RIGID MATERIALS HAVING HIGH SURFACE AREA AND LOW DENSITY

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to high strength, low density porous bodies derived from nitrogen-containing polymers.

2. Description of the Prior Art

Nitrogen-containing hydrogel polymers, especially chitin and chitosan, have been utilized for many different uses, exploiting their good surface activity and chemical reactivity of the polymers. Chitin is a polysaccharide of poly-N-acetyl-D-glucosamine, which is a constituent material of the outer shells of crustacea, such as shrimp and crab. Chitin is a highly crystalline substance and the intermolecular bonding by its aminoacetyl groups makes the material extremely stable, making chitin highly resistant to solubilization in a wide range of different solvents. Consequently, chitin has been modified a number of different ways to make it soluble and processable. One of such more easily processable derivatives of chitin is chitosan. Chitosan is deacylated chitin and is obtained by heating chitin with concentrated alkali. Chitosan is moderately soluble in water and is easily solubilized in dilute acidic solutions.

There exist many prior art references that disclose different applications utilizing nitrogen-containing polymers, especially chitin and chitosan. Such references include Japanese Patent Specification (Kokai) No. 58-57401, 1983; U.S. Pat. No. 4,125,708 to Masri et al. and U.S. Pat. No. 4,833,237 to Kawamura et al. Kokai No. 58-57401 discloses a process for making porous, granular chitosan bodies that are suitable for such use as chromatographic gels, catalyst carriers and enzyme fixing agents. The process consists of pouring an acidic solution of chitosan and an emulsifier into an aqueous alkali solution while stirring the alkali solution to coagulate and form granular, porous chitosan bodies. However, the resulting granular, porous bodies have a gel-like structure that collapses upon dehydration and has a poor mechanical strength.

Masri et al. discloses sulfite, sulfate, or chloride anion modified chitosan particles that bind superoxy-anion-forming metals, such as chromium, antimony and manganese. The modification process disclosed therein does not involve the steps of dissolving and re-solidifying the dissolved chitosan to form porous bodies, but consists of contacting chitosan particles with an aqueous solution of an appropriate modifying agent such as an acidic form of the above-mentioned anions or salts thereof to produce a compact material. Masri et al. also discloses that the anionically-modified chitosan may be subjected to an additional crosslinking modification, which may be accomplished with a crosslinking reagent, such as glyoxal, glutaraldehyde or dialdehyde starch, before or after the chitosan particles are anionically modified. The modified chitosan, particles of Masri et al. are non-porous particles having a small surface area, making it unsuitable for uses, such as, in high-throughput chromatography applications.

Kawamura et al. discloses a process for producing crosslinked porous chitosan bodies using a low molecular weight chitosan. The process disclosed by Kawamura et al. comprises dissolving a chitosan in an acid, pouring the chitosan solution into a basic solution to precipitate porous chitosan granules, transferring the chitosan granules to a polar solvent, and reacting the chitosan granules with an organic diisocyanate in a polar solvent. The crosslinked porous bodies provide improved strength and porosity. However, the crosslinking process disclosed in the patent subjects the porous bodies to go through a solvent exchange process, in which the porous bodies are exposed to an abrupt change from an aqueous solvent to a polar solvent. This solvent exchange process not only causes portions of the pores to collapse, but also requires additional manufacturing steps that accompanies the solvent exchange process. The collapse of the pores causes the resulting porous bodies to contain uncrosslinked portions that adversely affect dimensional stability of the porous bodies, allowing the porous bodies to shrink and swell upon exposures to different solvents.

SUMMARY OF THE INVENTION

There is provided in accordance with the present invention high-strength, highly porous bodies which are derived from nitrogen-containing polymers, and a process for producing the same. The porous body of the present invention comprises a nitrogen- containing polymer crosslinked with an anionic salt solution and further crosslinked with a covalent-crosslinking agent selected from the group consisting of dialdehydes, aromatic dihalides, formaldehyde, epichlorohydrin, imididates, disulfonyl chlorides, diacid halides, aliphatic dihalides, bisepoxides, diesters, diazides, carbodiimides, aromatic and aliphatic diisocyanates, aromatic and aliphatic diisothiocyanates, bis-azido compounds, 1-fluoro-2-nitro-4-azidobenzene, p-azidophenacyl bromide, N-(azidonitrophenyl)-γ- aminobutyrate hydroxysuccinimide ester, genipin, butene-3,4-oxide, pentafluorobenzaldehyde, chlorobenzaldehyde, fluorobenzaldehyde and mixtures thereof, wherein said porous body has an apparent bulk density of equal to or less than about 0.6 g/cm^3 and a surface area of at least 5 m^2/g.

The porous bodies of the present invention are produced by a process which comprises dissolving a nitrogen-containing polymer in water or an aqueous acid solution, contacting the dissolved polymer solution to an anionic salt solution to form ionically crosslinked bodies, and contacting the ionically crosslinked bodies to a covalent crosslinking agent to further crosslink covalently.

The porous bodies of the present invention exhibit high porosity and low density as well as high mechanical strength and dimensional stability, making the porous bodies to be suitable materials for use as chromatographic support, resins for biomolecule separation columns, fillers, absorbents, adsorbents, filters, membranes, insulation materials and the like.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic drawing which depicts a porous body of this invention and its open-celled 3-dimensional lattice structure. FIG. 1 depicts a section of the open-celled 3-dimensional lattice of a porous body of this invention. The porous body **10** has pores **11**, which form a continuous network of pores.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides highly porous bodies derived from nitrogen-containing hydrogel polymers.