The Seoul Journal of Medicine
Vol. 35, No. 4: 275-280, December 1994

Effect of Mechanical Deformation on in Vitro Calcification of Segmented Polyurethane

Soo Won Suh[1], Dong Keun Han[2],
Young Ha Kim[2], Byoung Goo Min[1]

Department of Biomedical Engineering[1], College of Medicine, Seoul National University, Korea
Polymer Chemistry Laboratory[2], Korea Institute of Science and Technology, Seoul, Korea

= Abstract = **To investigate why calcification is accelerated by mechanical flexure, in vitro calcification of segmented polyurethane (SPU) under static elongation and dynamic mechanical flexure was performed. After the calcification period, the amount of calcium deposition was increased by elongation, but the amount of calcium deposition per unit area of the elongated surface was relatively smaller as compared to that of the severe flexing area. Although the surface calcium concentration of the elongated SPU was relatively smaller than the flexed area, there was the increase of surface area by the elongation. The total amount of deposited calcium on the elongated SPU was increased as it is reduced to the original surface area. Therefore, the results reveal that certain changes of surface properties by the Mechanical deformation accelerate the calcium deposition onto the surface and the enlargement of surface area by the mechanical deformation results in the heavy calcification of the severe flexing area in the SPU.**

Key Words: *Calcification, Biomaterial, Mechanical deformation Elongation, Artificial organ*

INTRODUCTION

Due to its superior physical, chemical and mechanical properties and its excellent biocompatability, segmented polyurethane (SPU) has been used successfully in many kinds of short or long term implantable biomedical devices such as pacemaker insulator, catheters, vascular grafts, semiocclusive dressings, mammary implants and artificial heart valves because of its superior physical, chemical and mechanical properties and good biocompatibility. Many of these biomedical devices are long-term implanted devices.

The polyurethane elastomers are finding increasing acceptance as the biomaterial of choice in most applications that involve soft tissue or cardiovascular tissue (Szycher et al. 1991). Polyurethane elastomers and silicones are the only two biomedical-grade polymers that approximate the mechanophysical characteristics of human connective tissue. Silicones are biostable, histocom-

† This study was supported by a 1994 research grant from Seoul National University Hospital.
서울대학교 의공학 연구소: 서수원, 민병구
KIST 고분자 화학연구실: 한동근, 김영하

determined using an Inductively Coupled Plasma (ICP, Perkin-Elmer Plasma 40).

RESULTS

The surface morphology of the SPU after calcification is shown in Figure 4 & 5. As shown in The Figure, as incubation time increase, polyurethane surface was covered with calcium/phosphate deposits and the amoumt of the deposit was increased according to the elongation.

After the calcification, the amount of deposited calcium was estimated quantitatively according to the elongation and incubation time. The calcified SPU sheet of the static system and the SPU sac of the dynamic system were cut according to the elongation and the amount of calcium and phoshporus on the sample was measured using ICP. For the samples of the static system, there were no difficulties in cutting the samples according to the elongation. However, in case of the polyurethane sac of the dynamic system, there was no border that separated the areas of the sac having the same deformation. Therefore, the sac had been cut roughly according to it's deformation as shown in Figure 6. It indicates that area 1 and 2 are higher stress regions than area 3 and 4.

The amount of deposited calcium and phosphorus in the static and dynamic systems are shown in Table 1 & 2. The ratio of deposited calcium and phosphorus was about 1.6:1, irrespective of systems (static or dynamic). It means that the deposited compound is similar to HAP (Levy et al. 1983). The amount of calcium deposition was increased along with incubation time, and in both systems the amount of calcium deposition per unit area was also increased according to the elongation rate at the same incubation time. The SPU was more heavily calcified in the dynamic system than in the static system.

DISCUSSION

The amount of calcium deposition per unit area in the static system was increased by the mechanical elongation. Which infers that the surface property of the SPU was changed and become more susceptible to calcification by the elongation; but the difference of calcium depo-

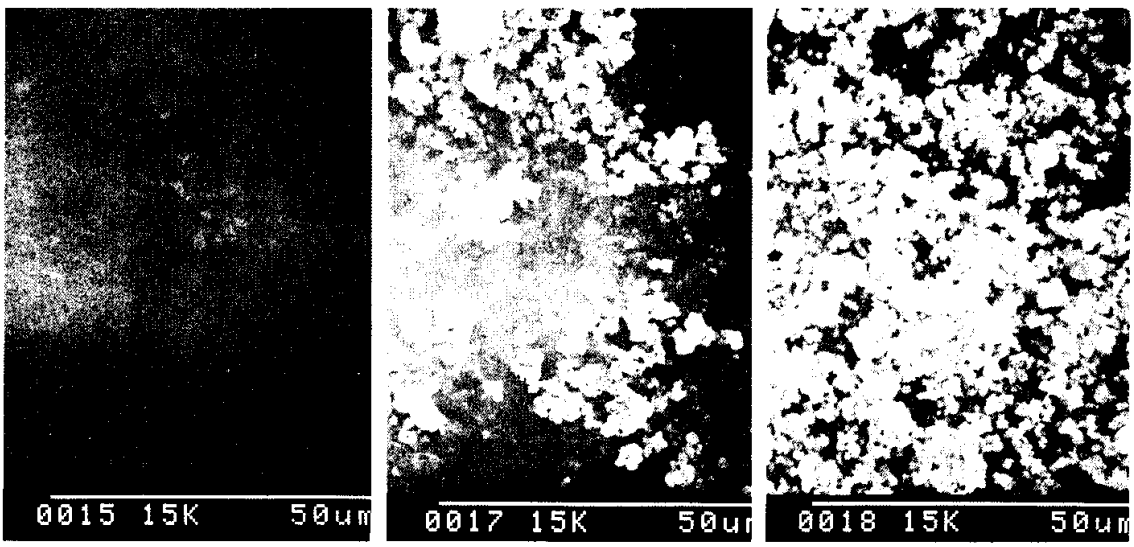

Fig. 4. SEM photograph of the samples incubated in the dynamic system for 30 days: (0) control, (1) Area 3 & 4, (2) Area 1 & 2.

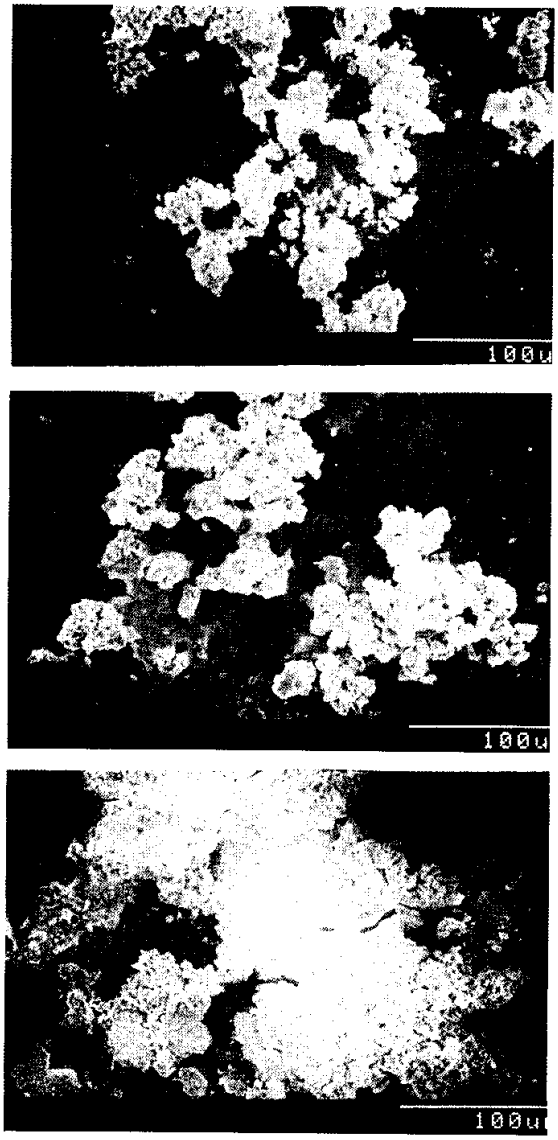

Fig. 5. SEM photograph of the samples incubated in the static system for 30 days: (a) 0% elongation, (b) 50% elognation, (c) 100% elongation.

sition between intact and elongated samples in static system was smaller as compared to the difference between highly flexing and non-flexing regions in the dynamic system. In clinical data, regions of high mechanical flexure are more calcified than other regions of less flexure (Dostal et al. 1990). Therefore, there may be some other reasons responsible for the accelerated calcification of implanted SPUs under the mechanical deformation.

One possible reason for the accelerated calcification of highly flexing SPU is the enlargement of surface area. When the SPU was elongated to the twice the original length (100% elongation), the

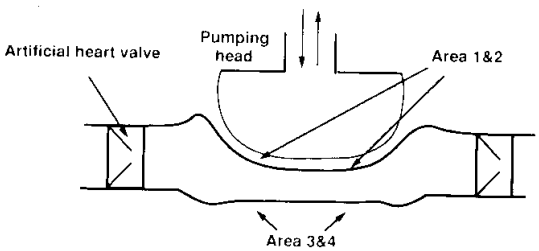

Fig. 6. A schematics of the sac deformation.

Table 1. Surface concentration of calcium and phosphate on the SPU incubated in the static system for 15 & 30 days

elongation / incubation days	Calcium (ug / cm²)	Phosphorus (ug / cm²)
5% / 15 days	13.3 (*3.5)	8.37 (1.5)
50% / 15 days	20.0 (1.5)	12.6 (4.3)
100% / 15 days	21.8 (2.1)	13.7 (1.3)
0% / 30 days	33.2 (3.6)	20.9 (2.3)
50% / 30 days	42.5 (3.0)	26.8 (2.2)
100% / 30 days	46.3 (5.3)	29.2 (3.4)

* S.D., N = 5

Table 2. Surface concentration of calcium and phosphate on the SPU incubated in the dynamic system for 30 days

	Calcium (ug / cm²)	Phosphorus (ug / cm²)
Area 1&2	101 (*8.4)	63 (7.2)
Area 3&4	38 (6.2)	23 (5.1)

* S.D., N = 5

surface area of the elongated SPU sample was enlarged to 147% of the original surface area. After calcification in the synthetic calcium solution for one month, about 85% of the enlarged surface area remained permanantly set, when the sample was taken from the sample holder and the elongation released. Therefore, the total amount of calcium deposited onto the elongated SPU is higher than the presented data when it is reduced to the original surface area.

In conclusion, by the mechanical deformation, the surface property of the SPU changes and becomes more susceptable to the calcification. This change, coupled with the enlargement of the surface area, accelerate the calcification of the surface, resulting in heavy calcification of the highly flexing area of the SPU.

REFERENCES

Coleman DL. Mineralization of blood pump bladders. Am Soc Artif Intern Organs, Transaction. 1981 : 708-13

Dostal M, Vascu J, Sotalova O, Vasku A, Dolezel S, Hartmannova B. Mineralization of polyurethane membranes in the total artificial heart (TAH) : a retrospective study from long-term animal experiments. Int J Artif Organs, 1990 ; 13 : 498

Golomb G. Calcification of polyurethane-based biomaterials implanted subcutaniously in rats : role of porosity and fluid absoption in the mechanism of mineralization J Mat Sci : Materials in Medicine. 1992 ; 3 : 272

Han, DK, Park KD, Jeong SY, Kim YH, Kim UY, Min BG. In vivo biostability and calcification resistance of surface-modified PU-PEO-SO3. J Biomed Mater Res 1993 ; 27 : 1063-73

Henig, E. and Bucherl ES. Mineralization of circulatory devices made of polymers. Polyurethanes in Biomedical Engineering. Elsvier, Amsterdam. 1984 : 109-134

Levy RJ, F. Schoen J, Levy JT, Nelson AC, Howard SL, and Oshry LJ. Biologic determinants of dystrophic calicfication and osteocalcin deposition in glutaraldehyde-preserved porcine aortic leaflets implanted subcutaneously in rats. Am J Pathol 1983 ; 113 : 142-55

Philips RE, Thoma RJ. Metal ion complexation of polyurethane : a proposed mechanism for calcification Polyurethanes in Biomedical Engineering. Elsvier, Amsterdam, 1987 : 91-108

Shunmugakumar N, and Jayabalan M. The pressure induced calcium deposition on crosslinked polyurethanes. Artificial Organs, 1992 ; 16 (3) : 256

Stokes K, Chem B. Envíronemntal stress cracking in implanted polyether polyurethanes. Polyurethanes in Biomedical Engineering. Elsvier, Amsterdam. 1984 : 243-55

Szycher M, Siciliano AA, and Reed AM. Polyurethanes in Medical Devices. Medical Design and Materials. 1991 ; Feb. : 18-25

Thoma RJ. Poly (ether)urethane reactivity with metal ion in calcification and environmental stress cracking. J Biomat Appl 1987 ; 1 : 449-86