Oxygen Barrier Materials from Renewable Sources: Material Properties of Softwood Hemicellulose-Based Films

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ABSTRACT: The aim of this study was to investigate the film-forming ability of the hemicellulose *O*-acetyl-galacto-glucomannan (AcGGM) and to evaluate its potential as a barrier material. The polymer film was evaluated by measurement of its oxygen permeability (Ox-Tran® Mocon), thermal properties (differential scanning calorimetry), and dynamic mechanical properties under a humidity scan (humidity-scan DMA). The AcGGM was isolated from industrial process water obtained from mechanical wood pulping. The self-supporting films were formed by solution-casting from water. As expected, a plasticizer was needed to avoid brittleness, and glycerol, sorbitol, and xylitol were compared. However, these additives resulted in higher sensitivity to moisture, which might be less beneficial for some applications. Interesting oxygen barrier and mechanical strength properties were achieved in a film obtained from a physical blend of AcGGM and either alginate or carboxymethylcellulose, both having a substantially higher molecular weight than AcGGM. No phase separation was observed, since all the components used were rich in hydroxyl functionalities. When a plasticizer was also added to the binary mixture, a compromise between (1) low O_2 permeability, (2) high mechanical toughness, and (3) flexibility of an AcGGM-based film was obtained. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2985–2991, 2006

Key words: hemicellulose; galactoglucomannan; mechanical properties; oxygen permeability; solution casting

INTRODUCTION

The study of biopolymers for films and coatings, based on polysaccharides, proteins, or lipids, is a research field that is rapidly expanding at the moment. In the food industry, there is a special interest in barrier layers with optimized properties based on biopolymers. The potential of polysaccharides and proteins as an edible coating on foodstuffs is well known, although it has not yet widely fulfilled in practice.[1–3] A growing demand for replacing existing barriers such as aluminum and synthetic polymers (e.g., polyvinyl alcohol, polyvinylidene chloride) is gaining an acceleration in the development of biopolymeric barrier layers in food packaging systems. The environmental benefits are primarily related to the renewability of the biopolymers. However, the environmental issues are not the only driving force. There are also other drawbacks in the use of common gas barriers. For example, aluminum barriers suffer from inferior mechanical properties and high costs.[4] Important properties for an oxygen barrier layer include not only low oxygen permeability but also good mechanical strength and a suitable degree of flexibility. Low water permeability is also often desired, but water is a general problem for polysaccharide and protein films.[5] Lamination[6] with a hydrophobic film or blending with hydrophobic components[7] are two basic approaches for improving the moisture tolerance.

Many naturally occurring polysaccharides have been proposed for use in coating and film formulations, including starch, starch derivatives, cellulose derivatives, chitosan, alginates, carrageenan, pectinates, and various naturally occurring gums.[8] An added plasticizer is often needed to achieve sufficient film flexibility.[9] An ideal plasticizer should also facilitate molecular motion and decrease internal friction within the biopolymer. Water has, for a long time, been known to function as a plasticizer and it is known, for example, to lower the glass transition temperature (T_g) of polysaccharides and proteins.[5] A general decrease in T_g by $10 \pm 5°C$ per wt % water present has been reported for polysaccharides.[10] Many polyols, such as glycerol and low molecular weight PEG, and alditols have a more lasting softening action than water, which evaporates easily, and they are thus often used in polysaccharide and protein films.[3,11] One approach to increase the mechanical strength properties of a polysaccharide film is to blend it with another
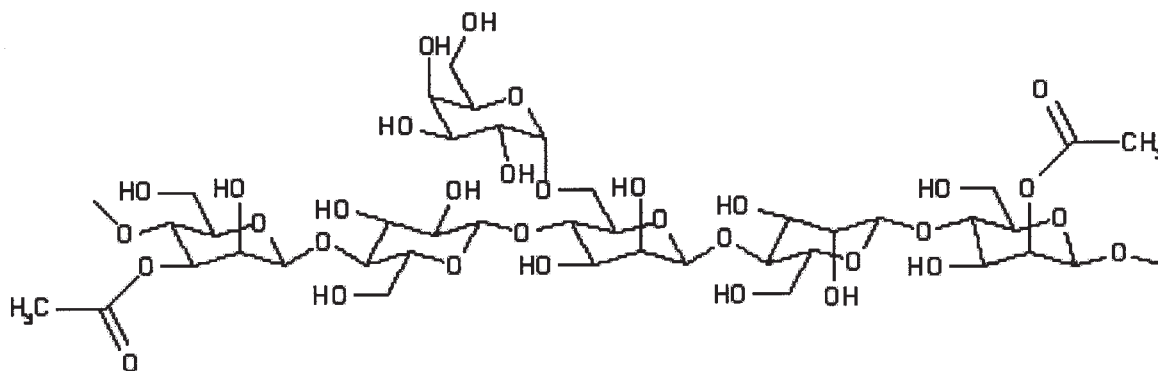
Scheme 1   A hypothetical element of *O*-acetyl-galactoglucomannan (AcGGM).

polysaccharide or polysaccharide derivative that either has a higher molecular weight or has more capability of bringing about strong interactions. Examples of this approach have been investigated for konjac glucomannan blended with sodium alginate,[12] carboxymethylcellulose (CMC),[13,14] and chitosan.[15]

Since polysaccharides generally possess a film-forming ability, which leads to modest or very good oxygen barrier properties depending on the structure,[8] we thought it would be of interest to study wood-derived hemicelluloses in this respect. Wood hemicelluloses are a heterogeneous class of short-chained polysaccharides that are biosynthesized through a different path than cellulose in the secondary cell wall. They constitute about 20–30% of the total weight of annual and perennial plants, and they are, thus, one of the most abundant natural polymers after cellulose. However, the industrial potential of hemicelluloses is still highly unexploited. The main hemicellulose in hardwood is *O*-acetyl-(4-*O*-methylglucurono)xylan, while the predominant one in softwood is *O*-acetyl-galactoglucomannan (AcGGM).[16] Water-soluble films of xylan extracted from kraft hardwood pulp together with, for example, glycerol were already prepared decades ago.[17] A glucuronoxylan isolated from aspen wood has recently been evaluated as a barrier film-forming material.[18]

AcGGM has a main chain of β-(1→4)-linked D-mannose and D-glucose with α-(1→6)-linked D-galactose moieties in various amounts, see Scheme 1. AcGGM is soluble in water as well as in organic solvents. The solubility properties can be attributed to a high degree of acetylation in combination with a low molecular weight. This particular molecular structure prevents the formation of hydrogen-bonded aggregates.[19,20] Hydrogels have recently been developed for medical purposes from AcGGM in collaboration within our group.[21,22] In these hydrogel studies, hemicellulose from steam-exploded spruce was utilized. Another highly attractive source for AcGGM is process water from mechanical pulping processes. The AcGGM present in these streams is not cur-

rently upgraded for commercial purposes. Instead, it contributes negatively to the chemical oxygen demand (COD), and this in turn increases the load on the biological purification treatment.

To our knowledge, acetylated galactoglucomannan originating from wood has not been evaluated with regard to its film-forming, mechanical, and barrier properties. The softening behavior of bioplastic materials as a function of humidity is furthermore rarely reported.

The present study aims at the development of films with low oxygen permeability and good mechanical properties from AcGGM isolated from industrial process water. Our intention has been to achieve films exclusively from renewable and biodegradable components. The effects of low-molar mass plasticizing additives and physical blends with high-molar mass renewable polymers have been evaluated. All films have been evaluated by measuring the storage modulus as a function of relative humidity (RH), using dynamic mechanical analysis (DMA) equipped with a humidity scan. The oxygen permeability of the films was measured using Ox-Tran® Mocon. Differential scanning calorimetry (DSC) was applied to study the thermal transitions of the different film compositions.

EXPERIMENTAL

Materials

O-acetyl-galactoglucomannan (AcGGM) isolate was obtained from thermomechanical pulping (TMP) process water. The AcGGM was concentrated by ultrafiltration from about 1 wt % to 15–20 wt % by STFI-Packforsk AB. Small molecules (i.e., salts, monomers, and oligomers < 1000 g mol^{-1}) were removed in this process. The concentrate was lyophilized into a fluffy powder cake, hereinafter referred to as the AcGGM isolate.

The molecular weight of the AcGGM isolate was determined by size-exclusion chromatography (SEC) calibrated with galactoglucomannan standards as-

Composition	Cast from 14 ml water
AcGGM	0.30[a]
AcGGM:Alginate	0.26:0.14
AcGGM:CMC	0.26:0.14
AcGGM:Glycerol	0.30:0.10
AcGGM:Sorbitol	0.26:0.14
AcGGM:Xylitol	0.26:0.14
AcGGM:Alginate:Glycerol	0.26:0.07:0.07

[a] Values given are in grams.

signed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS).[20] The AcGGM had an average molecular weight of about 10,000 g mol^{-1} ($\bar{D}P \sim 60$) and a polydispersity of 1.3. The carbohydrate composition of the AcGGM isolate was 1% xylan, 15% glucose, 63% mannose, 4% arabinose, and 17% galactose, as determined by enzymatic hydrolysis followed by capillary zone electrophoresis (CZE).[23] The degree of substitution of similar material, with respect to acetyl groups on the mannose units, was estimated to be 0.3 based on NMR measurements.[21]

The other materials used were alginic acid sodium salt from brown algae (Fluka, Steinheim, Germany; $M_w = 100,000–200,000$ g mol^{-1}), carboxymethylcellulose sodium salt (CMC) (Fluka, $M_w = 100,000–150,000$ g mol^{-1}), glycerol (Fluka, $\geq 98.0\%$, $M_w = 92.1$ g mol^{-1}), sorbitol (Acros Organics, Morris Plains, NJ; p.a., $M_w = 182.2$ g mol^{-1}), xylitol (Acros Organics, >99%, $M_w = 152.1$ g mol^{-1}), and magnesium nitrate hexahydrate (Riedel-de-Haën, Seelze, Germany; > 97%) as conditioning salt.

Methods

Casting of films

Films were cast from 14 mL aqueous solutions as indicated in Table I. The plasticizers used were glycerol, sorbitol, and xylitol, and the renewable polymers were alginate and carboxymethylcellulose (CMC). A physical blend film containing 0.07 g of each alginate and glycerol was also cast. Furthermore, a fragile film of pure AcGGM isolate was cast and tested with differential scanning calorimetry (DSC).

Firstly, all materials were weighed into an Erlenmeyer flask, and then mixed and heated in an oil bath at 95°C for 20 min under magnetic stirring. The AcGGM isolate dissolved rapidly in cold water, but heating ensured a complete mixing of the components. The solutions were poured into glass Petri dishes (diameter of 10 cm) coated with Teflon. The films were then left to dry under normal room conditions (~23°C, RH < 50%) for two days and finally

conditioned in a desiccator over magnesium nitrate hexahydrate for a minimum of 48 h prior to analysis. The desiccator conditions were 51.4 ± 3.1% RH and 21.2 ± 1.1°C.

Oxygen permeability

The oxygen transmission of the films was measured using a Mocon Ox-Tran® 2/20 apparatus (Modern Controls Inc., Minneapolis, USA) with a coulometric sensor in accordance with ASTM method D 3985–95. The area of measurement of the samples was 5 cm^2 and the analyses were made at 50% RH, which was instrumentally controlled. The room in which the instrument was kept had a humidity of 50.0 ± 6.2% RH and a temperature of 22.6 ± 1.1°C. The permeability was calculated on the basis of the transmission and the measured thickness of the films, and is presented as an average of two measurements with units (cm^3 μm)/(m^2 d kPa), where 1 d = 24 h. The thicknesses of the films were measured with a micrometer (Mitutoyo) at 10 different locations and inserted as mean values into the computer software. The thicknesses of the films varied between 30 and 60 μm. The films were preconditioned for a minimum of 48 h under conditions similar to those used during subsequent measurement (see Casting of films above). The films were further conditioned for 3 hours at 50% RH in the instrument itself before measurement began.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out on a Perkin–Elmer DMA 7 equipped with a custom-made cooling aggregate controlled by a separate computer (an instrument owned and developed by STFI-Packforsk AB). Films were kept in a desiccator for a minimum of 48 h under conditions similar to those used prior to oxygen permeability measurements. It was decided that maintaining the same conditioning histories for the two measurement methods would best facilitate comparison. Samples with a width of 3–5 mm and a height of 8–12 mm were cut for the dynamic mechanical testing. The dimensions of each sample were carefully, measured and the values were inserted into the instrument software as the mean of 10 measurement points per sample. For the measurement of storage modulus, the amplitude was varied between 2 and 4 μm with a frequency of 1 Hz. The static forces required varied between 55 and 160 mN. In the measurement chamber, the relative humidity could be controlled. A separate instrument (Optica chilled mirror precision hygrometer, General Eastern Instruments) connected to the cooling aggregate recorded the humidity in real time. One scan of three samples from each film was performed. The film sample was conditioned at 20% RH for two hours, after
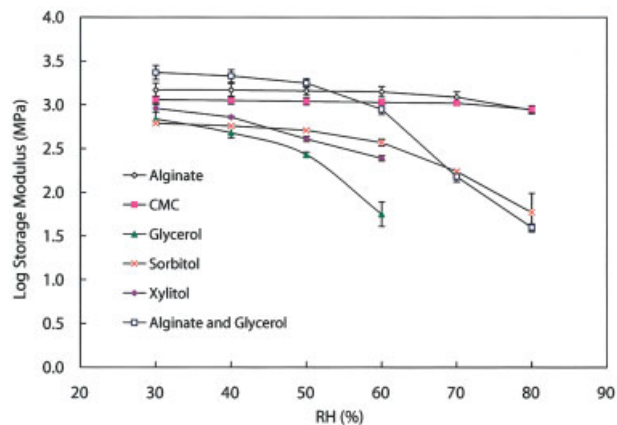
Figure 1 Storage modulus of AcGGM films as a function of varying moisture content (mean values of three samples per film). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

which a ramp up to 80% RH was applied during the DMA measurement at a rate of 1% RH per minute. The parameters were chosen to suit both the softer and the tougher materials.

Differential scanning calorimetry

DSC measurements were made with a Mettler Toledo DSC 820 with a method where the sample was heated in an aluminum crucible (40 μL) with a hole in the lid from $-70°C$ to $250°C$ at a rate of $10°C$ per minute with a nitrogen flow of 50 mL min^{-1}. The samples were lyophilized for 72 h prior to measurement (nonbound water was thereby removed).

RESULTS AND DISCUSSION

Film formation

All films were dry within 72 h when conditioned at $\sim23°C$ and RH $< 50\%$. It was observed that the one-component AcGGM films dried more quickly than the two-component films. This suggests that nonbound water molecules were more trapped within the net-

works of the two-component films and, therefore, evaporated more slowly.

The mechanism by which glycerol and other small molecules such as sorbitol and xylitol increase the mechanical plasticity of cast films is still not fully understood.[24] We assume that the plasticizers of low molecular weight intercalate between the hemicellulose chains and thus make the film easier to handle due to a loss of crosslinking hydrogen bonding. When a polysaccharide, or a derivative thereof, is added, the question of compatibility arises. By scanning electron microscopy (SEM), we observed that no phase separation had occurred as was predicted by the hydrophilicity of the components. This could also be seen as a good homogeneity of the casting solution. When the two-component film of AcGGM and alginate with glycerol was cast, it was assumed that the alginate would increase mechanical resilience while the plasticizer would improve the handling of the film. Such a blend could thus in a simple manner be expected to lead to a flexible, strong, and impermeable film.

Softening

The low molecular weight additives (glycerol, sorbitol, and xylitol) were applied as plasticizers to hemicellulose. As expected in a polysaccharide film containing a plasticizer,[11,25] a drop in storage modulus of these plasticized film samples was observed between ~35 and 50% RH on the DMA graph, as shown in Figure 1.

The glycerol-containing film clearly dampened most rapidly, while the decrease in storage modulus of the sorbitol- and xylitol-containing films was more or less comparable. A possible explanation is that glycerol is a liquid at room temperature whereas the alditols are solids.

The two-component films containing alginate or CMC and AcGGM formed hybrid films, which were mechanically the most resistant towards humidity and thus formed the most stable films (Table II).

When CMC was used almost no softening was observed up to 80% RH, whereas there was a small drop

TABLE II
Dynamic Softening of AcGGM Films

	Log storage modulus (MPa)					
	~30 %RH	$\sim40\%$ RH	$\sim50\%$ RH	$\sim60\%$ RH	$\sim70\%$ RH	$\sim80\%$ RH
Alginate	3.17 ± 0.08	3.17 ± 0.07	3.16 ± 0.05	3.15 ± 0.06	3.09 ± 0.06	2.94 ± 0.04
CMC	3.06 ± 0.04	3.05 ± 0.04	3.04 ± 0.04	3.03 ± 0.03	3.02 ± 0.03	2.95 ± 0.04
Glycerol	2.84 ± 0.08	2.68 ± 0.06	2.43 ± 0.03	1.75 ± 0.14	–	–
Sorbitol	2.79 ± 0.01	2.76 ± 0.02	2.71 ± 0.02	2.57 ± 0.04	2.24 ± 0.02	1.77 ± 0.22
Xylitol	2.96 ± 0.04	2.86 ± 0.01	2.61 ± 0.03	2.39 ± 0.03	–	–
Alginate and glycerol	3.37 ± 0.09	3.33 ± 0.08	3.25 ± 0.04	2.95 ± 0.04	2.18 ± 0.04	1.60 ± 0.06

TABLE III
Percentage Elongation of Samples after Dynamic Mechanical Analysis

	Elongation (%)
Alginate	4.1 ± 0.8
CMC	3.1 ± 0.1
Glycerol	195 ± 12
Sorbitol	16.9 ± 0.8
Alginate and glycerol	17.1 ± 2.6

in storage modulus for the film containing alginate at about 70% RH. The films made with low molecular weight additives were mechanically much weaker than the two-component films, and softened markedly when the moisture content was increased in the measurement chamber.

The two-component film of AcGGM and alginate containing glycerol as plasticizer had properties similar to those of the films made separately with either plasticizer or high molecular weight renewable polymer. All components were compatible due to their hydrophilicity, and homogeneous films could be produced, a conclusion that is supported by the smoothness of the DMA curve. The curve of the two-component film containing glycerol is situated between the curves of the films containing plasticizers and the films containing renewable polymer blends (Fig. 1). This film softened at a RH only slightly higher (at ~55% RH) than that at which the sorbitol-containing film softened, but well below the RH at which the AcGGM–alginate film softened slightly. This means that the incorporation of a plasticizer into the binary polysaccharide mixture results in a compromise between strength and flexibility.

Elongation

The percentage elongation of the film samples during the DMA moisture scans was determined. The elongation was calculated on the basis of the probe position before and after the measurement (a mean of three runs per film, Table III).

The film samples containing plasticizers were noticeably elongated during the measurements. The total elongation after measurement for the film containing glycerol was 195 ± 12%. The two-component film samples containing either alginate or CMC were mechanically the most resistant and also had the shortest elongations, 4 ± 1% and 3.1 ± 0.1%, respectively. The film containing AcGGM, alginate, and glycerol had an elongation of 18 ± 3%, suggesting that it is the larger alginate polysaccharide that contributes most to the mechanical properties of the film, while glycerol increases the elongation.

Oxygen barrier properties

Mixing alginate or CMC together with AcGGM to form a physical blend that could be dried into a two-component film gave the most resistant film towards oxygen permeation. As seen in Figure 2, the permeabilities measured were 0.6 and 1.3 (cm^3 μm)/(m^2 d kPa) for the films containing alginate and CMC respectively. In the case of the plasticizers, sorbitol addition gave a lower permeability, 2.0 (cm^3 μm)/(m^2 d kPa), than glycerol (4.6 (cm^3 μm)/(m^2 d kPa)) or xylitol (4.4 (cm^3 μm)/(m^2 d kPa)) addition. This sorbitol-containing film softened at a higher RH during DMA measurements than the other plasticized films, and this suggests that sorbitol packs together more tightly with the AcGGM than that of xylitol or glycerol.

Glycerol softens the AcGGM film already at about 35% RH (Fig. 1), and this film is thus the least tolerant to moisture, which may explain why permeability measurements at 50% RH were not possible for this film. Pinholes were probably formed in the film. The oxygen permeability of the glycerol-plasticized blend film was higher than that of the AcGGM–alginate film, 4.6 compared to 0.6 (cm^3 μm)/(m^2 d kPa). The network of alginate or CMC together with AcGGM is less permeable to oxygen than the network containing glycerol, sorbitol, or xylitol. In AcGGM–alginate and AcGGM–CMC films, strong energetic interactions between the polymer chains are expected due to the numerous polar pendant groups. This results in a more rigid polymer chain network combined with a low free volume between chains that may improve the barrier properties under humid conditions.

The oxygen permeability of the AcGGM films is similar to or lower than the values reported for films from glucuronoxylan[18] and other polysaccharides, such as starch[26] and chitosan,[27] and mixtures of various polysaccharides.[3] For example, a film consisting of
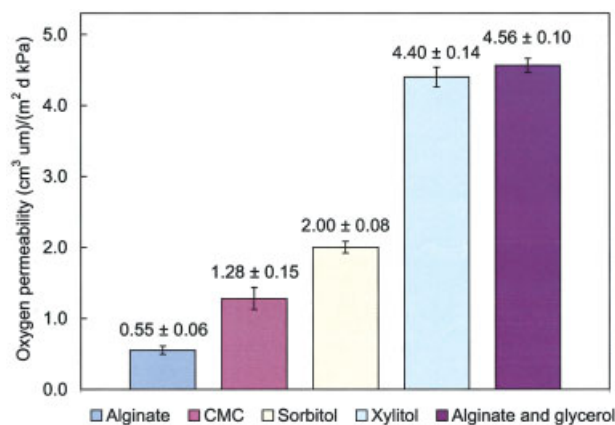

Figure 2 Oxygen permeabilities of AcGGM films containing given additives. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
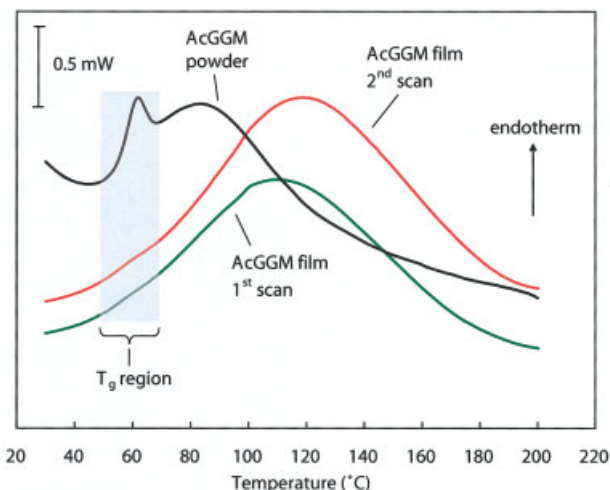
Figure 3 Differential scanning calorimetry of the AcGGM powder compared to the 1st and 2nd scans of an AcGGM film without additives. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

32.5 wt % soluble starch, 32.5 wt % methylcellulose, 30 wt % sorbitol, and 5 wt % water had a reported permeability of 5.7×10^{-11} cm^2 Pa^{-1} s^{-1}, which corresponds to 1200 (cm^3 μm)/(m^2 d kPa). [3] Furthermore, the barrier properties of AcGGM films are in the same range as those of conventional mineral-oil-based barrier materials, such as polyethylene vinyl alcohol (dry conditions,[28] humid conditions[29]) and polyvinylidene chloride.[28] Proteins like whey[30] and blends of proteins with polysaccharides[31] generally show higher permeabilities.

Thermal transitions

DSC was applied to detect first and second order transitional behavior in the AcGGM isolate. A thermogram of the AcGGM isolate—in both powder and film form—is shown in Figure 3. No thermal events occurred after 200°C except for exothermic peaks with an onset at about 230°C representing the beginning of thermal degradation.[32]

The endothermic peak occurring in the region from 30 to 200°C is attributed to water loss and represents the energy required to vaporize water present in the samples. The water seems to be trapped more in the film than in the powder as a consequence of various molecular and diffusional forces. A second run, immediately after the first, showed that water was still evaporating. In the DSC curve of the powder, an additional endothermic event resembling a glass transition was visible at 55–65°C (T_g). When inspected closely, the curves for the film sample showed a slight discontinuity in this temperature range. We suggest that this discontinuity is due to a glass transition of the sample.

For this reason, we studied the effect of plasticizer on this T_g. Results for a film with added glycerol and for an unplasticized film are shown in Figure 4. Firstly, it is evident that the broad endothermic peak of the glycerol-containing film had a much smaller area than the peak of the unplasticized AcGGM film.

This suggests that the water was much less trapped in the plasticized film and was almost as free as in the powder sample (compare Fig. 3). The discontinuities indicate that the T_g seemed to be about 5°C lower (than around 60°C) in the film containing glycerol as additive.

CONCLUSIONS

Acetylated galactoglucomannan (AcGGM) hemicellulose isolated from TMP process water was found to be an excellent candidate for making new renewable barrier materials intended for food packaging. To obtain good properties, an appropriate plasticizer and a high-molecular weight renewable polymer can be used with AcGGM in a physical blend. Low oxygen permeabilities were found, by analogy with many other films made from polysaccharides. The addition of a plasticizer such as glycerol, sorbitol, or xylitol resulted in increased film flexibility. Such an addition, however, also makes the film more susceptible to moisture. When a two-component system of AcGGM and a renewable high-molecular weight polymer was used, the mechanical strength and resistance towards humidity increased. The incorporation of a plasticizer resulted in a compromise between strength, low per-
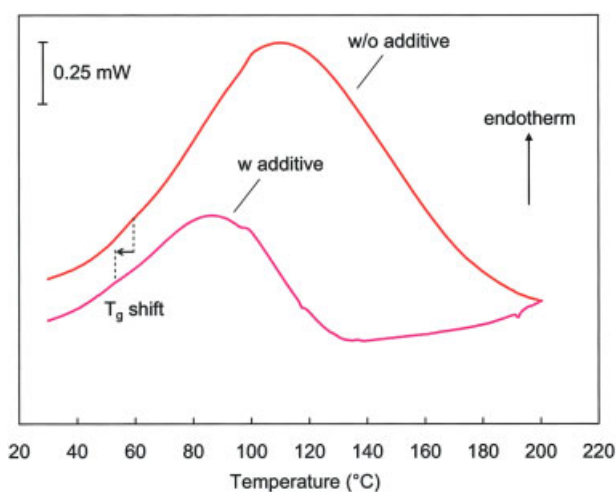

Figure 4 Differential scanning calorimetry of a lyophilized AcGGM film sample without additive (w/o additive) and of an AcGGM film with 25 wt % glycerol (w additive) scanned once. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

meability, moisture resistance, and handling properties. Since all the raw materials used were obtained from renewable sources and are completely biodegradable, this work strongly supports the idea of sustainable development.

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