

Characterization of a Polycarbonate-urethane elastomer for orthopedic applications.

⁺Bracco, P, ¹Zanetti, M, ¹Cipriani, E, ¹Costa, L

⁺University of Torino, Italy

pierangiola.bracco@unito.it

INTRODUCTION:

Polyurethane (PU) elastomers are used in a wide range of medical devices thanks to their versatility and peculiar mechanical properties. In the recent past, Polycarbonate urethane (PCU) has also been proposed as a suitable candidate to substitute UHMWPE as a bearing material in arthroplasty. [1,2]

PUs possess more complex chemical structures than many of the most widely produced polymers, such as polyethylenes. They typically comprise three reactive components: a diisocyanate, a soft segment (aliphatic polycarbonate in PCU) and a chain extender. PU elastomers typically show a two-phase structure in which hard segment microdomains are dispersed in a matrix of soft segments. These microdomains act as thermally labile physical cross-linking sites as well as fillers for the rubbery soft-segment matrix. This peculiar structure is responsible for the versatility in physical and mechanical properties. Nevertheless, small changes to this structural organization (induced for example as a consequence of, processing, sterilization, fluids absorption, etc.) can result in significant variations in the mechanical and chemical properties and potentially affect the material performances.

The objective of this study was the characterization of a commercial PCU, with a special attention to the changes induced to its chemical structure by thermal treatments.

METHODS:

The investigated PCU is Bionate[®] 80A (The Polymer Technology Group, Berkley, CA) in the form of pellets and was analysed as-received. One Bionate[®] 80A new acetabular component (Active Implant Corporation, Memphis, TN), not sterile, was also tested for comparison.

Thermogravimetry (TG) experiments were conducted in air and nitrogen, from room temperature to 800 °C at a heating rate of 10°C/min.

Differential scanning calorimetry (DSC) experiments were conducted in nitrogen, from -75°C to various temperatures, up to 250°C, at a heating rate of 20°C/min.

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectra were collected with a diamond crystal, using a resolution of 4 cm⁻¹ and 16 scans per spectrum.

RESULTS AND DISCUSSION:

Thermogravimetric curves obtained from Bionate[®] 80A (not shown) exhibit a quite simple decomposition path: the material starts to decompose at about 230°C, both in nitrogen and in air, and more or less no residue is observed after complete volatilization of the polymer. It must be pointed out that the onset of decomposition is not too far from the suggested processing conditions (180-210°C).

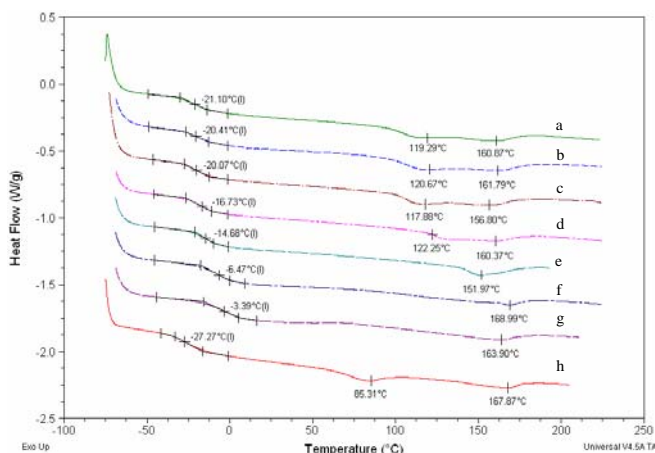


Figure 1

Figure 1a shows the DSC thermogram of the as-received Bionate[®] 80A. Three signals can be identified and, according to literature findings [3], have been attributed as follows: at -21°C the glass transition temperature (T_g) of the soft, polycarbonate-based segment, at 120°C an endotherm phenomenon due to disruption of the short-range ordered domains of the hard-phase, at 160°C an endotherm resulting from the

mixing of hard and soft phases. In order to investigate the thermal stability of this structural organization, DSC experiments were conducted on samples previously heated under nitrogen to: Figure 1b) 80°C, c) 100°C, d) 120°C, e) 140°C, f) 160°C, g) 180°C. It was found that the T_g of the soft phase shifted to progressively higher temperatures, indicating a “stiffening” effect due to incomplete recovery of the original structure after the first heating and suggesting a higher degree of hard-soft segment mixing. Also the first endotherm shifted to higher temperature, suggesting an increase in the average length of the hard segments involved.

Figure 1h shows the thermogram of a sample taken from the acetabular component. Both the T_g and the first endotherm are significantly shifted, compared with those of the original material.

Basically, these results indicate that the structural organization of this material appears to be very sensitive to the thermal history previously given to the material itself (for example during processing). In particular, the acetabular component exhibits quite different characteristics from the pristine material, possibly as a consequence of the manufacturing process and/or storage conditions.

Further DSC and FTIR studies demonstrated that, once perturbed the equilibrium-structure (i.e. by heating), the material tends to re-form a similar structure, but with a very slow kinetic.

Figure 2 shows the FTIR spectra of the original material and those of the same sample heated to 200°C and allowed to cool on the ATR crystal. Spectra have been recorded up to 60 hours after the thermal treatment.

The absorption peak at 1737 cm⁻¹ is characteristic of the soft polycarbonate-based segment (ν C=O carbonate), while that at 1700 cm⁻¹ can be attributed to the ordered, hard polyurethane-based segment (ν C=O urethane, hydrogen bonded). The shoulder appearing at 1720 cm⁻¹ after heating can be attributed to a shift of the latter, due to disruption of the short-range order (including H-bonding). It was observed that the subsequent spectra evolved towards that of the original material, but the equilibrium was not reached during the time-span of the experiment.

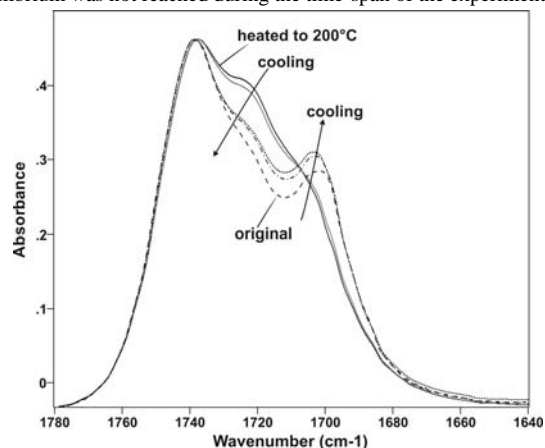


Figure 2

In addition, a residue was found on the ATR crystal once removed the original, unheated, sample. The same residue was observed after extraction of the sample in cyclohexane. Further experiments are in progress in order to investigate the nature of this residue.

It can be concluded that, even though PCU elastomers seem to be promising materials for arthroplasty, they exhibit a strongly significant thermal sensitivity. These preliminary results suggest that, in order to preserve the original properties, a particular care must be observed during processing, sterilization and storage of PCU devices.

REFERENCES:

- 1) Geary et al, J Mater Sci: Mater Med 2008 (19):3355–3363,
- 2) Kurtz et al. ORS 2009, 471.
- 3) Martin et al J Appli Polym Sci 1997 (64): 803-817