# Properties of Blood Compatible Crosslinked Blends of Pellethene®/Multiblock Polyurethanes Containing Phospholipid Moiety/C-18 Alkyl Chain

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**Abstract:** To improve the mechanical properties, dimensional stability and blood compatibility, the biomedical material Pellethene® was blended with multiblock polyurethane (MPU) containing phospopholipid /long alkyl chain (C-18) at the various MPU contents and crosslinked using dicumyl peroxide as a crosslinking agent. The maximum MPU content for stable Pellethene®/MPU blended films was approximately 30 wt%. The optimum crosslinking agent content and crosslinking time with respect to the mechanical properties were 4 wt% and 3 h, respectively. The mechanical properties (tensile strength and elongation at break) and water absorption of the crosslinked blend film increased with increasing MPU content. The test of platelet adhesion on the surfaces of the crosslinked blend film showed a decrease in the level of platelet adhesion from 70% to 6% with increasing MPU content from 0 to 30 wt%. These results suggest that the crosslinked Pellethene®/MPU-30 (MPU content: 30 wt%) sample has strong potential as a novel material for blood compatible material applications.

Keywords: polyurethane, phospholipids, biomaterials, platelet adhesion.

# Introduction

Among polymers frequently employed as biomaterial, segmented polyurethanes are widely used for various commercial and experimental blood-contacting and tissue-contacting applications. Although many successful results have been obtained when using polyurethanes in different biomedical devices, such as vascular prostheses, heat valves, blood pumps and artificial hearts, the inherent thrombogenicity of segmented polyurethanes has been a problem. Therefore, the development of non-thrombogenic biomaterials has remained one of the most elusive challenges in biomaterial field.

Generally, blood coagulates and causes blood clotting when it encounters foreign solid surfaces. This phenomenon is assumed to begin with the initial absorption of blood proteins, which is followed by platelet adhesion and activation of the coagulation pathway, leading to thrombus formation. Thus, several strategies have been proposed to improve the blood compatibility of biomaterials such as the incorporation of ionic groups on the polymeric surface, the alteration of the surface properties by grafting technique, the immobilization of heparin, functionalized dextrans, or biological compounds, and the introduction of hydrophilic polymers.<sup>8-10</sup>

Considerable attention has been paid to phospholipids because they are known to consist of hydrophilic and hydrophobic groups and form the lipid bilayer and are important building units of plasma membranes. It is believed that polymers containing the phospholipid moiety provide biomembrane mimicry and should be more compatible with the human body. Phosphorylcholine which is an electrically neutral and zwitterionic head group that represents the bulk of the phospholipid head groups present on the external surface of blood cell is inert in coagulation assays. The introduction of the phosphatidylcholine or its analogues into polymer is useful for improving blood compatibility. 13,14

The alkylation of blood contacting polymers with C-18 linear alkyl chains has been shown to reduce thrombus deposition at the blood/polymer interface. Munro *et al.* Munro *et al.* Proposed that the reduction of thrombus formation was a result of albumin adsorbing specifically and strongly to the alkyl chains. This specific absorption was postulated to increase the amount of albumin on the surface and to decrease the number of platelets on the surface available to aggregate into a thrombus. Some studies supported this hypothesis by showing that albumin absorption from single and binary protein solutions was increased when the polymers were derivatized with C-18 and C-16 alkyl chains. 16,17

These polyurethanes having phosphatidylcholine or its analogues showed good blood compatibilities but their

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mechanical properties and water resistance were poor. So, to improve mechanical properties, water resistance and blood compatibility, the high strength Pellethene® was blended with MPU synthesized from hexamethylene diisocyanate (HDI)/amphiphilic phospholid diol containing C-18/poly (ethylene oxide) (PEO)/poly(tetramethylene oxide) (PTMO) /poly(butadiene diol) (PBD)/1,4-butanediol (BD), and then crosslinked using dicumyl peroxide as a crosslinking agent. The effect of MPU content in Pellethene®/MPU blends on the water absorption behavior, mechanical properties, compatability between Pellethene® and MPU and blood compatibility was investigated in this study. The blood compatibility of the crosslinked blend films was evaluated by platelet rich plasma (PRP) contacting experiments and the results were observed by scanning electron microscopy (SEM).

### **Experimental**

Materials. A segmented biomedical grade polyurethane pellet (Pellethene® 2363-80AE, Dow Chemical Co., Midland, MI, USA) was used after being washed with methanol for 3 days and dried in a vacuum oven overnight at 60 °C. Poly (ethylene oxide) (PEO,  $M_n$ =3,400 g mol<sup>-1</sup>, Aldrich, Milwaukee, WI, USA) and poly(tetramethylene oxide) (PTMO, M<sub>n</sub> =2,000 g mol<sup>-1</sup>, Aldrich, Milwaukee, WI) were dried for 24 h at 80 °C in vacuum before use. Hexamethylene diisocyanate (HDI, Aldrich, Milwaukee, WI), polybutadiene diol (PBD, Aldrich, Milwaukee, WI), and 1, 4-butanediol (BD, Aldrich, Milwaukee, WI) were used after dehydration with 4 Å molecular sieves for one day. Triethylamine (TEA, Aldrich, Milwaukee, WI), 1-butanol (Aldrich, Milwaukee, WI), 1octanol (Aldrich, Milwaukee, WI), 1-dodecanol (Aldrich, Milwaukee, WI), 1-hexanol (Aldrich, Milwaukee, WI), 1octadecanol (Aldrich, Milwaukee, WI), 1-eicosanol (Aldrich, Milwaukee, WI), N-methyldiethanolamine (Aldrich, Milwaukee, WI), dibutyltin dilaurate (DBTDL, Aldrich, Milwauke, WI, USA) was used without further purification, and dicumyl peroxide (DCP, Aldrich, Milwaukee, WI) were used as provided.

Synthesis of Amphiphilic Phospholipid Diol Containing C-18: 2-[Bis(2-Hydroxyethyl) Methyl Ammonio]ethyl Stearyl Phosphate (BESP). 2-Chloro-1,3,2-dioxaphospholane [bp 45.5-46.5 °C at 15 mmbar; 45.5-47.0 °C at 15 mmbar] with 66% yield was prepared by the reaction of ethylene glycol with phosphorus trichloride in dichloromethane, according to the method of Lucas *et al.*..<sup>18</sup> 2-Chloro-2-oxo-1, 3, 2-dioxaphospholane (COP) [bp 103.5-105.0 °C at 1 mmbar; 79 °C at 0.4 mmbar] with 90% yield was obtained by oxidation reaction of 2-chloro-1, 3, 2-dioxaphospholane and oxygen according to the procedure of Edmundson.<sup>19</sup>

The solution of 1-octadecanol (0.037 mol)/TEA (0.041 mol)/ dry tetrahydrofuran (THF, 150 mL) was put into a three-necked round-bottomed flask, equipped with a mechanical stirrer,  $N_2$  gas inlet and dropping funnel, and then cooled at 10 °C. The COP (0.037 mol) was added dropwise to the solution over 1 h, and then triethylamine hydrochloride began to precipitate. The reacted mixture was maintained for 1 h at 10 °C under stirring and then allowed to heat to 15-20 °C. After keeping the mixture at 15-20 °C for 1.5 h, the precipitate (triethylamine hydrochloride) formed was filtered off and was washed out using dry THF. The white solid, 2-stearyloxy-2-oxo-1, 3, 2-dioxaphospholane (SOP, yield: 97%) was obtained by evaporating the mixture.

The solution of SOP (0.032 mol)/dry *N*,*N*-dimethylformamide (DMF, 100 mL) was put into a glass bottle. Then the *N*-methyldiethanolamine (0.048 mol) was rapidly added to the bottle. The bottle was sealed up and the reaction of SOP and *N*-methyldiethanolamine was continued for 20 h at 75 °C. The product 2-[bis(2-hydroxyethyl) methyl ammonio]ethyl stearyl phosphate (BESP, yield: 93%, pale yellow

Step II. HO 
$$(CH_2)_2$$
 OH  $\frac{PCl_3}{CH_2Cl_2}$   $\frac{H_2C-O}{H_2C-O}$  P-Cl  $\frac{O_2}{benzene}$   $\frac{H_2C-O}{H_2C-O}$  P-Cl  $\frac{P-Cl}{benzene}$   $\frac{P-Cl}{H_2C-O}$  P-Cl  $\frac{P-Cl}{benzene}$   $\frac{P-Cl}{H_2C-O}$  P-Cl  $\frac{P-C$ 

2-{Bis(2-hydroxyrthyl)methylammonio}ethyl swaryiphosphate: BESP

Scheme I. Synthetic scheme of phospholipid diol (BESP).

solid) was obtained by washing with acetone, dry chloroform, methanol, and diethyl ether. The synthetic scheme of phospholipid diol (BESP) is shown in Scheme I.

**BESP:** <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ = 0.88 ppm (s; -CH<sub>3</sub>, 3H), 1.26 ppm (s; C-(CH<sub>2</sub>)<sub>16</sub>-C, 32H), 3.12 ppm (s; N<sup>+</sup>-CH<sub>3</sub>, 3H), 3.4~4.2 ppm (m; OCH<sub>2</sub>CH<sub>2</sub>-N<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>O, PO-CH<sub>2</sub>CH<sub>2</sub>-N<sup>-</sup>, PO-CH<sub>2</sub>-C, 14H).

Synthesis of Segment Multiblock Polyurethanes (MPU). An appropriate amount of dried PEO ( $M_n = 3,400 \text{ g mol}^{-1}$ ) and three drops of dibutyltin diaurate as a catalyst were dissolved in THF. HDI was slowly added to the solution for 30 min and the reacted mixture was stirred for 4 h at 55 °C. Then PTMO, PBD, phospholipid diol (BESP), and BD were added separately to the mixture and reacted for 3 h, 2 h, 1 h, and 30 min respectively. The obtained MPUs were precipitated using n-hexane as a nonsolvent. The precipitated MPU was washed out with an excess amount of distilled water to remove any unreacted components and then they were dried for 2 days at 45 °C in a vacuum. The preparation procedure of MPU is shown in Scheme II. The compositions of MPU and Pellethene®(P)/MPU blends prepared in this study are shown in Table I.

Preparation of the Simple Blends (Pellethene®/MPUs) Films and Crosslinked Blends Films. The Pellethene® were dissolved in THF to form a 15 wt% solution. The MPU without DCP and with DCP for simple blends and crosslinked blends films were added to Pellethene® solution and the solutions of the mixtures were agitated homogeneously. Films were prepared by the solution casting from the solutions of the mixtures. The solvent was slowly evaporated at room temperature for 2 days in a desiccator cabinet followed by vacuum drying overnight at 60 °C. The crosslinking reaction was performed by heating the film in a vacuum oven at 120 °C for 3 h.<sup>7</sup>

In the preliminary experiment, it was found that the viscosity of blends containing above 40 wt% of MPU was too high to control film thickness and smoothness. The simple blends films containing above 40 wt% of MPU were found to be dissolved completely in water at 37 °C within 48 h. The MPU content should be higher to improve the proper-

Table I. Description and Composition of Multiblock Polyurethane Containing Phospopholipid/Long Alkyl Chain (C-18) (MPU) and Pellethene®(P)/MPU Blends

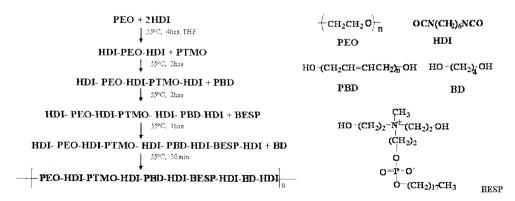
Sample Designation	Composition of Multiblock Polymer (Mole Ratio)		
	HDI/PEO/PTMO/Phospholipid Diol/PBD/BD		
MPU	2.8 / 1 / 0.26 / 1 / 0.04 / 0.5		
	Pellethene <sup>®</sup> /MPU		
P/MPU-5	95 / 5		
P/MPU-10 90 / 10			
P/MPU-20	P/MPU-20 80 / 20		
P/MPU-30	70 / 30		

ties of blends. However, the smooth surface films of Pellethene®/MPU blends were obtained when the MPU content was about 30 wt%, showing that the maximum MPU content in blends was 30 wt% in this study.

Characterization. The composition of blend (Pellethene®/MPUs) film surfaces were analyzed by x-ray photoelectron spectroscopy (XPS: Model ESCA 250 spectrometer). The XPS was equipped with AlKa radiation source at 1486.6 eV and 300 W at the anode. The survey scan, C<sub>1s</sub>, N<sub>1s</sub>, O<sub>1s</sub>, and P<sub>2P</sub> core level scan spectra were taken to analyze the surfaces of blend film. Curve fitting of the spectra was accomplished using a non-linear least squared method. A Gaussian Lorentizian function was assumed for the curve-fitting process.

The thermal dynamic mechanical behaviors of the non-crosslinked blends and crosslinked blends (Pellethene®/MPUs) films were measured at 3 Hz using DMA (DMA MK III, Rheometrics Scientific Inc., USA) with the heating rate of 3 °C/min. The dimension of crosslinked blend film was 5 mm×5 mm×0.2 mm for DMTA measurement.

The water absorption of the crosslinked blend films was examined by measuring the absorbed water content. After the weight of the dried films  $(W_{dry})$  was measured, the films were immersed in the purified water for 24, 48, and 120 h, and then were taken out from the water, wiped with tissue paper, and weighed again immediately  $(W_{wet})$ . Several runs (at least five runs) were made for each sample, and average



Scheme II. Synthesis of multiblock polyurethanes (MPU).

values were taken. Water absorption was determined as follows:

Water absorption (%) =  $(W_{wet} - W_{dry}) \times 100/W_{dry}$ 

The stress-strain measurement was carried out in a sample extension on dumbbell specimens using a tensile tester (United data system, Instron SSTM-1, Japan) at a cross-head speed of 30 mm/min. The Shore A hardness was measured using ASTM D2240.

Platelet Adhesion. The test procedure of platelet adhesion was described previously. 12,20 Briefly, human whole blood was collected from healthy human donors in sodium citrate (3.8%) as anticoagulant. Platelet-rich plasma (PRP) was obtained by centrifuging the blood at 1.500 rpm for 20 min. The crosslinked blend films were hydrated with phosphate buffered saline solution (PBS: pH 7.4) overnight. After removing the PBS, 1 mL of PRP, whose platelet density was adjusted to  $4.55 \times 10^5 / \mu L$ , was added and rotated for 3 h at 37 °C in a shaking incubator. The number of platelet was counted immediately with a Coulter counter (Blood Cell Calculator). The PRP incubated without films was used as a reference. The platelet adhesion (%) was determined from the percentage of the final number of platelet adhered to the film surface area (1 cm $^2$ : 1 cm  $\times$  1 cm) against the reference value. For the scanning electron microscopy observation, the adsorbed platelets were rinsed three times with PBS and then were fixed on the surface by immersing the film in 2.5 v/v% glutaraldehyde at room temperature for 2 h. The platelet adhering to the surface were dehydrated after being treated with gradual ethanol/distilled water mixtures from 50% to 100% ethanol (10% ethanol increment) for 10 min per each step and then dried at room temperature. The dried films were coated using evaporated gold, and the adherent platelets were observed with SEM (HITA-CHI-4200, Japan). Several runs (at least five runs) were made for each sample, and average values were taken.

#### Results and Discussion

Confirmation of Phosphorus Component in the Typical Sample P/MPU-30. XPS measurement is very useful for the characterization of a polymer surface. Figure 1 shows the comparison of XPS spectra of Pellethene® and the typical sample P/MPU-30. The C₁s spectra of Pellethene® and P/MPU-30 samples could be curve-fitted into three peaks assigned to alkyl carbon (-C-C-, binding energy 285.0 eV), ether carbon (-C-O-, 286.6 eV), and carboxylic carbon (O-C-O-, 289.1 eV). The N₁s of Pellethene® shows only one peak of urethane nitrogen (NHCOO, 400.5 eV). However, the N₁s peak of P/MPU-30 sample consists of two combination peaks of urethane nitrogen (NHCOO, at 400.2 eV) and phospholipid ammonium nitrogen (NHCOO, at 400.4 eV). The O₁s peak of P/MPU-30 at 532.5eV is wider than that of the Pellethene®, this should be attributed to the contribution of

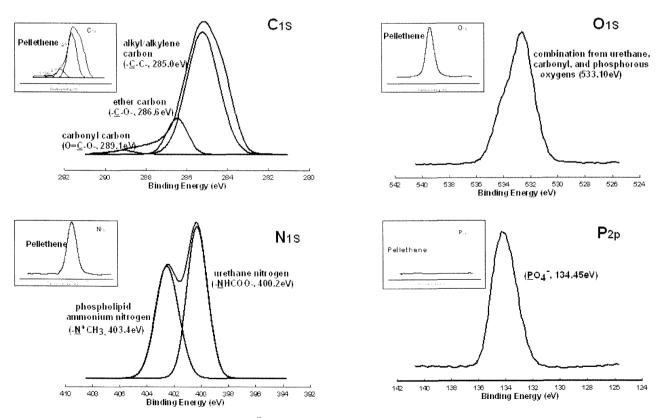


Figure 1. Comparison of XPS spectra of Pellethene® and a typical sample P/MPU-30.

Sample Designation	MPU Content	Tensile Strength (MPa)	Elongation at Break	Initial Tensile	Hardness	
	(wt%)		(%)	Modulus (MPa)	Shore A	Shore D
Pellethene®	_	54	787	20	80	45
P/MPU-5	5	63	1,077	22	83	47
P/MPU-10	10	68	1,223	25	83	47
P/MPU-20	20	72	1.324	30	85	49
P/MPU-30	30	80	1.520	47	88	50

Table II. Sample Designation and Mechanical Properties of the Pellethene® and Crosslinked Blend Films

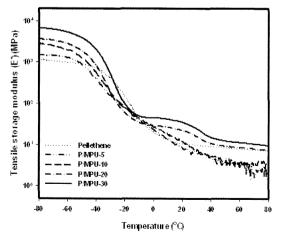
urethane oxygen (N-C $\underline{O}$ O and N-CO $\underline{O}$ ), ester oxygen (-C $\underline{O}$ O and -CO $\underline{O}$ -), and phosphorus oxygen (P $\underline{O}_4^-$ -). Pellethene® does not have P<sub>2P</sub> peak, however, P/MPU-30 sample has a phosphorus peak ( $\underline{P}$ O<sub>4</sub> -, 134.4 eV). These results confirm that phospholipid component is incorporated into P/MPU blend samples.

The XPS elemental composition of Pellethene® and the typical crosslinked blends films surfaces is shown in Table II. As the MPU content increased, the C<sub>1s</sub> spectrum increased, but O<sub>1s</sub>, N<sub>1s</sub> and P<sub>2P</sub> spectra decreased. This unusual phenomenon is attributed to the higher hydrophobic component on the film surface caused by phase separation between hydrophilic and hydrophobic components which was driven by amphiphilic phospholipid and C-18 alkyl chain component. Consequently, it is assumed that the matrix hydrophobic component C-18 alkyl groups are found on the outer surface of the film while the domain hydrophilic groups remain on the inside when the film is formed from blend solutions using THF as hydrophobic solvent.

**Dynamic Mechanical Analysis Result.** The tensile storage modulus (E') and tensile loss modulus (E'') of the Pellethene® and non-crosslinked Pellethene®/MPU blends samples are shown in Figure 2. The E' of Pellethene®/MPU increased with increasing MPU content from 0 to 30 wt%. One of the most indirect ways of examining the texture (i.e., how the phases are arranged in space) and miscibility of blends is observing the change of glass transition. The pure Pel-

lethene<sup>®</sup> had sharp E'' peaks near -40.7 °C assigned to the glass-transition temperature  $(T_{gs})$  of the soft segments. The T<sub>gs</sub> of Pellethene® decreased with increasing MPU content. The glass transition  $(T_{gh})$  of amorphous region with higher order and some polar groups showed a very broad peak near 15 °C. The  $T_{gh}$  increased with increasing MPU content. The decrease of  $T_{gs}$  and the increase of  $T_{gh}$  might be due to the increase of phase separation between soft segment amorphous region and higher order amorphous region containing polar groups. The phase separation should be attributed to the ionic moiety and long alkyl chain of MPU. This result indicated that the Pellethene® is compatible with MPU. The tensile storage modulus (E') and tensile loss modulus (E'')of crosslinked Pellethene®/MPU blends samples are shown in Figure 3. The change of E' and E'' according to temperature was almost the same as that of non-crosslinked blends samples. However, the E' values and their gap in the case of crosslinked samples showed slight increase compared to non-crosslinked blend samples. These increases might be due to the changes of morphology and their structure which occurred during crossliking process.

Effect of Crosslinking Condition on the Tensile Properties. Generally, DCP has been widely used as a crosslinking agent for polyethers such as PEO, PTMO and PPO.<sup>21-23</sup> Biomedical grade polyurethane Pellethene<sup>®</sup> used in this study contains about 50% polyether soft segments. The DCP could be used for crosslinking of Pellethene<sup>®</sup>/MPU containing



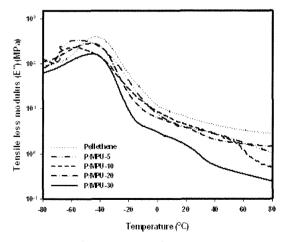
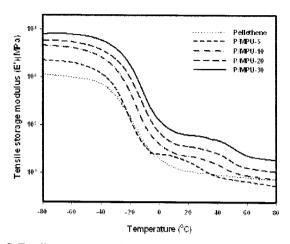
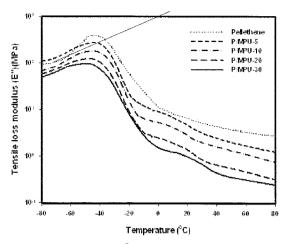


Figure 2. Tensile storage modulus (E') and tensile loss modulus (E'') of the Pellethene<sup>®</sup> and Pellethene<sup>®</sup>/MPU blends samples.





**Figure 3.** Tensile storage modulus (E') and tensile loss modulus (E'') of crosslinked Pellethene<sup>®</sup>/MPU blends samples.

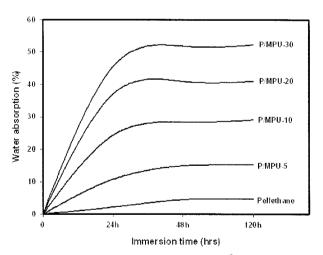
**Scheme III.** The mechanism of crosslinking via dicumyl peroxide (DCP).

PEO/PTMO. The DCP can be easily decomposed by heating or UV irradiation to produce peroxide radicals, which take hydrogen from polyether in Pellethene®/MPUs to generate carbon radicals, resulting in the crosslinking of Pellethene®/ MPU (see Scheme III). The crosslinking reaction was accomplished by heating blends with various DCP content (0-5 wt%) for various treatment times (0-4 h) at decomposition temperature of DCP (120 °C). The optimum DCP content and treatment time was determined from the changes of mechanical properties. The stress-strain results of the crosslinked blend films are shown in Table III. As the crosslinking agent content and crosslinking time increased up to 4 wt% and 3 h, tensile strength and elongation at break increased significantly, and then leveled off. From these results, it was concluded that the optimum DCP content and treatment time were 4 wt% and 3 h, respectively.

Effect of MPU Content on the Tensile Properties and Hardness. Previous studies on biocompatible materials seldom dealt with mechanical properties. The stress-strain curves of the crosslinked blend films are shown in Figure 4. The mechanical properties (tensile strength and elongation at break) and hardness of Pellethene® and the crosslinked

Table III. Effect of Crosslinking Agent (DCP) Content and Time on the Mechanical Properties of the Crosslinked Pellethene<sup>®</sup>/MPU Blend Films

Crosslin	king	Tancila Strangth	Elangation at	
DCP Content (wt%)	Time (h)	- Tensile Strength (MPa)	Elongation at Break (%)	
0	3	45	840	
1	3	58	996	
2	3	65	1,066	
3	3	71	1,139	
4	3	80	1,520	
5	3	79	1,518	
4	1	60	936	
4	2	68	1,057	
4	3	80	1,520	
4	4	80	1,510	



**Figure 4.** Water absorption of the Pellethene<sup>®</sup> and crosslinked blend films after immersion in water for 24, 48, and 120 h.

blend films were compared in Table IV. The Pellethene<sup>®</sup> film had 54 MPa of tensile strength and 788% of elongation at break. These properties of the crosslinked blend films

Table IV. XPS Elemental Composition (%) of Pellethene® and Crosslinked Blend Film Surfaces

Sample Designation	Atomic % <sup>a</sup>			0 /0	N. /C	D /C	
	C <sub>IS</sub>	O <sub>1S</sub>	N <sub>1S</sub>	$P_{2P}$	$O_{1S}/C_{1S}$	$N_{1S}/C_{1S}$	$P_{2P}/C_{1S}$
Pellethene (P)	70.51	26.86	2.63	_	0,3809	0.0372	-
P/MPU-5	74.30	21.03	2.14	2.53	0.2830	0.0288	0.0340
P/MPU-10	75.90	19.74	1.99	2.37	0.2600	0.0262	0.0312
P/MPU-20	78.50	17.82	1.66	2.02	0.2270	0.0211	0.0257
P/MPU-30	79.80	16.22	1.47	1.91	0.2032	0.0184	0.0239

<sup>&</sup>lt;sup>a</sup>Analyzed from survey scan spectra.

were found to be higher than those of the Pellethene® film and increased with increasing MPU content. The increase of tensile strength and elongation at break indicates the compatibility of Pellethene® and MPU molecular chains. The hardness (Shore A and Shore D) of crosslinked blend films also increased a little with increasing MPU content. This might be due to the crosslinking between Pellethene® and MPU molecular chains.

Effects of Crosslinking and MPU Content on the Water Absorption. The water absorption property of biomaterial films is an important parameter in many applications. In our previous study, it was found that the equilibrium water absorption of non-crosslinked blends samples were above 300%, too high for medical devices which comes in direct contact with blood. Therefore, the crosslinking of P/MPU blend samples is essential to reduce water absorption and to increase dimensional stability. Figure 5 shows the water absorption of the crosslinked blend film samples with immersion time. The water absorption increased with increasing immersion time in water at 30 °C, and then leveled off. The water absorption also increased markedly with increasing MPU content. The equilibrium water absorption of crosslinked P/MPU-30 film sample was about 55%, almost the same as that of the tissues of the human body. From this point, the crosslinked P/MPU-30 sample could be a good candidate for blood compatible materials.

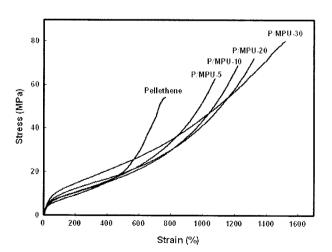
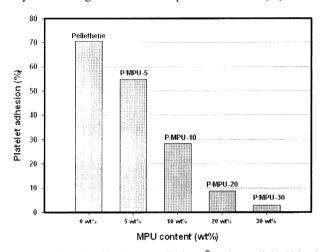
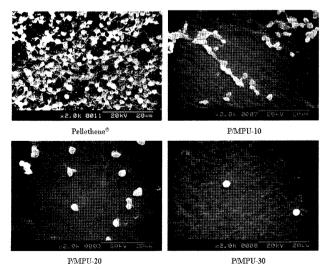


Figure 5. Stress-strain curves of Pellethene® and crosslinked blend films.

**Blood Compatibility.** The alkylation of polymers with C-18 linear alkyl chains has been shown to reduce thrombus deposition at the blood/polymer interface. Munro *et al.* Proposed that the reduction of thrombus formation was a result of albumin adsorbing specifically and strongly to the alkyl chains. Figure 6 shows the platelet adhesion (%) results



**Figure 6.** Platelet adhesion on Pellethene<sup>®</sup> and crosslinked blend film surfaces [platelet number/cm²: platelet density  $(4.55 \times 10^5 \text{ platelet number/}\mu\text{L}) \times \text{volume} (1 \text{ mL}=10^3 \mu\text{L}) / \text{area} (1 \text{ cm}^2: 1 \text{ cm} \times 1 \text{ cm}) \times \text{platelet adhesion} (\%)/100].$ 



**Figure 7.** Scanning electron micrographs of platelet adhering to the Pellethene<sup>®</sup> and typical crosslinked blend film surfaces.

for the pure Pellethane® and the crosslinked blend films having MPU with phospholid moiety/C-18 alkyl chain. The SEM micrographs of platelet adhered to the Pellethene® and typical crosslinked blend film surfaces are shown in Figure 7. As expected, the highest adhesion of platelet was observed on the Pellethene® surface. The platelet adhesion was markedly decreased with increasing MPU content, which indicated that the phospholipid moiety/C-18 alky chain of MPU played an important role to encourage platelet detachment. It is also supposed that C-18 alkyl chains absorb albumin generating albumin layers, thus preventing the absorption of platelets. This is in line with the conclusion of many related previous studies. 16.17 From these results, it was found that the crosslinked Pellethene®/MPU-30 (MPU content: 30 wt%) sample has high potential as a novel material for blood compatible material applications.

#### **Conclusions**

The MPU containing phospholipid moiety/long alkyl chain (C-18) was synthesized by polyaddition reaction using HDI/ PEO/PDMS/Phospholipid diol/PBD/BD. To enhance the mechanical property and blood compatibility of Pellethene®, Pellethene® was blended with MPU (5, 10, 20, and 30 wt%) and then crosslinked using DCP as a crosslinking agent. We reached a finding that the maximum content of MPU for stable Pellethene®/MPU blends was about 30 wt%. The tensile strength and elongation at break increased with increasing crosslinking agent content and crosslinking time up to optimum condition. The optimum crosslinking agent content and crosslinking time were found to be 4 wt% and 3 h, respectively. The XPS analysis confirmed that phsopholipid moieties were incorporated in the surface of the blend films, and that large amount of C-18 alkyl chains existed on the outer surface of film. The water absorption and mechanical properties (tensile strength and elongation at break) of the crosslinked blend film were markedly increased with increasing MPU content. The platelet adhesion on the crosslinked blend film surfaces greatly decreased with increasing MPU content. These results leave us with the conclusion that the crosslinked Pellethene®/MPU-30 (MPU content: 30 wt%) prepared in this study have strong potential as a new material for blood compatible material applications.

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#### References

- (1) J. H. Lee, Y. M. Ju, and D. M. Kim, *Biomaterials*, **21**, 683 (2000).
- (2) A. Korematsu, Y. Takemoti, T. Nakaya, and H. Inoue, *Biomaterials*, 23, 263 (2002).
- (3) K. D. Park, Y. S. Kim, D. K. Han, Y. H. Kim, E. H. Lee, H. Suh, and K. S. Choi, *Biomaterials*, 22, 851 (1998).
- (4) S. L. Cooper, J. Biomater. Sci.-Polym. E, 10, 679 (1999).
- (5) M. D. Lelah and S. L. Cooper, *Polyurethane in Medicine*, FL, CRC Press, 1986, pp 57-110.
- (6) Y. J. Li, T. Nakaya, and Z. Zhang, J. Biomater. Appl., 12, 167 (1997).
- (7) G. A. Abraham and J. S. Roman, *Biomaterials*, 23, 1625 (2002).
- (8) D. K. Han, K. D. Park, and Y. H. Kim, *J. Biomater. Sci. -Polym. E*, **9**, 163 (1998).
- (9) Y. Uyama, K. Kato, and Y. Ikada, Adv. Polym. Sci., 137, 3 (1998).
- (10) W. Marconi, A. Galloppa, A. Mattinell, and A. Piozzi, *Biomaterials*, 16, 449 (1995).
- (11) A. A. Durrani, J. A. Hayward, and D. Chapman, *Biomaterials*, 7, 121 (1986).
- (12) Y. J. Li, K. Mattews, H. M. Kodama, and T. Nakaaya, *Macro-mol. Chem. Phys.*, **196**, 143 (1995).
- (13) A. Korematsu, Y. J. Li, T. Murakami, and T. Nakaya, J. Mater. Res., 14, 378 (1999).
- (14) L. L. Yung and S. L. Cooper, *Biomaterials*, **19**, 31 (1998).
- (15) T. G. Grasel, J. A. Pierce, and S. L. Cooper, J. Biomed. Mater. Res., 21, 815 (1987).
- (16) M. S. Munro, R. C. Eberhart, N. J. Naki, B. E. Brink, and W. J. Fry, *Amer. Soc. Artif. Int. Organs J.*, 6, 65 (1983).
- (17) J. R. Frautschi, M. S. Munro, D. R. Lloyd, and R. C. Eberhart, Trans. Amer. Soc. Artif. Int. Organs, 29, 242 (1983).
- (18) R. S. Edmundson, Chem. Ind. (London), 20, 828 (1962).
- (19) F. E. Bailey and J. Y. Koleske, *Poly(ethylene oxide)*, Academic Press, New York, 1976, p 20.
- (20) J. H. Lee and S. H. Kim, Polymer(Korea), 21, 332 (1997).
- (21) J. G. F. Boats, L. van der Does, and A. Bantjes, *Biomaterials*, 7, 393 (1986).
- (22) J. G. F. Boats, L. van der Does, and A. Bantjes, *Brit. Polym. J.*, 19, 527 (1987).
- (23) E. Brinkman, A. Poot, T. Beugeling, L. van der Does, and A. Bantjes, *Int. J. Artif. Organs*, **12**, 390 (1989).