Carbohydrate Polymers 106 (2014) 283–292

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Modifying the flocculation of microfibrillated cellulose suspensions by soluble polysaccharides under conditions unfavorable to adsorption

Anni Sorvari[a], Tapio Saarinen[a], Sanna Haavisto[b], Juha Salmela[b], Maija Vuoriluoto[c], Jukka Seppälä[a,*]

[a] Polymer Technology, Department of Biotechnology and Chemical Technology, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland
[b] VTT Technical Research Centre of Finland, P.O. Box 1603, 40101 Jyväskylä, Finland
[c] Forest Products Surface Chemistry, Department of Forest Product Technology, Aalto University, P.O. Box 16300, 00076 Aalto, Finland

ARTICLE INFO

Article history:
Received 2 December 2013
Received in revised form 30 January 2014
Accepted 9 February 2014
Available online 18 February 2014

Keywords:
Microfibrillated cellulose
Rotational rheometry
Dispersant
Optical coherence tomography
Xanthan gum
Carboxymethyl cellulose

ABSTRACT

Carboxymethylcellulose (CMC) and xanthan gum were studied as dispersants for microfibrillated cellulose (MFC) suspension using a rotational rheometer and imaging methods. The imaging was a combination of photography and optical coherence tomography (OCT). Both polymers dispersed MFC fibers, although CMC was more effective than xanthan gum. The negatively charged polymer chains increased the viscosity of the suspending medium and acted as buffers in between the negatively charged fibers. This behavior decreased the number and strength of contacts between the fibers and subsequently dispersed the flocs. The stronger separation of the fibers was reflected in the frequency sweep where the MFC/polymer suspensions had lower gel strength than pure MFC suspension. Dispersing effect was also observed in the flow measurements, where the floc size was more uniform with polymers in the decelerating flow and after long, slow constant shear, which normally induces a heterogeneous structure with large flocs into the MFC suspension.

1. Introduction

Being a renewable raw material, wood and other cellulose resources are under constant investigations for new applications. Wood pulp can be disintegrated by mechanical shearing to microfibrillated cellulose (MFC) fibers, which have nanoscale diameters and length of several micrometers (Vartiainen et al., 2011). It is a potentially new material, for example, in nanocomposites (Nguyen et al., 2011; Svagan, Samir, & Berglund, 2007; H. Yano & Nakahara, 2004; H. Yano et al., 2005), paper making (Ahola, Österberg, & Laine, 2008; Eriksen, Syverud, & Gregersen, 2008), and as a rheology modifier (Turbak, Snyder, & Sandberg, 1983). As a rheology modifier, MFC has interesting properties in water suspensions, for example, gel formation at a very low concentration (~0.1%), thixotropy, and shear thinning behavior (Agoda-Tandjawa et al., 2010; Iotti, Gregersen, Moe, & Lenes, 2011; Karppinen et al., 2012; Pääkkö et al., 2007). These properties derive primaly from the inherent entangled network that forms when the fibers disintegrate to fibrils. A high fiber aspect ratio and partially disintegrated fibers strengthen the network within these suspensions (Pääkkö et al., 2007).

MFC suspensions, similar to many other fiber suspensions with a high aspect ratio, tend to form flocs when dispersed in water, unless specifically treated to prevent it. However, good dispersion and non-flocculated structure are required in many applications, for instance, transparent or high mechanical strength nanocomposites. Different means, for example, increasing the surface charge of the fiber (Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006) or adding dispersants (Myllytie, Holappa, Paltakari, & Laine, 2009) may be used to disrupt the flocs and achieve better dispersion. The origin of the MFC flocs is both mechanical and colloidal (Hubbe & Rojas, 2008). MFC fibers are flexible and long compared to their diameter, which enhances mechanical flocculation, as is known for pulp fibers (R.J. Kerekes, 2006; R.J. Kerekes, Soszynski, & Tam Doo, 1985). This can occur via hooking of the fibers or the fibers can bend in flowing suspension, and during decelerating flow, become strained between other fibers, forming a three dimensional network. The frictional forces between the fibers are important factors in this mechanism. As MFC fibers are smaller than pulp fibers, in the colloidal scale, the colloidal forces are also important in flocculation. DLVO theory (Derjaguin & Landau, 1941; Verwey & Overbeek, 1948) is often used to describe the effect of van der Waals and

* Corresponding author. Tel.: +358 9 4702 2614; fax: +358 9 462 373.
E-mail addresses: anni.sorvari@aalto.fi (A. Sorvari), tapio.saarinen@aalto.fi (T. Saarinen), sanna.haavisto@vtt.fi (S. Haavisto), juha.salmela@aalto.fi (J. Salmela), maija.vuoriluoto@aalto.fi (M. Vuoriluoto), jukka.seppala@aalto.fi (J. Seppälä).

http://dx.doi.org/10.1016/j.carbpol.2014.02.032
0144-8617/

electrostatic double layer interactions. Van der Waals forces arise from the interactions between permanent, induced, or transient electronic dipoles (Hubbe & Rojas, 2008), which display attraction between similar surfaces. The electrostatic double layer is caused by ions that accumulate close to the charged surface; these layers create repulsion between like-charged surfaces. The thickness of the electrostatic double layer is dependent on the electrolyte concentration; the higher the ionic strength, the thinner the electrostatic double layer is.

MFC fibers can also have non-DLVO interactions, such as steric and electrosteric interactions, in the presence of polymers or polyelectrolytes in the system. The effect of polymers on flocculation and rheology of pulp suspensions has interested researchers, as many polymers are used in paper making as, for instance, retention aids to retain fines and fillers on the fibers (Stenius, 2000). These polymers can be anionic, cationic or neutral. The molecular weight and charge density of the ionic polymers are the most characteristic properties of the deflocculants (Gregory & Barany, 2011). Often, adsorption of the polymer is needed and the interactions causing that may be electrostatic interactions, hydrogen bonding, hydrophobic interactions, or ion binding (Gregory & Barany, 2011). If a high amount of a polymer is adsorbed on the fibers, the polymer can sterically stabilize the system. This is normally achieved with highly cationic polymers (Gregory & Barany, 2011). Some polymers, such as gums and mucilages (de Roos, 1958) and carboxymethyl cellulose (Laine, Lindström, Nordmark, & Risinger, 2000), are known to adsorb on cellulosic fibers, thus reducing the fiber–fiber friction, and in turn, mechanical flocculation.

Adsorption is not always necessary for the dispersing effect of polymers. High molecular mass anionic polymers can be used as dispersants for pulp and MFC, even if they do not adsorb on cellulosic surfaces at low electrolyte concentration. They can deflocculate the suspension by changing the shear or elongational viscosity of the suspending medium. An increased shear or elongation viscosity of the suspending medium reduces the turbulence intensity and the velocity of the approaching fibers, thus diminishing flocculation (R.J. Kerekes, 2006; Lee & Lindström, 1989; Yan, Lindström, & Christiernin, 2006; Zhao & Kerekes, 1993).

In this study, we utilized two commonly known anionic polysaccharides, carboxymethylcellulose (CMC) and xanthan gum, for controlling the flocculation and rheology of MFC suspensions. CMC is an anionic, linear cellulose derivative which is known to adsorb on cellulosic fibers in certain conditions, although the fibers and polymer are both negatively charged (Laine et al., 2000). Adsorption can be expected at high temperatures, long adsorption time, and sufficiently high salt concentration. CMC is known to deflocculate pulp suspensions (Beghello, 1998; Giri, Simonsen, & Rochefort, 2000; Horvath & Lindström, 2007; Liimatainen, Haavisto, Haapala, & Niinimäki, 2009; Yan et al., 2006). The dispersion effect has been attributed to the ability of CMC to lower the frictional forces between the cellulosic fibers (Yan et al., 2006; Zauscher & Klingenberg, 2000, 2001) if it is adsorbed onto the fibers. Some researchers have also discovered that CMC can disperse pulp without adsorbing on the fibers. The proposed mechanism involves CMC forming a non-adsorbed layer near the fiber surfaces, thus reducing fiber-to-fiber friction due to the large physical size of the CMC molecules (Liimatainen et al., 2009), or that anionic CMC molecules creates repulsive forces between the fibers and thus prevents flocculation (Rantanen, Molarius, Pikkarainen, Knuutinen, & Pakarinen, 2006).

The other polymer used here is a negatively charged xanthan gum which is less studied as a dispersant for pulp or MFC than CMC. It is used in the food industry as a stabilizer and thickener, because it has high viscosity at low concentration and is shear-thinning with yield stress and it is non-toxic (Ahmed & Ramaswamy, 2004). Xanthan gum is produced by the bacterium *Xanthomonas campestris*. The main chain is composed of a 1–4 linked β-D-glucose units with trisaccharide side chains. Some of the side chains carry acetic and pyruvic acid groups which make the polymer anionic (García-Ochoa, Santos, Casas, & Gómez, 2000). Under certain temperature and salt concentration, xanthan gum backbone undergoes an order-to-disorder (or helix-to-coil) transition which is also reflected in the rheological properties (Norton & Goodall, 1984; Rochefort & Middleman, 1987). In distilled water and at room temperature, the backbone is disordered and highly extended due to the negative side chains which repel each other. The extended chains may align and associate via hydrogen bonding and form a weakly associated structure. With salt, the backbone takes a helical structure with the charged side chains inside the helix. In this conformation, the molecules align easily and are strongly associated resulting in gel-like structure (Rochefort & Middleman, 1987).

Previously (Saarinen, Haavisto, Sorvari, Salmela, & Seppälä, 2014), a novel method was introduced to investigate the rheology of a fiber suspension together with the information of its structure and flow profile inside the suspension using a combination of a rotational rheometer and optical coherence tomography (OCT). In this paper, the same system will be utilized to study MFC flocculation with polymers. The two polymers, CMC and xanthan gum, were studied as a rheology modifier and deflocculant for MFC. First, the adsorption of CMC and xanthan gum on MFC model surface by a quartz crystal microbalance with dissipation (QCM-D) and the rheology of the polymer solutions as such will be shown. This will be followed by measurements performed using a dynamic rotational rheometer with a normal digital camera and optical coherence tomography (OCT) device to study the MFC/polymer suspensions. With these methods, the ability of the polymers to change the flocculation and interactions between the MFC fibers under flow were studied, not only from outer surface of the rheometer geometry, but also inside the suspension.

2. Experimental

2.1. Materials

Microfibrillated cellulose (UPM Fibril Cellulose) was obtained from UPM-Kymmene Corporation. The material was prepared from never-dried bleached kraft birch pulp by mechanical disintegration. The pulp was changed to its sodium form and washed with deionized water to an electrical conductivity less than 10 μS/cm according to a procedure introduced by Swerin, Ödberg, and Lindström (1990) and subsequently ground three times in Supermasscolloider (Masuko Sangyo, Japan). The MFC was received, washed and ground and its initial solid content was 2% (w/w). The fiber diameters of similarly prepared MFC have been measured to be between 10 and 30 nm with some larger fibril aggregates (Vartiainen et al., 2011). Polymers were carboxymethylcellulose (CMC) from Sigma–Aldrich (M_w 700,000 g/mol, degree of substitution (DS) 0.9, sodium salt) and xanthan gum from CP Kelco (Kelzan XG, mesh size 381 μm). The charge of xanthan gum was determined to be approximately 1.6 meq/g by conductometric titration with cationic polydiallyldimethylammonium chloride. Both polymers were used without purification.

The polymers were dissolved in Milli-Q water (electrical conductivity <0.2 μS/cm at 25 °C) at room temperature and mixed with a magnetic stirrer for at least 2 h. The MFC suspensions were diluted with Milli-Q water and combined with polymer solutions using two different polymer concentrations, shown in Table 1. The suspensions were mixed with a Heidolph RZR 2051 control propeller mixer at 1400 rpm for 10 min. The diameters of the propeller and beaker