



Macromolecular Nanotechnology

Strengthening effect of nanofibrillated cellulose is dependent on enzymatically oxidized polysaccharide gel matrices

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ABSTRACT

Galactose oxidase (GaO)-catalyzed oxidation of the terminal galactosyl groups of guar galactomannan (GM) and tamarind seed galactoxyloglucan (XG) results in cross-linking of these polysaccharides via hemiacetal bonds and formation of elastic hydrogels (GMox and XGox, respectively), and enables the formation of aerogels. Nanofibrillated cellulose (NFC) was added at varying quantities to the aqueous GM and XG solutions and was entrapped in the three-dimensional structure of polysaccharides by enzyme mediated gelation. Addition of NFC up to 25% did not hinder the enzyme activity. The reinforcing effect of NFC on hydrogels was measured with rheometer and texture analyzer. The GMox hydrogels with 25% NFC exhibited higher elastic modulus than corresponding XGox hydrogels, but the latter showed higher compressive modulus. On the other hand, the lyophilized GMox aerogels containing 25% NFC showed the highest compressive modulus, 167 kPa. The reinforcing effect of NFC depended on the type of polysaccharides (GM/XG) and state of the material (hydro- or aerogel). Viewing the aerogels with focused ion beam scanning electron microscopy showed that the pores were approximately 125–250 μm in diameter.

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1. Introduction

Polysaccharides are abundant in nature and are sustainable resources for providing raw materials in modern industry. Polysaccharides are polymeric carbohydrate molecules composed of long chains of monosaccharide units linked via glycosidic bonds. Structural diversity ranges from linear to highly branched, and varying monosaccharide composition and molar mass make them versatile candidates for industrial applications. However, the physicochemical properties of polysaccharides are not always optimal for different applications. Enzymatic and chemical modifications, which mildly degrade the structure of the polysaccharides, add new functional groups, or create cross-links, are efficient methods for improving the functionality of polysaccharides and creating novel materials such as hydro- and aerogels [7,19,26,32].

Hydrogels are three-dimensional networks of chemically or physically cross-linked polymers, capable of holding large amount of water. Hydrogels from polysaccharides have many advantages over synthetic polymers, being non-toxic, biodegradable, and biocompatible, and showing peculiar physico-chemical properties suitable for many applications such

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as drug delivery systems [9], biomedical applications such as soft tissue regeneration and delivery of biologically active substances [20], and food materials [22]. Furthermore, hydrogels can be converted into highly porous materials of low density, formed by the removal of liquid from a gel/hydrogel, using techniques that maintain the gel structure. Such porous materials are called either aerogels, supercritically dried gels [18], cryogels, freeze-dried/lyophilized gels [23], or foams [17]. However, the term aerogel is becoming generally accepted for porous gel structures, regardless of whether they are lyophilized or supercritically dried [4,11,30]. During the last few decades, aerogels have drawn increasing attention as thermal and acoustic insulating materials as well as due to their excellent properties for water uptake, pharmaceutical and biomedical media, tissue engineering scaffolds, and packaging materials. As a result, numerous methods and techniques have been developed, so various types of raw materials can be used to form aerogels [11]. Recently, research efforts have focused on the development of materials from environmentally compatible renewable resources. The use of polysaccharides as aerogel matrices presents a great potential for developing bio-based materials [15,25]. Some native polysaccharides have already been studied in terms of aerogel formation: for example, cellulose-based aerogels [13,44] including cellulose nanocomposites [5] and alginate aerogels [37]. However, the conversion of polysaccharide hydrogels into aerogels and the connection between hydrogel texture and aerogel properties are not currently thoroughly understood.

Guar galactomannan (GM) and Tamarind seed galactoxyloglucan (XG) are galactose-containing plant polysaccharides and used in the food industry as thickeners and stabilizers [27,53]. GM and XG contain 40% and 16% terminal galactosyl groups, which are substrates for galactose oxidase (GaO) [52]. After enzymatic oxidation they form hydrogels [31] which can be lyophilized to aerogels [26]. Enzymatic oxidation is an environmentally friendly and safe technique for the derivatization of polysaccharides as the reaction is done in aqueous solution and enzyme only requires molecular oxygen as an electron acceptor.

Enzyme mediated gelation technique opens up new scenarios for preparing composite structures with reinforcing or active compounds within the matrix. The desired reinforcing agent can be mixed in the polysaccharide solution, following enzymatic gel formation to entrap the compounds inside the gel. Nanofibrillated cellulose (NFC) is widely studied as a reinforcing agent in composite materials to modify the materials properties [5,35]. NFC is a nanoscale fibril, generally obtained from chemical pulp by mechanical disintegration, often in combination with enzymatic or chemical pre-treatment of the pulp [1]. NFC is highly crystalline and has a high aspect ratio (3–5 nm wide and up to a few micrometers long), resulting in advantageous mechanical properties. NFC forms an entangled network in aqueous suspensions, which behaves like a gel due to physical gelation [28,29] and forms highly intertwined structure upon freeze drying [30].

Hydrogels in their swollen state behave as solid rubberlike material, and their mechanical and rheological properties depend on the structure of the polymer network and the water bound inside the hydrogel matrix [2,34]. GM and XG interact with NFC differently [12], which may define the structure formation of hydrogels during enzyme mediated gelation and the properties of hydro- and aerogels.

Our purpose is to develop NFC-reinforced polysaccharide-based aerogels with enhanced mechanical properties using the enzymatic oxidation technique. Homogeneous post-mixing of NFC to the hydrogels is difficult due to the high viscoelasticity of both materials. Herein, we present the idea of mixing NFC at different concentrations in GM and XG solutions before enzymatic oxidation to form hydrogels, and conversion to aerogels.

In the present work, the effect of added NFC on the rheological and textural properties of the hydrogels prepared by enzyme mediated gelation was studied, and the function of GM and XG combined with NFC was compared. Hydrogels were further converted into aerogels, and their morphological and mechanical properties were studied and correlated hydrogels' properties.

2. Experimental section

2.1. Materials

Galactose oxidase (GaO) used was from *Fusarium* spp., which was produced recombinantly in *Pichia pastoris*, and donated by Dr. Sybe Hartmans. The specific activity of GaO was 770 U/mg as measured with the chromogenic ABTS assay [46]. Nanofibrillated cellulose was prepared from never-dried birch kraft pulp by mechanical disintegration through a high-pressure fluidizer (Microfluidics, M-110Y, Microfluidics Int. Co., Newton, MA, USA) for six passes. Prior to disintegration, the sorbed metal ions were removed, and the carboxyl groups present in the pulp were converted to sodium form following the procedure described by Swerin [48]. No further enzymatic or chemical treatment was applied. Guar gum galactomannan (GM), horseradish peroxidase (HRP, P8250, Type II, 181 U/mg), and catalase (C30, from bovine liver, 22,000 U/mg) were obtained from Sigma–Aldrich (St. Louis, MO, USA). Tamarind seed xyloglucan (XG) was provided as a gift from Dainippon Sumitomo Pharma, Osaka, Japan.

2.2. Enzymatic oxidation and aerogel formation

GM and XG were stirred in Milli-Q water (10 mg/ml) at room temperature (RT), and the XG sample was heated to 50 °C during mixing. The samples were kept overnight at 4 °C for complete hydration. Nanofibrillated cellulose (NFC, 1% dry content) was added to GM and XG solutions at different ratios (5%, 15%, and 25% of the weight of the polysaccharides) and mixed

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