Synthesis of Biodegradable Poly(urea urethane) with Controllable Mechanical Properties

Zuwei Ma, William R. Wagner.
McGowan Institute for Regenerative Medicine, Dept. of Bioengineering, University of Pittsburgh, Pittsburgh, PA, USA

Statement of Purpose: Biodegradable elastomers with controllable mechanical properties matching with natural tissues are highly desired. Natural soft tissues are generally soft (low initial modulus), strong (high tensile strength) and resilient (high elongation at break and low permanent deformation). However, the design and development of a soft, strong and resilient biomaterial still remains a challenge [1]. Several biodegradable elastomers have been developed. Linear elastic polyesters such as PCL-co-LA and PTMC can undergo permanent creep easily, while cross-linked polyester elastomers like poly(diol citrates) and poly(glycerol sebacate) have drawbacks of being inherently weak and brittle [1]. Biodegradable polyurethanes with hydrolyzalbe polyester soft segments are tough materials with large elongation at break, but are also subject to permanent creep under long-term mechanical loading [1]. This is because of the weak hydrogen bond-based physical crosslinking between the hard segments. Poly(urea urethane) (PUU) contains urea groups which leads to stronger hydrogen bond interactions between hard segments. PCLdiol (Mw2000) has been used as soft segments for synthesis of biodegradable PUU [2]. The material showed high tensile strength (29Mpa) and elongation break (660%). However, due to the crystalline property of the PCL segments, the material is hard (initial modulus was 78MPa) and non-resilient. The purpose of this study is to synthesize biodegradable PUU which is soft, strong and resilient by controlling molecular structures of the soft segments.

Methods: ε-Caprolactone (CL), δ-Valerolactone (VL) and Trimethylene carbonate (TMC) were used to synthesize soft segment diols, PCL-diol 7200, PTMC-diol (1500, 2500, 5400) and PCL-co-VL50/50-diol (2250, 6000) by ring-open polymerization with diethylene glycol as initiator and $Sn(Oct)_2$ as catalyst. Molecular weight was characterized by NMR spectra. Soft segment PCL-diol 2000 was used as received from Sigma.

PUUs with different soft segments were synthesized using the two-step solution polymerization method described previously [2]. Soft segments diols were first reacted with 1,4-Diisocyanatobutane catalyzed by $Sn(Oct)_2$, followed by adding the chain extender (Putrescine) into the reaction system. The soft segments and PUUs' structure was studied by NMR and DSC. Tensile mechanical testing (10mm/min) was performed.

Results: All the PUUs showed high tensile strength (30-60MPa) and high elongation at break (600-1000%). The PCL-diol 2000 based PUU has the highest tensile strength (60MPa) due to the recrystalization induced by the stretching, which was confirmed by DSC test (Figure1). The PCL-diol 2000 based PUU also showed a high permanent deformation (~700%) because the material's T_m (50°C) is above the room temperature after the stretch (Figure 1). When non-crystalline soft segments PTMC-diol (1500, 2500) and PCL-co-VL50/50-diol 2250 was used, the PUUs showed much lower permanent deformation (80-120%), indicating improved resilience. Permanent deformation of the material can be further decreased to 10-20% by using longer non-crystalline soft segments PCL-co-VL50/50-diol 6000 and PTMC-diol 5400. Longer non-crystalline soft segments also gave lower initial modulus than the shorter ones do (Figure 2). With long crystalline soft segment PCL-diol (7200), the PUU obtained was not elastic at all due to its high crystallinity. The material showed no recovery after stretched (Figure 3). However, if the temperature is increased above 60ºC, the T_m of the PCL, the stretched material showed almost 100% recovery of the original shape, giving a thermal sensitive shape memory material (Figure 3).

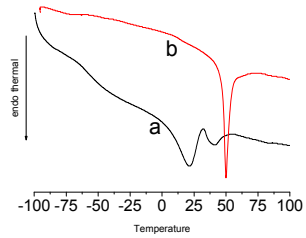

Figure 1. DSC curves of the PUU with PCL-diol 2000 as soft segment. (a) before stretch; (b) after stretch to break.

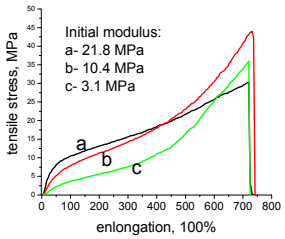

Figure 2. Tensile stress curve of PUUs with (a) PTMC-diol 1500, (b) PTMC-diol 2500 and (c) PTMC-diol 5400 as soft segment.

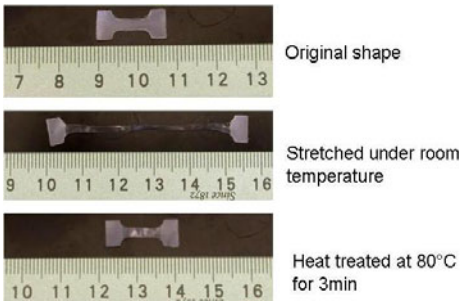

Figure 3. Shape memory property of the PUU with PCL-diol 7200 as soft segment.

Conclusions: PUUs prepared with non-crystalline soft segments are more resilient (lower permanent deformation) than those with crystalline soft segments. Longer non-crystalline soft segments give softer PUUs (low initial modulus) than shorter ones do. Therefore, soft, strong and high resilient PUUs were obtained using long non-crystalline soft segments PCL-co-VL50/50-diol 6000 and PTMC-diol 5400. Long crystalline soft segment PCL-diol 7200 gave a shape memorable PUU.

References:

1. Dey J, Biomaterials 2008;29:4637–4649
2. Guan JJ, J Biomed Mater Res 2002;61: 493–503.