

occur in-vivo after deployment in body fluid. A stent, catheter or cannula can be manufactured from this material, implanted while both ionically and covalently crosslinked, then in-vivo the device will soften as the ionic crosslinks are displaced. A device of this construction would provide stiffness for implantation and softness for patient comfort.

#### EXAMPLE 1

This example illustrates the preparation of tubing from a mixture of sodium alginate (Protanol LF 10/60 from Pronova Bipolymers A. S., Drammen, Norway) and polyvinylalcohol (PVA). A series of four different formulations were prepared as shown in Table 1.

TABLE 1

| PVA/alginate (wt. rat.) | 15/5   | 20/5   | 15/7.5 | 20/5    |
|-------------------------|--------|--------|--------|---------|
| Deionized water         | 72 g   | 67.5 g | 69.7 g | 74.25 g |
| PVA                     | 13.5 g | 18.0 g | 13.5 g | 19.8 g  |
| Sodium alginate         | 4.5 g  | 4.5 g  | 6.75 g | 4.95 g  |
| Bismuth subcarbonate    | 9.68 g | 9.77 g | 9.69 g | 9.9 g   |

The deionized water was weighed into a 4 oz. jar, while stirring the water, the PVA and sodium alginate were added and mixed until uniform. The jar was capped and heated to 100° C. to dissolve the ingredients. The jar was cooled to 37° C., then the bismuth subcarbonate (radiopaque filler) which had been sifted through a 325 mesh screen was added and the composition was mixed with a jiffy mixer until uniform. The samples were loaded into 30 cc syringes, centrifuged to remove air, then extruded through a tubing die into a coagulant solution. The coagulant solution was made from 100 grams of calcium chloride dihydrate, 30 grams of sodium chloride, 50 grams of boric acid and 820 grams of deionized water. The spun tubing was left in the coagulant solution overnight. Lengths of tubing were then soaked in a glutaraldehyde/coagulant solution mixture to covalently crosslink the sample. Glutaraldehyde levels were tested from 0.5% by weight to 12.5% by weight. pH was adjusted to 1.5 using 20% HCL solution. After reacting overnight at room temperature, the tubes were examined and then immersed in 0.4% sodium phosphate solution to strip the ionic crosslinks. Results are recorded in Table 2.

TABLE 2

| Glutaraldehyde (wt %)           | 0.5%           | 1.0%             | 5.0%                    | 12.5%          |
|---------------------------------|----------------|------------------|-------------------------|----------------|
| 15/5 (PVA/Alginate wt. ratio)   | soft, stretchy | slightly stiffer | stiffer, but still soft | stiff, brittle |
| 15/7.5 (PVA/Alginate wt. ratio) | soft, stretchy | slightly stiffer | much stiffer            | stiff, brittle |
| 20/5 (PVA/Alginate wt. ratio)   | soft, stretchy | slightly stiffer | stiff, brittle          | stiff, brittle |

Control samples which were not treated with glutaraldehyde were swollen and broken apart in the phosphate solution.

What is claimed is:

1. A method for forming a shaped medical device, comprising:

exposing a polymer composition to crosslinking conditions such that both ionic and non-ionic crosslinks are formed, thereby forming a crosslinked hydrogel;  
shaping the crosslinked hydrogel to form a shaped, crosslinked hydrogel; and

selectively removing one or more ionic crosslinks from the shaped, crosslinked hydrogel.

2. The method of claim 1, wherein the step of exposing to crosslinking conditions includes providing a crosslinking agent comprising a source of ions.

3. The method of claim 1, wherein the polymer comprises a cationic polymer and the ions are anions selected from the group consisting of phosphate, citrate, borate, succinate, maleate, adipate, and oxalate ions.

4. The method of claim 1, wherein the shaped medical device is selected from the group consisting of stents, catheters, cannulas, plugs, constrictors, and biological encapsulants.

5. The method of claim 1, wherein non-ionic crosslinks are formed prior to forming ionic crosslinks.

6. The method of claim 1, wherein ionic crosslinks are formed prior to forming non-ionic crosslinks.

7. The method of claim 1, wherein the non-ionic crosslinks are covalent crosslinks.

8. The method of claim 1, wherein the polymer comprises one or a mixture of polymers, selected from the group consisting of polyhydroxyethylmethacrylate, polyvinyl alcohol, polyacrylamide, poly(N-vinylpyrrolidone), polyethylene oxide, hydrolyzed polyacrylonitrile, polyacrylic acid, polymethacrylic acid, polyethylene amine, alginate, pectinic acid, carboxy methyl cellulose, hyaluronic acid, heparin, heparin sulfate, chitosan, carboxymethyl chitosan, chitin, pullulan, gellan, xanthan, carboxymethyl starch, carboxymethyl dextran, chondroitin sulfate, cationic guar, cationic starch, and salts and esters thereof.

9. The method of claim 1, wherein the polymer comprises one or a mixture of cationic polymers selected from the group consisting of chitosan, cationic guar, cationic starch, and polyethylene amine.

10. The method of claim 1, wherein the crosslinking conditions comprise providing a crosslinking agent selected from the group consisting of carboxyl, hydroxy, epoxy, halogen, and amino functional groups.

11. The method of claim 1, wherein the crosslinking agent is selected from the group consisting of glutaraldehyde, epichlorohydrin, dianhydrides, and diamines.

12. The method of claim 11, wherein the crosslinking agent is glutaraldehyde.

13. The method of claim 8, wherein the polymer comprises alginate.

14. The method of claim 13, wherein the alginate comprises an ester of a C<sub>2</sub> to C<sub>4</sub> alkylene glycol.

15. The method of claim 14, wherein the alkylene glycol is propylene glycol.

16. The method of claim 8, wherein the polymer comprises a mixture of alginate or pectinic acid and polyvinylalcohol.

17. The method of claim 1, wherein the shaped medical device is in the form of a cylindrical, hollow tube.

18. The method of claim 5, wherein the step of selective removing occurs prior to the step of forming non-ionic crosslinks.

19. The method of claim 1, wherein the step of shaping occurs after ionic crosslinks are formed but before the non-ionic crosslinks are formed.

20. The method of claim 1, wherein the step of shaping occurs after the non-ionic crosslinks are formed but before the ionic crosslinks are formed.