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For the special issue of ISP2010

DIFFERENT TYPES OF MICROFIBRILLATED CELLULOSE AS FILLER MATERIALS IN POLYSODIUM ACRYLATE SUPERABSORBENTS

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Abstract Microfibrillated cellulose (MFC) is known to provide strong reinforcing effects in polymer nanocomposites, and has also been shown to be highly efficient as a filler material in polysodium acrylate superabsorbents (SAPs), altering swelling and mechanical properties. In this study three types of MFC with differences in structure and surface charge were used at low concentration as filler materials in SAPs. The swelling of the composite hydrogels was determined in 0.9 % NaCl solution as well as in deionized water. The shear modulus of the samples was determined through uniaxial compression analysis after synthesis and after swelling in 0.9 % NaCl solution. Furthermore, the ability to retain filler effects after washing was investigated. The results showed that all of the investigated MFCs had a strong reinforcing effect on the shear modulus after synthesis. The filler effect on swelling, and on the associated shear modulus of swollen samples, showed a more complicated dependence on structure and surface charge. Finally, it was found that the filler effects were reasonably retained after washing and subsequent drying. The results confirm that MFC holds great potential as a filler material in superabsorbent applications. Furthermore, the results provide some insight on how the structural properties and surface charge of MFC will affect gel properties depending on swelling conditions. This information should be useful in evaluating the use of different types of MFC in future applications.

Keywords SAP, MFC, Microfibrillated cellulose, Polyacrylic acid, Hydrogels

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Suggested abbreviated title: DIFFERENT MFCs AS FILLERS IN SUPERABSORBENTS

INTRODUCTION

Hydrogels are a class of materials that has been and currently is researched intensively. This is because of their use and potential in applications such as hygiene products, drug delivery, cell scaffolds, sensing systems, etc. [1-4]. Polyacrylic acid (PAA) neutralized with sodium ions is commonly used in superabsorbent hydrogels as it is cheap and easy to produce. The performance of such polysodium acrylate superabsorbents (SAP) is highly dependent on their swelling and shear modulus (G) [5]. The swelling and shear modulus are in turn strongly connected, as seen from the equation describing the swelling pressure of a gel [6-8]:

$$\pi = \pi_{mix} + \pi_{ion} + \pi_{elastic} \quad (1)$$

where π_{mix} is osmotic pressure from the mixing of the polymer chains with the solvent, π_{ion} is the osmotic pressure derived from counterions within the gel and $\pi_{elastic}$ is the opposing elastic pressure derived from the deformation of the polymer network during swelling. That is, the positive contribution from mixing of the polymer chains with the solvent and the osmotic pressure from the counterions, which are constrained to the hydrogel due to charge neutrality, is opposed by the deformation of the network. Thus, the swelling of a SAP decreases with the ionic strength of the swelling medium and with increasing shear modulus of the swollen hydrogel. Conventionally, the shear modulus of SAPs is varied by the amount of crosslinker incorporated into the hydrogel network, where a high crosslink density corresponds to a high shear modulus.

Much work has been done on composite hydrogels, *e.g.* using different fillers to improve gel properties. One filler material being of great interest is microfibrillated cellulose (MFC), as it has interesting structural properties in combination with the raw material cellulose being abundant and renewable [9-11]. In a previous study we showed that MFC, utilized at low concentrations, as a filler material in SAP was highly efficient in increasing the shear modulus of the swollen gels [5]. The effect of MFC on swelling and shear modulus was in fact equivalent to that of the same mass of conventional covalent crosslinker. However, the structure and surface charge of MFC will differ greatly depending on raw material and method of preparation, and even more so if also including cellulose whiskers and nanocrystals [10, 12-14].

From traditional filler theory the reinforcing effect will be greatly dependent on the aspect ratio of the filler particles, where a high aspect ratio is expected to increase the reinforcement and to cause filler

interactions to become important at lower concentrations [15]. The reinforcing effect is also known to be dependent on the filler-network interactions, where two extreme cases can be identified [16]: 1) No interactions; at small deformations this results in a decrease in gel modulus with volume fraction of filler. 2) Strong interactions; at small deformations this results in an increase in gel modulus with volume fraction of filler. For swelling systems the strength of the filler-network interactions will determine the degree to which the filler modifies the equilibrium swelling of the systems. For perfectly adhering, *i.e.* strongly interacting systems, the swelling of the polymer network will be restricted at the filler-network interface but will be increasingly unaffected with increasing distance from the filler. On the other hand, for non interacting systems, swelling will cause detachment of the network from the fillers, creating a liquid vacuole around the fillers [17, 18]. This liquid vacuole will cause an overestimation of the network swelling if determined from sample mass, and should cause a decrease in shear modulus. For interactions in between the two extremes, the limiting effects on swelling will be increasing with increasing filler-network interaction, as reasoned in the work by Kraus [17].

In the special case of nano-fillers, the surface area per mass is very high, and the distance between filler particles is small even at low volume fractions [5, 19]. This will cause the interfacial filler-network regions to occupy large volume fractions and to percolate at relatively low concentrations of filler [18]. However, it has also been shown and stated that nano-fillers are not very “nano” when utilized in composites [20]. Ubiquitous aggregation was reported to cause nano-fillers with different structural properties to actually behave similarly in most cases.

In this study we investigated how three different types of MFC, having differences in structural content and surface charge (see Materials section), differed in their reinforcing effect when used at low concentration as filler materials in superabsorbents. The swelling of the samples was investigated in deionized water and in 0.9 % NaCl solution using gravimetric analysis. The shear modulus of the samples was determined using uniaxial compression analysis. Finally, the reinforcing effect after washing and drying was investigated.

EXPERIMENTAL

Materials

The three different types of microfibrillated cellulose were: MFC1 bought from the Paper and Fibre

Research Institute PFI, Trondheim, Norway. MFC1 had been prepared from commercial bleached kraft pulp using a mechanical pre-treatment followed by homogenization according to Eriksson et al [21]. MFC1 has previously been characterized as highly heterogeneous, having structural content ranging from micro to nanoscale [5]. MFC2 prepared from softwood sulfite pulp through a pre-treatment step involving enzymatic degradation and mechanical beating, followed by a homogenization process using a Microfluidizer M-110EH (Microfluidics Ind., U.S.A.). MFC2 nanofibers have a width in the 10-40 nm range and a length of several micrometers, as previously described [22]. MFC3 prepared by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation combined with one pass through a Microfluidizer. The resulting nanofibers have a regular width of 4-5 nm and a length of several micrometers. Furthermore, MFC3 has a high carboxylate content (negative surface charge) compared to MFC1 and MFC2, this due to the conversion of primary hydroxyl groups to sodium carboxylate groups during the TEMPO-mediated oxidation [23].

The following used chemicals were of analytical grade and were used as received; acrylic acid [AA] (Fluka, Belgium), N,N'-methylenebisacrylamide [MBA] (Sigma-Aldrich, Germany), sodium chloride (Sigma-Aldrich, Germany), sodium hydroxide (Sigma-Aldrich, Germany), potassium persulfate [KPS] (Sigma-Aldrich, Germany). Used H₂O was of Milli-Q grade.

Methods

Synthesis

The SAP hydrogels were synthesized by free radical copolymerization as follows: A stock solution of AA was drop wise neutralized on ice, to 60 mol%, with 30 w/w NaOH solution. The MFC suspensions were diluted to the same concentration (0.87 % w/w) using Milli-Q water. To the neutralized AA stock solution the crosslinker MBA was added for a MBA:AA ratio of 1:1000 followed by addition of KPS to a concentration of 39 mmolal, all on ice. To Erlenmeyer-flasks containing 4.7 ml of the different MFC suspensions (or pure H₂O) 5.3 ml of the stock solution was added. The mixtures were bubbled with N₂ gas under stirring while kept on ice for about 30 minutes. The samples were then immediately transferred to 7x40 mm autosampler vials (NTK KEMI), which were placed in a water bath at 70 °C for 6 h for the synthesis solutions to polymerize. Finally the samples were allowed to settle over night at room temperature before breakage of the vials and further analyses.

Shear modulus determination

The shear modulus of the gels was determined as previously described [5]. Briefly, gel cylinders were analyzed using uniaxial compression. For the uniaxial compression of Gaussian chain networks the following equation is valid [24]:

$$P = G(\alpha - \alpha^{-2}) \quad (2)$$

where P is the pressure, G is the shear modulus and α is the ratio deformed length to initial length. For deformation ratios up to 20 % the shear modulus was determined as the slope of the linear region in the graph P versus $(\alpha - \alpha^{-2})$, similar to previous works [5, 25-29]. The non linear data for low strains was discarded as it is derived from imperfect geometries of the sample ends [27, 29].

Swelling analysis

Samples were prepared for swelling by cutting of and discarding the uppermost part of the gel cylinders. For samples to be swollen in NaCl solution after synthesis, the weights were recorded and the theoretical dry weights were calculated, assuming a yield of 100% from the synthesis, as previously described by others [30, 31] and by us [5]. Samples were swollen for 6 days in 900 ml 0.90 % NaCl solution or in 5 l deionized water, after which their equilibrium weights were recorded. The deionized water was replenished daily (washing). After the washing, the samples were dried at 80°C and the dry weights were determined. Washed samples were again swollen in NaCl solution, as described above. The swelling degree was calculated as:

$$Q = \frac{m_{eq} - m_{dry}}{m_{dry}} \quad (3)$$

where m_{eq} is the mass of the swollen gels and m_{dry} is the mass of the dry gels, calculated or measured.

RESULTS AND DISCUSSION

Synthesis of Hydrogels

During the preparation of synthesis solutions containing the different MFCs, it was observed that the synthesis solution containing MFC3, prepared by TEMPO-mediated oxidation, was rather heterogeneous. The solution contained regions of more gel like character in combination with more liquid regions. Probable causes for this behavior are entanglement of the cellulose fibers, due to their very small diameter and high aspect ratio and incompatibility of the negatively charged surface of the MFC3 fibers with the acidic synthesis solution. MFC1 and MFC2 were more homogeneously dispersed, even though

the MFC2 containing synthesis solution was more viscous than the one containing MFC1. Despite the differences between the three synthesis solutions, high quality gels were produced, appearing homogenous on the macroscopic scale (see Fig. 1). The visual appearances of the gels were; MFC1 – opaque, MFC2 – slightly opaque and MFC3 – clear with some diffuse light scattering effects dispersed through the gel. In conclusion, MFC1 was the easiest to handle during synthesis, MFC2 was manageable, whilst MFC3 was out right difficult to use.

Shear Modulus after Synthesis

The analysis of the shear modulus after synthesis revealed that all of the used MFCs had a strong reinforcing effect on the hydrogels; with MFC2 having the greatest effect (Fig. 2). To evaluate the reinforcing effect, the increase in modulus was compared with traditional hard filler theory for spherical fillers, utilizing the simple Einstein-Smallwood equation [32]:

$$G = G_m(1 + 2.5\phi) \quad (4)$$

where G_m is the shear modulus of the matrix, and ϕ is the volume fraction of filler. Assuming a density of 1 g / cm³ for the filler and the gel matrix, the reinforcing effect of the MFCs is approximated to be 30-60 times greater per volume fraction of filler than expected for hard spherical fillers. Finally, the small error bars presented in Fig. 2 also indicate that the samples are of good quality, homogeneous on the macroscopic length scale, this despite the inhomogeneous appearance of the synthesis solution containing MFC3.

Hydrogel Swelling

To evaluate how the different MFCs influenced the equilibrium swelling degree (Q) of the SAPs, swelling studies were conducted. Samples were swollen in 0.90 % NaCl solution and in deionized water (washing) for 6 days, at which point the samples were close to equilibrium. In addition, washed samples were swollen in 0.9 % NaCl solution to evaluate if the reinforcing effect remained after swelling. As seen from Fig. 3a, the swelling in 0.9 % NaCl solution was reduced with the addition of all investigated MFCs. The swelling after synthesis was reduced similarly much by MFC1 and MFC2, whilst MFC3 had less impact on the swelling. For swelling in deionized water MFC2 reduced the swelling the most, whilst MFC1 and MFC3 had less effect on the swelling (see Fig. 3b). For the re-swelling of washed samples in 0.90 % NaCl, again looking at Fig. 3a, it is seen from the increase in swelling that some of the reinforcing effect had been lost. However, much of the filler effect still remained, in particular for MFC2.

Taken together, the swelling of samples in deionized water and of washed samples indicates that upon washing some of the interactions between filler and matrix were destroyed. Furthermore, it seems from the swelling data as if the reinforcement of MFC2 was less affected by washing, possibly due to a stronger filler matrix interface leading to less detachment of the matrix from the filler during washing.

Shear Modulus after Swelling

To evaluate the mechanical performance of the swollen hydrogels, non-washed samples swollen in 0.90 % NaCl were subjected to uniaxial compression analysis and the shear modulus (G) was determined. As seen in Fig. 4, all of the MFC containing samples displayed an increased shear modulus. In addition the order of the modulus was well in agreement with the swelling results. MFC1 and MFC2 containing gels displayed a similarly high modulus, for the MFC3 containing gels, the modulus was still increased as compared to pure SAP, but not nearly as much as for MFC1 and MFC2. In order to evaluate the actual performance of the samples, i.e. the modulus at a given equilibrium swelling degree, the shear modulus at equilibrium swelling was compared with the data from our previous work [5] in a plot of $\log G$ versus $\log Q$ (Fig. 5). In that work, MFC1 was used as a filler material at different concentrations in SAP gels with different degree of crosslinking. For a swollen polymer network, where only the degree of crosslinking changes, such a plot of $\log G$ versus $\log Q$ should be linear if only the degree of crosslinking changes within the network [33-35]. As seen in Fig. 5, the data points from this study correlates well with the data from our previous work. It can be concluded that even though MFC3 had somewhat less reinforcing effect on swollen hydrogels than MFC1 and MFC2, all of the investigated gels displayed a shear modulus at equilibrium swelling similar to what would be expected for samples with traditional covalent crosslinker at the same equilibrium swelling.

CONCLUDING REMARKS

In this study we investigated how microfibrillated cellulose prepared by different methods, having differences in structural content and surface charge, performed when utilized as filler materials in superabsorbent polysodium acrylate hydrogels. All of the investigated MFCs showed a strong reinforcing effect on the hydrogels after synthesis. However, for swollen samples MFC prepared by TEMPO mediated oxidation was the least effective in altering the gel properties, despite its very small dimensions and high aspect ratio. This is most likely due to repulsion between the negatively charged surface of that

MFC and the negatively charged polymer network, i.e. the filler-network interaction is weak and is disrupted during swelling. The MFCs prepared by purely mechanical treatment and enzymatic pretreatment showed similar reinforcing effect on non-washed samples swollen in NaCl solution. However, in deionized water the enzymatically pretreated MFC showed a greater reinforcing effect, possibly due to the more homogeneous high aspect fiber content. The enzymatically pretreated cellulose also retained the most of the reinforcing effect after washing, this being important for many applications. All investigated samples showed shear modulus at their equilibrium swelling that would have been expected if addition of covalent crosslinker had been used to achieve the same equilibrium swelling. This indicates that the gels were of good quality with good structural integrity. Finally, for applications it is concluded that MFC prepared by TEMPO-mediated oxidation probably is not very suitable to reinforce negatively charged hydrogel networks. This given its limited reinforcing effect compared to the other MFCs in combination with it being difficult to handle during gel synthesis. On the other hand, both purely mechanically prepared and enzymatically pretreated MFC shows good potential as reinforcement materials in SAP gels. For applications where samples need to be washed under high swelling conditions and where a reinforcing filler material is wanted, it seems as if the enzymatically pretreated MFC would be beneficial to use. However, additional more detailed studies on different MFCs should be performed to substantiate this observation.

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FIGURE CAPTIONS

Fig. 1 Photograph showing synthesised gels with the different MFCs and a pure SAP gel as reference.

Fig. 2 Shear modulus after synthesis for gels with the different MFCs and for pure SAP gels. Error bars indicate Min/Max (n = 2).

Fig. 3 (a) Equilibrium swelling degree in 0.90 % NaCl per calculated dry weight for samples swollen after synthesis (grey, error bars indicate Min/Max, n = 2) and per real dry weight for washed samples (black). (b) Equilibrium swelling degree in deionized water.

Fig. 4 Shear modulus for gels with the different MFCs and for pure SAP at equilibrium swelling in 0.90 % NaCl. Error bars indicate Min/Max (n = 2).

Fig. 5 Plot of $\log G$ versus $\log Q$ for the samples in this study (●) in comparison with previously published data (×) for SAPs with different degree of crosslinking, utilizing MFC1 at different concentrations (Larsson et al., 2010, *Soft Materials*, 8: 3, 207 - 225)

FIGURES

Fig. 1

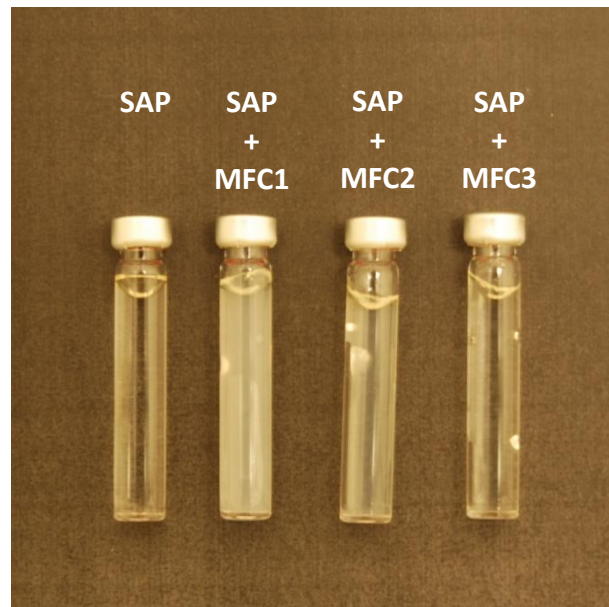


Fig. 2

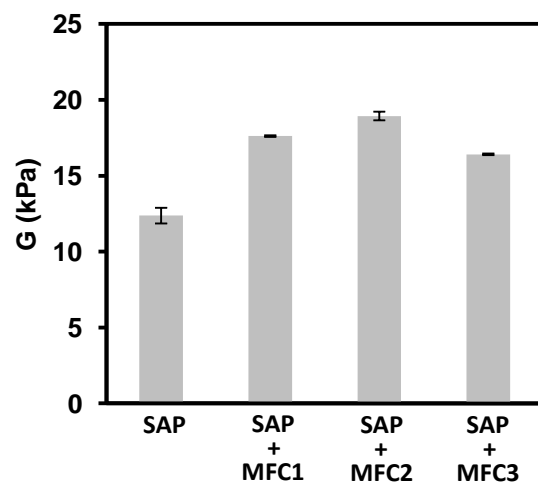


Fig.3

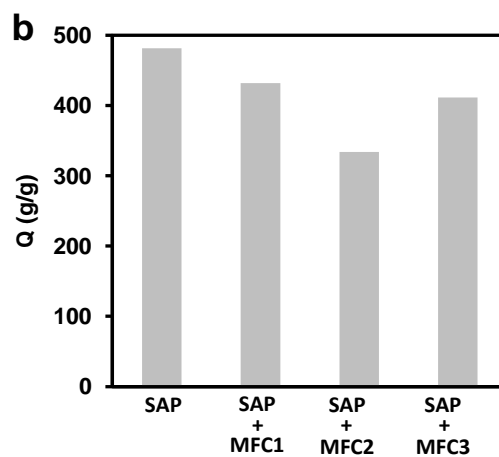
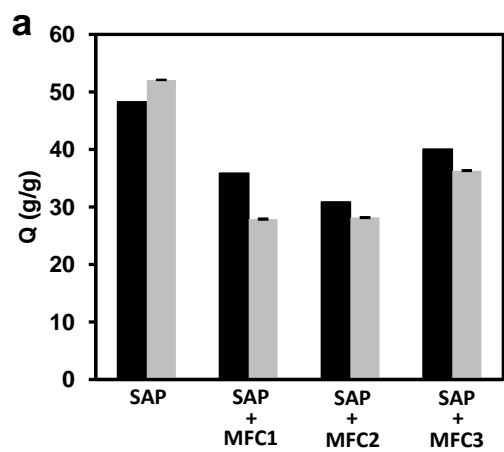


Fig. 4

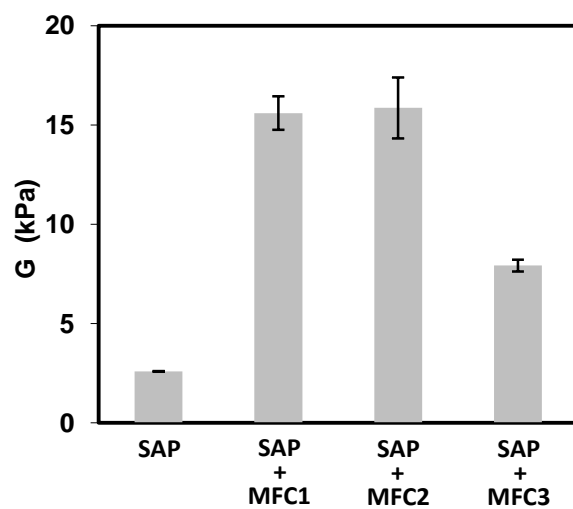
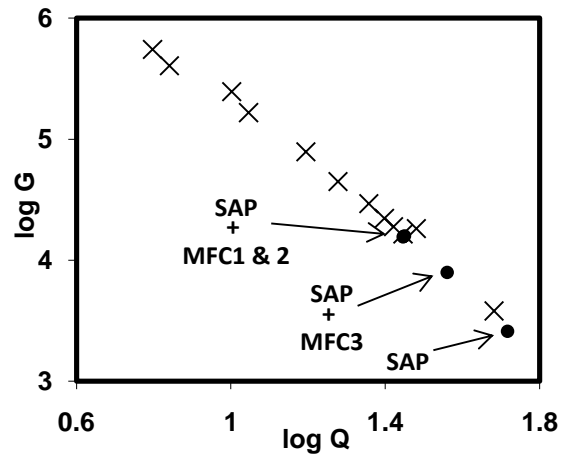


Fig. 5



Graphical abstract

DIFFERENT TYPES OF MICROFIBRILLATED CELLULOSE AS FILLER MATERIALS IN POLYSODIUM ACRYLATE SUPERABSORBENTS

Mikael Larsson, Qi Zhou and Anette Larsson

Three types of microfibrillated cellulose (MFC) with differences in structure and surface charge were used at low concentration as fillers in superabsorbents. The results showed on differences between different MFCs that were also dependent on swelling conditions.

