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Plasticized xyloglucan for improved toughness—Thermal and mechanical behaviour

Elina Mabasa Bergström[a], Lennart Salmén[a,c,*], Joby Kochumalayil[b], Lars Berglund[b,c]

[a] INNVENTIA AB, Fibre & Material Science, Box 5604, SE-114 86 Stockholm, Sweden
[b] Department of Fibre and Polymer Technology, Royal Institute of Technology, SE-100 44 Stockholm, Sweden
[c] Wallenberg Wood Science Centre, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

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ABSTRACT

Tamarind seed xyloglucan is an interesting polysaccharide of high molar mass with excellent thermomechanical properties. Several plasticizers were studied in order to facilitate thermal processing and improve toughness (work to fracture) of xyloglucan film materials: sorbitol, urea, glycerol and polyethylene oxide. Films of different compositions were cast and studied by thermogravimetric analysis (TGA), calorimetry (DSC), dynamic mechanical thermal analysis (DMA) and tensile tests. Results are analysed and discussed based on mechanisms and practical considerations. Highly favourable characteristics were found with XG/sorbitol combinations, and the thermomechanical properties motivate further work on this material system, for instance as a matrix in biocomposite materials.

1. Introduction

There is a growing trend in research and industry for possible replacement of fossil and coal based materials with those that are biobased (Gandini, 2008; Petersen et al., 1999). Among the more common materials studied are polysaccharides such as starch, hemicelluloses from wood or grains, and cellulosic fibrils (Bastioli, 1998; Berglund & Peijs, 2010; Hansen & Plackett, 2008; Henriksson, Berglund, Isaksson, Lindström, & Nishino, 2008). However, wood hemicelluloses are generally of rather low molecular weight exhibiting modest mechanical properties while starch is competing with the food chain, which is why polysaccharides with better properties from non-food resources are of high interest. To this end, a polysaccharide – xyloglucan – derived from the seed of tamarind (*Tamarindus indica*) is an appealing alternative. It can be extracted from de-oiled tamarind kernel powder as a water soluble polymer (Edwards, Dea, Bulpin, & Reid, 1985). At present it is commercially utilized as a food thickener and as a sizing agent in textile, paper and jute industries and most recently in some specific applications such as drug-delivery technology (Mishra & Malhotra, 2009).

Being a primary cell wall constituent of plants, xyloglucan (XG) has been extensively studied and characterized from a botanic point of view by several authors (Fry, 1989; McNeil, Darvill, Fry, & Albersheim, 1984; Whitney, Brigham, Darke, Reid, & Gidley, 1995; Whitney, Gothard, Mitchell, & Gidley, 1999), but it is only recently that research into the use of XG as an engineering material has been performed (Kochumalayil, Sehaqui, Zhou, & Berglund, 2010). Xyloglucan, or galactoxyloglucan, is a common name given to a group of $\beta(1 \rightarrow 4)$ linked glucan chains identical to cellulose chains, with up to 75% of the glucose residues substituted with $\alpha(1 \rightarrow 6)$ linked xylose, where some of these xylose groups have a $\beta(1 \rightarrow 2)$ linked galactose residue (Gidley et al., 1991; Urakawa, Mimura, & Kajiwara, 2002).

Tamarind XG has previously been shown by Kochumalayil et al. (2010) to be easily cast into films, attributed to its high molecular mass of the order of more than 2 MDa. In characterizing the thermal properties of XG, a glass transition of ca. 260 °C at a frequency of 1 Hz is observed (Kochumalayil et al., 2010). The unusually high thermal stability of XG with a degradation temperature above its glass transition makes XG a very interesting polymer for the use in applications such as in film forming. Still, the high T_g makes thermal processing a difficult and uneconomical route which is why it is of interest to explore the use of plasticizers to reduce this high softening temperature. Previous work (Kochumalayil et al., 2010), utilized glycerol showing a good response at about 10 wt% plasticizer addition. However higher amounts of glycerol may have led to phase separation. The difficulty in plasticization is attributed to the solution architecture of XG where the macromolecules are in self-aggregated state rather than separate individual chains (Gidley et al., 1991; Lang & Kajiwara, 1993; Lang, Kajiwara, & Burchard, 1993). The plasticizing action was on these molecular aggregates

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* Corresponding author. Tel.: +46 8 6767340; fax: +46 8 4115518.
E-mail address: lennart.salmen@innventia.com (L. Salmén).

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rather than the individual chains. In order to further explore the possibilities of modifying the properties of XG different plasticizers were investigated: urea, PEG 600, glycerol and sorbitol in different weight percentages and a modified mixing procedure was adopted for effective plasticization. The thermo-mechanical characteristics of such plasticized XG films were investigated. Since many polysaccharides tend to be brittle, it is of particular interest to increase ductility (strain to failure) and toughness (work to fracture, area under stress–strain curve in tension).

2. Experimental

2.1. Preparation of XG solution

Industrially purified XG from tamarind seeds was acquired from Innovassynth Technologies Ltd., India. The powder was further purified by preparing an aqueous solution of 0.5 wt% XG in distilled water, heating it at 60 °C for 60 min before centrifuging at 4000 rpm for 30 min to separate protein matter. This was followed by filtration using a Büchner funnel having glass microfiber filters (Whatman GF/A, pore size 1.6 μm). The solution was then freeze dried to obtain pure XG for further experiments.

2.2. Plasticizers

The plasticizers in this study were chosen so as to interact with the hydroxyl groups of the XG; sorbitol (sugar alcohol), glycerol (alcohol), urea (amine) and polyethyleneoxide (polyoxide). They were purchased from laboratory suppliers such as Sigma–Aldrich. The properties of these plasticizers are given in Table 1.

2.3. Film casting

The XG was first mixed with deionised water and to ensure dissolution of the material it was heated at 60 °C for 60 min under continuous magnetic stirring. The solution was further mixed through the use of a small micro-fluidizer, Ultra-Turrax®, for 15 min at 9500 rpm. Four different plasticizers – urea, glycerol, polyethylene glycol 600, and sorbitol – were used and the desired plasticizer was mixed with the XG solution in the range of 10–40 wt% under magnetic stirring for 2 h. This was followed by an intense mixing at 8000 rpm for 15 min using the micro-fluidizer. Once cooled to 30 °C, centrifuging at 4000 rpm for 20 min ensured removal of air bubbles. The solution was then spread over a Petri dish and placed on a levelled oven shelf at 35 °C. The dried films were peeled-off, and conditioned at 23 °C, 50% RH.

2.4. Thermogravimetric analysis (TGA)

TGA measurements were conducted on a Perkin-Elmer TGA7 in order to determine the thermal stability of the samples. About 4 mg of samples of XG as well as XG containing 40 wt% of different plasticizers were tested. An initial drying of 15 min at 35 °C was followed by a temperature scan of 5 °C/min up to 400 °C. Helium gas was used for sample purge and nitrogen gas for balance purge. The gas flow rates were 26 ml/min and 40 ml/min, respectively.

2.5. Differential scanning calorimetry (DSC) analysis

DCS tests were done on a TA Instruments Q1000 Auto MDSC to determine the glass transition temperature, T_g, of the samples. About 2 mg of each film composition prepared was tested in duplicate runs. Prior to testing samples were dried in an oven, stored in desiccators and then hermetically sealed in a dry atmosphere. Modulated DSC scan (±1 °C every 60 s) with a ramp rate of 3 °C/min was used. The temperature interval was 30–260 °C. The nitrogen flow rate was 50 ml/min. The upper range was set to be below the temperature at which the plasticizers evaporated/phase separated. A shift in baseline of the heat capacity (C_p) of the reversible C_p was utilized to determine the glass transition.

2.6. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties were determined in temperature scans using a Perkin-Elmer DMA 7 operating in tensile mode. The sample size was 20 mm × 5 mm × 0.02 mm. A measuring frequency of 1 Hz and an amplitude 5 μm was used. Temperature scans with an initial drying and conditioning sections were used with a ramp rate of 3 °C/min in the interval 30–300 °C. Helium at a flow rate of 40 ml/min was used as sample purge.

2.7. Tensile testing

Tensile testing was carried out on a Perkin-Elmer DMA 7e operating in tensile mode in an environment of 50%RH, 30 °C. The humidity was controlled using a SETARAM WetSys Humidity Controller with a flow rate of 50 ml/min that mixed dry air and water-saturated air to the desired humidity. The sample size was 20 mm × 5 mm × 0.02 mm. The films were conditioned at 50%RH for 48 h prior to testing. The applied loading rate was 500 mN/min. Only the pure XG films and XG plasticized films with 20 and 30 wt% sorbitol were evaluated; ten specimens per film tested. Young's modulus was calculated from the tangent of the initial slope of the linear part of the stress–strain cure (ca 1% strain).

2.8. Brabender mixing and compression moulding

Thermal processing of the samples was evaluated using vacuum compression moulding: blending in a twin screw Brabender PL2000 with $L/D = 30$ and $D = 25$ mm, and compression moulding in a Fontyne press. The plasticized XG solution containing 30 wt% sorbitol was first mixed with Ultra-Turrax and freeze dried, subsequently a paste was prepared by adding 125 ml of water to 15 g of XG before mixing in the Brabender. Mixing was done at 120 °C for 25 min at 32 rpm. A continuous water feed during mixing maintained the material as a paste. The paste was evenly distributed in the mould before compression. Vacuum compression was performed at 210 °C, with a pressure of 200 kN for 1 min before cooling, maintaining the pressure at 200 kN.

3. Results

3.1. Film formation

The film casting from the different solutions (different types of plasticizer and plasticizer content) resulted in all cases in cohesive more or less transparent films. The intense mechanical treatment reduced the molecular aggregation in the solution as noticed by the change in the viscosity (which decreased from 120 cP to 80 cP after 15 min of Ultra-Turrax mixing) without changing the molecular weight. However a phase separation occurred in films containing 20 or more wt% urea. This was noted as visible patches of white urea crystals on the film surface. Higher concentrations of urea led to a larger surface area covered by such crystals. Only those films with concentrations of 10 wt% urea were characterized.

3.2. Thermal properties

Fig. 1 shows that the pure XG has extremely good thermal stability for being a polysaccharide. Only at about 300 °C degradation started, being partly completed at around 370 °C. This is similar

Table 1
Properties of some plasticizers.

Plasticizer	Mol. wt. (g/mol)	Specific gravity (g/cm$^{3)}$	T_g (°C)[a]	T_m (°C)[a]	T_b (°C)[a]	Water solubility
D-Sorbitol $C_6H_{14}O_6$	182.17	1.506	−2.3	96.8	362	Soluble
Glycerol ($C_3H_8O_3$)	92.09	1.26	−83	18	290	Miscible
Poly(ethylene) oxide-600 $(C_2H_4O)_n$ H_2O	Average 600	1.13/1.33	−67/−27	61/73	–	Soluble
Urea $(NH_2)_2CO$	60.06	1.3230	∼ −3[b]	133	135 (decomposes)	Highly soluble

[a] As reported in literatures (Angell, Sare, & Sare, 1978; Gombás, Szabó-Révész, Regdon, & Erős, 2003; Schaber et al., 2004; Van Krevelen & Te Nijenhuis, 1990; Yan & Suppes, 2008).

[b] Calculated using the Bayer–Beaman rule as applied to organic compounds (i.e. ratio of T_g/T_m is 2/3) (Beaman, 1952).

to the observations made for cellulose, with a pyrolysis temperature in the range of 300–400 °C (Alen, Kuoppala, & Oesch, 1996; Yang, Yan, Chen, Lee, & Zheng, 2007). Hemicelluloses generally show a lower thermal stability than cellulose, probably due to their lack of crystallinity. This can be exemplified with the pyrolysis behaviour of spruce galactoglucomannan (Mikkonen et al., 2010) and xylan (Yang et al., 2007) with most of the weight loss appearing at 220–300 °C with a maximum at around 250 °C. The unusual thermal stability of XG could be explained partly with its stiff cellulose back-bone and the chain packing of the long polymer molecules.

As seen all the plasticized XG films showed lower thermal stability. With sorbitol as a plasticizer weight loss begins around 250 °C. Nearly 40% of the weight was lost up to 300 °C most probably due to evaporation of the sorbitol exhibiting increasing vapour pressure in the range of 250–350 °C (Yan & Suppes, 2008). The remaining degradation followed that shown for the pure XG. For the glycerol containing film a weight loss of more than 20% occurred between 130 °C and 170 °C most probably being related to evaporation of much of the smaller glycerol molecules although the glycerol has a boiling point of 290 °C. A somewhat similar result may be deduced from the PEG containing film. Presumably an evaporation of the lower molecular weight components of the PEG 600 started at about 180 °C and then progressed throughout the temperature scan. For the urea containing film this was, as discussed above, a blend of a plasticized XG film containing 10–15% urea with the remaining part of the urea being phase separated into urea crystals. The weight loss of about 30% seen between 150 and 200 °C was probably caused by a degradation of the phase separated urea crystals. A decomposition temperature of 135 °C has been noted for pure urea. The remaining part of the urea, presumably more closely interacting with the XG, seemed to result in a further increase in the thermal stability of the mixture up to a temperature of 280 °C where further degradation occurred. This anomalous behaviour of urea could be explained by the formation of an inclusion complex in H-bonded xyloglucan as noted for the dissolution of cellulose fibres in the urea–NaOH system (Cai et al., 2008).

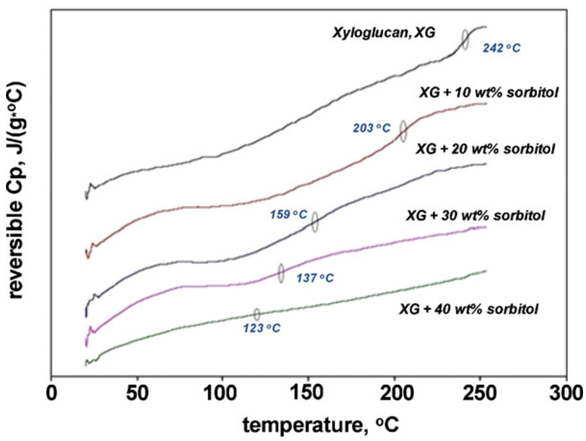

Fig. 2. Reversible heat capacity, C_p, of XG and XG plasticized with 10, 20, 30, and 40 wt% sorbitol respectively; T_g encircled.

The DSC runs showed phase transitions, as changes in baseline of the reversible heat capacity (C_p), indicating glass transitions as exemplified by the plasticizing of XG by sorbitol in Fig. 2. With increasing amounts of sorbitol the glass transition temperature was progressively reduced.

In Fig. 3 the effect of increasing plasticizer content on the T_g for the different plasticizers are compared. For the use of PEG 600 no distinct T_g was observable by the DSC runs, except for the lowest amount 10% for which the XG T_g seemed to be unaffected. The reason could be the molecular weight distribution of the PEG resulting in a heterogeneous softening of XG rendering a rather broad softening region. Both sorbitol and glycerol decreased the T_g of XG as expected based on their respective T_g and compatibility with XG, the glycerol being somewhat more effective due to its lower T_g of

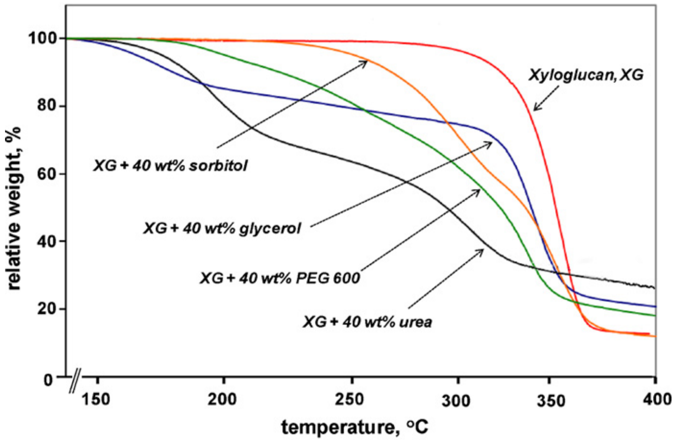

Fig. 1. Thermogravimetric analysis of xyloglucan, XG as well as plasticized XG-films, containing 40 wt% urea, glycerol, sorbitol and PEG 600 respectively.

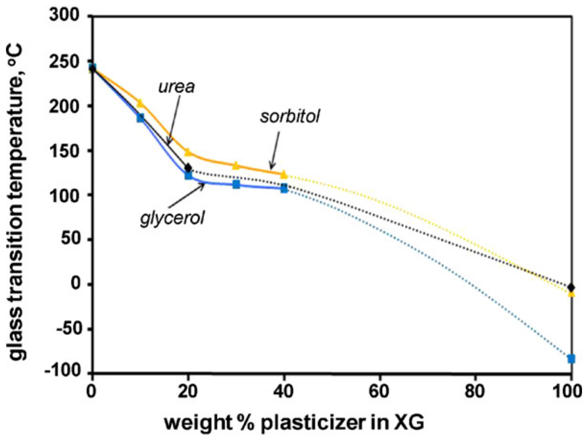

Fig. 3. Effect of plasticizer content, wt%, on the glass transition temperature of XG-films.

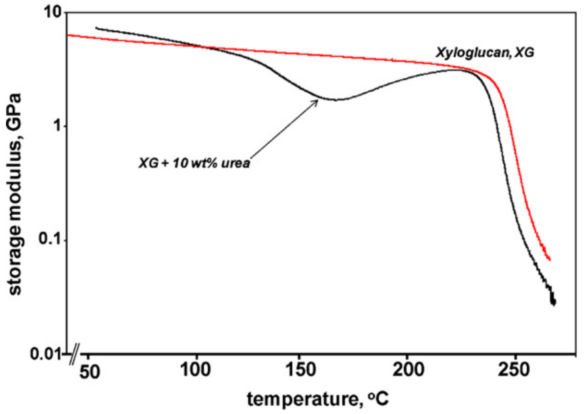

Fig. 4. Storage modulus at 1 Hz versus temperature for pure XG film as well as an XG film containing 10 wt% urea.

the pure solvent. One should also recognize that the molar weight of the glycerol is only half of that of the sorbitol. The urea containing samples were difficult to measure due to phase separation problems and thus uncertainity with regard to the exact composition of the sample. The result at 20 wt% urea indicated a behaviour similar to sorbitol and glycerol. Also previously urea has been found to have similar plasticizing effects as compared to sorbitol and glycerol (Lourdin, Coignard, Bizot, & Colonna, 1997).

The thermomechanical properties of the different films were examined at a frequency of 1 Hz. For the urea containing film only the one containing 10% urea was tested as films with higher amount of urea showed phase separation. As seen in Fig. 4 the urea caused a softening of the film at about 130 °C followed by an antiplasticization at 150 °C. The probable cause of this was a decomposition of the urea as discussed above. The final softening of the film occurred only at a slightly lower temperature than that of the originally pure XG film.

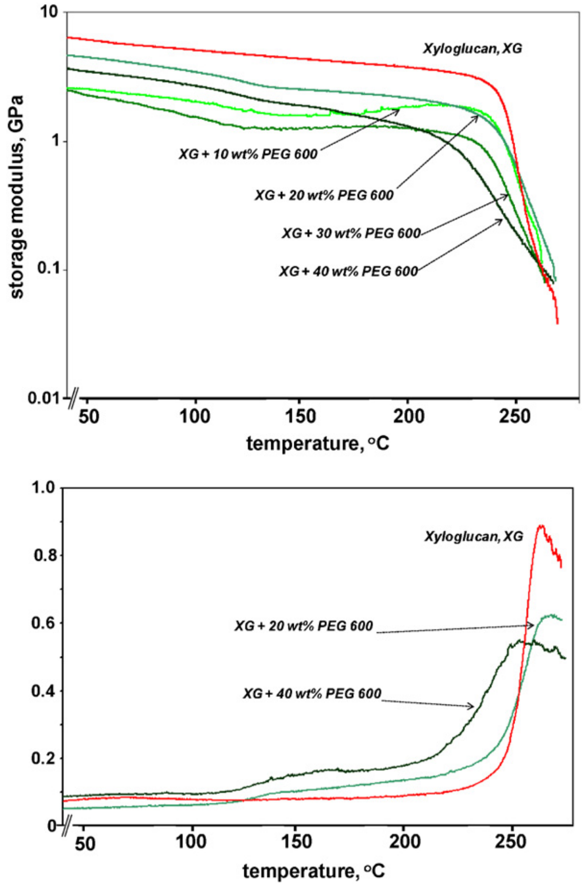

Fig. 5. Storage modulus and examples of tan δ at 1 Hz versus temperature for pure XG as well as XG films containing 10, 20, 30 and 40 wt% PEG 600.

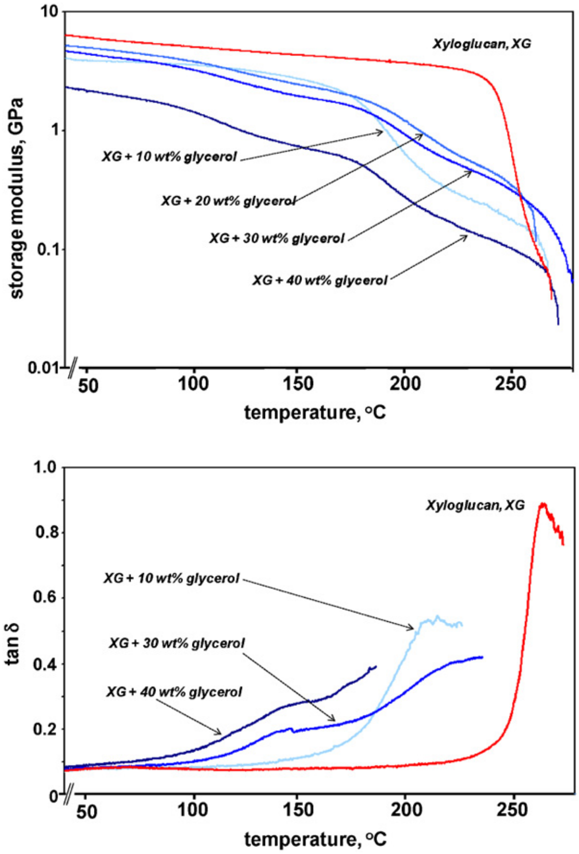

Fig. 6. Storage modulus and examples of tan δ at 1 Hz versus temperature for pure XG as well as XG films containing 10, 20, 30 and 40 wt% glycerol.

Fig. 5 displays the properties of the PEG containing films. Obviously a minor softening effect occurred with increasing PEG content despite the fact that some of the PEG probably started to evaporate at about 170 °C; see the TGA measurements above.

For the glycerol containing films (Fig. 6) the behaviour seems complex. The softening temperature occurs here in the region of glycerol evaporation. Only the sample containing 10% glycerol showed a clear and large stiffness drop of the film corresponding to the expected glass transition temperature of the glycerol/XG mixture. At higher glycerol contents an indication of softening was seen at lower temperatures, decreasing with increased glycerol content and closely matching the T_g of the mixture as seen from Fig. 3. However the degree of softening was probably highly affected by a simultaneous evaporation of the glycerol being extensive above 120 °C; compare Fig. 1. For all these mixtures a second softening was apparent above 180 °C, closely matching the softening of the 10% glycerol/XG mixture. This could indicate a more closely association between glycerol and XG at the lower glycerol content somewhat hindering the evaporation of this remaining glycerol. At temperatures above this softening, up to the softening of pure XG it seems as also the remaining glycerol may have evaporated. This type of behaviour was earlier noted for glycerol/XG mixtures where the role of possible "cross-linking" effects in glycerol–starch systems were addressed (Kochumalayil et al., 2010).

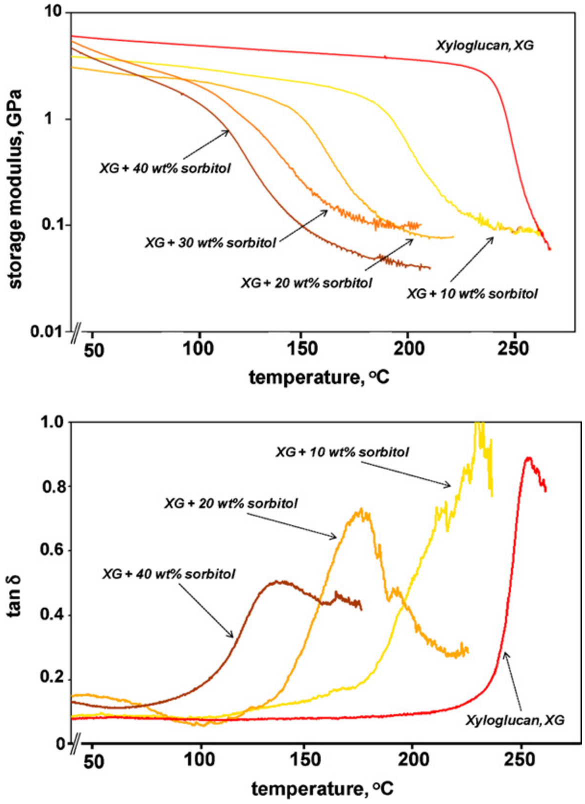

Fig. 7. Storage modulus and examples of tan δ at 1 Hz versus temperature for pure XG as well as XG films containing 10, 20, 30 and 40 wt% sorbitol.

For the films containing sorbitol a clear softening effect was evident with a progressive lowering of the softening temperature with increasing content of sorbitol (Fig. 7). This softening corresponds with the T_g of the sorbitol/XG mixture as evident from Fig. 3. Thus with sorbitol as a plasticizer the softening of the XG film may be lowered to below the evaporation or decomposition temperature of the plasticizer making sorbitol a good candidate for extrusion moulding of XG-softener mixtures.

3.3. Tensile properties

The stress–strain properties of XG films were compared for films containing 20 and 30% sorbitol with that of a pure XG film. XG films do absorb moisture why the samples here were tested at an RH of 50%. Evidently as seen from Fig. 8, although XG absorbs moisture acting as a softener, the pure XG films were somewhat brittle with a strain to failure of only about 4%. In contrast the XG film with 20 wt% sorbitol showed a ductile behaviour with a strain to failure above 25%. Still the films had very good strength and modulus as evident from Table 2. Qualitatively, it is also clear from Fig. 8, that the work to fracture (area under stress–strain curve) was much improved with sorbitol addition.

Fig. 9. Hot pressed XG film with 30 wt% sorbitol (0.1 mm thick).

3.4. Industrial application

3.4.1. Vacuum compression moulding

The industrial applicability of sorbitol plasticized XG films was looked at with regard to mouldability for a 30 wt% mixture of sorbitol and XG. The hypothesis was that a film could be hot pressed from such a XG/sorbitol paste possessing a T_g below 150 °C. As seen in Fig. 9 the hot pressing performed at 210 °C resulted in a thin film of 0.1 mm thickness. The film formed was ductile and tough as well as transparent. Some discolouration due to the press was observed but could probably with a more continuously applied process be avoided. As seen from Fig. 10, the thermomechanical

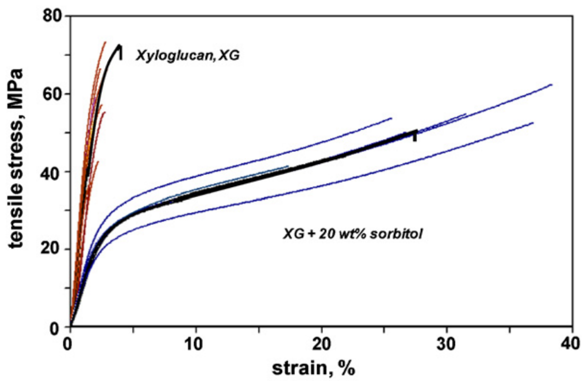

Fig. 8. Stress–strain curves for pure xyloglucan, XG, films as well as XG films containing 20 wt% sorbitol.

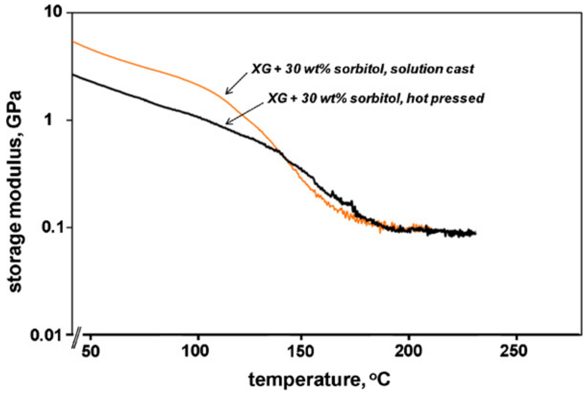

Fig. 10. Storage modulus of solution casted and hot pressed xyloglucan films containing 30 wt% sorbitol.

Table 2
Average values of Young's modulus (E), strength (σ) and strain to failure (ε) for the XG film and XG film with 20 and 30 wt% sorbitol. Values in brackets are standard deviations.

	Strain to failure, ε (%)	Strength, σ (MPa)	Young's modulus, E (GPa)
XG	2.3 (0.7)	67.7 (4.0)	4.1 (0.3)
XG + 20 wt% sorbitol	27 (7)	50(6.5)	1.17 (0.09)
XG + 30 wt% sorbitol	50 (13)	43 (10)	0.65 (0.11)

properties were close to those of the solution cast films although a broader softening region was experienced. An improvement in the homogenisation of the paste may probably improve the material properties.

4. Conclusions

The investigation of the effect of different types of plasticizers on the softening of xyloglucans, has demonstrated the attractive combination of modulus, strength and toughness (area under stress–strain curve) for XG with 20–30% sorbitol. In addition, the plasticized material showed considerable thermal stability with a glass transition temperature exceeding 130 °C for those compositions. Due to the very high T_g of XG (≈250 °C), several plasticizers studied have disadvantages in the form of either evaporating or decomposing at temperatures lower than that of the softening temperature achieved of the XG/plasticizer mixture. With moderate amounts of sorbitol (20%), strong ductile films were formed from solvent casting. As an application demonstrator, it was also shown that compressing moulding of XG/sorbitol mixtures produces transparent films with good mechanical properties.

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