

## FILMS FROM SPRUCE GALACTOGLUCOMANNAN BLENDED WITH POLY(VINYL ALCOHOL), CORN ARABINOXYLAN, AND KONJAC GLUCOMANNAN

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The improvement of mechanical properties of spruce galactoglucomannan (GGM)-based films was sought by blending GGM with each of poly(vinyl alcohol) (PVOH), corn arabinoxylan (cAX), and konjac glucomannan (KGM). The blend ratios were 3:1, 1:1, and 1:3 (w/w), and in addition films were made from each of the polymers alone. Glycerol was used as plasticizer. Adding other polymers increased the elongation at break of GGM blend films. The tensile strength of films increased with increasing amount of PVOH and KGM, but the effect of cAX was the opposite. Dynamic mechanical analysis showed two separate loss modulus peaks for blends of GGM and PVOH, but a single peak for all other films. Optical and scanning electron microscopy confirmed good miscibility of GGM with cAX and KGM. In contrast, films blended from GGM and PVOH showed phase separation when examined by microscopy.

*Keywords:* Galactoglucomannan; Films; Blends; Mechanical properties; Dynamic Mechanical Analysis; Scanning Electron Microscopy

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### INTRODUCTION

Hemicelluloses are structural cell wall components that comprise 20–35% of the dry weight of wood and annual plants, and thus they are the most common plant polysaccharides other than cellulose (Sjöström 1993; Ebringerová and Heinze 2000). *O*-acetyl galactoglucomannans (GGM) are the main hemicelluloses in softwoods. They consist of backbones of  $\beta$ -1,4-D-mannopyranosyl and  $\beta$ -1,4-D-glucopyranosyl units carrying single  $\alpha$ -D-galactopyranosyl residues that are 1,6-linked to mannose units, and acetyl substituents attached to C-2 or C-3 positions of mannose (Sjöström 1993). The ratio of mannose/glucose/galactose of water-soluble spruce GGM is approximately 4:1:0.5, and the degree of acetylation is about 30%. GGM with a molar mass of approximately 30–60 kDa can be recovered as a by-product from process water of mechanical pulping of spruce at a yield of 5 kg/ton pulp (Willför et al. 2003; Xu et al. 2007). GGM is a remarkable natural resource with great potential, but it is not currently isolated for industrial use (Willför et al. 2007). At the laboratory scale, GGM has been

tested for use as a raw material for biodegradable films. GGM-based films have the capacity for acting as oxygen barriers, but their tensile strength and elongation at break are rather low (Hartman et al. 2006a,b; Mikkonen et al. 2006).

Improved mechanical properties of films based on biopolymers have been sought by blending them with other natural or synthetic polymers. The toughness and elongation at break of e.g. pectin / starch-based films were increased by addition of poly(vinyl alcohol) (PVOH) (Coffin and Fishman 1996; Fishman et al. 2004; Fishman et al. 2006). PVOH is a water-soluble polymer produced by methanolysis of poly(vinyl acetate). The solubility of PVOH in water depends on its molar mass and the degree of ester hydrolysis (Hassan et al. 2002). PVOH has excellent film-forming properties and can be used as a barrier to oil, grease, organic solvents, and oxygen (Kirwan and Strawbridge 2003). The biodegradability of PVOH is arguable, as some micro-organisms produce PVOH-degrading enzymes, but the occurrence and overall number of those micro-organisms in nature is rather limited (Chiellini et al. 1999; Chen et al 2007).

Corn fiber, which is the main low-value by-product of the corn wet and/or dry milling process, contains large quantities of arabinoxylans (cAX) (Doner and Hicks 1997). The backbone of cAX consists of 1,4-linked  $\beta$ -D-xylopyranosyl units, to which short side chains of  $\alpha$ -L-arabinofuranosyl units are connected by 1,3- and/or 1,2-glycosidic linkages. D-galactopyranosyl and D-xylopyranosyl residues are attached to the arabinofuranosyl branches. cAX also carries  $\alpha$ -D-glucopyranosyluronic acid and feruloyl groups (Saulnier et al. 1995). Exploitation of cAX as a film former has been suggested (Fredon et al. 2002; Peroval et al. 2002; Zhang and Whistler 2004). Films have successfully been prepared also from other cereal arabinoxylans (Höije et al. 2005; Tenkanen et al. 2007).

Konjac glucomannan (KGM) occurs as a storage polysaccharide in tubers of *Amorphophallus konjac* (Takigami 2000). Its chemical composition resembles that of GGM, except that KGM does not contain galactose side groups, and it has significantly higher molar mass, approximately 1000 kDa (Li et al. 2006a). The mannose/glucose ratio of KGM is 1.6:1 and the degree of acetylation about 5%. KGM forms strong films by itself and as blends with various substances, including PVOH (Yue et al. 1995; Xiao et al. 2000a; Xiao et al. 2000b; Xiao et al. 2001a; Xiao et al. 2001b; Li and Xie 2004; Cheng et al. 2006; Li et al. 2006b; Ye et al. 2006; Cheng et al. 2007). The aim of the present study was to increase the tensile strength and elongation at break of GGM-based films by blending GGM with PVOH, cAX, and KGM. To study the homogeneity of the blend films, their thermal behavior was examined using dynamic mechanical analysis (DMA) and the film structure was viewed with optical and scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials

GGM was prepared from thermomechanical pulp of spruce according to Willför et al. (2003), with the exception that pulp taken after the second refiner in a two-stage refining system was used. The mannose content of the dried powder was determined by gas chromatography following methanolysis and trimethyl silylation (Sundberg et al.

1996). The GGM content was estimated from the mannose content and the mannose/glucose/galactose ratio of 4:1:0.5 to be 77 mole% of carbohydrates. The main non-GGM residual components were other polysaccharides, mainly pectic acids and arabinogalactans. Molar mass and the degree of acetylation of GGM were determined as described by Xu et al. (2007) to be approximately 50 kDa and 18%, respectively.

The cAX sample was isolated by alkali extraction from de-oiled and de-starched fiber fractions from commercial corn wet milling (ADM Research, USA). The method of isolation, as well as the characteristics of the obtained product (CFG-1), were described in detail by Yadav et al. (2007). PVOH (98–99% hydrolyzed, Mw 146,000–186,000 as reported by the supplier) and glycerol were from Sigma and KGM (BJ-C1) from Baoji, China.

### Preparation of Films

The blend ratios of GGM with each of PVOH, cAX, and KGM were 1:0, 3:1, 1:1, 1:3, and 0:1 (w/w). Glycerol was used as plasticizer at 40% (w/w of the polymers). Polymers and glycerol were dissolved in de-ionized water at 95°C to produce a final polymer concentration of 10 g/L. Solutions containing cAX and a reference sample from pure GGM and glycerol were filtered through a steel sieve with 45 µm pore size to remove a small amount of insoluble particles. Air was removed by ultrasonication under vacuum for 5 min. Films with an average thickness of approximately 70 µm were prepared by casting 50 ml of solutions on polystyrene petri dishes (diameter 9 cm) and drying overnight at 60°C.

### Mechanical Properties

An updated Instron 1122 mechanical property tester (Instron Corp., Norwood, MA, USA) with a 100 N load cell and TestWorks 4 data acquisition software (MTS Systems Corp., Minneapolis, MN, USA) was used to determine the tensile strength and elongation at break of films. The initial grip distance was 25 mm and the rate of grip separation 5 mm/min. The measurements were done at 21°C and 65% RH (in a climate room) and the films were stored at these conditions for at least three days before measurement. From those films that could be handled at this RH, two films of each type and five replicate specimens from each film were measured. The specimens were 5 mm wide and approximately 60 mm long. The thickness of the specimens was measured with a micrometer (Ames, Waltham, MA, USA, precision 1 µm) at three points and an average was calculated.

### Dynamic Mechanical Analysis

Dynamic mechanical analysis was done on a Rheometrics RSA II solids analyzer (Piscataway, NJ, USA) using a film-testing fixture. Specimens of 7 mm × 38 mm were dried under vacuum for 30 min prior to testing. Specimen thickness was measured at three points with the micrometer and width at two points with a millimeter ruler, and averages were calculated. The gap between the jaws at the beginning of the test was 23.0 mm. A nominal strain of 0.1% was applied with a frequency of 10 rad/s (1.59 Hz). Storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) were determined as a function of temperature from –100°C to 50°C at a heating rate of 10°C/min. The peak

temperature of  $E''$ , determined by fitting a parabolic curve to  $E''$  data with Origin 7.2 (OriginLab Corporation) software, was taken as glass transition temperature ( $T_g$ ) (Kalichevsky and Blanshard 1993). All analyzes were done in triplicate.

## Microscopy

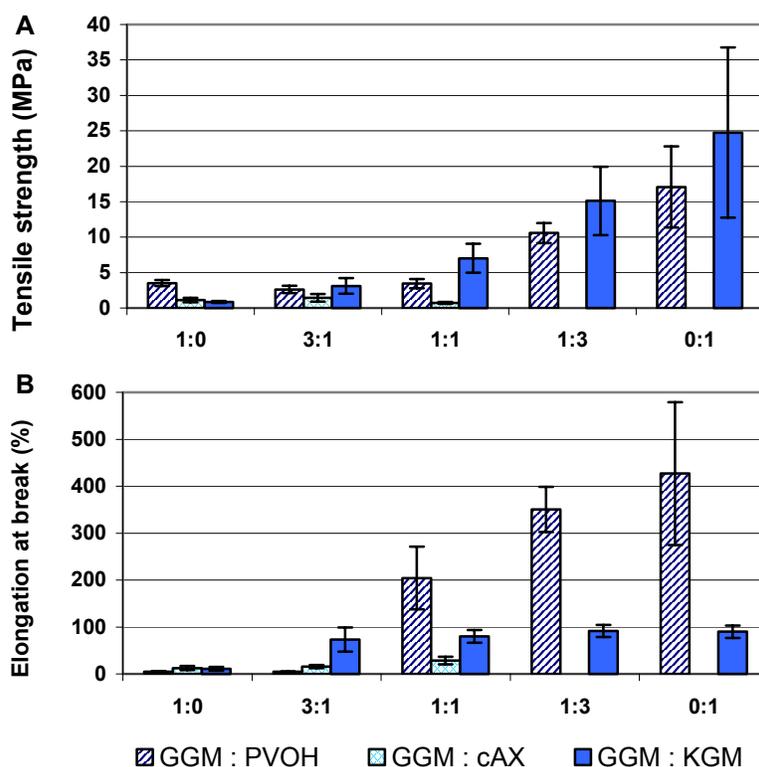
Optical and fluorescence imaging of film surfaces was done with a model MZ FLIII stereofluorescence microscope equipped with a DC200 charge-coupled device camera (Leica Microsystems, Inc., Bannockburn, IL, USA) and oblique, transmitted illumination from a fiber optic bundle connected to a 150 W halogen lamp in an Intralux 5000-1 lamphouse (Volpi Manufacturing, Auburn, NY, USA). Matching epifluorescence images of sample areas were excited with violet light ( $\sim 425$  nm) from a 50 W Hg lamphouse and digital images of blue fluorescence ( $> 475$  nm) were collected.

The cross-sections of the films were viewed with scanning electron microscopy (SEM). Rectangular strips of approximately  $5 \text{ mm} \times 40 \text{ mm}$  were excised from the films with a razor blade and dehydrated by immersion in 10 ml of absolute ethanol. The samples were stored in sealed vials for three days, during which the ethanol was replaced twice. Film segments were quickly blotted dry, plunged into liquid nitrogen, and cooled for 5 min. The frozen film segments were fractured manually using tweezers by bending the strips against the surface of a brass block in liquid nitrogen. Fractured fragments were removed from the liquid nitrogen, thawed by immersion in ethanol, and subsequently critical point dried from liquid carbon dioxide. Dry fragments were trimmed and mounted on aluminium stubs using Duco Cement (ITW Performance Polymers, Riviera Beach, FL, USA) and colloidal silver adhesive (Electron Microscopy Sciences, Hatfield, PA, USA) and coated with a thin layer of gold by direct current sputtering. Images of oriented fracture faces were collected using a Quanta 200 scanning electron microscope (FEI Co., Hillsboro, OR, USA) operated in the high vacuum-secondary electron imaging mode.

## RESULTS AND DISCUSSION

### Mechanical Properties

Both the tensile strength and elongation at break of pure GGM-based films were low, as expected (Fig. 1). On average, the elongation at break was slightly higher and the tensile strength somewhat lower than when measured previously at lower RH (50% RH) with another instrument and different specimen dimensions (Mikkonen et al. 2006). Water has a plasticizing effect on biopolymer-based films (Talja et al. 2007), which is a probable explanation for the different results obtained at 65% RH in the present study. The mechanical testing of pure GGM-based films was repeated with each set of blend films (GGM / PVOH, GGM / cAX, and GGM / KGM) and some variation in the results was found. The tensile strength of pure GGM-based films was  $3.5 \pm 0.4$ ,  $1.1 \pm 0.3$  and  $0.85 \pm 0.2$  MPa when the films were prepared and measured together with its blends with PVOH, cAX, and KGM, respectively. The values of elongation at break of the corresponding films were  $4.9 \pm 1\%$ ,  $12.5 \pm 4\%$ , and  $10.9 \pm 4\%$ .



**Fig. 1.** (A) Tensile strength and (B) elongation at break of films from GGM blended with PVOH, cAX, and KGM at different ratios and plasticized with 40% (w/w of polymers) glycerol. Each average is based on  $n = 10$  observations, and the error bars indicate standard deviations. GGM / cAX films with ratios of 1:3 and 0:1 could not be measured.

The tensile strength of films clearly increased when PVOH was used in GGM / PVOH at ratios of 1:3 and 0:1 (Fig. 1A). At lower PVOH levels, the differences in the tensile strength of GGM / PVOH blend films were small. The elongation at break of GGM / PVOH films increased almost linearly with increasing PVOH content from GGM : PVOH ratio of 3:1 to 0:1, but a small addition of PVOH did not have an effect as the elongation at break of GGM : PVOH 3:1 films was similar to that of films from pure GGM (Fig. 1B).

Adding cAX to GGM at a GGM : cAX ratio of 3:1 did not significantly affect the tensile strength of the films, but at the ratio of 1:1, the tensile strength decreased to almost zero (Fig. 1A). In contrast, the elongation at break of films increased slightly with increasing cAX content (Fig. 1B). The mechanical properties of GGM : cAX 1:3 and 0:1 films could not be measured, because cAX was very sensitive to changes in ambient RH, and these films were difficult to handle at 65% RH, which was used for tensile testing. cAX is more branched than the other studied polymers. It may absorb more water, which can lead to plasticization and softening of the films. We also tested pure cAX-based films using lower glycerol contents (25% and 10% w/w) and GGM / cAX blends using 25% glycerol, but even those films were too soft to measure at 65% RH. When prepared without added plasticizer, cAX films had a tensile strength of  $4.2 \pm 1.5$  MPa and elongation at break of  $21 \pm 9\%$ . In the future, it can be worthwhile to test if cAX has

potential as a film forming and flexibility increasing component in blend films if treated as plasticizer, so that the amount of other plasticizers is decreased with increasing cAX content.

An increasing amount of KGM increased the tensile strength of the films (Fig. 1A). The increase was slow at low KGM contents, but escalated at high KGM contents. Even a small amount of KGM notably enhanced the elongation at break of films, which was high for all films containing KGM (Fig. 1B).

In a previous study, a moderate decrease in the degree of polymerization of guar gum galactomannan resulted in an increase of tensile strength and elongation at break of films (Mikkonen et al. 2007). Similarly, films from partially acid-hydrolyzed KGM showed higher tensile strength than native KGM-based films, when the acid treatment was relatively mild (Cheng et al. 2007). In both studies, however, a stronger hydrolysis of the polymeric chain led to decreased film mechanical properties. Suggested mechanisms of the initial improvement of tensile strength with decreasing molar mass were altered chain flexibility and mobility, and an optimal decrease of viscosity of the polysaccharide solution leading to better orientation of the film-forming polymers. GGM was found to decrease the viscosity of aqueous KGM solution (Xu et al. submitted) and therefore a small addition of GGM to KGM could have been expected to somewhat strengthen the films.

Several studies on KGM-based blend films have shown that there is an optimum polymer ratio that gives higher film tensile strength than either of the two polymers alone (Yue et al. 1995; Xiao et al. 2000a; Xiao et al. 2000b; Xiao et al. 2001a; Xiao et al. 2001b; Li and Xie 2004; Li et al. 2006b; Ye et al. 2006). For example, blends of KGM and PVOH reached a maximum tensile strength at 20% PVOH content (Xiao et al. 2000a), and also in the presence of glutaraldehyde, the tensile strength of KGM / PVOH blends was higher than that of films purely from either KGM or PVOH (Li and Xie 2004). Relatively similar or high molar masses of the both blended polymers could promote synergism. The molar mass of GGM is significantly lower than that of PVOH and KGM, and in the present study there was not an optimum blend ratio, as the films from pure PVOH and KGM had clearly higher tensile strength than any of the GGM / PVOH or GGM / KGM blends.

### Dynamic Mechanical Analysis

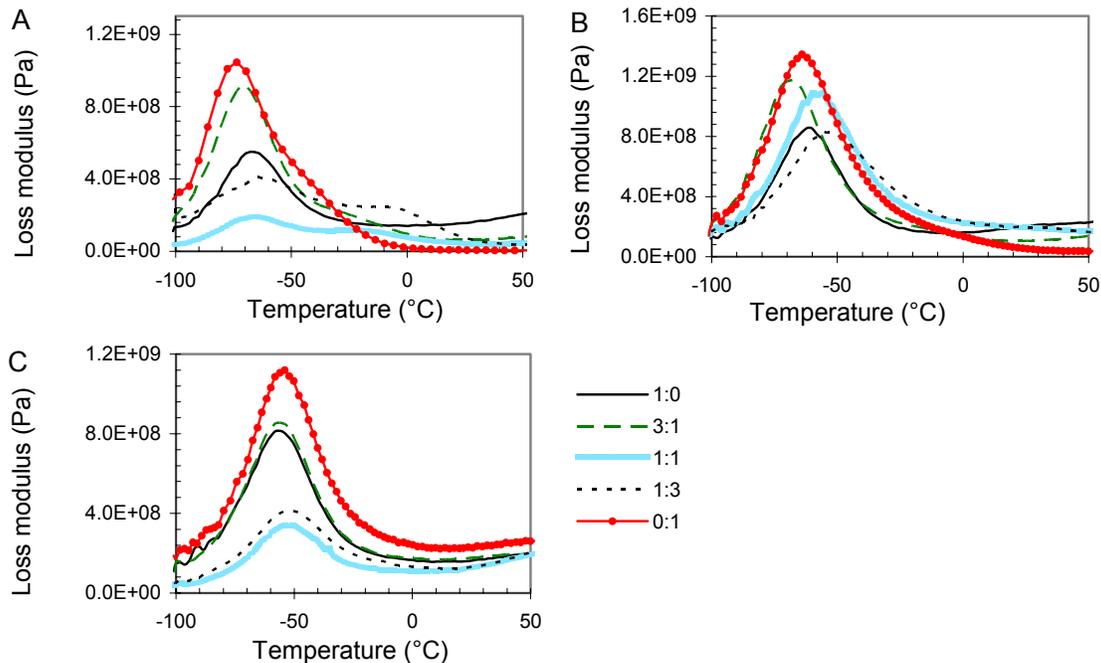
The DMA tests of pure GGM-based films were also repeated with each set of blend films. The average  $T_g$  of pure GGM-based films measured at different times varied from  $-56$  to  $-70^\circ\text{C}$  (Table 1). The standard deviation between the replicate specimens was small each time. An attempt was made to control the plasticizing effect of water by vacuum-drying the film specimens before DMA testing. Despite that, the films probably absorbed some water from the air during attachment of the film strips in the instrument. The films from individual sets were generally analyzed within a few days, but the time between the analyses of the different sets was up to several weeks. Thus changes in the ambient RH might have affected the detected  $T_g$  values. This complicates the comparison of the  $T_g$  values of films from different sets, but most likely not of the films from the same set.

**Table 1.** Glass Transition Temperature ( $T_g$ ) of Films from GGM Blended with PVOH, cAX, and KGM at Different Ratios and Plasticizer with 40% (w/w) of Glycerol (Mean Value  $\pm$  SD from Triplicate Analysis).

Ratio	GGM / PVOH*		GGM / cAX	GGM / KGM
	$T_{g1}$ ( $^{\circ}$ C)	$T_{g2}$ ( $^{\circ}$ C)	$T_g$ ( $^{\circ}$ C)	$T_g$ ( $^{\circ}$ C)
1:0	$-70 \pm 3$	nd	$-62 \pm 0.9$	$-56 \pm 1$
3:1	$-70 \pm 0.9$	$-36 \pm 3$	$-67 \pm 2$	$-57 \pm 1$
1:1	$-66 \pm 0.1$	$-25 \pm 1$	$-57 \pm 0.05$	$-53 \pm 2$
1:3	$-66 \pm 0.8$	$-19 \pm 7$	$-50 \pm 2$	$-52 \pm 2$
0:1	$-72 \pm 2$	nd	$-65 \pm 2$	$-53 \pm 1$

\*Two glass transitions were detected for blends of GGM and PVOH. nd = not detected.

Figure 2 shows that there were two peaks in the  $E''$  spectra of films containing both GGM and PVOH, indicated as  $T_{g1}$  and  $T_{g2}$  in Table 1. The second peak at approximately  $-20$  to  $-30^{\circ}$ C was more pronounced for GGM : PVOH 1:1 and 1:3 films than for films with the GGM : PVOH ratio of 3:1. The  $E''$  curves of pure PVOH-based films had a single peak with a shoulder. Distinct glass transitions clearly indicate that GGM and PVOH were incompatible and that phase separation took place. Interestingly, the  $T_g$  values of the films from pure GGM and PVOH were close to each other and to the first detected  $T_g$  of the blends ( $T_{g1}$ ), but the second  $T_g$  of the blends ( $T_{g2}$ ) was clearly higher. It is possible that glycerol was unevenly distributed in the two separate phases, the GGM-rich and PVOH-rich phase. Plasticization decreases  $T_g$ , so the  $T_{g1}$  could have resulted from the phase containing more glycerol and  $T_{g2}$  from the phase with less glycerol.



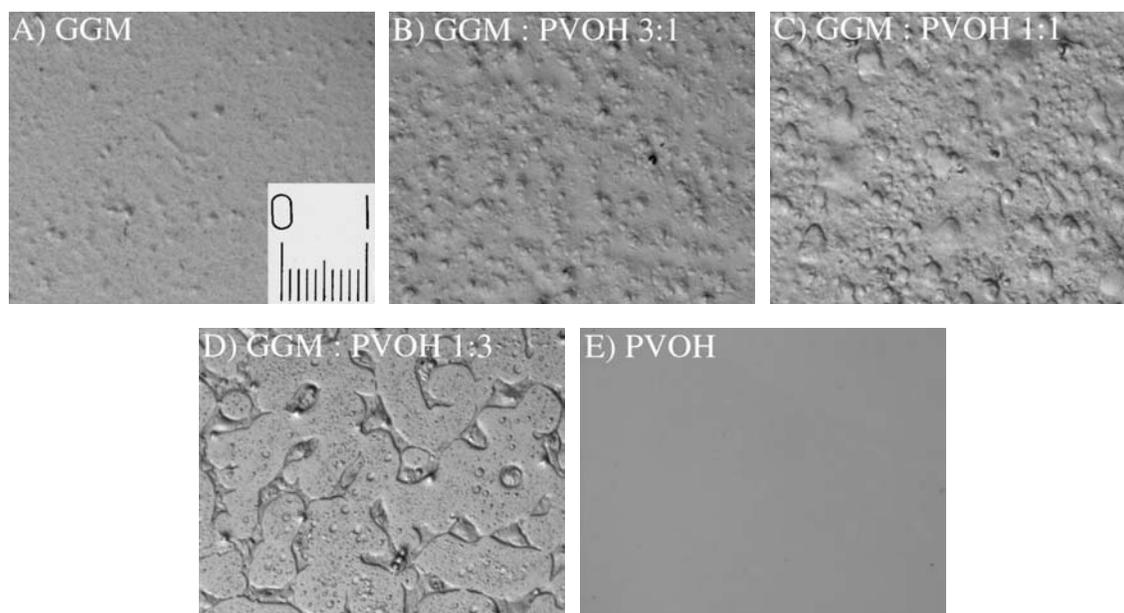
**Fig. 2.** Typical loss modulus spectra of films from GGM blended with (A) PVOH, (B) cAX, and (C) KGM at different ratios plasticized with 40% (w/w) of polymers glycerol.

All GGM / cAX and GGM / KGM films had a single glass transition (Fig. 2). The  $T_g$  of GGM / cAX blends increased with increasing cAX content, but the  $T_g$  of pure cAX-based films was lower and close to that of films based on pure GGM. The  $T_g$  of GGM / KGM films varied within only a narrow range. The  $E''$  peak heights of all films varied notably, which was probably due to differences in the thickness of the films but is not expected to affect the peak temperature.

### Microscopy

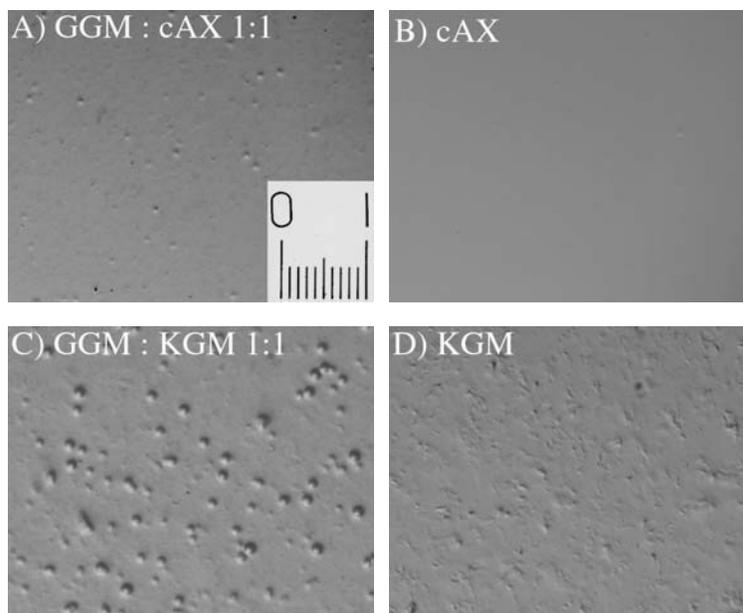
Optical microscopic imaging with visible light showed that pure GGM-based films had a slightly grainy surface (Fig. 3A). GGM contained a small amount of insoluble particles, some but not all of which were removed by filtration through the 45  $\mu\text{m}$  sieve used in the preparation of GGM / cAX sample set. Those particles most probably formed the elevated spots seen by optical microscopy using visible light. The same spots autofluoresced, indicating that they could have contained residual aromatic structures originating from spruce wood. Because the aromatic substances are present in GGM only in trace amounts, reliable analytical data of their composition has not been obtained up to date. However, it is most likely that these structures arise from fragments of lignin-like moieties, possibly from so-called lignin-carbohydrate complexes.

Addition of PVOH resulted in increased unevenness of the film surfaces (Fig. 3). Films with GGM : PVOH ratios of 3:1 and 1:1 had a much rougher surface than the films from pure GGM. The films with GGM : PVOH ratio of 1:3 had a pattern of irregular minor shapes immersed in a continuous phase. In contrast, the surfaces of pure PVOH-based films were very smooth.



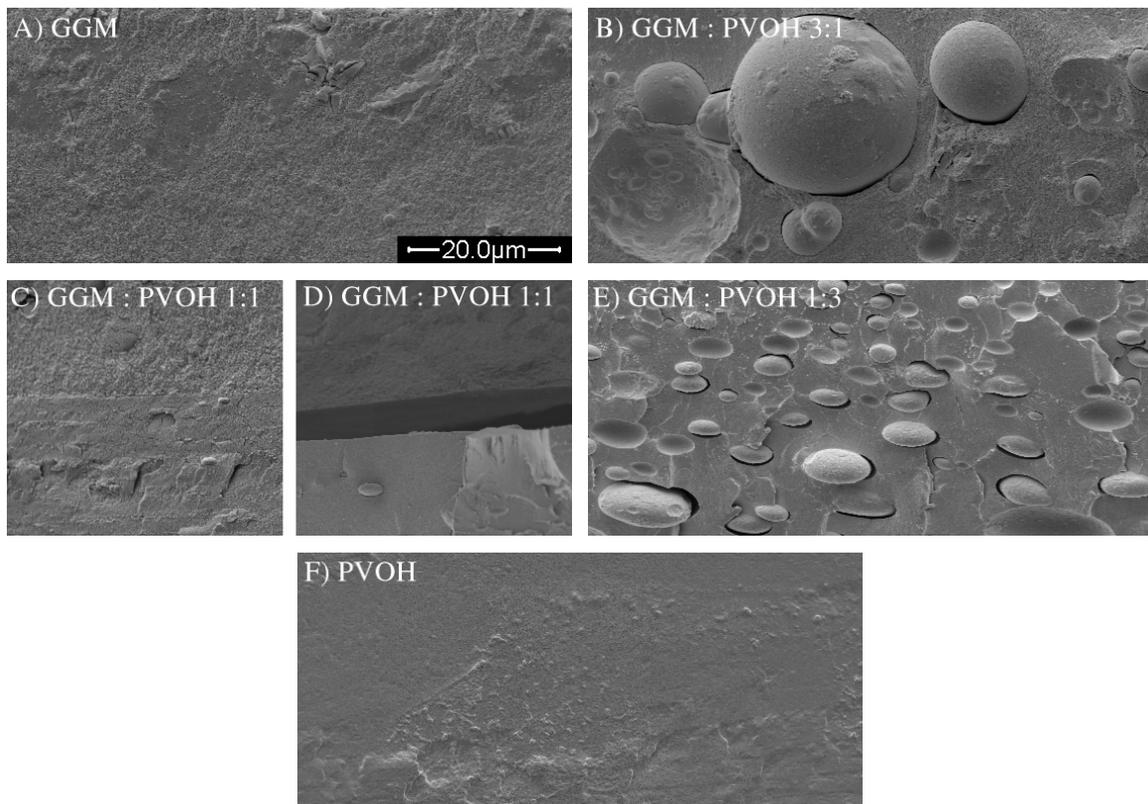
**Fig. 3.** Optical microscopic images of surfaces of films from (A) GGM; (B) GGM : PVOH 3:1; (C) GGM : PVOH 1:1; (D) GGM : PVOH 1:3 and (E) PVOH obtained using visible light. Scale bar = 1 mm. All images are at the same magnification.

The surfaces of GGM / cAX and GGM / KGM blend films looked much alike. Figure 4 presents images of films with GGM : cAX and GGM : KGM ratios of 1:1 and 0:1 as examples. Films containing GGM had a somewhat grainy surface, whereas those from pure cAX were smooth and those from pure KGM had some fiber-like formations. Films not containing GGM did not show significant fluorescence.

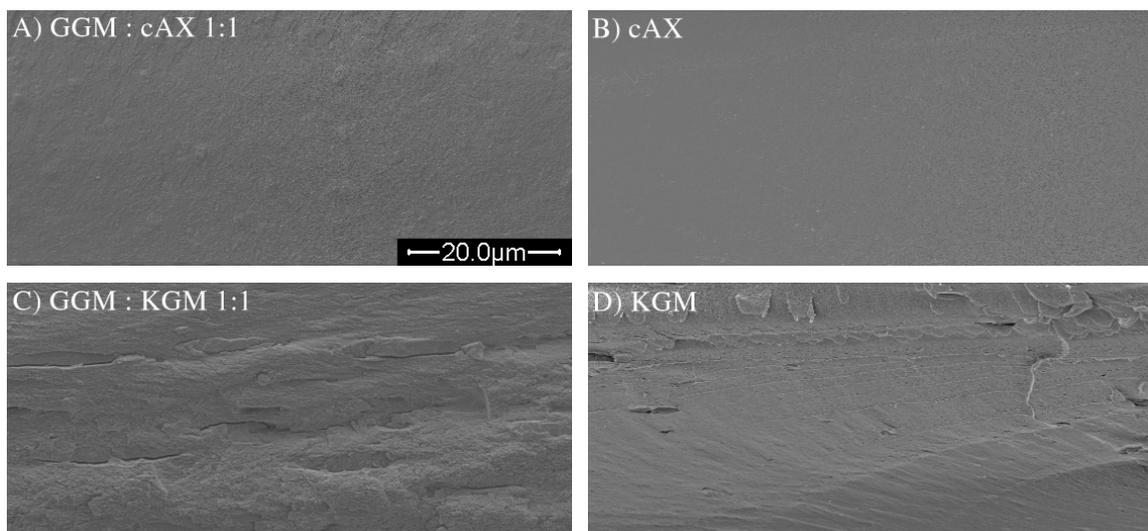


**Fig. 4.** Optical microscopic images of surfaces of films from (A) GGM : cAX 1:1; (B) cAX; (C) GGM : KGM 1:1 and (D) KGM obtained using visible light. Scale bar = 1 mm. All images are at the same magnification.

The cross-section of pure GGM-based film, viewed with SEM, was somewhat grainy with some dark and dense areas (Fig. 5A). There was a great contrast to images of blend films from GGM with PVOH, which clearly showed separation into two distinct phases. The film with GGM : PVOH ratio of 3:1 (Fig. 5 B) had spherical particles of different sizes in a continuous phase that resembled the cross-section of the film from pure GGM. When the ratio of GGM to PVOH was 1:1, the two phases were formed as layers on top of each other (Fig. 5C) and in some areas they had separated (Fig. 5D). At the GGM : PVOH ratio of 1:3 (Fig. 5E), the continuous phase looked similar to the cross-section of pure PVOH-based film (Fig. 5F), and there were small round and oval particles inside. The cross-sections of GGM / cAX and GGM / KGM blend films showed a homogeneous structure consisting of a single phase (Fig. 6).



**Fig. 5.** Scanning electron micrographs of cross-sections of films from (A) GGM; (B) GGM : PVOH 3:1; (C and D) GGM : PVOH 1:1; (E) GGM : PVOH 1:3 and (F) PVOH. Scale bar = 20 μm. All images are at the same magnification.



**Fig. 6.** Scanning electron micrographs of cross-sections of films from (A) GGM : cAX 1:1; (B) cAX; (C) GGM : KGM 1:1 and (D) KGM. Scale bar = 20 μm. All images are at the same magnification.

Microscopic studies by Xiao et al. (2000a) showed phase separation of PVOH and KGM, the latter of which has similar sugar composition to GGM. They found with IR spectroscopy that there was some hydrogen bonding between the two polymers, but not as much as between KGM and other polysaccharides. This could also explain the results of the present study. GGM might form strong hydrogen bonding and homogeneous mixtures with the other studied polysaccharides cAX and KGM, but not with PVOH, which has only one hydroxyl group attached to every second carbon atom of the polymeric chain. Based on SEM imaging, it can be reasoned that the mechanical properties of the GGM blend films were determined mainly by the properties of the continuous phase, which was formed of a homogeneous mixture of two polysaccharides in GGM / cAX and GGM / KGM blends, but of either GGM-rich or PVOH-rich phase in the films made from those two polymers.

### Application Potential

Previously, Hartman et al. (2006a; 2006b) found that GGM can form films with low oxygen permeability. They showed decrease of storage modulus of plasticized GGM films with increasing ambient RH, but did not determine their tensile strength and elongation at break, which are important parameters concerning film applications. The present study proves that the tensile properties of GGM films were significantly enhanced by the addition of KGM or PVOH. Although the latter two polymers formed stronger and more flexible films alone than as blends with GGM, the estimated low cost of GGM makes it an interesting component of biodegradable films (Persson et al. 2007). To further evaluate the potential of GGM films in e.g. food packaging applications, water vapor barrier properties need to be studied.

### CONCLUSIONS

1. GGM / KGM blend films were homogeneous and had higher tensile strength than the films from pure GGM. Even a small addition of KGM notably increased the elongation at break of GGM-based films. Blending GGM with KGM was found to be an effective way to improve the mechanical properties of GGM-based films.
2. Although the use of PVOH increased the mechanical properties of GGM / PVOH blend films, DMA and microscopic study showed that the two polymers were immiscible.
3. GGM and cAX formed homogeneous blend films, but they were very sensitive to high relative humidity.

### ACKNOWLEDGMENTS

Chunlin Xu is acknowledged for the isolation of GGM and for the mannose content analysis, Guoping Bao for skillful technical assistance in SEM imaging of films, and David Coffin for assistance in DMA. Foundation for Research of Natural Resources in Finland, Finnish Funding Agency for Technology and Innovation (Tekes), and Academy of Finland are thanked for financial support.

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Article submitted: November 2, 2007; Peer-review completed: Jan. 5, 2008; Revised version received and accepted: Jan. 17, 2008; Published: Jan. 19, 2008.