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Superabsorbent hydrogels via graft polymerization of acrylic acid from chitosan-cellulose hybrid and their potential in controlled release of soil nutrients

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ABSTRACT

Superabsorbent polymers fabricated via grafting polymerization of acrylic acid from chitosan (CTS) yields materials that suffer from poor mechanical strength. Hybridization of chitosan with cellulose (Cell) via chemical bonding using thiourea formaldehyde resin increases the flexibility of the produced hybrid (CTS/Cell). The hybridization process and post graft polymerization of acrylic acid was followed using Fourier transform infrared (FTIR). Also, the obtained structures were homogeneous and exhibited uniform surface as could be shown from imaging with scanning electron microscopy (SEM). Thus, the polymers derived from the grafting of polyacrylic acid from (CTS/Cell) gave rise to much more mechanically robust structures ((CTS/Cell)-g-PAA) that bear wide range of pH response due to presence of chitosan and polyacrylic acid in one homogeneous entity. Additionally, the obtained structures possessed greater water absorbency 390, 39.5 g/g in distilled water and saline (0.9 wt.% NaCl solution), respectively, and enhanced retention potential even at elevated temperatures as revealed by thermogravimetric analysis (TGA). This could be explained by the high grafting efficiency (GE%), 86.4%, and grafting yield (GY%), 750%. The new superabsorbent polymers proved to be very efficient devices for controlled release of fertilizers into the soil which expands their use in agriculture and horticultural applications.

1. Introduction

Hydrogels are a type of crosslinked polymeric materials with high retaining capacity of water. When the retaining capacity of such materials is in the range of several hundreds of their original weight they are categorized as superabsorbents. This depends upon their three dimensional structure and the content of their free hydrophilic polymers. This characteristic feature expands their innovative applications in many areas in particular medicine, food and agricultural field [1–5].

The principal drawbacks of simple hydrogels are their high production cost and poor mechanical properties especially after high water absorption. This depends mainly on the way of their preparation. Major route for hydrogel preparation is through grafting polymerization of hydrophilic vinyl monomers from various polysaccharide backbones [6–15] especially chitosan and cellulose. The interest on chitosan originates from its distinct chemical nature (a partially deacetylated form of chitin) which holds the advantages of chitin and chitosan thus this favors chelation and crosslinking and imparts biocompatibility, bio-degradability, low toxicity and antibacterial action for the superabsorbents derived from it [16–21]. However, the hydrogels derived from grafting of vinyl monomers from chitosan suffer from inferior mechanical integrity which limits their use and restricts any long-term applications of these materials. Several solutions were introduced for solving this problem including inorganic reinforcing filler [22] as well as cellulosic materials or what is so ever in order to increase the mechanical strength along with the handling [23,24].

So we were motivated in the current work to merge the benefits of chitosan and cellulose by following a simple chemical procedure to couple them in one stable hybrid that can serve as integral backbone for post graft copolymerization of acrylic acid resulting in a novel superabsorbent with improved chemical activity, higher water absorption capacity, and elevated mechanical strength as compared to either cellulose or chitosan alone.

Some superabsorbent materials were reported to prolong the fertilizers time frame of release in soil which was for the sake of plants and increased their growth [25]. This is required to ensure

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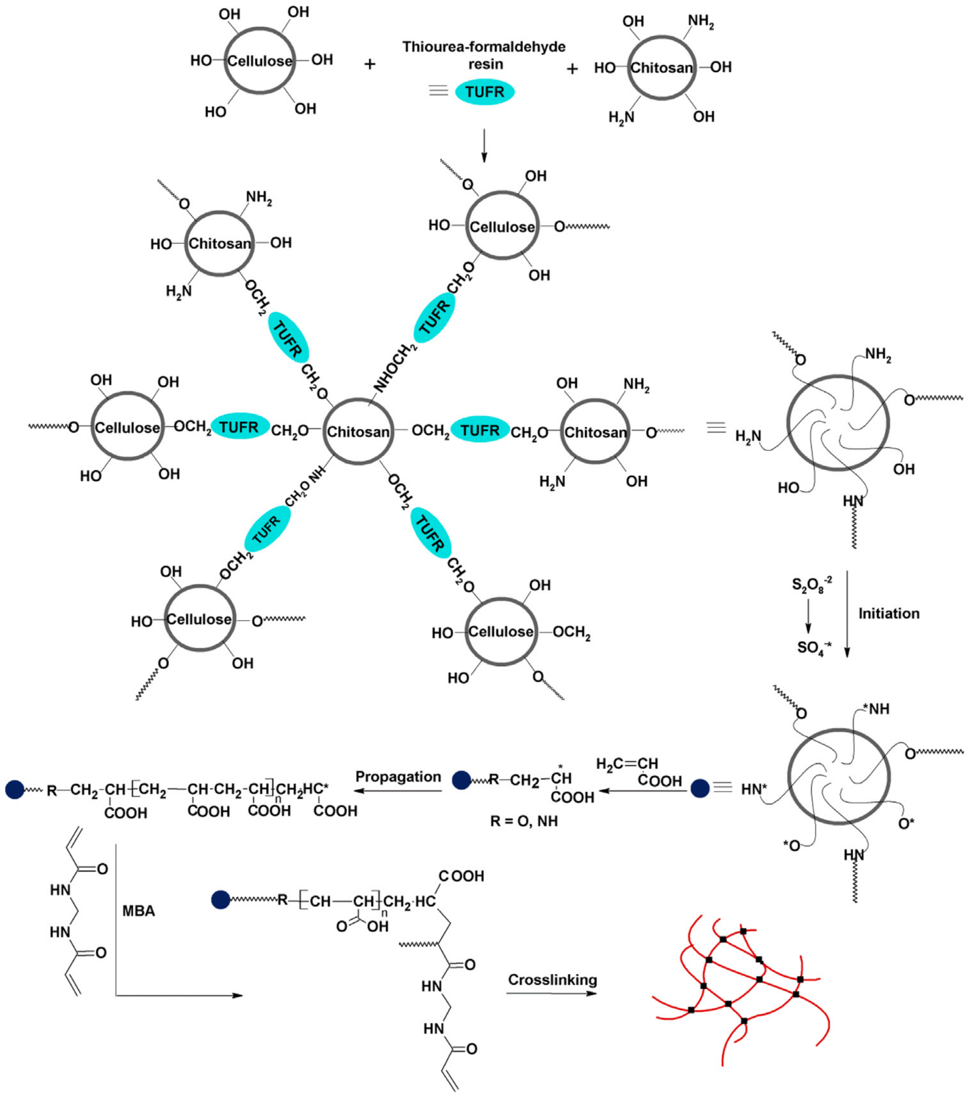

Scheme 1. Steps involved in the coupling of cellulose and chitosan into crosslinked backbone (CTS/Cell) and successive graft polymerization of acrylic acid from this backbone.

steady release of the nutrients according to the plants necessities. The developed superabsorbent in this work is an environment-friendly system and is expected to offer more ability to bind soil nutrients and provide more control over their release, which is useful in agricultural and horticultural applications.

2. Experimental

2.1. Materials

Acrylic acid (AA) and ammonium persulfate (APS) were purchased from Sigma-Aldrich, USA. Chitosan (CTS, with deacetylation above 85%) was purchased from Euromedex, France. Cellulose (Cell) and potassium hydroxide were supplied from Sd. fine Chem., India. *N,N'*-methylenebisacrylamide (MBA) was ordered from Merck, Germany. Potassium dihydrogen phosphate and ammonium nitrate (denoted together as NPK) were bought from Fluka. Other chemicals were all of analytical grade.

2.2. Crosslinked chitosan-cellulose hybrid (CTS/Cell)

A crosslinked structure comprising both chitosan and cellulose was prepared after the method introduced by Chanachai et al. [26]. Briefly, 1.2 g of chitosan was dissolved in 100 mL of 2 wt.% aqueous solution of acetic acid. Similarly, 1.2 g of cellulose was suspended in 100 mL distilled water under vigorous magnetic stirring at 60 °C for 24 h. The dispersion was slightly turbid. Thus, the chitosan solution was filtered and both solutions were mixed together, and the stirring was performed at room temperature for additional 24 h. The resulting solution was poured into a glass plate and dried at room temperature for 4 days then the blend was removed from the plate. At this stage the chitosan became entrapped completely within the cellulose. The blend components were then coupled together through chemical crosslinking by immersing 1 g in a homogenized mixture, representing thiourea formaldehyde resin as a crosslinking agent, including 2.5 wt.% thiourea, 2.2 g formaldehyde solution, and 2.5 wt.% sulfuric acid solution dissolved in 100 mL ethanol-water (1:1) at room temperature for 2 h [26]. The blend particles were washed several times with deionized water and eventually dried at room temperature for 2 days. After drying, the yield was around 1.22 g, and the produced particles were subjected to further grinding and sieved to a size of less than 75 μm.

2.3. Superabsorbent hydrogels derived from crosslinked CTS/Cell hybrid

The superabsorbent hydrogels were prepared under similar conditions to that reported elsewhere [19,24]. Crosslinked (CTS/Cell) particles (1 g) were dispersed in 30 mL distilled water