Correlation between Viscoelasticity and Microstructure of a Hierarchical Soft Composite Based on Nanocellulose and κ-Carrageenan

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ABSTRACT

A soft composite consisting of a gel (κ-carrageenan) reinforced with two type of nano-cellulose (microfibrillar cellulose, MFC, and nano-crystalline cellulose, NCC) was evaluated using transmission electron microscopy and viscoelastic measurements. MFC addition did not show significant difference as compared to a pure κ-carrageenan gel structure, whereas the addition of NCC promoted aggregation in the κ-carrageenan gel structure.

INTRODUCTION

Soft composites reinforced with cellulose fibers have not been widely investigated. It is known that fibers improve mechanical properties of even a soft material, which can have several applications such as mimicking human tissue for biomedical application[1,2].

K-carrageenan is a polysaccharide extracted from red marine algae. A solution of κ-carrageenan forms strong thermally reversible gels upon cooling in the presence of specific cations such as potassium, sodium or calcium. However, potassium ions have a specific and strong effect on the gel formation [3-5]. Carrageenans have been used in a variety of commercial in food and non-food application [6-8].

Cellulose is another polysaccharide which occurs in plant cell walls. Native cellulose is a semicrystalline fibrillar material containing amorphous and crystalline regions[9]. The entire fiber consists of amorphous and crystalline region known as MFC, microfibrillated cellulose, which can be extracted by mechanical disintegration of the native cellulose [10,11]. In contrast, nano-crystalline cellulose, NCC, only consists of the crystalline region of the fibrills and can be described as rods approximately 200 nm long and 20 nm in diameter. They can be obtained by enzymatic or chemical disintegration of native cellulose to separate the crystalline from the amorphous region[10, 12-15]. The crystalline regions of the microfibrils are responsible for the strong mechanical properties along the longitudinal direction[10, 14-16]. This is one of the reasons why cellulose fibers have been widely used as a structural material in a number of industrial fields and products [10, 11, 14-16].

In this study we have focused on the interaction between the κ-carrageenan and the nano-cellulose and how this influences the final biomaterial structure and viscoelastic properties. Two soft composites were reinforced with two types of nano-cellulose (MFC and NCC). The samples were evaluated using transmission electron microscopy and viscoelastic measurements.

MATERIALS AND METHODS

The κ-carrageenan was supplied in powder form by Danisco (Demark). The powder contained 0.35 w/w% Na^+, 10 w/w% K^+ and 0.16 w/w% Ca^+; indicating the sample is predominantly in the potassium form with very little free salt.

Two different nano-cellulose fibers were used, one semi-commercial microfibrillar cellulose (MFC) kindly provided by Södra Cell and prepared by The Paper and Fiber Research Institute PFI (Trondheim, Norway) and nano-cristalline cellulose (NCC) prepared by sulfuric acid hydrolysis as described by Hasani et al., 2008. The dry weight content in the aqueous suspensions of cellulose fibers was 1 and 1.2 w/w % for MFC and NCC, respectively.

In a constant κ-carrageenan concentration of 0.5 w/w% naturally containing 6.7 mM; 0.09 M of potassium chloride (Merck, Darmstadt, Germany) was added to enable temperature induced gel formation. The suspensions of nano-cellulose fibers and κ-carrageenan were mixed under stirring for 30 min at 90 °C.

The rheological measurements were carried out using an ARES G2 (TA Instruments, New Castle, USA), a controlled strain rheometer equipped with a concentric cylinder measuring system with an 18 mm diameter bob. The hot solutions for the soft composite or the individual component (κ-carrageenan or nano-celluloses) were poured into the cup which was pre-heated to 90°C. The sample was cooled at a cooling rate of 1.5°C/min from 90 to 20°C. The rheometer was used in the oscillatory mode at 6.28 rad/s and 0.1% strain which was in the linear viscoelastic domain. Samples were covered with paraffin oil to prevent evaporation during measurements. Each measurement was performed in triplicate (n = 3).

The samples for the microscopy studies were all prepared using the same preparation procedure. The samples were let to cool from 90 °C to room temperature to allow gel formation. Small pieces of the nano-composite and the κ-carrageenan gel were chemically fixated in 2% glutaraldehyde and 0.1 w/w% ruthenium in the corresponding salt solutions as used for gel preparation. Samples were dehydrated in a grade ethanol series, followed by infiltration in a resin, LR White (TAAB laboratories, Aldermaston, UK), and polymerized. Thin sections of 60 nm were cut using a diamond knife and stained with uranyl acetate and lead citrate. The sections were examined in a transmission electron microscope, LEO 906 E (LEO Electron Microscopy Ltd., Cambridge, UK) at an accelerating voltage of 80 kV.

RESULTS AND DISCUSSION

Effect of the fiber addition on the κ-carrageenan structure and rheological properties

Two soft composite based on κ-carrageenan solution and nano-cellulose ere developed. The mixed of both polysaccharides formed a gel upon cooling in the presence of potassium. The gelation for all samples was monitored by oscillatory measurements as temperature was decreased from 90 to 20°C.

Pure potassium κ-carrageenan

Fig. 1A shows the storage modulus G', of pure 0.5% κ-carrageenan in 0.09 M KCl. An increase in G' up to a pronounced maximum (above 10^3 Pa) at 50°C was observed. After the peak, the storage modulus decreased, and G' stabilized at a lower value (~ 10^2 Pa). This rheological behavior of κ-carrageenan has also been reported by other authors [5, 16]. In our case, κ-carrageenan was able to form a strong gel with modulus above 10^3 Pa at only 0.5% concentration due to the high concentration of potassium in the solution.

Figure 1B shows TEM micrographs of 0.5% κ-carrageenan in 0.09 M KCl. TEM micrograph shows a structure dominated by superstrands. The superstrands formed an open network structure similar to the previously published microstructure of pure κ-carrageenan in 0.1 M KCl [5]. The formation of

the superstrand network structures caused a peak in the storage modulus as also observed for the soft composites in the present study.

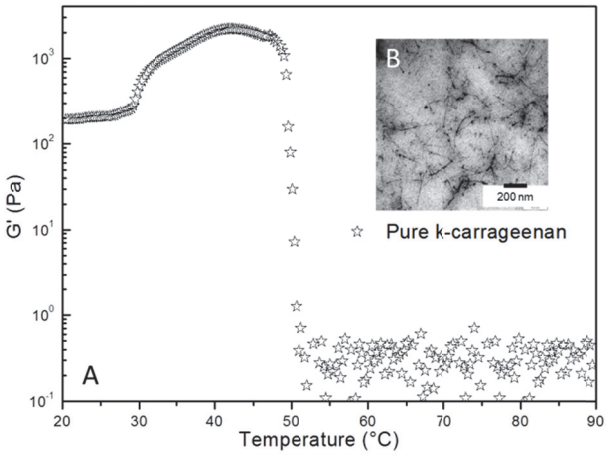

Figure 1. Gelation during cooling (A) and TEM micrographs (B) of pure 0.5% κ-carrageenan in 0.09 M KCl

Soft-composite based on MFC and K^+ κ-carrageenan

Fig. 2A shows the storage modulus G', of 0.5% κ-carrageenan in 0.09 M KCl with 0.25% MFC. An increase in G' up to a pronounced maximum (above 10^3 Pa) at 50°C for all the samples was observed. After the peak, the storage modulus decreased, and G' stabilized at a lower value (~ 10^2 Pa). As compared with the pure κ-carrageenan gel no significant difference was found by the addition of MFC. The soft composite with MFC showed a similar structure and viscoelastic gelation behavior as compared to pure κ-carrageenan (see Figs. 1 and 2).

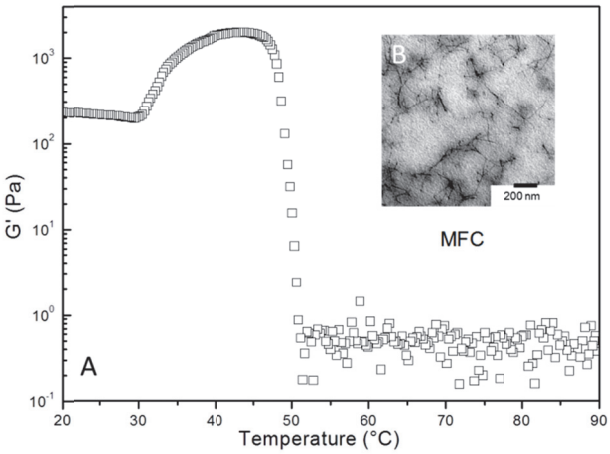

Figure 2. Gelation during cooling (A) and TEM micrographs (B) of 0.5% κ-carrageenan in 0.09 M KCl with 0.25% MFC.

Soft-composite based on NCC and K^+ κ-carrageenan

Fig. 3A shows the storage modulus G', of 0.5% κ-carrageenan in 0.09 M KCl with 0.25% NCC. The addition of NCC led a significant increase in G′ from 90 to 50°C. After that a sudden increase in G′ occurred over a wider temperature range. Finally, the storage modulus decreased, and G' stabilized at a lower value (~ 10^2 Pa) similar to the samples with MFC and pure κ-carrageenan without nano-cellulose.

The NCC soft composite formed a continuous and flexible network structure which filled the whole volume of the sample (Fig. 3B). The superstrands formed were slightly thicker as compared both to the MFC soft composite and to pure κ-carrageenan. We believe that NCC addition promoted the aggregation of superstrands in κ-carrageenan due to that the pores between the superstrands were more evenly distributed and larger than for the pure κ-carrageenan. This is also supported by the sharp peak in G' of the NCC soft composite, see Fig. 3A.

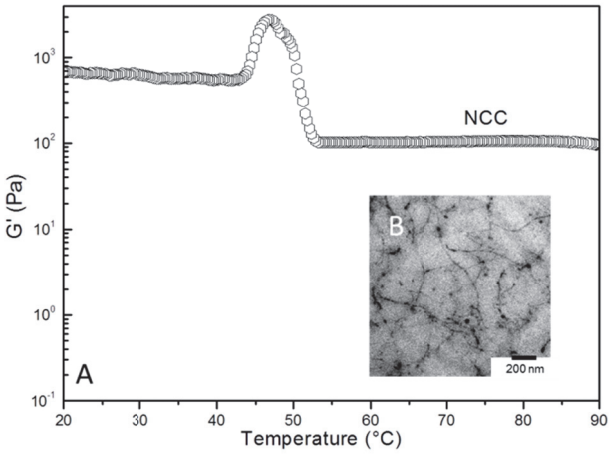

Figure 3. Gelation during cooling (A) and TEM micrographs (B) of 0.5% κ-carrageenan in 0.09 M KCl with 0.25% NCC.

CONCLUSIONS

The viscoelasticity and microstructure of the soft composites comes from both the fiber and carrageenan and is also dependent on the interaction. The soft composite with MFC showed a similar rheological behavior and structure to pure κ-carrageenan. However, a significant increase in G´ and a more pronounced maximum compared to the pure carrageenan gel and the sample containing MFC was observed. NCC addition promoted the aggregation of superstrands in κ-carrageenan.

The results of this study will make it possible to tailor hierarchical biomaterials with specific properties suitable for industrial applications such as strong absorbents, soft bio-mimicking composites or release systems.

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