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Molecular mechanisms in deformation of cross-linked hydrogel nanocomposite

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ABSTRACT

The self-folding behavior in response to external stimuli observed in hydrogels is potentially used in biomedical applications. However, the use of hydrogels is limited because of its reduced mechanical properties. These properties are enhanced when the hydrogels are cross-linked and reinforced with nanoparticles. In this work, molecular dynamics (MD) simulation is applied to perform uniaxial tension and pull out tests to understand the mechanism contributing towards the enhanced mechanical properties. Also, nanomechanical characterization is performed using quasi static nanoindentation experiments to determine the Young's modulus of hydrogels in the presence of nanoparticles. The stress–strain responses for chitosan (CS), chitosan reinforced with hydroxyapatite (HAP) and cross-linked chitosan are obtained from uniaxial tension test. It is observed that the Young's modulus and maximum stress increase as the HAP content increases and also with cross-linking process. Load displacement plot from pullout test is compared for uncross-linked and cross-linked chitosan chains on hydroxyapatite surface. MD simulation reveals that the variation in the dihedral conformation of chitosan chains and the evolution of internal structural variables are associated with mechanical properties. Additional results reveal that the formation of hydrogen bonds and electrostatic interactions is responsible for the above variations in different systems.

1. Introduction

Stimuli responsive hydrogel is a promising material in the biomedical industry as sensors and drug encapsulation. These materials are mostly in the form of hydrogels, a three-dimensional polymer network holding large amounts of water. The rapid change in its physical properties when exposed to pH, temperature, magnetic field, UV or electric field can be utilized autonomously in different applications [1–5]. Self-folding is used to obtain complex shapes suitable for drug encapsulation and microgrippers for surgery. Self-folding is achieved with tethered connections or tether less external medium [4]. The folding behavior is dependent on the swelling characteristics of hydrogels [6], porosity [1], attachment of functional groups to the hydrogel backbone, the degree of cross-linking and filler loading. Most importantly, the folding is a function of mechanical properties observed in the material.

Chitosan (CS) is a natural bio adhesive polymer and it is biocompatible, biodegradable and anti-infective. CS is widely used in various fields such as biomedical industry in drug delivery, tissue engineering, wound healing [7,8] and food industry in the form of edible films and food packaging [9]. However, their application in the biomedical industry gets limited because of its poor mechanical properties. The mechanical properties of CS can be enhanced by cross-linking, reinforcing with nanoparticles and by blending with other polymers.

Addition of nano sized fillers into the polymer can alter the mechanical, thermal, barrier properties of polymer material [10–12]. Recent studies have revealed that most of the biopolymers, proteins and tissues interact with filler materials mainly through electrostatic interactions and hydrogen bond formation at the interface [13,14]. Here, hydroxyapatite (HAP) nanoparticle, a biocompatible ceramic material is applied as nanofillers to reinforce chitosan. Though, the mechanical properties of chitosan and interactions between CS/HAP are available in the literature, the absence of detail interaction mechanisms like conformational behavior and hydrogen bond analysis (CS/HAP) during the deformation process have motivated us to perform this work [14,15]. This work will be helpful in engineering the mechanical properties of the CS/HAP system.

Apart from reinforcing hydrogels with filler material, the presence of cross-linking improves the mechanical properties of hydrogels. The mechanical properties of CS and its stability in the different pH media can be enhanced either by ionic or covalent cross-linking [15,16]. In this work, glutaraldehyde (GA) is used as a cross-linking agent. The formation of a three-dimensional network structure improves the mechanical properties and their stability in a solvent medium.

Abbreviations: CS, chitosan; HAP, hydroxyapatite; GA, glutaraldehyde; DOC, degree of cross-linking.

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Though different techniques are used to improve the mechanical properties, we have to compromise with properties like elasticity and swelling behavior. As the filler loading increases, the tensile strength of nanocomposites shows an increasing trend. With further increase of filler loading beyond a critical percentage of nanoparticles, the tensile strength is found to be decreased [17]. At higher cross linker content, the hydrogels turn into a brittle material, which shows reduced swelling behavior [18]. Incorporating nanoparticle into cross-linked hydrogels is a suitable technique to have a material with improved mechanical properties besides efficient swelling behavior. Addition of nanoparticles with hydrophilic groups provides attractive sites for water and modifying the swelling behavior of hydrogels. Therefore, hydrogels reinforced with nanoparticles require a lesser degree of cross-linking. This reduces the effect of cross-linking on water absorption capacity of hydrogels. Therefore, an optimized degree of cross-linking and nanofiller content is required to obtain essential mechanical and swelling properties for self-folding applications.

Self-folding observed in hydrogels is primarily a bending phenomenon because of differentially stressed films [1,4,6]. Uniaxial tension test is the most fundamental technique to determine the mechanical properties. It is one of the simplest tests which can help in modeling the folding behavior of hydrogel in the presence of nanoparticle and cross-linking. Besides understanding the deformation behavior, it is extremely important to explore the interaction mechanisms between hydrogel matrix, nanoparticles and cross-linking agent at an atomistic level. This study can assist in designing hydrogel films with a desired folding nature. Molecular dynamics simulation is used to predict mechanical properties as well as the interaction mechanisms of various materials like collagen/hydroxyapatite, polyethylene and epoxy [13,19,20]. Therefore, we have applied molecular dynamics (MD) simulations to address the deformation behavior and interaction mechanisms. These interaction studies will also be helpful in understanding the self-folding behavior of hydrogels in a trigger based physiological environment.

In this work, we focus on the interaction mechanisms present in HAP/CS matrix with different HAP loading and glutaraldehyde cross-linked chitosan systems. The deformation behavior of particle reinforced hydrogel is dependent on the filler loading and it is evaluated using stress–strain characteristics. The evolution of internal structural variables over the deformation is used to relate the microscopic mechanisms and different regimes observed in stress–strain curves. To explore the interaction between CS and HAP in the presence of cross-linking agent, uncross-linked/cross-linked chitosan chains were pulled along an axis in the vicinity of HAP. Experimentally, the enhancement of

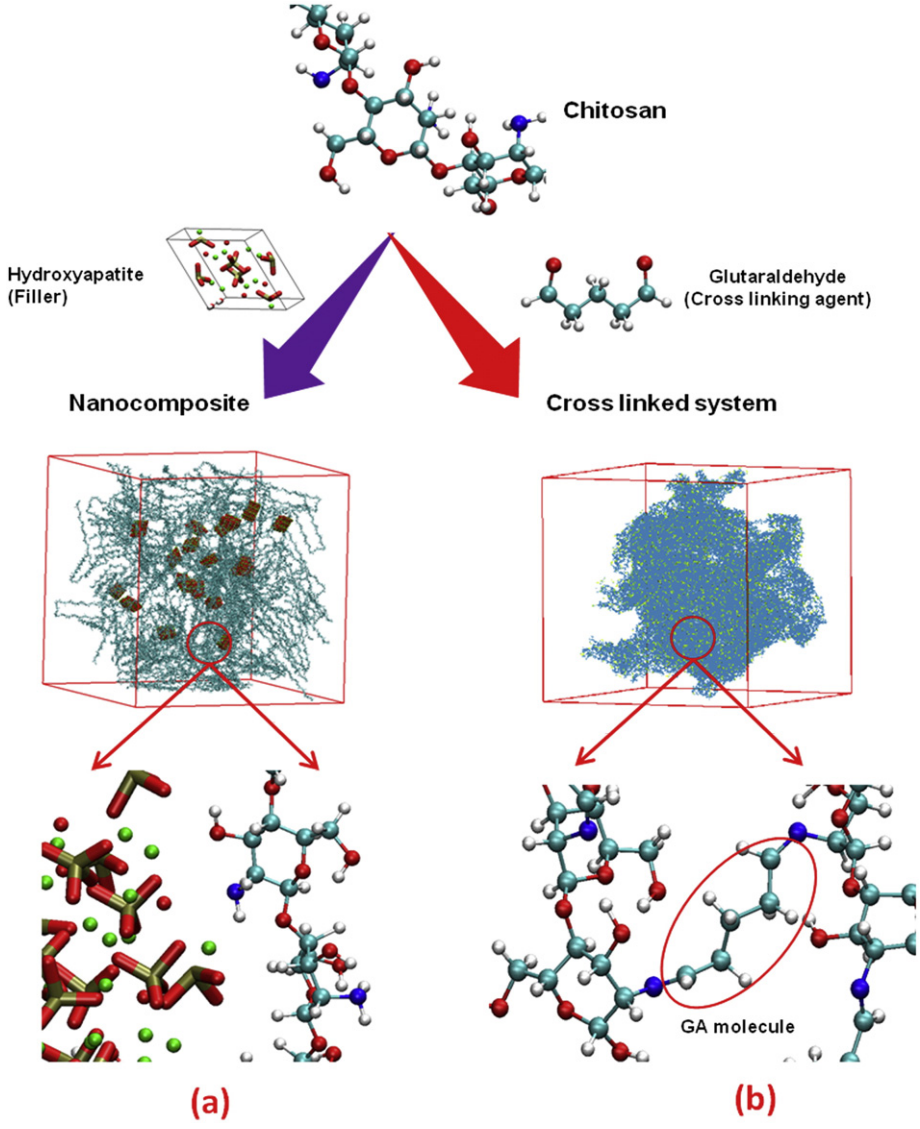

Fig. 1. (a) Chitosan reinforced with HAP (b) chitosan cross-linked with glutaraldehyde (GA). (Cyan — carbon; red — oxygen; white — hydrogen; blue — nitrogen; green — calcium; gold — phosphorous).