and a crosslinking agent. A generally water-soluble, modified polysaccharide is then added to the mixture, wherein the surface of the modified polysaccharide becomes crosslinked. The water-soluble, modified polysaccharide is swellable in the mixture. The modified polysaccharide is then dried.

The present invention further concerns a surface-crosslinked, modified polysaccharide. The surface-crosslinked, modified polysaccharide comprises a substantially non-crosslinked, generally water-soluble, modified polysaccharide core. Surrounding the core is a crosslinked, generally water-insoluble, modified polysaccharide shell.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** illustrates the apparatus for determining the Absorbency Under Load values of an absorbent material.

FIG. **2** illustrates, in the form of a graph, the results of the physical property testing set forth in Table 1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In one aspect, the present invention concerns a method for producing a surface-crosslinked, modified polysaccharide. The method comprises the steps of forming a mixture comprising water and a crosslinking agent. A generally water-soluble, modified polysaccharide is then added to the mixture comprising water and a crosslinking agent. The water-soluble, modified polysaccharide absorbs at least a portion of the water and crosslinking agent mixture, and the surface of the modified polysaccharide becomes crosslinked. The modified polysaccharide is then dried.

Modified polysaccharides, suitable for use in the present invention, are generally water soluble. As used herein, a modified polysaccharide will be considered to be water soluble when it either dissolves in water to form a true solution or swells in water to such an extent that it appears to lose its initial structure even though a true solution may not be formed. As a general rule, the water-soluble, modified polysaccharides will be free from a substantial degree of crosslinking, as crosslinking tends to render the modified polysaccharides water insoluble.

Modified polysaccharides suitable for use in the present invention include, without limitation, the carboxylated, sulfonated, sulfated, and phosphated derivatives of polysaccharides, their salts, and mixtures thereof. Exemplary of suitable polysaccharides are cellulose, starch, carrageenan, agar, gellan gum, chitin, and the like, and mixtures thereof. The preferred modified polysaccharide is a carboxyalkyl polysaccharide such as a carboxyalkyl cellulose, for example, carboxymethyl cellulose, carboxyethyl cellulose, or the like.

When the modified polysaccharide is a carboxyalkyl cellulose, the carboxyalkyl cellulose suitably has an average degree of substitution of from about 0.3 to about 1.5, preferably from about 0.4 to about 1.2. The degree of substitution refers to the average number of carboxyl groups present on the anhydroglucose unit of the cellulosic material. When the carboxyalkyl cellulose has an average degree of substitution greater than about **0.3**, the carboxyalkyl cellulose is generally water soluble.

When the modified polysaccharide is a carboxyalkyl cellulose, those carboxyalkyl celluloses having a relatively high molecular weight are generally preferred for use in the present invention. Nonetheless, a broad range of molecular weights are suitable for use in the present invention. It is generally most convenient to express the molecular weight of carboxyalkyl cellulose in terms of its viscosity in a 1.0 weight percent aqueous solution at 25° C. Carboxymethyl celluloses suitable for use in the present invention will generally have a viscosity in a 1.0 weight percent aqueous solution at 25° C. of from about 10 centipoise to about 40,000 centipoise or higher, preferably from about 500 centipoise to about 40,000 centipoise, and most preferably from about 1000 centipoise to about 40,000 centipoise.

Preferred carboxyalkyl celluloses have a relatively high degree of substitution and a relatively high molecular weight.

It is generally preferred that the modified polysaccharides be relatively dry when employed in the process of the present invention. It is, however, not necessary that the modified polysaccharide be completely water free. In fact, modified polysaccharides may contain a relatively high weight percent of water prior to the addition of the modified polysaccharide to the mixture of water and crosslinking agent and still be suited for use in the present invention. For example, commercially available carboxymethyl cellulose generally comprises about 8 weight percent water. Applicant has found that, at water concentrations greater than about 500 weight percent (5 grams of water per gram of modified polysaccharide prior to the addition of the modified polysaccharide to a mixture of water and crosslinking agent), the performance of the surface-crosslinked, modified polysaccharides is deleteriously affected.

Modified polysaccharides, in a wide variety of shapes, may be employed in the process of the present invention. Specifically, it is possible for the modified polysaccharide to be in the form of individual particles, flakes, films, fibers, and the like. When the modified polysaccharide is a carboxyalkyl cellulose, suitable carboxyalkyl celluloses are commercially available from a number of commercial sources. Exemplary of such a commercially available carboxyalkyl cellulose is a carboxymethyl cellulose commercially available from Aqualon Company under the trade designation AQUALON™ or BLANOSE™ cellulose gum.

Crosslinking agents suitable for use in the present invention are generally water soluble and comprise a compound having at least two functional groups or functionalities capable of reacting in an aqueous solution with the carboxyl, hydroxyl, and/or amino groups of a modified polysaccharide. The crosslinking agent is suitably selected from the group consisting of metal cations having a valency of at least 3; organic compounds comprising at least two, preferably at least four, carbon atoms and having at least two functional groups or functionalities capable of reacting in an aqueous solution with the carboxyl, hydroxyl, and/or amino group of a modified polysaccharide; phosphoryl chloride; and phosphoryl bromide. Examples of suitable organic crosslinking agents include dialdehydes, dianhydrides, polyamines, polyacids, succinyl dichloride, and the like, and mixtures thereof. Suitable metal cations having a valency of 3 or greater include those of aluminum, chromium, cerium, zirconium, cobalt and the like, and mixtures thereof. The preferred crosslinking agent is an aluminum cation having a valency of 3.

Without intending to be bound thereby, Applicant hypothesizes that it is desirable to employ a metal cation having a valency of at least 3 to encourage intermolecular bonding between adjacent polymeric chains. Applicant has found that crosslinking with a divalent metal ion appears to encourage intramolecular bonding within a single polymer chain rather than intermolecular bonding between adjacent polymer