Physical Properties and Morphology of Films Prepared from Microfibrillated Cellulose and Microfibrillated Cellulose in Combination with Amylopectin

David Plackett,[1] Harvey Anturi,[2] Mikael Hedenqvist,[2] Mikael Ankerfors,[3] Mikael Gällstedt,[3] Tom Lindström,[3] István Siró[1]

[1]*Risø National Laboratory for Sustainable Energy, Technical University of Denmark (DTU), Roskilde 4000, Denmark*
[2]*School of Chemical Science and Engineering, Fibre and Polymer Technology, Royal Institute of Technology (KTH), Stockholm SE-100 44, Sweden*
[3]*Innventia AB, Stockholm SE-114 86, Sweden*

Received 14 December 2009; accepted 11 February 2010
DOI 10.1002/app.32254
Published online 12 May 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two types of microfibrillated cellulose (MFC) were prepared using either a sulfite pulp containing a high amount of hemicellulose (MFC 1) or a carboxymethylated dissolving pulp (MFC 2). MFC gels were then combined with amylopectin solutions to produce solvent-cast MFC-reinforced amylopectin films. Tensile testing revealed that MFC 2-reinforced films exhibited a more ductile behavior and that MFC 1-reinforced films had higher modulus of elasticity (E-modulus) at MFC loadings of 50 wt % or higher. Pure MFC films had relatively low oxygen permeability values when data were compared with those for a variety of other polymer films. MFC 1 and MFC 2 films had similar opacity but differences in appearance which were attributed to the presence of some larger fibers and nanofiber agglomerates in MFC 2. Field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) were used to illustrate the morphology of MFC nanofibers in pure films and in an amylopectin matrix. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3601–3609, 2010

Key words: microfibrillated cellulose; nanocomposites; amylopectin; barrier; biodegradable

INTRODUCTION

Over the past 20 years, there has been an increasing interest in nanocomposite materials. The field of nanocomposites literally exploded when Toyota researchers successfully developed nanoclay/nylon nanocomposites for under-the-hood applications in the automotive industry.[1] Since then there has also been a growing interest in bionanocomposite materials. Nanocellulosic materials can conveniently be classified in terms of cellulose whiskers, bacterial cellulosic materials, and microfibrillated cellulose (MFC) made from delaminated plant cell walls. Research on MFC can be dated back to work at ITT-Rayonnier in the 1980s.[2,3] A significant part of the past work on nanocomposite cellulose materials has been performed utilizing cellulose whiskers,[4,5] usually produced through hydrolysis of various cellulosic materials. The general field of nanocellulose applications has been covered in recent reviews.[6,7]

The early research on MFC focused on its commercial exploitation as a rheology modifier in foods, whereas in more recent work the properties of MFC have been explored in relation to a range of applications. In the past MFC was never commercialized on a large scale because of the very high energy consumption required for cell wall delamination using various types of homogenizers. At Innventia (previously STFI-Packforsk), several routes to decrease the energy consumption during homogenization have been explored. Enzymatic pretreatment[8,9] as well as carboxymethylation[10,11] have been shown to be efficient means of decreasing energy consumption. Another route using TEMPO oxidation has recently been explored by French and Japanese teams.[12–15] The exploration of MFC use in bionanocomposites has been the subject of extensive research[16,17] and is under investigation for potential uses in the field of packaging.[18] For example, previous researchers have examined the properties of MFC films and MFC-starch films in terms of such applications.[19–24]

Svagan et al.[25] combined MFC with a viscous amylopectin–glycerol blend and cast homogeneous films with 10–70% MFC content. The films with 70% MFC content showed high tensile strength, high tensile modulus, and very high work of fracture.

Correspondence to: I. Siró (isir@risoe.dtu.dk).
Contract grant sponsor: EU Sixth Framework Programme SUSTAINPACK Project.

Recently, the same authors demonstrated that cellulose nanofiber addition at 70 wt % reduced the moisture uptake to half the value of the pure plasticized amylopectin film.[26] Reduction in moisture uptake of thermoplastic starch as a result of MFC addition was also reported by Mondragón et al.[27]

López-Rubio et al.[28] studied the reinforcement of amylopectin with MFC. In this research, gelatinized films of amylopectin, glycerol plasticizer, and MFC were cast at 50% relative humidity and the properties were investigated after 10 days of storage. Amylopectin films were brittle and impossible to handle unless glycerol was added at 38 wt %. However, when MFC was added it was possible to produce films that could be handled without the addition of glycerol.

The purpose of the research described here was to compare the performance of two types of MFC produced at Innventia in terms of polymer reinforcement. The two types were generation 1 (MFC 1), produced from relatively high ($\sim$ 14%) hemicellulose content sulfite pulp[9] and generation 2 (MFC 2), produced by carboxmethylation of a dissolving pulp followed by high-shear homogenization.[10,11] Since amylopectin has been the focus of earlier related research on MFC reinforcement,[28] it was considered a suitable polymer matrix in which to compare the performance of MFC 1 and MFC 2. To our knowledge, this is the first study in which different generations of MFC have been compared in respect to their film-forming and reinforcing potential.

EXPERIMENTAL SECTION

Materials

Maize amylopectin (M_r or relative molar mass = 10^6–10^7; ash $\leq$ 0.1%; one terminal group per 25 glucose units) obtained from Fluka Biochemika (Sigma Aldrich Chemie GmbH, Steinheim, Germany) was used as matrix material. Glycerol, 99% GC (Sigma Aldrich Chemie GmbH, Steinheim, Germany) was used as a plasticizer. For the manufacture of MFC 1, a commercial bleached sulfite softwood pulp (Domsjö ECO Bright, Domsjö Fabriker AB, Sweden) consisting of 40% pine (*Pinus sylvestris*) and 60% spruce (*Picea abies*) with a hemicellulose content of 13.8% and a lignin content of 1% was used. For the manufacture of MFC 2, a commercial sulfite softwood dissolving pulp (Domsjö Dissolving Plus, Domsjö Fabriker AB, Sweden) with a hemicellulose content of 4.5% and a lignin content of 0.6% was used. These composition data were obtained from the pulp supplier. Both pulps were thoroughly washed with deionized water before use.

MFC preparation

MFC 1 was prepared using a combined refining and enzymatic pretreatment followed by a high pressure homogenization described in detail by Pääkkö et al.[9] MFC 2 was prepared using a carboxymethylation pretreatment followed by high pressure homogenization described previously by Wågberg et al.[11] As a result of the different manufacturing procedures, the two types of MFC have different fibril sizes and surface charge densites. The MFC 1 fibrils have widths of about 17–30 nm,[9] whereas the MFC 2 fibrils are somewhat smaller[11] ($\sim$ 15 nm). The MFC 1 gel is more opaque than MFC 2 gel at the same concentration, which might be attributable to differences in fibril dimensions between the two types of MFC. The charge density is 40 μeq g^{-1} for MFC 1 and 586 μeq g^{-1} for MFC 2, measured using conductometric titration.[29]

Film casting

Amylopectin films containing MFC were cast from dispersions in deionized water containing 2 wt % amylopectin. The preferred mixing procedure, as described by López-Rubio et al.,[28] involved heating of amylopectin to 90°C with stirring for about 10 min to ensure gelatinization. Then, MFC 1 or MFC 2 dispersions were added in amounts designed to achieve a range of final dry weight loadings between 0 and 100 wt % and the mixtures were stirred for another 10 min. The dispersions were then poured into Petri dishes and stored uncovered at ambient conditions for several days to allow water evaporation. Pure MFC films were cast either from mixtures of 2 wt % MFC 1 and distilled water at 1 : 1 weight ratio or 2 wt % MFC 2 and distilled water at 1 : 2 weight ratio after stirring at 90°C for 10 min. Since MFC 2 gel had much higher viscosity than MFC 1 gel, it was necessary to use approximately twice as much water to prepare a suspension that could be easily poured or mixed with amylopectin. To confirm and quantify this viscosity difference MFC suspensions of the two types with concentrations in water of 1 wt % and 0.67 wt %, respectively were measured using a Schott-Geräte glass capillary viscometer (501/33, Schott Geräte GmbH., Mainz, Germany). Films were stored at 23°C and 50% relative humidity (RH) for at least 3 days before each test. The equilibrium moisture content of the conditioned films was 6–7% for the pure MFC films, 10% for the amylopectin films, and 7–10% for the composite films depending on their MFC content.

Tensile tests

Tensile tests were performed according to ASTM D-882[30] at 23°C and 50% RH on an Instron 5566 instrument operated at a crosshead speed of 10 mm

min^{-1}. In the first tensile test run, dumbbell-shaped specimens were punched out from films containing 0–20 or 100 wt % MFC. These specimens were 4 mm in width and 20 mm in length in the narrow section. The 50 and 75 wt % MFC samples were too brittle to be punched and as a result they were cut into rectangular specimens with a width of about 4 mm. For purposes of comparison, 100% MFC films with this geometry were also tested. The starting clamp distance was 30 mm. The number of replicates was typically between 10 and 15 and all the tested films were unplasticized. Film thickness was measured using a micrometer screw gauge and for calculation purposes was taken as the mean of four measurements.

Permeability

Since initial oxygen permeability tests gave lower than expected values for MFC films, we decided to utilize two different test methods to cross-check and validate the data. A series of permeability experiments was carried out using a PBI-Dansensor OPT-5000 instrument (PBI-Dansensor A/S, Ringsted, Denmark) at 23°C and 50% RH and with measurements made in triplicate for each film type. The tested film samples included 100% amylopectin and 100% MFC films as well as 15 and 50% MFC 1 or MFC 2 in amylopectin. In addition, a duplicate series containing 33 wt % glycerol plasticizer was tested. The oxygen permeability of some films was also determined using an Ox-Tran® 2/20 (Mocon, Minneapolis). Measurements were again performed at 23°C and 50% RH. The film samples included at least three replicates each of 100% MFC 1 and 2 as well as 50% MFC films. Poly(ethylene terephthalate) (PET) films were tested as a reference material. The Mocon Ox-Tran® instrument for measuring oxygen permeation through films relies upon a coulometric electrochemical oxygen sensor, whereas the PBI-Dansensor OPT 5000 utilizes a ceramic-based sensor to determine the partial pressure concentration of oxygen. The operating range of these instruments is reported to be 0.1 to 144,000 mL m^{-2} day^{-1} for the Ox-Tran® instrument and 0.1 to 10,000 mL m^{-2} day^{-1} for the OPT 5000.

Field emission scanning electron microscopy

Field emission scanning electron microscopy (FE-SEM) was used to explore the morphology of MFC-amylopectin film fracture surfaces as well as the fracture and top surfaces of pure MFC films. The instrument used at Risø DTU was a Zeiss Supra 35 FE-SEM (Karl-Zeiss SMT AG, Germany) equipped with an HKL Technology Channel 5.6 electron backscattering diffraction detector and a Noran System Six Model 300 EDS detector. Some of the films were examined at KTH in Stockholm using a Hitachi S-4300 FE-SEM (Hitachi High-Technologies Europe GmbH, Krefeld, Germany).

Atomic force microscopy

The surface topography of MFC films was examined using a PSIA XE150 atomic force microscope (Park Systems, South Korea). Standard silicon cantilevers of theoretical spring constant 40 N m^{-1} with an approximate resonance frequency of 300 kHz and a silicon tip of typical radius 10 nm were utilized (BS-Tap300Al, BudgetSensors®, Innovative Solutions Bulgaria Ltd., Sofia, Bulgaria). Film squares of 1 and 5 μm on each side were scanned in tapping mode at a scan rate of 0.5 Hz. All AFM images were collected in air under ambient conditions. Images were processed using Gwyddion (http://gwyddion.net), a modular freeware program for scanning probe microscopy data visualization and analysis.

Film transparency and opacity

Light transmittance of films was measured over the 400–800 nm wavelength range using a Shimadzu 1700 UV–Visible spectrophotometer (Shimadzu Europe GmbH, Duisburg, Germany). Film opacity was determined using a procedure described by Gontard et al.[31] The absorbance spectrum (400–800 nm) of film samples was recorded for each sample and then film opacity was defined as the area under the recorded curve and calculated by an integration procedure. The opacity was expressed as absorbance units × nanometers (AU nm) and was normalized to a film thickness of 25 μm. LLDPE (linear low-density polyethylene) and EVOH (ethylene vinyl alcohol) reference films were also tested. Opacity values were determined in triplicate for each film type.

RESULTS AND DISCUSSION

Film casting

Cast films containing 0, 5, 10, 15, 20, 50, 75, and 100 wt % MFC were obtained using either MFC 1 or MFC 2 in combination with amylopectin. The viscosity of suspensions prepared with MFC 1 was notably lower than that of the corresponding suspensions prepared with MFC 2. For example, the measured kinematic viscosities for MFC 1 and MFC 2 using capillary viscosimetry were 97 mm^2 s^{-1} and 765 mm^2 s^{-1} at concentrations of 1 wt % and 0.67 wt %, respectively. The charged nature of the MFC 2 nanofiber surfaces could be a significant factor contributing to the observed viscosity difference between MFC 1 and MFC 2 suspensions; however, the role of

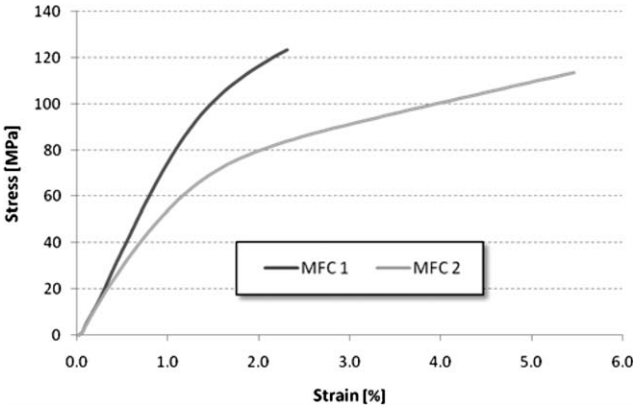

Figure 1 Stress–strain curves for 100% MFC 1 and 100% MFC 2 films.

other factors such as hemicellulose content and nanofiber dimensions cannot be discounted. As a result of the different dilutions, the drying time for the MFC 2 films was longer (4–5 days) than that required for MFC 1 films (2–3 days). MFC 2 films also appeared to shrink more after drying under ambient conditions and were generally less flat than films prepared using MFC 1.

Tensile tests

Tensile test plots of stress versus strain for 100% MFC 1 or 100% MFC 2 films are shown in Figure 1 and indicate that MFC 2 films showed a more pronounced nonlinearity/yield and more ductile behavior than MFC 1 films, which were generally more stiff and brittle. This behavior was also exhibited by MFC-reinforced amylopectin films. The nonlinear stress–strain behavior of MFC films is also reported elsewhere. Henriksson and Berglund[32] interpreted this phenomenon in MFC films as due to deformation mechanisms at the scale of the individual nanofiber level. The tensile test results for the full range of films are illustrated in Figure 2 and in Table I.

The higher average stiffness of MFC 1-based films at MFC loadings of 50% or more is shown in Figure 2(a). Tensile strength data illustrated in Figure 2(b) show an increase in film strength with increasing MFC content over the whole range, but no statistically significant difference was observed between the two film types at any concentration. This increase in film strength might be explained by the crack-stopping capability of MFC nanofibers at higher load as suggested by Nakagaito and Yano.[33] The higher extensibility of MFC 2-based films is apparent in Figure 2(c) at MFC loadings of 20% or higher. Interpretation of the mechanical test data must be qualified by the use of the rectangular specimen shape for the 50, 75, and 100% MFC films and the use of the clamp-distance elongation method as a means of recording approximate strain values.

López-Rubio et al.[28] investigated the mechanical properties of MFC-reinforced amylopectin films and reported Young's modulus, stress at break, and strain at break values of 1.8 ± 0.12 GPa, 38.8 ± 5.0 MPa and 3.0 ± 0.6%, respectively, for films containing 10 wt % MFC and stored at 50% RH. These values are similar to those reported here for amylopectin films with the same MFC content. Berglund[34] noted the interesting mechanical properties of MFC films and suggested that despite random in-plane orientation it should be possible to obtain films with

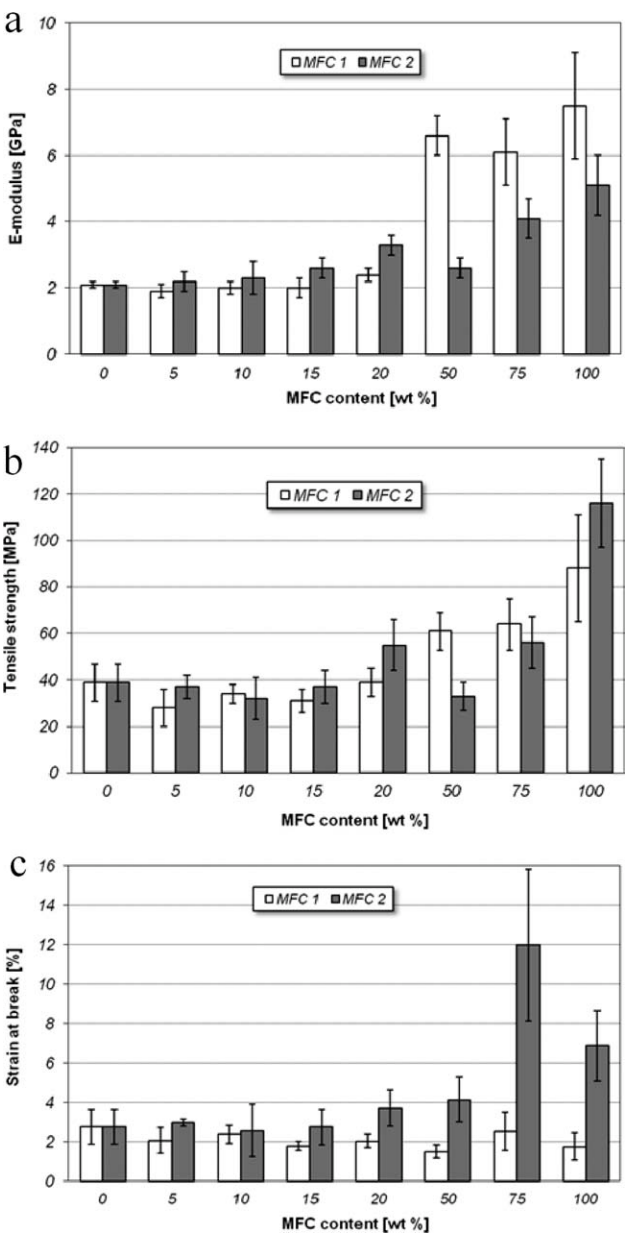

Figure 2 (a) E-modulus; (b) tensile strength; (c) strain at break as a function of MFC content in amylopectin films. Data are presented as the mean values of at least ten replicates and error bars show standard deviations.

TABLE I
Tensile Properties of MFC-Amylopectin Films as a Function of MFC Content

	MFC content (wt %)	Max. stress (MPa)	Strain at break (%)	E-modulus (GPa)
MFC 1	0	39 ± 8	2.8 ± 0.9	2.1 ± 0.1
	5	28 ± 8	2.1 ± 0.7	1.9 ± 0.2
	10	34 ± 4	2.4 ± 0.5	2.0 ± 0.2
	15	31 ± 5	1.8 ± 0.2	2.0 ± 0.3
	20	39 ± 6	2.0 ± 0.4	2.4 ± 0.2
	50	61 ± 8	1.5 ± 0.3	6.6 ± 0.6
	75	64 ± 11	2.5 ± 1.0	6.1 ± 1.0
	100	88 ± 23	1.8 ± 0.7	7.8 ± 1.6
MFC 2	0	39 ± 8	2.8 ± 0.9	2.1 ± 0.1
	5	37 ± 5	3.0 ± 0.2	2.2 ± 0.3
	10	32 ± 9	2.6 ± 1.3	2.3 ± 0.5
	15	37 ± 7	2.8 ± 0.9	2.6 ± 0.3
	20	55 ± 11	3.7 ± 0.9	3.3 ± 0.3
	50	33 ± 6	4.1 ± 1.1	2.6 ± 0.3
	75	56 ± 11	12.0 ± 3.8	4.1 ± 0.6
	100	116 ± 19	6.9 ± 1.8	5.1 ± 0.9

Data are presented as the mean values of at least ten replicates ± standard deviations.

Young's modulus approaching 20 GPa and a strength of 240 MPa; however, data obtained here for 100% MFC films indicate significantly lower modulus and strength values. Svagan et al.[25] tested a series of MFC-reinforced amylopectin films based on 50 : 50 glycerol/amylopectin as the matrix and various percentages of MFC. As expected, strain at break was high at low MFC loadings but 100% MFC films had an average modulus of 13 ± 1 GPa, tensile strength of 180 ± 7.8 MPa, and strain at break of 2.1 ± 0.38%. As in our research, MFC was prepared at Innventia but there were differences between the method we used to prepare suspensions for casting and that reported by Svagan et al.[25] In particular, Svagan et al. magnetically stirred MFC suspensions for 6 days and then subjected the resulting product to high-shear mixing for a short period. It is conceivable that this method might generate films with more tightly packed nanofiber networks than was the case in our films and at least partly explain the reported differences in mechanical properties of 100% MFC films.

Henriksson and Berglund[32] worked with MFC as a potential reinforcement in melamine-formaldehyde films and found stress at break approaching 100 MPa and Young's modulus of 14 GPa for 100% MFC films. These authors noted that the MFC used in their research appeared to perform as well as MFC studied by Nakagaito and Yano[33]; however, these authors acquired MFC from Daicel Chemical Industries and did not directly report the mechanical properties of 100% MFC films. Recently, Henriksson et al.[24] investigated tensile properties of 100% MFC films prepared by vacuum filtration using pulp with an average degree of polymerization (DP) varying from 410 to 1100. It was found that a higher cellulose DP was associated with higher modulus, tensile strength, and strain at break in MFC films. Their tensile values were significantly higher when compared with the corresponding MFC films in our study (MFC 1≈DP = 800; MFC 2≈DP = 1100). These differences might be explained by the anomalies between the mixing procedures applied. It is likely that high speed mixing could result in better dispersion of MFC in water than in the case of samples prepared by magnetic stirring.

Permeability

The results from oxygen permeability testing of various MFC and MFC-reinforced amylopectin films using the PBI-Dansensor equipment are shown in Table II. Pure and plasticized amylopectin films were impossible to measure as they cracked during testing leading to false OTR values. These results are therefore not presented in Table II. However, a number of the tested samples exhibited relatively low permeability values with low measured standard deviation. The oxygen permeability of amylopectin films decreased with increasing MFC content; however, no statistically significant difference was observed between amylopectin films with 50 wt % MFC content and 100% MFC films. Plasticized samples showed higher oxygen permeability compared with unplasticized films, which is in agreement with expectation. Plasticizers increase the free volume or

TABLE II
Oxygen Permeability of MFC and MFC-Reinforced Amylopectin Films as Measured at 23°C and 50% RH

Film type	Glycerol content (wt %)	MFC/amylopectin weight ratio	Average O_2 permeability at 23°C, 50% RH (mL mm m^{-2} day^{-1} atm^{-1})
MFC 1	0	15/85	0.037 ± 0.004^{a}
	0	50/50	0.020 ± 0.007^{b}
	0	100/0	0.016 ± 0.001^{b}
MFC 2	0	15/85	0.034 ± 0.007^{a}
	0	50/50	0.013 ± 0.001^{b}
	0	100/0	0.013 ± 0.005^{b}
MFC 1P	33	15/85	1.087 ± 0.151^{c}
	33	50/50	0.427 ± 0.013^{d}
	33	100/0	0.774 ± 0.179^{c}
MFC 2P	33	15/85	1.400 ± 0.158^{e}
	33	50/50	0.382 ± 0.082^{d}
	33	100/0	0.980 ± 0.089^{c}

1P and 2P were glycerol-plasticized samples (33 wt % glycerol content). Data are expressed as mean values of at least three replicates ± SD. Means with different superscripts (a–e) are significantly different at $P \leq 0.05$.

TABLE III
Oxygen Permeability Values for Polymer Films Reported in the Literature

Polymer	O_2 permeability at 23°C, 50% RH (mL mm m^{-2} day^{-1} atm^{-1})	Method	Reference
Ethylene vinyl alcohol (EVOH)	0.001–0.01	Ox-Tran 2/20	40
Chitosan	0.01–0.04[a]	Ox-Tran 1000	41
Poly(vinylidene chloride) (PVDC)	0.01–0.3	Ox-Tran 2/20	40
Poly(vinyl alcohol) (PVOH)	0.02	Ox-Tran 2/20	40
Amylose	0.7[a]	Ox-Tran 2/90	42
Amylopectin	1.4[a]	Ox-Tran 2/90	42
Polyamide (PA)	0.1–1.0	Ox-Tran 2/20	40
Poly(ethylene terephthalate) (PET)	1.0–5.0	Ox-Tran 2/20	40
Poly(vinyl chloride) (PVC)	2.0–8.0	Ox-Tran 2/20	40
Poly(hydroxyalkanoate) (PHA)	10–15[b]	Method not specified	43
Poly(lactic acid) (PLA)	16–20[b]	Method not specified	43
Polypropylene (PP)	50–100	Ox-Tran 2/20	40
Polyethylene (PE)	50–200	Ox-Tran 2/20	40
Polystyrene (PS)	100–150	Ox-Tran 2/20	40

[a] Values recalculated from the original paper.
[b] Values estimated from diagrams in the original paper.

molecular mobility of polymers by reducing hydrogen bonding between polymer chains, and as a consequence, diffusive processes within the matrix would become more rapid.[35,36] In the case of MFC films, the addition of glycerol plasticizer could disrupt the highly packed nanofiber network and thereby contribute to an increase in measured oxygen permeability. In plasticized film samples, no clear correlation was observed between MFC content and oxygen permeability and it appears that the

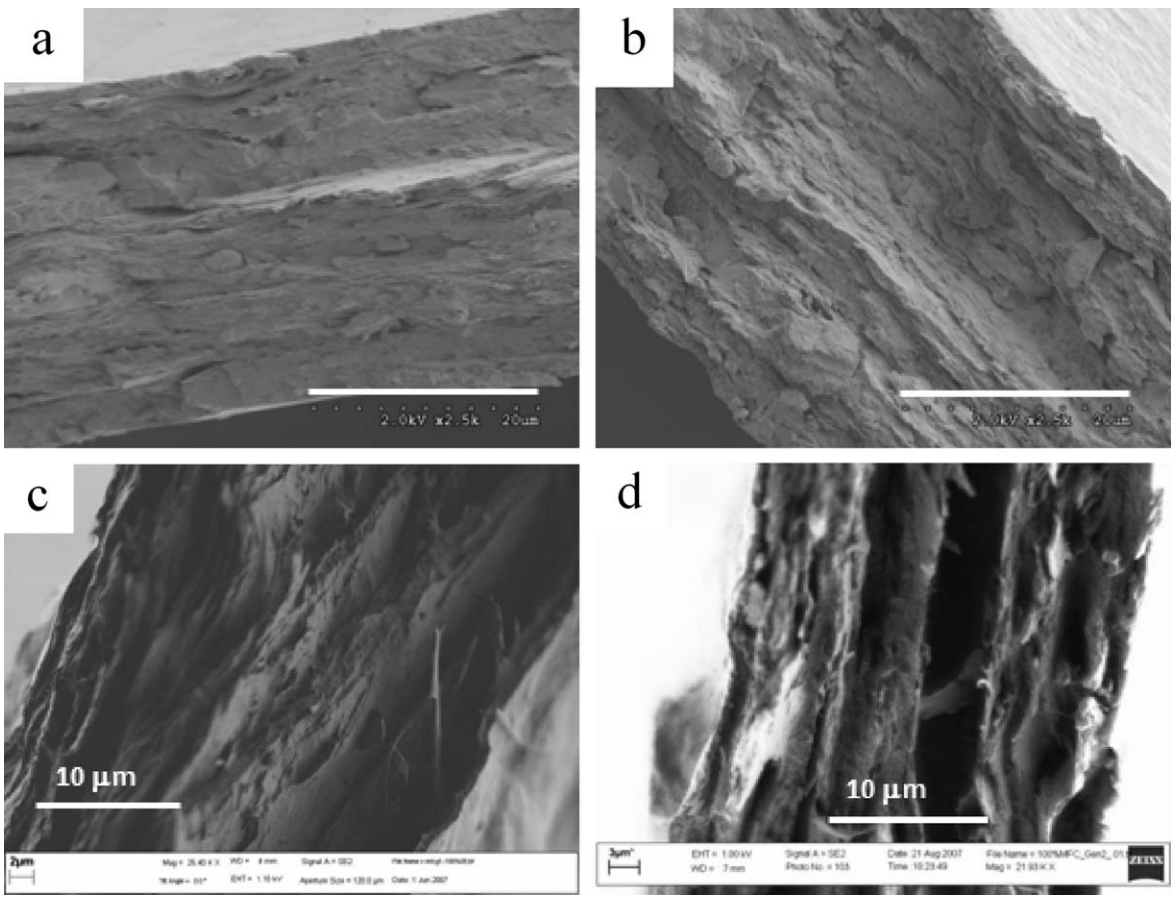

Figure 3 FE-SEM images of the tensile fracture surfaces of (a) MFC 1- and (b) MFC 2-reinforced amylopectin films and (c) 100% MFC 1, (d) 100% MFC 2 films. Images 3a and 3b were obtained at KTH, whereas 3c and 3d were obtained at Risø-DTU. Scale bars correspond to 20 µm in images a and b, and 10 µm in images c and d.

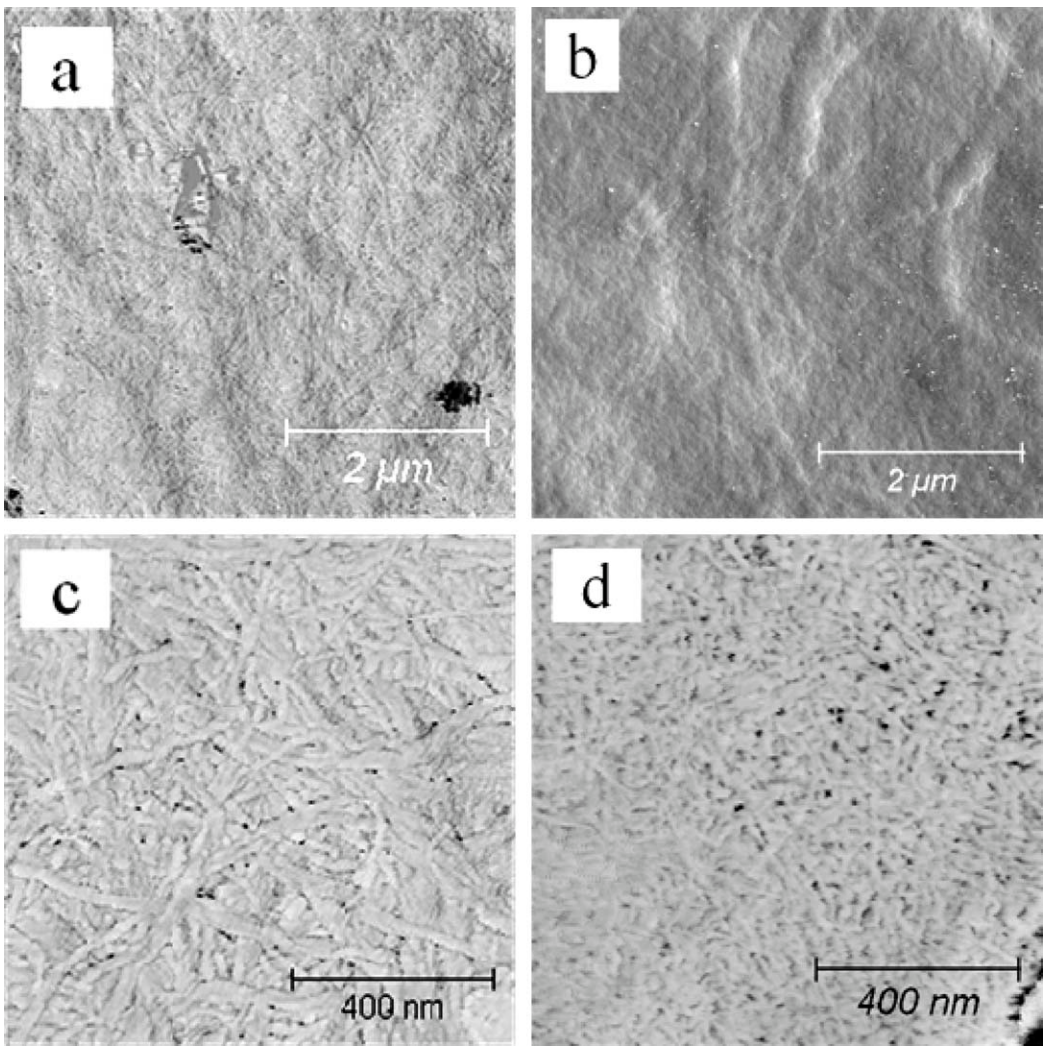

Figure 4 AFM phase images in tapping mode of (a) 5 × 5 μm area of MFC 1 film, (b) 5 × 5 μm area of MFC 2 film, (c) 1 × 1 μm area of MFC 1 film, and (d) 1 × 1 μm area of MFC 2 film. Scale bars correspond to 2 μm (a and b images) or 400 nm (c and d images).

positive influence of MFC in terms of improving barrier properties was counteracted by the addition of glycerol.

The oxygen permeability of selected MFC films was also determined using the Mocon Ox-Tran® oxygen permeability tester and values obtained were in good agreement with permeability results for the corresponding films measured by PBI-Dansensor equipment (data not shown). Oxygen permeability tests demonstrated that MFC films possess a relatively low permeability when compared with values cited in the literature for other polymers (Table III). One can conclude that the oxygen permeability obtained for pure MFC 1 or MFC 2 film is comparable to that of poly(vinylidene chloride) or poly(vinyl alcohol). This finding suggests that the packing of MFC nanofibers in films under some circumstances can create a rather impermeable material with closed pores in a typical cross section. Recently, the oxygen permeability of MFC films was measured by Syverud and Stenius at 23°C and 0% RH using a Mocon Coulox oxygen sensor and reported to be 0.37 mL mm m^{-2} day^{-1} atm^{-1}. It should be noted that these authors used a different MFC source as well as different homogenization equipment and film-forming procedure, all of which might explain the higher permeability when compared with our data. Syverud and Stenius[37] suggest high cellulose crystallinity as a factor which might contribute to good film barrier properties as the crystalline region of cellulose is reported to be impermeable to oxygen molecules.[38,39] Fukuzumi et al.[14] also noted that oxygen permeability of a polylactic acid (PLA) film decreased by a factor of ~ 750 when coating with a thin TEMPO-oxidized MFC layer.

Field emission scanning electron microscopy

FE-SEM images of the tensile fracture surfaces of 50 wt % MFC-amylopectin films and pure MFC films

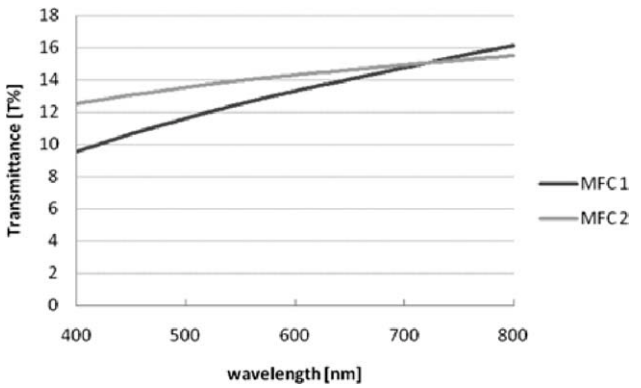

Figure 5 Light transmittance spectra for 100% MFC 1 and MFC 2 films. Data were normalized to 25 μm film thickness.

are shown in Figure 3. The images suggest a brittle fracture with little to distinguish MFC 1 or MFC 2 at this magnification (Fig. 3a,b) and also reveal the paper-like layered structure of pure MFC films (Fig. 3c, d).

Atomic force microscopy

The results of MFC film examination using AFM are illustrated in Figure 4. AFM phase images of 5 × 5 μm sections of MFC 1 and MFC 2 films (Fig. 4a and b) show the pattern of individual nanofibers or nanofiber agglomerates in the case of MFC 1 whereas much larger nanofiber agglomerates are revealed within the MFC 2 film. The AFM phase images of 1 × 1 μm sections of MFC 1 and MFC 2 films (Fig. 4c and d) clearly reveal the entangled network of nanofibers in each case as well as suggesting the more uniform distribution of nanofiber dimensions in MFC 2.

Film transparency and opacity

The transparency of MFC 1 and MFC 2 films was compared at 580 nm, chosen as the center of the visible wavelength spectrum from 380 to 780 nm. Light transmittance of MFC 2 films was slightly higher (14.1 ± 0.27 T%) than that of MFC 1 films (13.0 ± 1.2 T%); however, this difference was not statistically significant ($P \leq 0.05$). The normalized opacity of MFC films was calculated from the spectra shown in Figure 5 according to the method of Gontard et al.[31] Opacity is inversely proportional to transparency.

Based on the finer nanofiber dimensions of MFC 2, it was expected that the opacity of MFC 2 film would be much lower than that of MFC 1 film. However as shown in Figure 5 this is not the case and, as with the transparency measurements, differences between the opacity of MFC 1 (356.0 ± 16.3) and MFC 2 (340.7 ± 3.9) films were not statistically significant. An explanation for the limited measured transparency of MFC 2 films may be provided by the presence of large nanofiber agglomerates in these films. We have since demonstrated that these nanofiber agglomerates can be disintegrated by further homogenization steps. Although both MFC films had significantly higher opacity than either the LLDPE (20.2 ± 1.6) or EVOH (20.3 ± 1.4) reference films, by elimination of large fiber fragments and fibril aggregates highly transparent MFC 2 films can be produced. This research is the subject of a forthcoming publication.

CONCLUSIONS

An investigation into the use of two types of MFC as reinforcement in amylopectin films has shown differences in mechanical behavior under tensile load as a function of MFC type and concentration in the film. Stiffer films can be obtained when using MFC 1, containing a significant content of hemicellulose, at relatively high loadings. Oxygen permeability measurements on a range of pure MFC and MFC-amylopectin films have given relatively low values when compared with data for other polymers considering that MFC films should have a porous structure. The use of FE-SEM indicated that both types of 100% MFC film had a layered paper-like structure and that tensile fracture surfaces of MFC-reinforced amylopectin films had a brittle appearance regardless of MFC type. Both atomic force microscopy and FE-SEM techniques revealed the finer and more homogeneous distribution of nanofibers, but also the presence of some larger nanofiber agglomerates on the surface of MFC 2 films. The presence of these larger nanofiber agglomerates may explain why the transparency of MFC 2 films was lower than expected based on nanofiber dimensions.

The authors would like to express their gratitude for the valuable help provided by a number of other researchers. In particular, the authors are grateful for the assistance with scanning electron microscopy provided by Jørgen Bilde-Sørensen (Risø-DTU) and David Nordqvist (KTH). David's help with aspects of the tensile testing is also noted. Guidance in the use of atomic force microscopy from Noemi Rözlösnik (DTU Nanotech) is appreciated. Åsa Blademo at Innventia is acknowledged for the production of MFC 1 and 2 gels.

References

1. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. J Mater Res 1993, 8, 1185.
2. Herrick, F. W.; Casebier, R. L.; Hamilton, J. K.; Sandberg, K. R. J Appl Polym Sci Symp 1983, 37, 797.
3. Turbak, A. F.; Snyder, F. W.; Sandberg, K. R. J Appl Polym Sci Symp 1983, 37, 815.
4. Berglund, L. In Natural Fibers, Biopolymers and Biocomposites; Mohanty, A. K., Mishra, M., Drazal, L. T., Eds.; CRC

Press Taylor and Francis Group: Boca Raton, FL, 2005; pp 807–832.
5. Dufresne, A. Can J Chem 2007, 86, 484.
6. Klemm, D.; Schumann, D.; Kramer, F.; Hessler, N.; Hornung, M.; Schmauder, H. P.; Marsch, S. Polysaccharides 2006, 205, 49.
7. Kamel, S. Express Polym Lett 2007, 1, 546.
8. Henriksson, M.; Henriksson, G.; Berglund, L. A.; Lindström, T. Eur Polym J 2007, 43, 3434.
9. Pääkkö, M.; Ankerfors, M.; Kosonen, H.; Nykanen, A.; Ahola, S.; Österberg, M.; Ruokolainen, J.; Laine, J.; Larsson, P. T.; Ikkala, O.; Lindström, T. Biomacromolecules 2007, 8, 1934.
10. Wågberg, L.; Winter, L.; Odberg, L.; Lindström, T. Colloids Surf 1987, 27, 163.
11. Wågberg, L.; Decher, G.; Norgren, M.; Lindström, T.; Ankerfors, M.; Axnas, K. Langmuir 2008, 24, 784.
12. Saito, T.; Nishiyama, Y.; Putaux, J. L.; Vignon, M.; Isogai, A. Biomacromolecules 2006, 7, 1687.
13. Saito, T.; Kimura, S.; Nishiyama, Y.; Isogai, A. Biomacromolecules 2007, 8, 2485.
14. Fukuzumi, H.; Saito, T.; Wata, T.; Kumamoto, Y.; Isogai, A. Biomacromolecules 2009, 10, 162.
15. Saito, T.; Hirota, M.; Tamura, N.; Kimura, S.; Fukuzumi, H.; Heux, L.; Isogai, A. Biomacromolecules 2009, 10, 1992.
16. Sorrentino, A.; Gorrasi, G.; Vittoria, V. Trends Food Sci Technol 2007, 18, 84.
17. Pandey, J. K.; Kumar, A. P.; Misra, M.; Mohanty, A. K.; Drzal, L. T.; Singh, R. P. J Nanosci Nanotechnol 2005, 5, 497.
18. Rhim, J. W. Food Sci Biotechnol 2007, 16, 691.
19. Taniguchi, T.; Okamura, K. Polym Int 1998, 47, 291.
20. Yano, H. Cellul Commun 2005, 12, 63.
21. Nakagaito, A. N.; Yano, H. In Cellular Nanocomposites: Processing, Characterization, Properties; Oksman, K., Sain, M., Eds.; American Chemical Society: Washington, DC, 2006; Vol. 938, p 151.
22. Yano, H. Sen'1 Gakkash 2006, 62, 356.
23. Nakagaito, A. N.; Yano, H. Cellulose 2008, 15, 323.
24. Henriksson, M.; Berglund, L. A.; Isaksson, P.; Lindström, T.; Nishino, T. Biomacromolecules 2008, 9, 1579.
25. Svagan, A. J.; Samir, M. A. S. A.; Berglund, L. A. Biomacromolecules 2007, 8, 2556.
26. Svagan, A. J.; Hedenqvist, M. S.; Berglund, L. Compos Sci Technol 2009, 69, 500.
27. Mondragón, M.; Arroyo, K.; Romero-García, J. Carbohydr Polym 2008, 74, 201.
28. López-Rubio, A.; Lagaron, J. M.; Ankerfors, M.; Lindström, T.; Nordqvist, D.; Mattozzi, A.; Hedenqvist, M. S. Carbohydr Polym 2007, 68, 718.
29. Katz, K.; Beatson, R. P.; Scallan, A. M. Sven Papperstidn 1984, 87, R48.
30. ASTM D 882. Standard Test Method for Tensile Properties of Thin Plastic Sheeting. ASTM International: West Conshohocken, PA, USA. Available at: www.astm.org.
31. Gontard, N.; Guilbert, S.; Cuq, J. L. J Food Sci 1992, 57, 190.
32. Henriksson, M.; Berglund, L. A. J Appl Polym Sci 2007, 106, 2817.
33. Nakagaito, A. N.; Yano, H. Appl Phys A Mater Sci Process 2005, 80, 155.
34. Berglund, L. Proceedings of the 27th Risø International Symposium on Materials Science: Polymer Composite Materials for Wind Power Turbines: Risø National Laboratory, Roskilde, Denmark, 2006; p 1.
35. Banker, G. S.; Gore, A. Y.; Swarbric. J. J Pharm Pharmacol 1966, 18, 457.
36. Sothornvit, R.; Krochta, J. M. J Agric Food Chem 2000, 48, 6298.
37. Syverud, K.; Stenius, P. Cellulose 2009, 16, 75.
38. Lagaron, J. M.; Catala, R.; Gavara, R. Mater Sci Technol 2004, 20, 1.
39. Fendler, A.; Villanueva, M. P.; Giménez, E.; Lagarón, J. M. Cellulose 2007, 14, 427.
40. Lange, J.; Wyser, Y. Packaging Technol Sci 2003, 16, 149.
41. Butler, B. L.; Vergano, P. J.; Testin, R. F.; Bunn, J. M.; Wiles, J. L. J Food Sci 1996, 61, 953.
42. Rindlav-Westling, A.; Stading, M.; Hermansson, A. M.; Gatenholm, P. Carbohydr Polym 1998, 36, 217.
43. van Tuil, R.; Fowler, P.; Lawther, M.; Weber, C. J. In Biobased Packaging Materials for the Food Industry; Weber, C. J., Ed.; KVL Department of Dairy and Food Science: Frederiksberg, Copenhagen, 2000; pp 13–44.