Biostable, Highly Swellable Polyether-urethane-ureas and Polyether-siloxane-urethane-urea: A Preliminary Report

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Statement of Purpose: Polyurethanes represent a main class of synthetic elastomers used in long-term medical implants as they present tunable chemical and excellent mechanical properties. Polyether-urethane-ureas, a subgroup of elastomeric polyurethanes, have long been considered ideal for use in many implanted devices. The use of aromatic diisocyanate as intermediates in these polymers has been associated with a number of cited drawbacks which include (1) generation of toxic aromatic diamines; (2) thermal degradation and/or crosslinking which limit their use for melt-processable devices; and (3) limited solubility in traditional organic solvents which limit their use for solution castable medical devices.[1,2] However, recent findings at Poly-Med on the attributes of fully aliphatic hydroswellable segmented heterochain polymers, including aliphatic polyether-urethane-ureas and polyether-siloxane-urethane-ureas for the production of novel biomedical devices[3-5] prompted the pursuit of this study. Specifically, the present communication describes the synthesis and evaluation of these polymers for use as cartilage-like materials.

Materials and Methods: Preparation of a biostable polyether-urethane-urea (PEUU) involved a two step polymerization process. In the first step, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPG-PEG), poly(tetramethylene glycol) (PTMG), 1-6-diisocyanatohexane, and N,N-dimethylacetamide (DMAC) were mixed/dissolved and stirred at 100ºC for 2 hours. In the second step, ethylene diamene (EtDA) and DMAC were mixed/dissolved and added to the product of the first step while stirring at room temperature. Preparation of a biostable polyether-siloxane-urathane-urea (PESiUU) involved the same process used in the preparation of PEUU with the exception that 20% of the PTMG portion was replaced with a carbinol terminated polydimethylsiloxane (PDMS). The resulting polymers were purified by precipitation and inherent viscosities were measured. Films were prepared with a thickness of ~0.70 mm by casting from 2,2,2-trifluoroethanol (TFE). Films were hydrated in water for a period of 24 hours prior to burst testing. The burst testing fixture used a 20 mm diameter hole and a ball type plunger with a diameter of 11.40 mm. Physical properties of the films were characterized by swell testing in a 1% methyl cellulose solution for a period of 16 hours at 37ºC. Sample weights were taken pre and post hydration to determine percent weight increase.

Results and Discussion: Two polymers were synthesized/designed to be hydroswellable and biostable. The first of these polymers, PEUU, is almost entirely comprised, by weight, of polyether. The second of these polymers, PESiUU, has a portion of the polyether component in PEUU replaced with a PDMS. PDMS was incorporated to make a more biostable polymer, as polyethers may be susceptible to oxidation. Both of these polymers have been shown to be highly hydroswellable. As summarized in Table I, films made with PEUU and PESiUU have similar swelling properties with a gain of ~64.8% and ~62.6%, respectively, of their original weight in water. However, mechanical testing of the films reveals that addition of the PDMS causes a marked reduction in strength, as noted in Table II. This difference in mechanical strength can be attributed to the PDMS addition as the viscosities of the two materials are very similar.

Table I. Polymer Characterization

Polymer	Swell Testing				Inherent Viscosity (dL/g)
	Sample #	Initial Wt. (mg)	Hydrated Wt. (mg)	% add on	
PEUU	1	0.1334	0.2188	64.0%	4.55
	2	0.1334	0.2201	65.0%	
	3	0.1319	0.2182	65.4%	
PESiUU	1	0.2007	0.3329	65.9%	4.25
	2	0.2036	0.3273	60.8%	
	3	0.1960	0.3158	61.1%	

Table II. Mechanical Properties of Films

Polymer	Film #	Film Thickness (mm)	Peak Load (N)	Ext. at Max Load (mm)
PEUU	1	0.69	136	63.65
	2	0.73	130	63.08
	3	0.70	136	63.53
PESiUU	1	0.71	64	47.55
	2	0.73	83	53.31
	3	0.71	74	50.89

Conclusions: Two polymers (PEUU and PESiUU) were synthesized to have a fully aliphatic structure and were solvent cast into films using a traditional organic solvent. Film swell and mechanical testing revealed properties that suggest the polymers may be attractive for use as cartilage substitute materials, without the drawbacks associated with traditional polyurethanes.

References:

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