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PART XIII

Structure and Properties of Biomaterials
SOFTENABLE, SHAPE-MEMORY THERMOPLASTIC
FOR USE IN BIOMEDICAL DEVICES

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Many implantable biomedical devices could benefit from a material with a strongly temperature-dependent modulus. Catheters made from such a material could be inserted as a stiff plastic, and upon reaching body temperature, would soften dramatically to minimize erosion of adjacent tissue. Sutures could be stiff during placement in an incision, heated slightly to form a shape to hold the suture in place, and then cooled. A new family of materials known as softenable, shape-memory thermoplastics have a distinct and adjustable thermal transition that produces a dramatic change in modulus at a predetermined temperature (range).

Shape-memory is the ability of a material to be deformed into a temporary shape and then returned to its original shape, usually upon heating. Nitinol is an expensive nickel-titanium alloy with well-known shape-memory properties [1].

Calo-MER® softenable, shape-memory polymers achieve their shape-memory properties without the use of covalent crosslinks. Two thermodynamically compatible molecular structural units with different glass transitions will generally combine to give an intermediate Tg which is linearly related to the volume fraction of each unit. This allows systematic variation of Tg for a variety of end uses. They are nonreactive thermoplastics (e.g. polyurethane or polyester thermoplastic elastomers) which may be formed by a variety of economical melt processing methods, including extrusion and injection molding. Compounding with many fillers and pigments gives them versatility without interfering with their shape-memory properties.

THERMAL PROPERTIES

The softenable and the shape-memory properties of Calo-MER® thermoplastics depend upon the glass transition temperature (Tg) of the polymer. At temperatures below the Tg, molecular movement is restricted and the material is rigid and stiff. At temperatures at or above the Tg, the free volume for thermal motion of the molecular backbone increases and the material behaves as a rubbery or high viscosity liquid. For biomedical devices the Tg range of interest is between about room temperature and body temperature (20-37°C) [2,3,4].
A block copolymer in which two chemically-different segments or blocks retain their dominant thermal transition temperatures can exhibit shape-memory properties. The lower Tg of the soft segments or blocks lies within the range of use temperatures and the upper Tg or crystalline melting point (Tm) of the hard segment or block is at a much higher temperature than the use temperature. Figure 1. shows the schematic structure of a shape-memory polymer at various temperatures.

![Figure 1. Schematic Structure of a Softenable, Shape-Memory Polymer at Various Temperatures Relative to Its Two Thermal Transitions](image)

At temperatures above the Tg of the soft block and below the Tg or Tm of the hard segment, the soft block is rubbery and flexible while the hard block is stiff and rigid. The polymer behaves like a thermoplastic elastomer. The chemical structure and molecular weight of the soft segment give it considerable mobility at this temperature so that it easily undergoes viscous deformations and stress relaxation. The rigid block is constrained by lack of free volume and behaves like a springy plastic.

At temperatures below the Tg of the soft block and the Tg or Tm of the hard block, the entire polymer backbone is constrained. At these temperatures the modulus increases dramatically and formed devices made from the material are capable of storing energy that will not be released until one or both of the thermal transitions are exceeded.

At temperatures above the thermal transition of the hard block, the entire polymer chain is a viscous liquid and can be formed by extrusion and injection molding processes into what can be considered the permanent shape of the device. Quenching below the upper processing temperature locks in the shape. Some examples are a catheter that is a concentric tube and straight along its axis, or one that has been formed to have a curved tip. Different permanent shapes can be formed by heating to these temperatures, reforming, and quenching. This process, which occurs
at the melt processing temperature, can also be done at temperatures below the melt processing temperature, but close to the onset of the dominant upper thermal transition, as measured by DSC, for example.

Temporary shapes are "locked into" the device by heating to a temperature between the soft and hard block thermal transitions. In this temperature range, only the soft block is viscous and deformable. Cooling to temperatures below the lower Tg locks in the temporary shape. When the lower Tg is exceeded, the device returns to the permanent shape that was formed during the high temperature process.

Figure 2 shows two possible shape-memory situations. In one case, a tube or rod with a permanent helical shape has been given a temporary straight shape. Upon reaching body temperature, exceeding the lower Tg, the tube releases the internal stresses associated with the temporary shape and winds into a helix. The second case illustrates a temporary helix in an article that is permanently straight. The helix is rigid and springlike at room temperature but softens, uncoils and relaxes at body temperature.

<table>
<thead>
<tr>
<th>SHAPE CHANGE</th>
<th>BELOW LOWER Tg</th>
<th>ABOVE LOWER Tg</th>
</tr>
</thead>
<tbody>
<tr>
<td>STRAIGHT TO CURVED</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CURVED TO STRAIGHT</td>
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</table>

Figure 2. Two Examples of Axial Deformation Shape-Memory

The shape-memory properties in the axial direction described above also exist in the radial direction of a tube as shown in Figure 3. Tubing made from this material exhibits excellent kink resistance compared to the commercially available catheters made from polyurethanes and FEP. If a perfectly round tube is bent or folded at temperatures below the lower Tg, heating above the lower Tg will return the tube to roundness. Another property of shape-memory tubing is diameter change. Either larger or smaller diameters than the permanent diameter can be temporarily locked in, by heating to the intermediate temperature range. Heating to above the lower Tg results in free expansion or contraction to the permanent diameter. An example of large-to-small diameter change
is similar to the diameter change that occurs in heat shrink tubing, except the shrinkage could occur at body temperature. The third example in Figure 3 depicts a small diameter catheter that following insertion into the body, would grow into a larger diameter.

<table>
<thead>
<tr>
<th>SHAPE CHANGE</th>
<th>BELOW LOWER TO</th>
<th>ABOVE LOWER TO</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLAT TO ROUND</td>
<td></td>
<td></td>
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<tr>
<td>LARGE DIAMETER TO</td>
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<td>SMALL DIAMETER</td>
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<tr>
<td>SMALL DIAMETER</td>
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<tr>
<td>LARGE DIAMETER</td>
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Figure 3. Three Examples of Radial Deformation Shape-Memory

Thermomechanical Analysis (TMA) [5] can be used to determine a polymer's thermal transitions. A flat sample is placed in the furnace of the TMA with a probe resting on its surface. As the sample is heated and the transition temperatures are exceeded, the sample softens, and the probe penetrates the sample. Figure 4 is a thermogram of a softenable, shape-memory polymer with a composition consisting of 73% soft segment and 27% hard segment. This actual TMA plot represents the ideal response of a thermoplastic shape-memory polymer, i.e. two nearly horizontal plateaus and two sharp transitions.

Figure 4. TMA of Softenable, Shape-Memory Thermoplastic
PHYSICAL PROPERTIES

Solid-state rheology changes dramatically as the thermal transitions occur. At temperatures below the lower Tg, the polymer exhibits a stress-strain curve typical of a stiff, ductile plastic. At temperatures above the lower Tg, the stress-strain behavior changes to that of a low modulus elastomer. For catheter use, the elastomeric properties are preferred for contact with a blood vessel, but the rigid plastic is required for ease of insertion and placement. Table I lists the changes in the physical properties (mean ± standard deviation, N=5) of a specific softenable, shape-memory thermoplastic as the soft segment Tg = 40°C is exceeded.

Table I. Physical Properties as a Function of Temperature

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Initial Modulus (psi)</th>
<th>Tensile Strength (psi)</th>
<th>Ultimate Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 (Tg-10*)</td>
<td>113000 ± 8000</td>
<td>4800 ± 700</td>
<td>182 ± 30</td>
</tr>
<tr>
<td>40 (Tg)</td>
<td>31000 ± 3800</td>
<td>4000 ± 300</td>
<td>290 ± 10</td>
</tr>
<tr>
<td>50 (Tg+10*)</td>
<td>3400 ± 500</td>
<td>1600 ± 280</td>
<td>350 ± 20</td>
</tr>
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</table>

The rate of softening of an implantable device will depend upon the rate at which the material is heated to body temperature by the surrounding blood or tissue. This, in turn, will depend upon the thickness of the device and the original temperature. For a thin-walled catheter with the soft segment Tg below body temperature, softening will occur very quickly after exposure to a 37°C environment. Such a rapid change would eliminate the advantage of the high modulus as an aid to insertion.

This problem can be avoided by relying on the plasticizing effect of water to lower the Tg following insertion. When the Tg is set slightly above 37°C, little softening occurs immediately following insertion. As water is absorbed by the device, the Tg is shifted slightly lower. It takes several minutes for the Tg to fall to body temperature, at which time the modulus will change dramatically. This allows sufficient time for insertion and placement of the device.

APPLICATIONS

If softenable shape-memory polymers and particulate fillers are combined on a twin-screw extruder, pelletized thermoplastic compounds can be produced that are suitable for a variety of biomedical applications (e.g. catheters, wound closures, endotracheal tubes, etc.). The extent of
modulus change exhibited by a particular compound can be varied through the hard segment/soft segment ratio in the polymer. Devices can be produced by commonly-used methods of melt processing. Permanent shapes can be set in the original conversion process or by postforming in an oven. Temporary shapes can be set by cold forming or by heating above the lower Tg and then quenching in the desired shape. Softenability without shape recovery is achieved by omitting the temporary shape forming step, making the temporary and permanent shapes identical.

Sterilization of biomedical devices made from softenable, shape-memory polymers must be done at temperatures low enough for the temporary shape to be retained, when this shape differs from the permanent shape. If the sterilization temperature exceeds the lower Tg, packaging must be designed to constrain the component during the sterilization cycle. Temperature extremes in shipping product can be handled in the same way.

CONCLUSION

The availability of softenable, shape-memory thermoplastics suited to high-volume methods of polymer processing provides great potential for designers of biomedical devices. With or without radiopaque fillers and pigments, these materials provide a range of moduli previously unavailable in commercial polymers. Their shape-memory properties appear to be unique among thermoplastic polymers and have some of the interesting properties of much more expensive shape-memory metals.

REFERENCES

1. L. McDonald Schetky, Scientific American, 441, (5), 74-82, (1979)