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Enhanced film forming and film properties of amylopectin using micro-fibrillated cellulose

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Abstract

This work describes a novel approach to produce amylopectin films with enhanced properties by the addition of microfibrillated cellulose (MFC). Aqueous dispersions of gelatinized amylopectin, glycerol (0–38 wt%) and MFC (0–10 wt%) were cast at ambient temperature and 50% relative humidity and, after 10 days of storage, the tensile properties were investigated. The structure of the composite films was revealed by optical, atomic force and transmission electron microscopy. The moisture content was determined by thermogravimetry and the temperature-dependent film rigidity was measured by thermal mechanical analysis. Synchrotron simultaneous small- and wide-angle X-ray measurements revealed that the solutions had to be heated to above 85 °C in order to achieve complete gelatinization. Optical microscopy and atomic force microscopy revealed uniformly distributed MFC aggregates in the films, with a length of 10–90 μm and a width spanning from a few hundred nanometers to several microns. Transmission electron microscopy showed that, in addition to aggregates, single MFC microfibrils were also embedded in the amylopectin matrix. It was impossible to cast amylopectin films of sufficient quality with less than 38 wt% glycerol. However, when MFC was added it was possible to produce high quality films even without glycerol. The film without glycerol was stiff and strong but not brittle. It was suggested that this remarkable effect was due to its comparatively high moisture content. Consequently MFC acted both as a "conventional" reinforcement because of its fibrous structure and also indirectly as a plasticiser because its presence led to an increase in film moisture content.

Keywords: Amylopectin films; Microfibrillar cellulose; Glycerol; Mechanical properties; Plasticiser

1. Introduction

There is a continuous development of "environment-friendly" biodegradable plastic films from starch and its main constituents (amylose and amylopectin) to compete with and replace synthetic polymers in several applications. Although starch is promising because of its low price and its ready availability, the huge variety of starch sources makes it difficult to establish a general route for the fabrication of starch-based films. The is due particularly to the variation in content of the two high-molecular weight components of starch: amylose and amylopectin.

Amylose constitutes the linear glucan fraction of starch, while the amylopectin molecules are highly branched (Ritzl, Regev, & Yerushalmi-Rozen, 1998). It has been observed that the functional properties, e.g., the film ductility and the barrier properties, of amylose films are, in general, slightly better than those of amylopectin films (Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998). In addition, the crystallinity of amylose is relatively stable, unlike that of amylopectin which crystallizes to various extents during

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ageing (Biliaderis, 1991; Lionetto, Maffezzoli, Ottenhof, Farhat, & Mitchell, 2005; Myllärinen, Buleon, Lahtinen, & Forssell, 2002; Paton, 1987; Rindlav-Westling et al., 1998). On the other hand, amylopectin films have a higher clarity than those of amylose.

The brittleness of amylopectin films (and also of amylose and starch) necessitates the use of a plasticiser. The plasticiser improves the flexibility and extensibility of the films but, due to the reduction in intermolecular cohesive forces, it also leads to an increase in the gas, vapour and liquid permeabilities (Mali, Grossmann, Garcia, Martino, & Zaritzky, 2002).

Recently, composite materials based on cellulose and/or its derivatives have become a topic of intense research (Averous & Boquillon, 2004; Berglund, 2005; Borges, Godinho, Martins, Trindade, & Belgacem, 2001; Chiellini, Cinelli, Imam, & Mao, 2001; Dufresne, Dupeyre, & Vignon, 1999; Seavey, Ghosh, Davis, & Glasser, 2001). The reasons are that cellulose fibres are (i) renewable and biodegradable, (ii) abundant and inexpensive; (iii) available in a large variety of different morphologies, geometries and surface properties depending on the source and/or separation process and (iv) comparable in specific strength to commodity fibres, including glass fibres (Borges et al., 2004). In addition, it has been demonstrated that cellulose fibres show good compatibility with polysaccharide matrices. The armouring component is the crystalline cellulose in the 3.5–20 nm wide microfibrils (Cousins & Brown, 1995; Heigler, 1985).

In the early 1980s, Turbak, Snyder, and Sandberg (1983) and Herrick, Casebier, Hamilton, and Sandberg (1983) developed a method for the liberation of these microfibrils. The material is referred to as microfibrillated cellulose (MFC) and consists of long nano-scale bundles of microfibrils, which form entangled networks. MFC is normally prepared by the delamination of delignified wood fibres in high-pressure homogenisers and the diameter of the MFC manufactured from Scandinavian softwood pulp is approximately 17–30 nm (Pääkkö et al., 2006). The high specific strength of MFC enables strong composite materials to be manufactured (Berglund, 2005; Nakagaito & Yano, 2004; Nakagaito, Iwamoto, & Yano, 2005; Nakagaito & Yano, 2005).

Apart from the source of the starch and the type of plasticiser used (Elder & Schoch, 1959; Swinkels, 1985; Takahashi & Nakamura, 1970), which are all fixed in this investigation, a number of additional factors influence the properties of the films. These are the temperature during mixing, the composition of the film, the temperature and relative humidity during film formation/casting and the film storage conditions. In the present investigation, some of these factors were varied systematically to optimise the properties of the pure and fibre-reinforced amylopectin films.

In order to obtain acceptable film properties, it is essential that the degree of gelatinization is as high as possible before casting. The gelatinization of starch involves hydration, swelling, loss of birefringence and loss of crystallinity, and it has been monitored using, e.g., differential scanning calorimetry (Kohyama, Matsuki, Yasui, & Sasaki, 2004; Souza & Andrade, 2002), X-ray scattering (Jenkins & Donald, 1998), light scattering (Funami et al., 2005), optical microscopy (Thiré, Simao, & Andrade, 2003) and NMR spectroscopy (Cooke & Gidley, 1992). In this investigation, the extent of gelatinization of amylopectin was monitored by optical microscopy and, for the first time, by synchrotron simultaneous small- and wide-angle X-ray scattering.

The purpose of the present investigation was (1) to establish an adequate film-making process and (2) with the help of MFC, to enhance the mechanical properties of the films.

2. Experimental

2.1. Materials

For this study, maize amylopectin from Fluka Biochemika (Sigma–Aldrich Chemie GmbH, Steinheim, Germany) was used. The plasticiser used was glycerol (99.5% purity) which was purchased from Karlshamn Tefac AB (Karlshamn, Sweden).

2.2. Preparation of microfibrillated cellulose

The preparation of MFC is described in detail in the work of Pääkkö et al. (2006) and will therefore only by summarised here. Bleached sulphite softwood pulp (Domsjö ECO Bright; Domsjö Fabriker AB) consisting of 40% pine (*Pinus sylvestris*) and 60% spruce (*Picea abies*) with a hemicellulose content of 13.8% (measured as solubility in 18% NaOH, R18) and a lignin content of 1% (estimated as 0.165* Kappa number (SCAN C 1:00)) was used as a source for MFC. The pulp was used in its never-dried form. The cell wall delamination was carried out by treating the pulp in four separate steps: a refining step using an Escher–Wyss refiner in order to increase the accessibility of the cell wall to the subsequent enzyme treatment, an enzymatic treatment step using monocomponent endoglucanase, a second refining stage and finally passing the pulp slurry through a high-pressure microfluidizer. The phosphate buffer used during the enzymatic treatment, with a pH between 6.8 and 7.2, was prepared from 11 mM KH_2PO_4 to 9 mM Na_2HPO_4. A microbiocide, 5-chloro-2-ethyl-4-isothiazolin-3-one, was added to the MFC in order to prevent bacterial growth.

2.3. Film preparation

Amylopectin (AP) films were cast from aqueous dispersions with 2 or 3 wt% of amylopectin (concentrations with respect to the total weight of the film-forming solution) and glycerol as a plasticiser (0, 20, 33 or 38 wt% with respect to the total dry mass) and MFC pulp (0, 5 or 10 wt% of dry MFC with respect to the total dry mass).

The total dry mass is the mass of the dried film, i.e., containing the non-volatile components (amylopectin with or without glycerol and fibres). Amylopectin was gelatinized by heating the dispersion at 5 °C/min to 90 °C where it was kept for 5 min. The gelatinized dispersion was then decanted into Petri dishes with a Teflon cover and allowed to dry under ambient conditions (50% RH and 21 °C). The films produced were stored for 10 days at room temperature (15% RH or 50% RH), before analysis. The nomenclature for the films is: D/C–wt% glycerol–wt% fibre, where D and C refer, respectively, to dilute (2 wt%) and concentrated (3 wt%) amylopectin dispersions. Thus D-20-10 refers to a film made from 2 wt% amylopectin dispersion and containing 20 wt% glycerol and 10 wt% MFC. It should be noted here that the reason why MFC films with 0, 20 and 33 wt% glycerol were compared with an MFC-free film containing 38 wt%, instead of 33 wt% glycerol, was that the 33 wt% MFC-free film was too brittle to be tensile tested.

2.4. Thermal analysis

Thermogravimetry was carried out using a Mettler–Toledo thermobalance (TGA/SDTA 851^e) at a 10 °C/min heating rate between 30 and 800 °C on 3–4 mg samples. The sample thickness was recorded during heating at 10 °C/min between 40 and 180 °C using a Mettler–Toledo TMA-40 thermal mechanical analyser. The film was placed between two silica discs and a force of 0.1 N was applied using a 1.1 mm diameter glass rod during the heating run.

2.5. Optical microscopy

Polarized light microscopy was performed using a Leitz Ortholux II POL-BK optical microscope, equipped with a hot-stage. The amylopectin dispersion was heated from 40 to 100 °C at a heating rate of 5 °C/min in order to determine the gelatinization point.

2.6. Atomic force microscopy (AFM)

AFM was conducted using a Multimode™ Nanoscope IIIa Atomic Force Microscope, Veeco Metrology Group. The films were studied in the tapping mode with standard silicon tips at a scan angle of 0°, a scan rate of 0.10 Hz and a drive frequency of 316 kHz. The scan size was 15 μm and the tip velocity was limited to 3 μm/s to obtain good topographic information.

2.7. Tensile testing

Tensile testing was carried out at 50% RH with an Instron Testing Instrument 5566 according to ASTM D-882 for thin plastic sheeting at 23 °C. The crosshead speed was 10 mm/min and a full-scale load of 100 N was selected. Dumb-bell-shaped specimens (50–60 μm thick) were used (width and length of narrow section: 4 and 20 mm, gauge length: 30 mm). Five replicates were tested on each sample.

2.8. X-Ray diffraction

Simultaneous small (SAXS) and wide angle (WAXS) X-ray scattering experiments were carried out as a function of temperature using the synchrotron radiation source in the polymer beam A2 at Hasylab (DESY) in Hamburg (Germany). Scattering patterns were recorded using a unidimensional detector and an incident radiation wavelength, λ, of 0.15 nm. SAXS and WAXS data were corrected for detector response and beam intensity and calibrated against PET and rat-tail standards. The temperature needed to achieve a complete loss of molecular order (the final gelatinization temperature) was determined during a time-resolved experiment by heating an amylopectin dispersion from 30 to 95 °C at a heating rate of 5 °C/min (temperature accuracy: ±0.5 °C). For this temperature experiment, the amylopectin dispersion was sealed between aluminium films and O-ring rubber seals inside screwed rectangular cell compartments.

2.9. Transmission electron microscopy

AP/MFC films were replicated in two stages using cellulose acetate for the first impression, shadowed with Au/Pd in a vacuum evaporator (JEOL JEE-4b), coated with carbon, transferred to a copper grid and examined in a Philips Technai 10 100 kV transmission electron microscope.

3. Results and discussion

3.1. Film formation

3.1.1. Mixing temperature

Fig. 1 illustrates, as an example, the gelatinization of amylopectin in the presence of water. The increase in the granule diameter due to swelling and the loss of birefringence due to the loss of crystallinity are clearly observed as the temperature is increased. Although, in agreement with data for maize starch (Souza & Andrade, 2002), very few granules are birefringent at 76 °C, crystalline order is still present, as indicated by the SAXS/WAXS diffractograms in Fig. 2 on the same system. According to the SAXS/WAXS measurements, complete loss of crystallinity seemed to occur between 85 and 90 °C. This means that the loss of birefringence is not necessarily an indication of complete gelatinization. It was also observed that, below 80 °C, a whitish precipitation rather than a proper film consisting of amylopectin granules was formed. In the case of starch, regardless of its origin, Jenkins and Donald (1998) showed that complete loss of crystallinity occurred at ~100 °C. Moreover, SAXS experiments on gelatinizing maize starch indicated that, if samples are heated to a few degrees below the tempera-

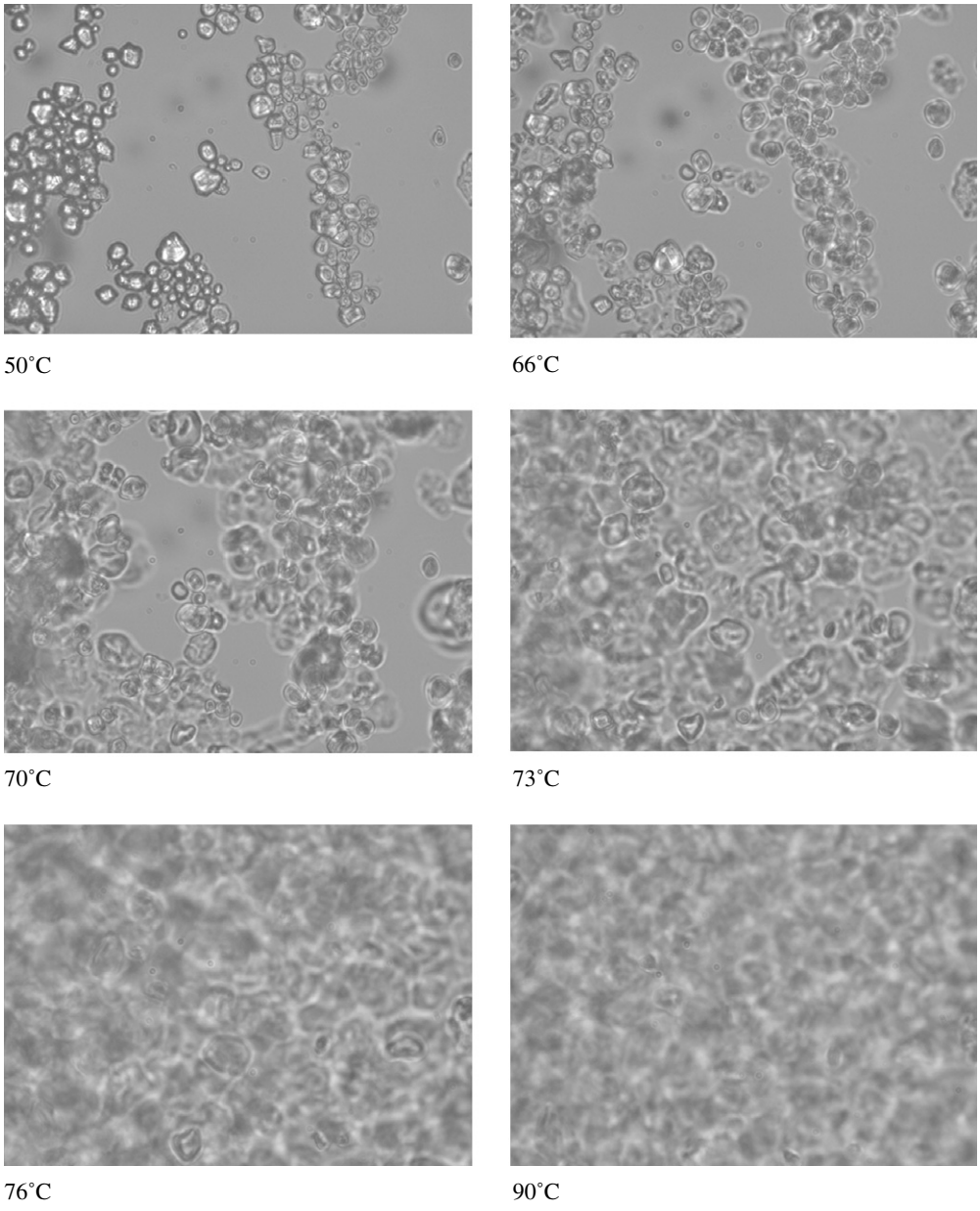

Fig. 1. Photomicrographs showing the temperature range of gelatinisation of amylopectin granules in excess of water. The width of the figures correspond to 420 μm.

ture at which the long period completely disappears, the crystalline order can be recovered upon cooling (Waigh, Gidley, Komanshek, & Donald, 2000).

When comparing Figs. 1 and 3 it is observed that the addition of glycerol and MFC did not change the degree of gelatinization at 90 °C to any significant degree. Based on these findings, all amylopectin dispersions were here heated to 90 °C. Note that what is observed as impurities in the amylopectin/MFC micrographs in Fig. 3 are actually fibres or fibre fragments.

3.1.2. Composition of the solution and drying conditions

It was observed that dispersions with 2 wt% amylopectin and glycerol did not yield films that were continuous over the whole petri dish. However, continuous films were obtained with a 3 wt% amylopectin solution. The amount of plasticiser needed to avoid brittleness was however high (38 wt%). A high glycerol content, typically above 25 wt%, leads to extensive amylopectin–glycerol phase separation (Lourdin, Ring, & Colonna, 1998) and this was also the case here (Fig. 4). Amylopectin films have been produced elsewhere from 1 to 3 wt% amylopectin dispersions and 0–40 wt% glycerol, but no details have been given as to how the film integrity varied with composition (Forssell, Lahtinen, Lahelin, & Myllärinen, 2002; Myllärinen et al., 2002; Myllärinen, Partanen, Seppälä, & Forssell, 2002; Rindlav-Westling et al., 1998).

Interestingly, when MFC was added, it became possible to produce films that were continuous with only 2 wt% amylopectin in the dispersion and these films were ductile

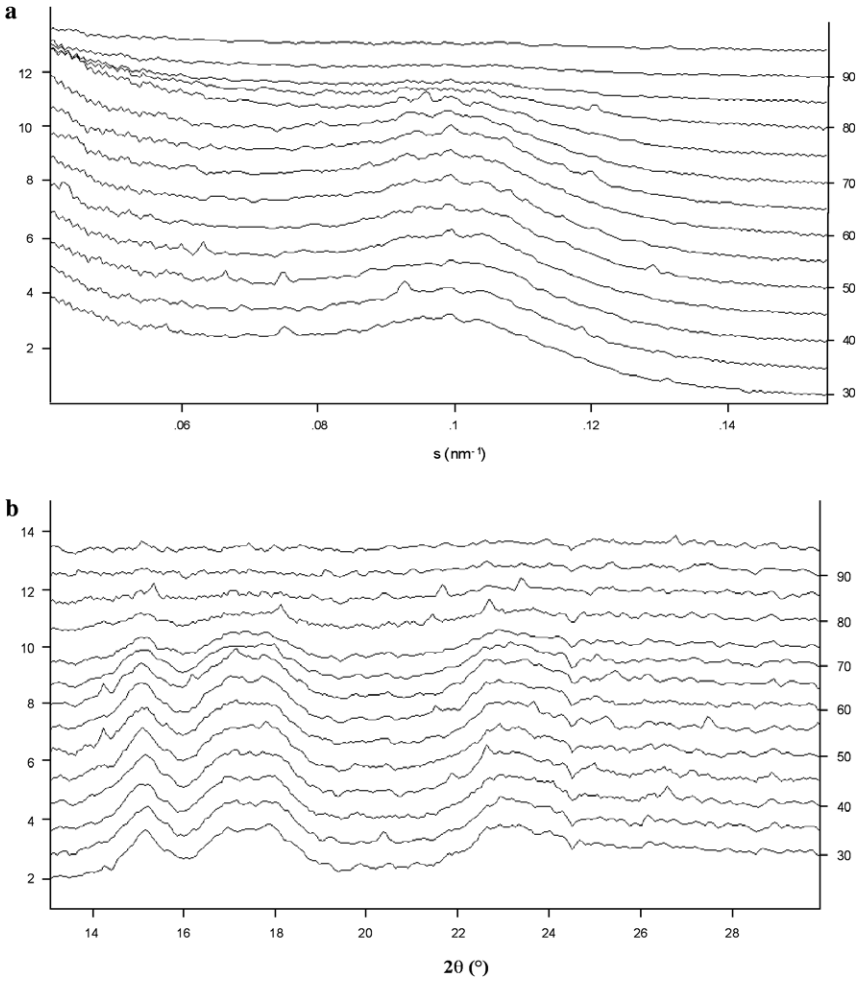

Fig. 2. SAXS (upper figure) and WAXS diffraction patterns of an amylopectin/water dispersion as a function of temperature.

enough to be handled without fracturing, even without glycerol (e.g., the D-0-10 film). They could easily be folded 180° between two hands, an impossible task for a pure amylopectin film. The most plausible explanation of this is that MFC retains a sufficient amount of moisture to keep the film ductile. The moisture content is discussed later in this paper.

3.2. Film properties

3.2.1. Distribution of MFC

The MFC formed a homogeneous mixture with the amylopectin dispersion and the resulting films were therefore also homogeneous on a large scale, 1–4 mm^2, with well dispersed microfibril aggregates, observed as light objects in Fig. 5. This was achieved without the need for a high shear rate or a long mixing time and it did not require any plasticiser. The light scattering microfibrillar entities observed in the optical micrographs were 20–90 μm long and 3–10 μm thick. According to Pääkkö et al. (2006), this MFC contains a large fraction of 17–30 nm thick and a smaller fraction of 100–150 nm thick microfibrils. The MFC is nevertheless opaque, which indicates that even larger fibre fragments were present. The fibrillar network in the MFC scatters light and it is possible that the light regions in the film in Fig. 5 are structures originating from the MFC.

The addition of MFC significantly changed the appearance of the film as revealed by optical microscopy (Fig. 6). Furthermore, the surface roughness increased significantly with the addition of only 5 wt% MFC. This indicated that it should be possible to observe fibrillar entities simply by examining the film surface with AFM or TEM. It was therefore decided to examine further the most interesting material, the D-0-10 film, at a higher resolution. By using AFM directly on the film surface it was possible to observe microfibrillar aggregates with a thickness of a few hundred nanometres and a length of more than 10 μm (Fig. 7). By means of AFM it was not feasible to reveal finer structures with high resolution and, therefore, TEM replication of the film surface was also performed. Single microfibrils with a thickness of the order of a few tens of nanometres were discerned by TEM as part of the complex morphology of the MFC-reinforced amylopectin film (Fig. 8).

3.2.2. Aging with and without MFC

A qualitative idea on the variation of crystallinity/retrogradation among the films was obtained by careful examination of the content and size of the semicrystalline

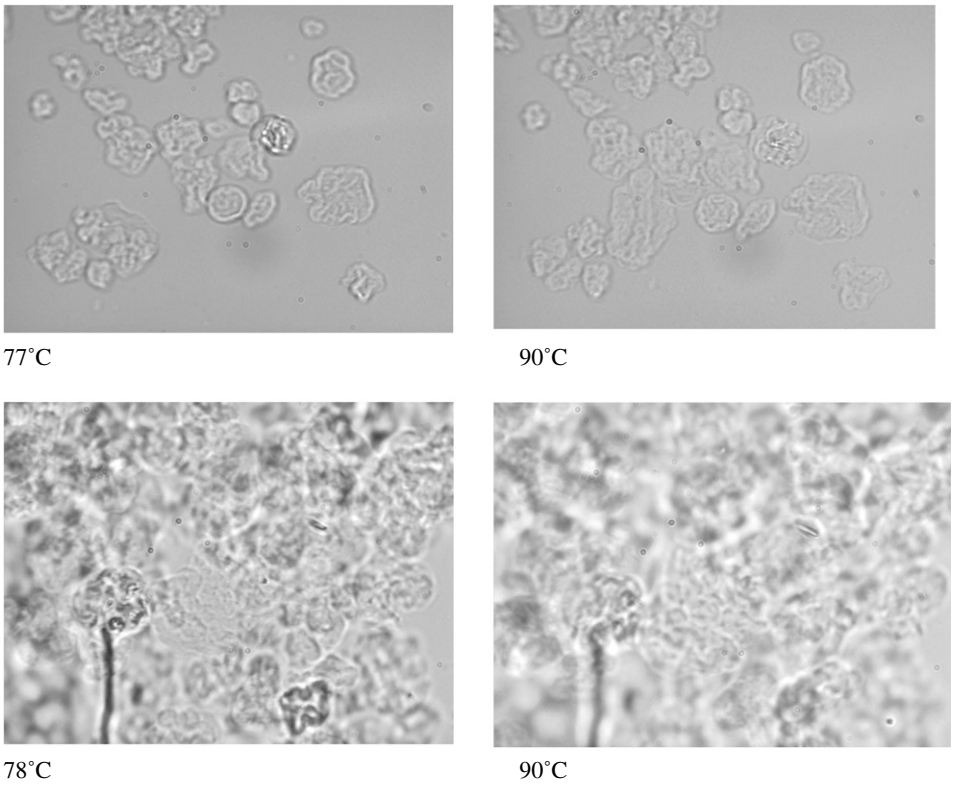

Fig. 3. Photomicrographs showing the gelatinization process for amylopectin granules in a water/glycerol (upper two figures) and in a water/glycerol/MFC dispersion (lower two figures). The relative contents, in excess of water, in the dispersions was 70/30 for amylopectin/glycerol and 57/33/10 for amylopectin/glycerol/MFC. The width of the figures correspond to 420 μm.

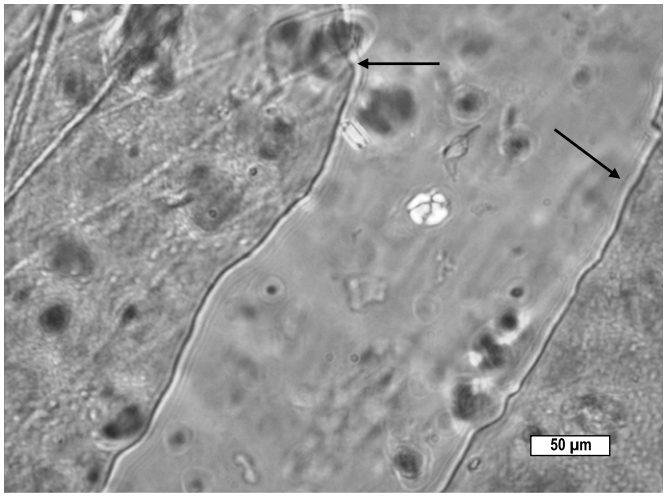

Fig. 4. Photomicrograph of a C-38-0 film. Arrows point at two glycerol microdomains (small channels) in the film.

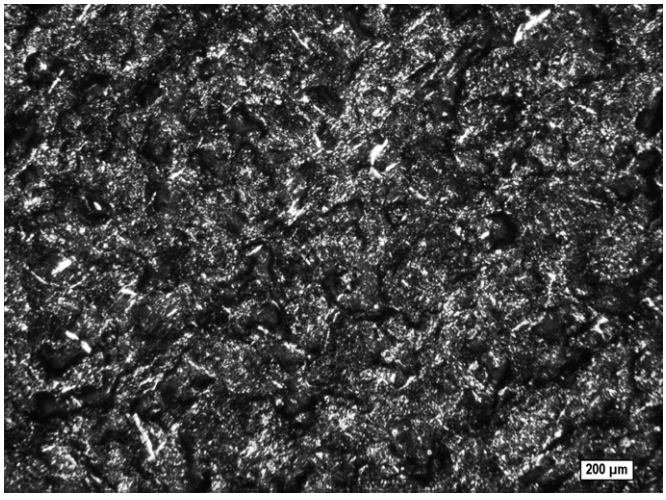

Fig. 5. Photomicrograph of a D-0-10 film.

birefringent maltese crosses that develop during crystallisation. This technique was chosen based on the findings of Myllärinen et al. (2002) that is difficult to obtain accurate values for the amylopectin crystallinity with X-ray when a large amount of glycerol is present. Glycerol contributes with a broad reflection overlapping the amylopectin reflections. It was observed that the content and size of the maltese crosses were not dramatically affected by the presence of MFC and glycerol. The number of these crosses was always small (Fig. 9) and probably too small to yield any X-ray crystallinity, in accordance with the findings of Myllärinen et al. (2002).

Rindlav-Westling et al. (1998) showed that amylopectin films with and without 30 wt% glycerol and dried at 15% RH were amorphous. In addition, Myllärinen et al. (2002) observed that amylopectin films with a plasticiser content below 30 wt% did not crystallise on aging for 2 months

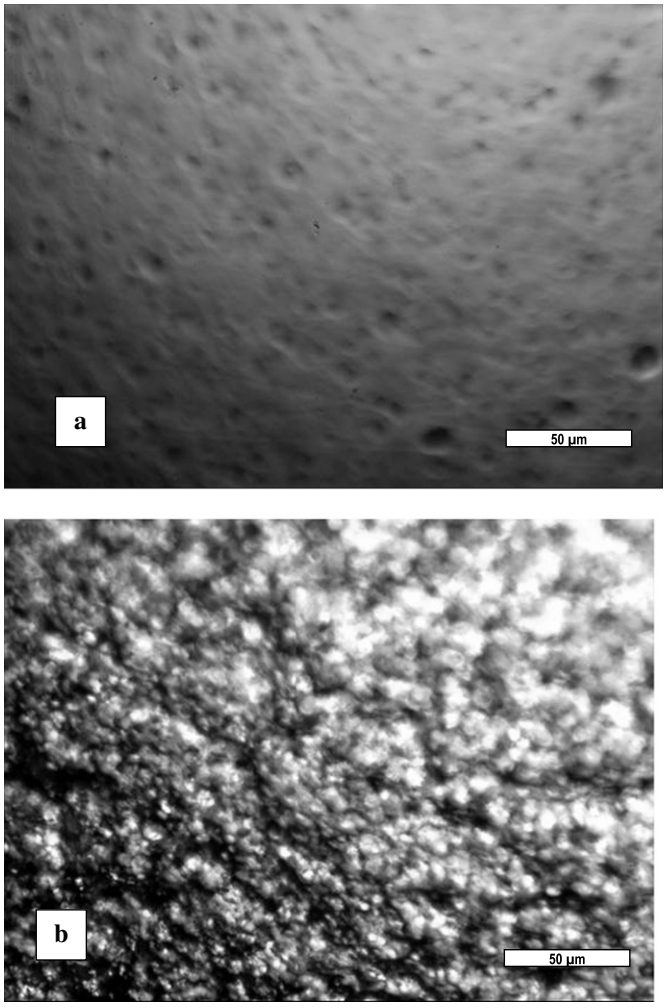

Fig. 6. Photomicrographs of (a) C-38-0 and (b) D-33-5 films.

(⩽91% RH). A combination of very moist conditions (91% RH) and a high glycerol content (30 wt%) was required for amylopectin to crystallise. An amylopectin film stored for 2 months under these conditions was 19% crystalline. Thus, as indicated in Fig. 9, it was improbable that any of the present films crystallised to any significant degree.

3.2.3. Moisture content

Table 1 shows the moisture content in the films estimated from TGA data using the mass loss between 30 and 120 °C (Fig. 10). This desorbed moisture therefore corresponds to the easily evaporating moisture, i.e., the water that is neither compositional water nor water intimately bound to the film constituents. 120 °C was chosen as the upper boundary since glycerol begins to evaporate at about 140 °C and this makes further moisture content determination impossible. It seems, however, that most moisture had left the glycerol-containing films at this temperature, as indicated by the flattening out of the TGA curve prior to the onset of glycerol loss (in the vicinity of the arrow in Fig. 10). In the case of the glycerol-free film, moisture seemed to have left the film continuously up to a temperature of 160–180 °C (Fig. 10, where the curves intersect). It

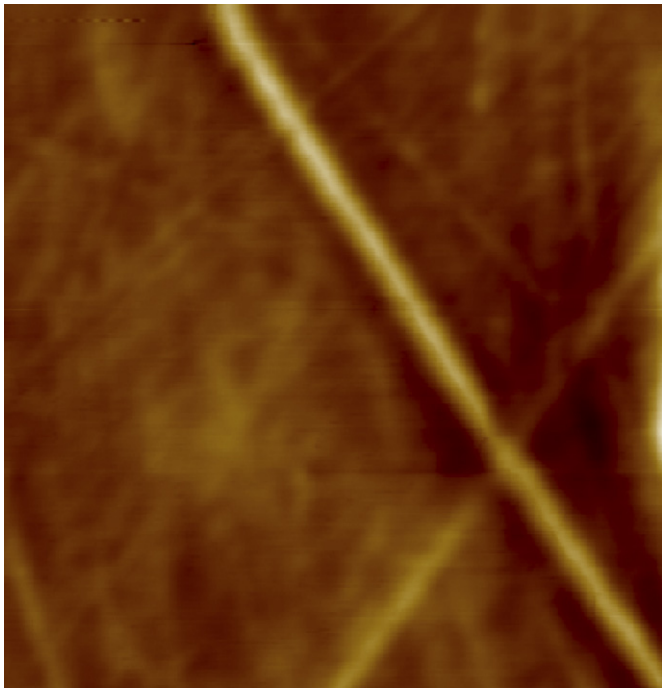

Fig. 7. AFM-micrograph of the D-0-10 film surface. The width of the figure is 15 μm and the brightest regions are 200 nm above the darkest region.

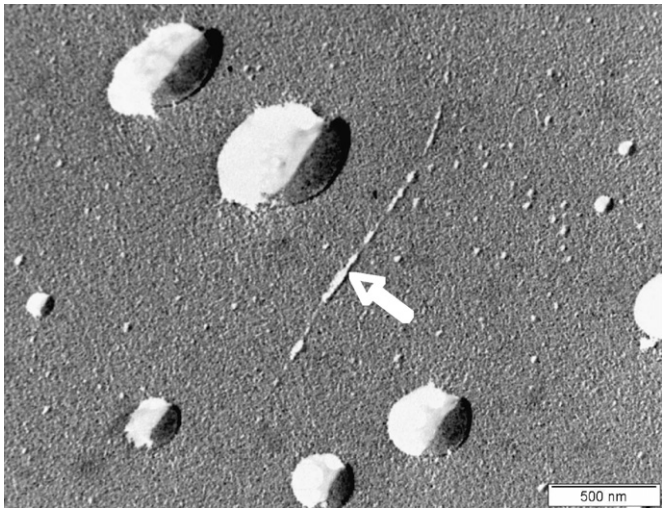

Fig. 8. TEM replicate of the D-0-10 film surface. The arrow point at the microfibril. The spherical objects are commonly observed replicate artifacts.

was interesting that the highest moisture content was found in the film without glycerol (the D-0-10 film in Table 1). In addition, for the films with the same fibre content (10 wt%), it was observed that the moisture content was decreasing with increasing glycerol content. There are at least two possible explanations of this: (1) glycerol may compete with water for accessible sites in the polymer, (2) there may be a shift of "non-bonded" water in the polymer to bound water located in the glycerol domains in the sample. The former explanation is probably more realistic. It should be noted that the trend in moisture content among the films was the same at 15 and at 50% RH (Table 1).

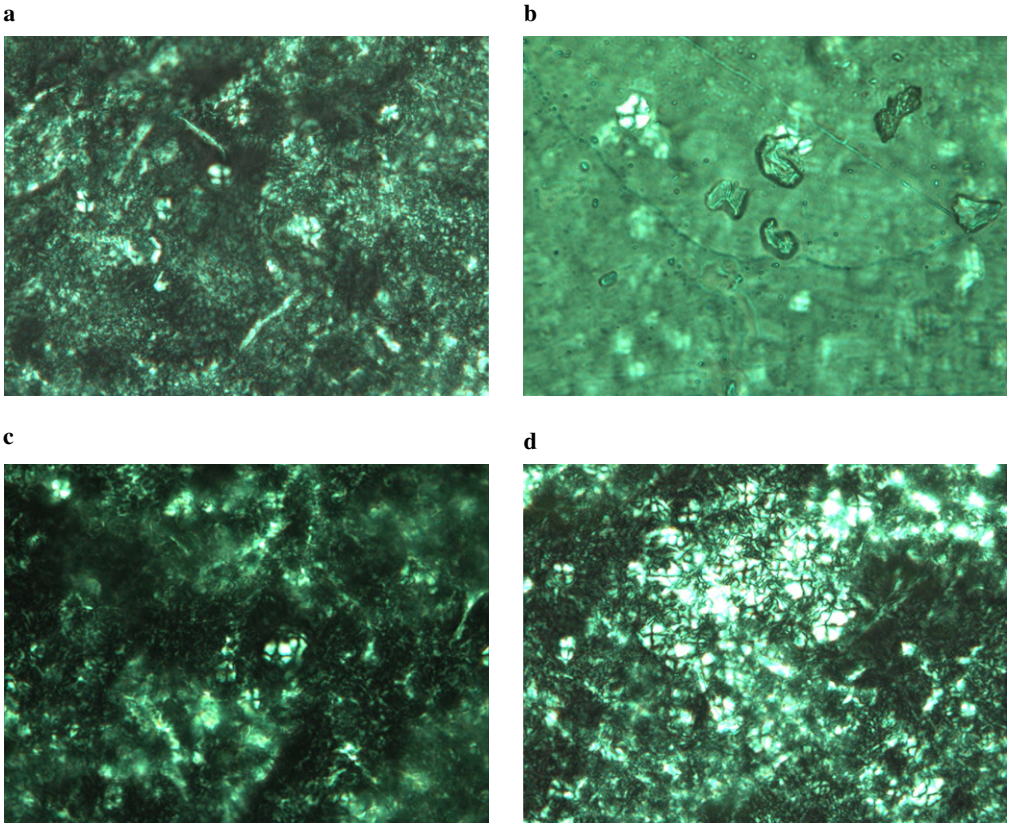

Fig. 9. Photomicrographs of (a) D-0-10, (b) C-38-0 and (c) D-33-10 films. To illustrate the difference between these samples and a sample with a large amount of maltese crosses, a D-33-10 film, aged for 10 days in a refrigerator (4 °C, 53% RH), is given in (d). The width of the figures correspond to 420 μm.

Table 1
Moisture content (wt%) in AP films under different conditions of relative humidity

	15% RH	50% RH
D-0-10	2	7
D-20-10	1.5	5
D-33-10	1	4
D-33-5	~0.3	3.5
C-38-0	1	4

The nomenclature for the films is: D/C–wt% glycerol–wt% fibre, where D and C refer, respectively, to dilute (2 wt%) and concentrated (3 wt%) amylopectin dispersions.
The estimated standard deviation was 0.25 wt%.

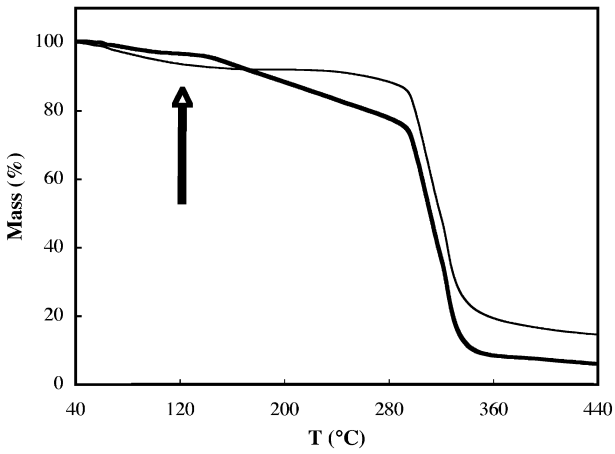

Fig. 10. Mass (wt%) as a function of temperature for D-0-10 (bold line) and C-38-0 (thin line) stored at 50% RH. The arrow indicates the upper temperature limit (120 °C) from which the moisture content was calculated.

3.2.4. Tensile properties

Young's modulus (E), stress at break (σ_b) and strain at break (ε_b) for the amylopectin films are given in Table 2. At 50% RH, the amylopectin films with $\geqslant 33$ wt% glycerol showed typical elastomeric stress-strain properties, with a low stiffness and strength and a large strain at break, as previously observed by Myllärinen et al. (2002). The scatter in mechanical data was high, both at 15% and 50% RH, for these films, reflecting the heterogeneous glycerol microdomain/amylopectin matrix structure. The MFC-free amylopectin films with less than 38 wt% glycerol were too brittle to be tensile tested.

Table 2 shows that the stiffness and strength decreased and that the ductility increased significantly with increasing glycerol content (compare the D-0-10, D-20-10 and D-33-10 films). The effect of changing the MFC content was not significant, at least not at a high glycerol content (compare D-33-5 and D-33-10).

Again it is worth drawing attention to the remarkable mechanical properties of the glycerol-free MFC-amylo-

Table 2
Young's modulus (E, MPa), stress at break (σ_b, MPa) and strain at break (ε_b, %) for the AP films at different storage conditions

		D-0-10	D-20-10	D-33-10	D-33-5	C-38-0
15% RH	E	2033 ± 114	1637 ± 71	822 ± 279	666 ± 315	683 ± 294
	σ_b	33.5 ± 6.7	20.8 ± 4.8	15.3 ± 4.2	14.3 ± 4.3	16.4 ± 6.6
	ε_b	1.9 ± 0.4	1.4 ± 0.4	2.4 ± 0.8	4.3 ± 0.5	3.8 ± 0.7
50% RH	E	1799 ± 123	1132 ± 59	175 ± 57	135 ± 66	24 ± 11
	σ_b	38.8 ± 5.0	16.3 ± 3.8	5.1 ± 0.8	4.1 ± 1.2	1.8 ± 0.4
	ε_b	3.0 ± 0.6	1.9 ± 0.7	21.0 ± 10.2	33.6 ± 4.4	120.4 ± 23.1

Values are given with ± standard deviations.

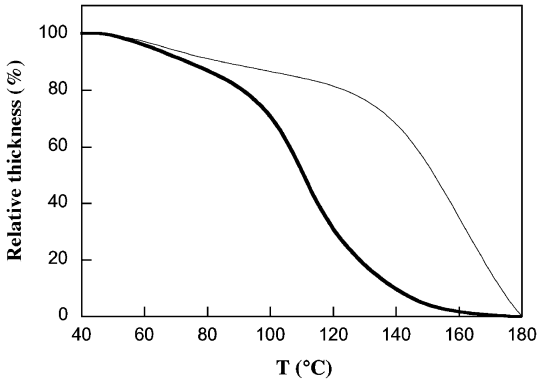

Fig. 11. Relative decrease in thickness measured by TMA as a function of temperature for D-0-10 (thin line) and C-38-0 (bold line) stored at 15% RH.

pectin film. Its modulus of 2 GPa and stress at break of 30–50 MPa indicated a relatively stiff and strong film, and yet it was ductile enough to be tested (ε_b: 2–7%). The fibrous MFC network yields a strong film and its ability to hold moisture ensures sufficient ductility for many applications. The resulting film is, in many ways, a competitive choice instead of e.g., polypropylene (Seavey et al., 2001).

Another advantage of using MFC instead of glycerol is that the fibre network, in contrast to glycerol, provides mechanical support at high temperatures as it increases the temperature at which the AP film collapses. Fig. 11 illustrates the greater film rigidity at higher temperature for the MFC composite compared to that of the glycerol-containing film (TMA data).

4. Conclusions

When MFC was added it was possible to obtain plasticiser-free amylopectin films of sufficient ductility to be easily handled. This was a remarkable effect; it seemed as MFC acted indirectly as a reinforcing "plasticiser". Thermogravimetry revealed that the amount of moisture was highest in the glycerol-free MFC film and it was suggested that this moisture was responsible for the observed plasticisation power of MFC. Optical microscopy revealed that MFC aggregates were uniformly distributed on a large scale in the films, and transmission electron microscopy indicated that single MFC microfibrils also existed in the films.

Overall, the success in making high quality amylopectin films, relies on the ability to fully gelatinize the polymer before casting. It has been shown here that synchrotron simultaneous small- and wide-angle X-ray spectroscopy can be used to assess the proper mixing temperature for complete gelatinization and the associated loss in crystallinity.

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