

Comparison of Water Absorption and Shore Hardness for Novel Polyurethanes to Bionate®

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Statement of Purpose: Polyurethanes (PUs) are unique and versatile materials that are used in many medical device applications. Recently, PUs have been utilized in orthopedic implants, such as the Tribo-Fit Hip Buffer™ by Active Implants Corporation¹, wherein Bionate® (DSM, Exton, PA) is used as a wear surface for a hip prosthesis. Bionate® PCU is a widely accepted medical-grade polycarbonate urethane, and modified versions of this material are making their way into the medical device industry. As new PUs have been surfacing in the field, Poly-Med, Inc., Anderson, SC., has been developing a series of aliphatic polyurethanes (Theraprene®-P), as disclosed in US Patent Application No. 12/380,391². These PUs demonstrate a wide range of properties that can be tailored for specific medical applications. For instance, initial screening studies of the PUs indicate that these materials mimic properties similar to natural cartilage, especially in regards to water absorption and wear properties. We propose that the PUs can be improved further through chemical modifications, such as cross-linking, in order to obtain more durable materials that still maintain the desired water absorption, coefficients of friction and Shore hardness. We hypothesize that the introduction of cross-linking has a direct effect on water absorption and Shore hardness, and that through careful manipulation the PUs can be synthesized with enhanced properties relative to Bionate® PCU. As shown in Table 1, hard segments for the PUs are derived from hexamethylene diisocyanate (HMDI), ethylene diamine (ED) and tetra-amine.

Methods: Polymers were synthesized by a two-step method, with the exception of PEU8K. Prepolymers were synthesized by reacting soft segments with HMDI using Tin(II) ethyl-2-hexanoate as catalyst at elevated temperature for at least two hours under nitrogen. The second reaction step involved addition of diamine to prepare linear PUs. Crosslinked PEUU1X was synthesized by incorporating tetra-amine during the second reaction step. However, for PEU8K, crosslinking was achieved by extensive heating of the prepolymer. Materials were characterized by DSC, inherent viscosity, and percent water absorption. Certain PEUs were solvent cast into films for Shore hardness testing and compared to published values for Bionate®. Shore hardness was determined for dry and hydrated films. Water absorption was assessed for all materials by weighing polymer samples before and after soaking in deionized water for at least 16 hours at 37 °C.

Results: Table 1 includes test results from I.V. analysis and % water absorption for four PUs. Water absorption ranges from 23% to 128%. Table 2 compares Shore hardness values and percent water absorption of PEUs to published specifications for Bionate®³. As shown, Bionate® demonstrates minimal water absorption.

Conclusions: Interestingly, the polymers with the highest and lowest swelling (other than Bionate®) were the two

cross-linked materials. PEUU1X absorbed 128% of its weight in water, whereas PEU8K absorbed 23%. This

Table 1. Properties and Compositions of Select PUs.

PU Type	Hard Segment	Soft Segment (wt%)	Cross-linking (Y/N)	IV (dL/g)	% Water Abs.
PEUU1	HMDI, ED ¹	70/30 PTMG ⁴ /Pluronic ²	N	6.05	65%
PEUU2	HMDI, ED ¹	70/30 PTMG/PEG8400	N	3.34	88%
PEUU1X (X-linked)	HMDI, ED ¹ , tetra-amine	70/30 PTMG/Pluronic ²	Y (low density)	NA*	128%
PEU8K (X-linked)	HMDI, ED ¹	70/30 PTMG/PEG8000	Y (high density)	NA*	23%
Bionate®	MDI ³	Poly-carbonate	N	--	0.8-1.2%

* - I.V. analysis could not be performed because cross-linked sample was insoluble in HFIP

1 - ED = ethylene diamine

2 - Pluronic = poly(ethylene glycol-block-propylene glycol-block-ethylene glycol), 82.5% PEG

3 - MDI = diphenylmethane diisocyanate

4 - PTMG = poly(tetramethylene glycol)

Table 2. Comparison of Shore Hardness of PUs to Bionate®.

PU Type	Shore Hardness (dry)	Shore Hardness (hydrated)	% Water Absorption
PEUU1	50-58A	34-40A	65%
PEU8K	46-51A	29-42A	23%
PEUU1X	50-72A	35-48A	128%
Bionate®	83A-73D	--	0.8-1.2%

difference could be attributed to PEUU1X being lightly crosslinked, whereas PEU8K was highly crosslinked. The extensive crosslinking in PEU8K would significantly limit the expansion of the bulk polymer upon solvation of polymer chains by water, thereby limiting the overall water absorption. The minimal water absorption reported for Bionate® can be explained by the polycarbonate soft segments, which are less hydrophilic than the polyether materials utilized in PMI's PUs. Future studies will address the percent crosslinking more extensively and the effect it has on water absorption. In addition, coefficient of friction and wear testing will be performed on promising PU candidates that could serve as wear surfaces within articulating joints. Tables 1 and 2 show the differences in composition between PMI PUs and Bionate®, especially demonstrating lower Shore hardness and increased water absorption. These enhanced properties would make these PUs more suitable for articulating surfaces as these properties more closely mimic natural cartilage.

References:

- Steinberg, A., Active Implants Corp., Cushion Bearing Implants for Load Bearing Applications, US Patent No. 7,572,295 B2.
- Shalaby et al., Poly-Med, Inc., Hydroswellable, Segmented, Aliphatic Polyurethanes and Polyurethane Ureas; US Patent Application No. 12/380,391.
- Bionate® Thermoplastic Polycarbonate Polyurethane (PCU), http://www.dsm.com/content/dam/dsm/medical/en_US/documents/bionate%28r%29-pcu-product-sheet.pdf