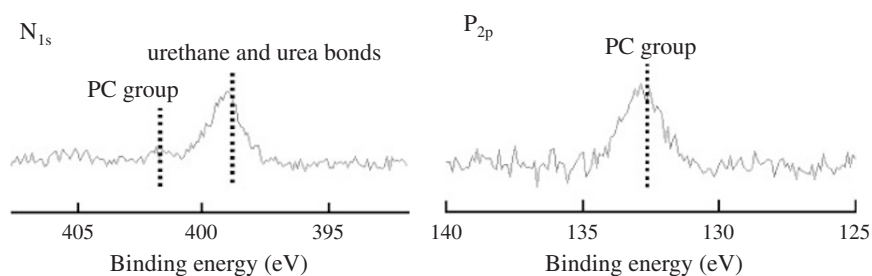


Figure 2. XPS spectra of SPUU-1c film.

exhibited the durability to common organic solvents such as alcohols and the higher thermal stability, whereas the MPC polymer were easily soluble in common organic solvents and softened at T_g of below 100 °C.

Surface Property

The surface analysis of the polymer films was carried out, in order to clarify the effect of PC group on the surface property of SPUU-1 and SPUU-2 series. Figure 1 shows the time-course of contact angle of water on the surface of polymer films after the films were immersed in water. In the cases of SPU-1 and SPU-2 without PC unit, the contact angle showed almost no change after immersed in water during 1–24 h, where the film surfaces became slightly hydrophilic by the contact with water to give a certain decrease of contact angle at the first stage. The value of SPU-2 was higher than that of SPU-1, which would be due to the hydrophobic PDMS segment of SPU-2. On the other hand, the contact angles of the SPUU-1 and SPUU-2 films were significantly decreased after the films were immersed in water, where SPUU-1c film showed the great decrease of the contact angle with contacting time of water. Therefore, the surface of the polymer membrane became hydrophilic by the introduction of PC unit and by contacting the surface with water. This result indicated that SPUU-1 and SPUU-2 film surfaces were largely swelled by water and the PC group of polymers was oriented to the water-side. The similar tendency was observed for polyamides containing PC unit in the side chain.²⁷

Furthermore, the surface chemical structure of SPUU-1c film was analyzed by X-ray photoelectron spectroscopy (XPS), as shown in Figure 2. The XPS signals observed at 133, 398 and 402 eV in P_{2p} and N_{1s} regions were attributed to phosphorus of the phosphate group, the nitrogen atoms in the urethane or urea bond (-NH-) and the ammonium group (-N⁺(CH₃)₃), respectively. Then, PC group was clearly observed on the SPUU-1c film surface. However, these peaks were not so clear on the surfaces of SPUU-1a, SPUU-1b, SPUU-2a and SPUU-2b films. Therefore, in this poly-(urethane-urea) system, PC content should be over *ca.* 15 wt. % to make the PC group clearly appear on the surface of polymer film.

Biocompatibility

The blood compatibility of the polymer films was evaluated by contacting the films with a human blood, to reveal the effect of PC unit on the biocompatibility of polymers. Figure 3 shows the number of platelets adhered on the polymer films and the SEM pictures of SPU-1 and SPUU-1c films after contact with PRP for 1 h. The numerous adherent human platelets on the SPU-1 film surface were observed as large aggregates. On the contrary, the platelets were significantly suppressed on the SPUU-1b, SPUU-1c and SPUU-2b film surfaces as shown in Figure 3. The numbers of adhered platelets on SPUU-1b, SPUU-1c and SPUU-2b films were 3.0, 1.5 and 3.3 ($\times 10^6$ cells/cm²), whereas those on SPU-1 and SPU-2 films were 8.4

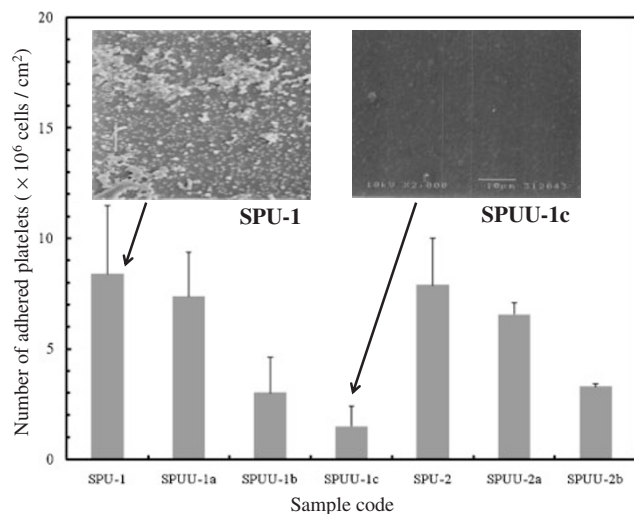


Figure 3. Number of adherent platelets and SEM pictures ($\times 2,000$) on the polymer surfaces after contact with human platelet rich plasma (PRP) for 60 min. Each bar represents mean \pm S.E. for 4 experiments.

and $7.9 (\times 10^6 \text{ cells/cm}^2)$, respectively. These results clearly indicated that **SPUU-1b**, **SPUU-1c** and **SPUU-2b** exhibited the excellent blood compatibility and that PC unit in the poly(urethane-urea) was an appropriate component to develop the blood compatibility, where *ca.* 10 wt. % of PC content was enough to reduce the adhesion of platelets. Furthermore, the composition of the PC unit was a dominant factor in the reduction of the blood cell and platelet adhesion, which was revealed from the result that the number of adhered platelets was much decreased on **SPUU-1c** film rather than **SPUU-1b** and **SPUU-2b** films. Thus, the PC content of 16.5 wt. % in **SPUU-1c** was necessary to sufficiently reduce the adhered platelets on the polymer surfaces, which would be an enough content of the PC unit located at the surface of the polymer film.

However, the reduction of the adhered platelets on the MPC polymer (PMB) film was more effective than **SPUU-1c**, where the number of adhered platelets on PMB surface was less than $1 \times 10^6 \text{ cells/cm}^2$ in the same condition. Probably, the density of PC group on the surface of **SPUU-1c** would be lower than that of MPC polymer, because of the limitation of PC content in this polyaddition system.

Mechanical Property

The mechanical properties of **SPU** and **SPUU** films were evaluated in order to reveal the effect of introduction of PC unit on the mechanical property of polyurethane backbone. Figure 4 shows the stress-strain behaviors of all the polymer films prepared in this study, and the Young's modulus, the tensile strength and the elongation to break were summarized in Table II. As seen in Figure 4, the similar tendency was observed in all of the polymer films except **SPUU-1c**, although the tensile strength of **SPU-2** and **SPUU-2b** series was higher than that of **SPU-1** and **SPUU-1** series. Consequently, there

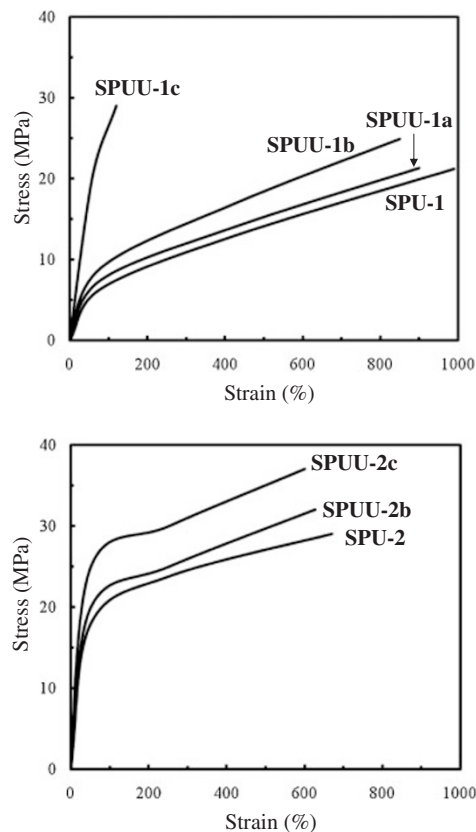


Figure 4. Stress-Strain behaviors of SPU and SPUU films. Gauge length: 50 mm, Width: 15 mm, Thickness: 0.1–0.2 mm, Elongation rate: 12 mm/min.

Table II. Mechanical properties of SPU and SPUU films

Code	Young's modulus (MPa)	Tensile strength (MPa)	Elongation to break (%)
SPU-1	106	21.2	1010
SPUU-1a	119	21.3	912
SPUU-1b	132	24.9	850
SPUU-1c	345	31.6	120
SPU-2	208	28.9	670
SPUU-2a	220	31.7	627
SPUU-2b	281	37.0	600
PMBH*	15	3.6	390

*PMBH: poly(MPC-co-2-ethylhexyl methacrylate) (MPC content: 26 mol%), the values of which were described in the literature.²⁰

was almost no change in such elastic stress-strain behaviors between **SPU** and **SPUU** series, the PC content of which was less than 12 wt. %. However, **SPUU-1c** containing 16.5 wt. % of PC unit exhibited also the elastic property, although the elongation at break of **SPUU-1c** was lower than that of **SPUU-1a** and **SPUU-1b**. Furthermore, the Young's modulus and the tensile strength increased with the increase of PC unit of **SPUU-1** and **SPUU-2** series, as listed in Table II. The increase of the mechanical strength would be due to the increase of urea bond, which would enhance the molecular interaction in the hard segments rather than urethane bond. In addition, as shown

Table III. Gas permeability and solubility and diffusion parameters of SPU-2 and SPUU-2b films

Sample code and parameters	Gas permeability coefficient (<i>P</i>) and <i>S</i> , <i>D</i> parameters ^{a)}					
	H ₂	CO ₂	O ₂	N ₂	CH ₄	C ₂ H ₆
SPU-2						
<i>P</i> (Barrer ^{b)})	105	428	77.3	32.8	103	251
<i>S</i> (10 ⁻⁵ cm ³ (STP)/cm ³ ·cmHg)	24.1	769	112	26.5	203	1150
<i>D</i> (10 ⁻⁷ cm ² /s)	437	55.6	69.1	123	50.9	21.8
SPUU-2b						
<i>P</i> (Barrer ^{b)})	124	505	91.5	40.0	124	306
<i>S</i> (10 ⁻⁵ cm ³ (STP)/cm ³ ·cmHg)	95.5	1150	125	56.2	267	1630
<i>D</i> (10 ⁻⁷ cm ² /s)	130	44.0	73.2	71.2	46.5	18.7

^{a)} *S*: Solubility parameter, *D*: Diffusion parameter. ^{b)} 1 Barrer = 10⁻¹⁰ cm³(STP)·cm/cm²·s·cmHg

in Table II, the mechanical properties of these poly(urethane-urea)s and MPC polymer (PMEH) films were quite different, where Young's moduli of SPUU-1c and PMEH were 345 and 15 MPa, respectively. These physical properties of these polymers obviously depended on the elastic segmented polyurethane backbone.

Gas Permeability

As described above, it was found that PC group was effective to change the polymer film surface when the PC content was above 10 wt. %, and that the tough films could be prepared from these polymers. Then, the gas permeabilities of SPU-2 and SPUU-2b were evaluated to reveal the effect of PC unit on the gas permeability of polymer film, which consisted of the high permeable polysiloxane segment. Gas permeability coefficients of SPU-2 and SPUU-2b films for nitrogen, oxygen, hydrogen, carbon dioxide, methane and ethane were evaluated, as listed in Table III. It was noticed from this table that the gas permeability of the two films were relatively high according to the PDMS backbone component. Interestingly, the gas permeability coefficients of SPUU-2b film were slightly higher than those of SPU-2. Therefore, the solubility and diffusion parameters were also calculated from the time lag in the slope of time-pressure curve, dp/dt , to predict the mechanism. As a result, the solubility parameters of all of the gases on the SPUU-2b film surface were higher as compared with SPU-2 film, as shown in Table III. It was speculated that the surface property, which was derived from the introduction of PC group, increased the gas permeability of polymers due to the increase of gas solubility on the polymer surface. Iwasaki *et al.* have been reported the oxygen permeability in water through the skin films consisted of MPC polymer, poly(MPC-co-dodecyl methacrylate) (PMD), adhered on a polyethylene porous membrane, where the oxygen permeability coefficients were increased as the increase of MPC content.²⁸ The tendency of gas permeability of SPUU-2b film corresponds to those results of composite films containing MPC polymer, although the permeabilities have been investigated in different conditions and the mechanism of such improved gas permeability by PC unit has been still unclear.

If the high gas permeable and biocompatible membrane is developed, several applications will be expected, such as the artificial lung or the separation membranes without adhesion of

bio-components. Thus, we are planning to develop the higher permeable membrane materials with a biocompatibility based on PC group.

CONCLUSION

An aromatic diamine compound containing PC group, DAPC, was used as a coupling reagent in the synthesis of segmented polyurethane to yield poly(urethane-urea)s with different PC contents. The introduction of such a polar group of phospholipid was effective to improve the blood compatibility even in the segmented polyurethane system, which would be due to the surface property covered with PC moiety. Furthermore, the elastic mechanical properties of segment polyurethane were maintained when the PC unit was introduced up to 17 wt.%. On the other hand, the gas permeability of the poly(urethane-urea) film, which consisted of the high permeable siloxane soft segment, slightly increased as compared with polyurethane film due to the effect of surface rearrangement by PC moiety. Consequently, it is expected that such poly(urethane-urea)s containing PC group will be useful polymeric biomaterials to develop a new generation of biomedical devices, because of the different solubility, the higher mechanical strength and the similar biocompatibility as compared to the MPC polymer.

However, it is considered that the PC content should be increased to improve the biocompatibility, which is not enough for the practical use. To improve the PC content in this system, the molecular design of the higher reactive diamine monomer containing PC unit must be developed, which is now in progress.

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