



Oscillatory rheometric tracing of dextran crosslinking reaction in aqueous semidilute solutions – Effects of formulation on the gelation properties

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ABSTRACT

Rheological characteristics evolved during chemical gelation of semidilute dextran solutions are reported at different temperatures, levels of epichlorohydrin (ECH as a cross-linker), polymer concentration, and amount of catalyst *i.e.*, NaOH. Increasing temperature, cross-linker, polymer and NaOH concentrations, all lead to faster gelation. Gelation at higher temperatures resulted in weaker incipient gels, whereas higher ECH addition or increasing polymer concentration gave rise to higher values of the gel strength parameter *S*. The results disclosed that for all systems the gelation process proceeds over a long time, and both the complex viscosity and the power law exponent reveal that solid-like gel structures are formed in the post-gel region. These results clearly show that the rheological characteristics of the incipient dextran hydrogels can be tuned by changing the conditions of temperature, polymer and cross-linker concentration, as well as the amount of catalyst.

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1. Introduction

Hydrogels can be produced through the introduction of intermolecular cross-links in semidilute aqueous polymer solutions with the aid of a chemical cross-linker [1]. Most of the natural polysaccharides are hydrophilic macromolecules suitable for fabrication of hydrogels that can be readily utilized for medical implants, diagnostics, biosensors, bioreactors, and drug delivery systems since they retain high water contents in their structure like body tissues and are highly biocompatible [2–4]. One important member of this class is dextran [5,6], a linear, bacterial polysaccharide consisting of α -(1 → 6) linked D-glucose repeating units positioned on the main chain with varying proportions of linkages and branches depending on the bacterial species used for its production. This biopolymer consists of repeating units of a single monomer *i.e.*, glucose and can be activated and cross-linked through its hydroxyl groups by a number of chemical methods that are efficient for coupling with other molecules.

Several approaches have been employed to prepare dextran hydrogels, and it is well-known that dextran is easily cross-linked

by various functional organic and inorganic cross-linker [7] such as glycidyl acrylate with *N,N'*-methylene bisacrylamide as an additional cross-linker [8], glutaraldehyde [9], and the commonly used epichlorohydrin (ECH) [5,10]. Crosslinking of dextran with ECH in semidilute solutions in the presence of sodium hydroxide (NaOH) [11] gives commercial products known as Sephadex for gel filtration chromatography and Debrisan, a wound-cleansing agent that significantly shortens the healing process of secreting wounds [6]. In spite of some studies on dextran gelation using ECH, there is a lack of understanding of the macroscopic gelation process occurring at different circumstances like the reaction temperature, and the reactants or catalyst concentration. This systematic information is important for the development of dextran hydrogels for various practical applications.

In the present work, by using rheological methods we investigate the time evolution of dextran gels under the influence of ECH at different conditions of polymer concentration, level of cross-linker addition, temperature, and NaOH concentration. This will facilitate a better understanding of the gelation process for dextran gels and to optimize the settings for producing tailor-made macroscopic gels. This study will show that all the mentioned variables are important for the features of the incipient macroscopic gel. To the best of our knowledge, this is the first study where the impact of catalyst concentration on the gelation features of

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dextran solutions is reported. Furthermore, this is the only systematic investigation where the effects of polymer concentration, cross-linker addition, temperature, and NaOH concentration on the gelation process are compared.

2. Experimental

2.1. Materials and preparation of solutions

In this work, the USP grade dextran 70 ($\bar{M}_n = 45,040 \text{ g mol}^{-1}$, polydispersity index = 1.47) was purchased from Pharmacosmos A/S (Holbaek, Denmark) and it was employed as a precursor for the synthesis. The cross-linker, epichlorohydrin (ECH) was supplied by Merck Chemical Co. (Darmstadt, Germany), and used without further purification. Millipore water was used for the preparation of all solutions.

The aqueous alkaline dextran solutions (12.5–50%w/v of the polymer) were prepared by weighing the components, followed by stirring over night at room temperature to obtain homogeneous solutions. The strong alkaline conditions are necessary to catalyze the cross-linking reaction in the mixture. The used polymer concentrations are all far into the semidilute concentration regime.

Prior to commencement of experiment, the prescribed amount of the cross-linker ECH was added to the sample and a fast homogenization of the solution was performed by stirring, and shortly afterward the experiment was initiated. This was accomplished by shaking the reaction mixture vigorously for 1 min using the vortex mixer before use. The concentrations of the cross-linker used in the

dextran solutions were 4, 6, 8 and 12%w/v. Here, weight-volume percentage refers to the cross-linker weight added to a specific volume of the polymer solution.

The cross-linking in the dextran solutions occurs between intermolecular side-chain reactions of dextran-hydroxyl groups with epichlorohydrin-epoxy group. The chemical structures of the cross-linker and dextran, as well as the proposed mechanism for the main cross-linking reaction are depicted in Fig. 1(a) [12].

2.2. Rheological experiments

Oscillatory sweep experiments were carried out in an Anton Paar-Physica MCR 301 rheometer using a cone-and-plate geometry, with a cone angle of 1° and a diameter of 75 mm. This geometry was employed constantly in all measurements. To prevent evaporation of the solvent, the free surface of the sample was always covered with a thin layer of low-viscosity silicone oil (the value of the viscosity is practically not affected by this layer). The measuring device is equipped with a temperature unit (Peltier plate) that gives an effective temperature control ($\pm 0.05^\circ \text{C}$) over an extended time for the temperatures (25, 30, 35, 40, and 50°C) examined in this work.

To study the influence of temperature on the network formation, the mechanical spectra of dextran solutions were recorded, immediately after the addition of ECH, in a stepwise sequence during the reaction process at 25, 30, 35, 40 and 50°C ; a small strain (γ) of 0.03 was applied to minimize the perturbation of the network during the gel evolution.

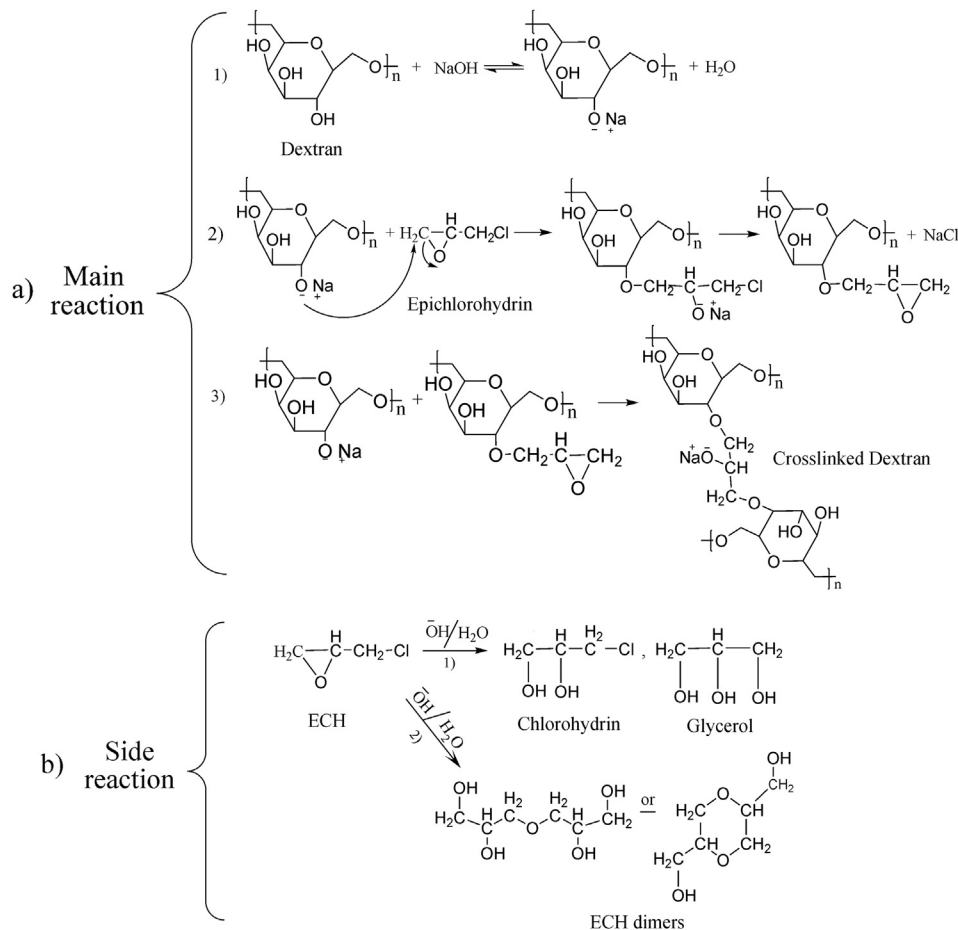


Fig. 1. A schematic representation of the chemical reaction mechanism between dextran and ECH and the possible chemical structures for side reactions products [12].

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