THE FORMATION AND CHARACTERIZATION OF SUSTAINABLE LAYERED FILMS INCORPORATING MICROFIBRILLATED CELLULOSE (MFC)

Galina Rodionova,*[,a] Solenne Roudot,[a] Øyvind Eriksen,[b] Ferdinand Männle,[c] and Øyvind Gregersen [a]

Microfibrillated cellulose (MFC), TEMPO-pretreated MFC, and hybrid polymer/MFC mix were used for the production of layered films with interesting properties for application in food packaging. The series of samples were prepared from MFC (base layers) using a dispersion-casting method. The same procedure as well as a bar coating technique was applied to form top layers of different basis weights. The barrier properties and formation of the layered films were investigated in relationship to the preparation procedures, combination of layers, and areal weight (basis weight). Characterization was done with respect to oxygen transmission rates (OTR), water vapor transmission rates (WVTR), tensile properties, and contact angles (CA) with water. The produced layered films yielded OTR values of 4 mL m^{-2} day^{-1} and fulfilled oxygen barrier requirements for a modified atmosphere packaging (MAP). Hornification of the MFC films, however, occurred during drying, which may result in a loss of the film's beneficial properties.

Keywords: Layered films; Microfibrillated cellulose (MFC); Barrier properties; Basis weight; Hornification

Contact information: a: Department of Chemical Engineering, Norwegian University of Science and Technology, 7491 Trondheim, Norway; b: Paper and Fibre Research Institute, 7491 Trondheim, Norway; c: SINTEF Materials and Chemistry, 0373 Oslo, Norway.
**Corresponding author: galina.rodionova@chemeng.ntnu.no*

INTRODUCTION

Microfibrillated cellulose, or MFC, is a biodegradable film-forming material widely studied for its industrially interesting properties and possible applications in food packaging. It offers advantages such as high strength and large aspect ratio of its fibrils. Films made from MFC may be used for the preparation of multifunctional barriers. The majority of currently used packaging materials are produced from fossil-derived plastics. Even fiber-based packaging solutions usually incorporate one or more layers of synthetic polymers to obtain reliable barrier properties of the package. MFC is produced from sustainable cellulosic resources, and due to the relatively high crystallinity (Aulin *et al.* 2009), it has excellent oxygen barrier properties, as well as broad possibilities for the chemical derivatization to alter its hydrophobicity.

MFCs are extensively investigated for use as a coating layer of paper substrates with the aim to improve barrier properties and reduce surface porosity. Koga (2000) presented a method based on the use of one or several layers of MFC and fabricating a

gas and moisture resistant paper laminate. The product was claimed to be applicable in food packaging. Several more studies have shown that MFC may be successfully used as a barrier in paper coating or as an individual monolayer (Aulin *et al.* 2009; Syverud and Stenius 2009). In spite of the many advantageous properties and ability to cover larger pores on the paper surfaces, the MFC films themselves may have a significant porosity (Henriksson and Berglund 2007; Henriksson *et al.* 2008).

Organic/inorganic hybrid polymers based on polyhedral oligomeric compound silsesquioxane (POSS) represent a large potential for chemical derivatization and interesting properties for use in polymer blends of packaging multilayer materials (Männle *et al.* 2011). Polymeric materials, functionalized with POSS, exhibit enhanced mechanical strength, thermal stability, and barrier properties (Cordes *et al.* 2010). Cellulose microfibrils and hybrid polymers potentially have excellent properties for cross-linking. Combining them may enhance mechanical properties and provide effective barrier performance against water or water vapor.

In this work, due to the occurrence of drying hysteresis and an irreversible loss of swelling ability (hornification), specific attention was given to the different drying methods of the films. The hornification phenomenon defines the irreversible, or partially reversible, as well as changes in the fiber structure upon the removal of water, typically resulting in a decrease of the strength properties (Fernandes Diniz *et al.* 2004; Park *et al.* 2006). Laivins and Scallan (1993) demonstrated that intra-fiber walls are irreversibly linked during drying of cellulose fibers, and this may cause a significant loss of large pores. The concept of pore closure implies a partial or total removal of water as the main cause of hornification. The effect of drying conditions on the hornification of the fibers was studied by Weise (1998). He suggested that the hornification due to drying is caused by a change in the microscopic morphology.

Combination of multiple MFC layers in a single film, or coating MFC films with higher water barrier polymers could possibly improve barrier properties as well as provide other benefits. The aim of this research was to make layered films incorporating coating formulations based on different grades of MFC. The coating materials were produced by high-pressure homogenization in combination with TEMPO-mediated oxidation of pulp suspension or mixing the pulp fibers with a hybrid polymer before mechanical treatment. The influence of varying basis weights and coating compositions on the film's barrier properties were investigated using water repellency, oxygen, and water vapor permeability tests. Two methods of top layer formation, as well as different drying techniques, were applied to study their effect on the film's barrier properties and the hornification effect.

EXPERIMENTAL

Materials

MFC1: MFC was produced from Norway spruce kraft pulp (containing 83.6% cellulose and 15.6% hemicelluloses) by pre-treatment in a Claflin mill combined with homogenization as described by Eriksen *et al.* (2008). The MFC1 suspension had a solids content of 0.37 %.

MFC2: TEMPO-mediated pre-treatment of the pulp by TEMPO/NaBr/NaClO system was carried out before the mechanical homogenization for preparation of MFC2. 2 g of pulp fibers (dry weight) were placed into a reaction vessel containing distilled water (150 mL), NaBr (0.25 g), and TEMPO (0.025 g). All of the above-listed chemicals were purchased from Sigma-Aldrich Chemie GmbH. The desired amount of NaClO solution, corresponding to 3.8 mmol g^{-1} cellulose, was added to the fiber suspension. The mixture was maintained at pH 7 by adding 0.5 M of 37 % HCl (Merck Chemicals). The MFC2 suspension had a solids content of 0.37 %.

MFC3: An organic/inorganic hybrid polymer (HP) was prepared by a sol-gel conversion process. The hybrid polymer was of the type FunzioNano, a polyhedral oligomeric silsesquioxane. The synthesis of the FunzioNano has been performed by using a mixture of salicylic acid (95 % w/w) and 3-hydroxy-2-naphthoic acid as modifiers (Männle *et al.* 2011). The FunzioNano was added to the pulp suspension before the mechanical homogenization. The produced MFC3 suspension consisted of MFC and FunzioNano (50:50 %) suspension and had a solids content of 0.7 %.

Preparation of Films

Base-layer MFC films with basis weights of 2, 10, 15, 20, and 30 g m^{-2} were manufactured by a dispersion-casting of aqueous dispersions of microfibrils. The films were made from a suspension of 0.1 % MFC1 in water by simple filtration through a paper filter, supported by a metal mesh and a polyamide filter cloth. After draining most of the water, the films were dried at 100°C for 2 h (Rodionova *et al.* 2011). The filter paper was dried at the same conditions before casting the film.

Top layers of MFC2 and MFC3 were applied on the MFC1 films by the same dispersion-casting procedure or by using a laboratory bar coating system. The bar coating was done in one direction using a metal rod wound with a metal wire for metering the wanted basis weight of microfibril suspensions. The coating layer basis weights were 0.5 and 1 g m^{-2}.

Characterization of Films

Density/thickness measurement

Apparent thickness of the MFC films was determined as an average of 12 measurements using a L&W Micrometer (Lorentzen & Wettre, Sweden) according to ISO 534 standard for paper and board materials. The density was calculated from the apparent thickness values and areal weights (basis weights) of the films.

Contact angle (CA)

The alterations of the water repellency of the MFC film's surface were estimated by CA measurements. The test was done using a DAT1100 Dynamic Contact Angle Tester (FIBRO system ab, Sweden) at 23°C and 50 % RH. A droplet of water (4 μL) was deposited on the specimen surface. Series of images were captured and analysed. The dynamic wetting (contact angle) was measured as a function of time between 0 and 180 seconds. A minimum of ten readings were taken for each sample.

Water vapor transmission rate (WVTR)

Water vapor permeability of the layered films was evaluated by the gravimetric WVTR test according to TAPPI T 448. The films were placed on top of a test dish containing sufficient amount of desiccant (anhydrous calcium chloride). The assembled dishes were placed in the testing room at 23°C and 50% RH and weighed every 24 h until constant rate of weight gain was attained.

Oxygen transmission rate (OTR)

The OTR was measured using a Mocon oxygen transmission rate tester (OX-TRAN Model 1/50) according to ASTM D3985. The test gas contained 21% of oxygen and was applied to the film area of 5 cm^2 at 2.2 bar partial oxygen pressure (2 parallels for each sample, RH = 0).

Tensile test

The tensile strength was measured using a Zwick/Roell test machine at 20 mm min^{-1} strain rate (23°C, 50 % RH). Specimen dimensions were 14.6 × 20 mm. Tensile indexes of the MFC films were calculated from the basis weight of every single film, thickness, and tensile rupture strength.

Scanning electron microscopy (SEM)

The film's surfaces were examined using a Hitachi S-3000N scanning electron microscope at 5 kV acceleration voltage. To avoid sample charging, the films were coated with carbon and observed in a secondary electron imaging mode (SEI) at 50/500× magnification.

RESULTS AND DISCUSSION

There are several methods to characterize barrier properties of the films and estimate their applicability for the food packaging applications. The single layer MFC films, prepared by the dispersion-casting technique, were tested with respect to their permeabilities/mechanical properties and showed encouraging results. The layered films, combining different materials, were characterized according to the same procedures and considerable improvement of the properties compared to single layer MFC films was registered.

Single Layer MFC1 Films

A series of MFC1 films with the basis weights from 2 to 30 g m^{-2} were made by the dispersion-casting technique. An examination of the filter paper surface coverage by the MFC was done to establish the minimal thickness of a film that was separable from the filter paper. The morphological investigation by scanning electron microscopy (SEM) clearly demonstrated that 2 g m^{-2} of MFC1 was not sufficient to cover the porous structure of the filter paper sheet (Fig. 1A and 1B). It was possible to obtain freestanding films starting at 10 g m^{-2} (Fig. 1C). Films having this basis weight, together with films of

20 g m^{-2}, were chosen for the preparation of the base MFC1 layers of the layered films in this work.

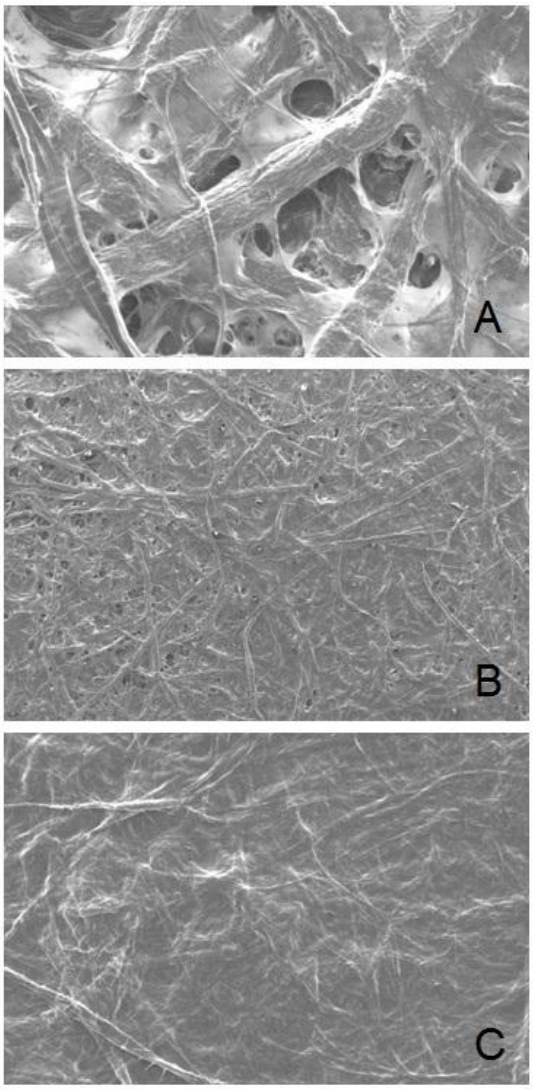

Fig. 1. SEM images of the 2 g m^{-2} MFC1 film (A at 500×, B at 50×) and 10 g m^{-2} MFC1 film surfaces

A short investigation was carried out to study the effect of the thicknesses and areal weights (basis weights) on the WVTR of the single layer MFC1 films (Fig. 2). Obviously, it is more difficult for the water vapor molecules to pass through the thicker films. It was confirmed that the water vapor permeability was negatively correlated to the film's thickness and basis weight. However, for the thicker films of 25 and 30 g m^{-2}, the WVTR stabilized at around 170 g m^{-2} day^{-1}, and no further reduction was registered. It can also be suggested that in spite of the large surface porosity (Henriksson and Berglund 2007), the internal pores are not interconnected through the film thickness, which will slow down penetration of the water molecules.

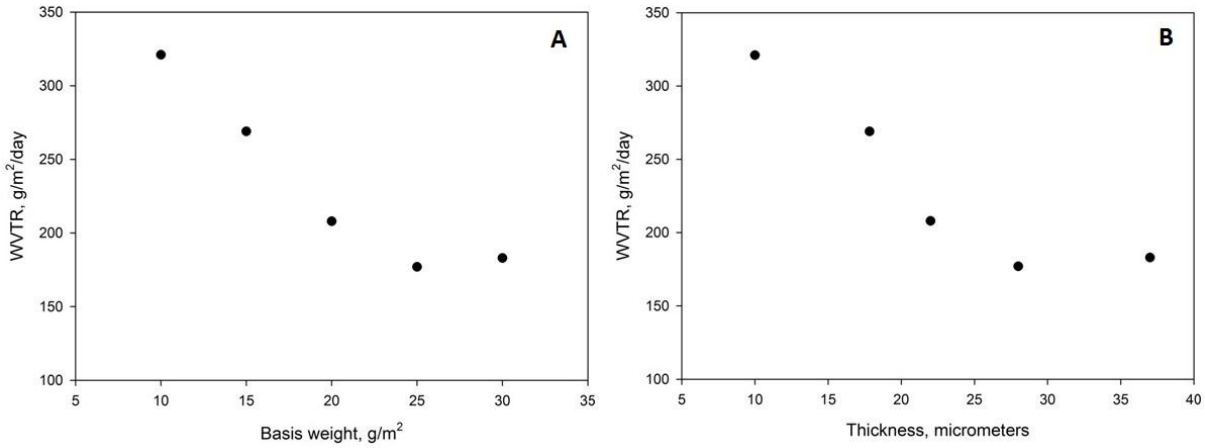

Fig. 2. WVTR of the MFC1 films at variable basis weights (A) and corresponding thicknesses (B)

As expected, contact angles of the single layer films showed no correlation with their basis weights. The obtained values were in the range from 40 to 50°, which is in agreement with the hydrophilic nature of the films made from the mechanically produced MFC (Rodionova *et al.* 2011).

Analysis of the oxygen permeability was carried out on the corresponding MFC1 films, and the results are presented in Table 1. Possibly due to presence of macroscopic pores in the films, the films showed no barrier against oxygen at the 10 g m^{-2} basis weights. The oxygen transmission rates (OTR) of the films with 20 g m^{-2} basis weights were in a good agreement with literature values (Syverud and Stenius 2009).

Table 1. Oxygen Transmission Rates of the Monolayer MFC1 Films of Different Basis Weights

Basis weight [g m^{-2}]	OTR [ml m^{-2} day^{-1}]
10	>2000
15	9.3 ± 0.7
20	5.4 ± 0.8

Tensile indexes of the 10 and 20 g m^{-2} MFC1 films were estimated (Table 2). The films of higher basis weights showed better strength as well as elongation. These values are also in agreement with the measurements of Syverud and Stenius (2009). It seems that the oven drying has no effect on the mechanical properties of the films.

Table 2. Elongation and Tensile Indexes of the Monolayer MFC1 Films

Basis weight [g m^{-2}]	Elongation [%]	Tensile index [Nm g^{-1}]
10	3.5 ± 0.5	78.1 ± 7.7
20	5.3 ± 0.6	102 ± 2.8

Layered Films

The layered films with MFC2 top layers of about 1 g m^{-2} were prepared by the dispersion-casting method. After introducing the top layer, films were dried either at room conditions (22°C) or in the oven at 100°C. WVTR measurements showed a significant effect of the basis weights as well as the drying conditions on the capacity of the films to absorb water vapor (Fig. 3). The films of highest basis weights had the lowest permeability. After applying the MFC2 layer, the oven dried films showed an unexpected increase in WVTR, whereas the two-layer films dried at 20°C, as expected, got a reduced WVTR. This might be explained by morphological changes. According to Stone and Scallan (1965), hydrogen bonding causes shrinkage of the cellulose microfibrillar network upon drying, and as a result, causes loss of the pores in the cell wall. Rewetting might only partially reopen the tightly packed structure.

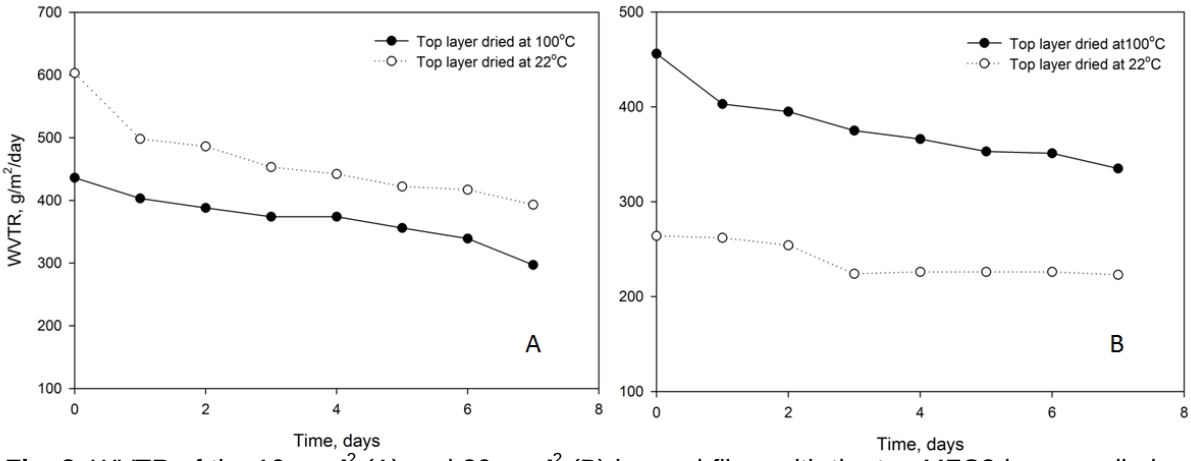

Fig. 3. WVTR of the 10 g m^{-2} (A) and 20 g m^{-2} (B) layered films with the top MFC2 layer applied by the dispersion-casting method

The WVTR for the layered films prepared using a bar coating system are given in Table 3. The values were reduced when the top layer was made using the MFC3, as the polymer in the MFC3 mixture has better water vapor barrier resistance than the other component, MFC1. Packaging needs an efficient water vapor barrier; polyethylene, which is normally used for this purpose, may provide water resistance in a range of about 1 g m^{-2} day^{-1} (Combellick 1985). In this study, the lowest WVTR was obtained for the MFC3 coated films (173 g m^{-2} day^{-1}). This moisture barrier is low when compared to the single layer MFC films but still not sufficient for application in food packaging and has to be improved.

Table 3. WVTR of Mono- and Multi-layer MFC Films at Variable Basis Weights

Basis weight: base + top layer [g m^{-2}]	WVTR [g m^{-2} day^{-1}]	
	MFC2 top layer	MFC3 top layer
20 + 0	208	208
20 + 0.5	213	174
20 + 1.0	211	173

The OTR were measured on the films made by both dispersion-casting and bar coating and showed an improvement compared to single layer 20 g m^{-2} MFC1 films. It was concluded that the composition of the coating layer in this case had no effect on the OTR. The values registered for the films prepared using the bar coater and top layers of MFC2 and MFC3 were lowest with a similar transfer rate, about 4.0 mL m^{-2} day^{-1}. These films had oxygen barrier comparable with synthetic polymers, commonly used in an oxygen sensitive food packaging.

The CA of the layered films prepared by different methods with both MFC2 and MFC3 top layers are shown on Fig. 4. The measurements were done on the films prepared with both 10 and 20 g m^{-2} MFC1 base layers. However, the MFC1 grammage had no effect on the film's hydrophilicity. CA variations within the standard deviation were registered for both coating formulations and grammages when using the dispersion-casting method. The bar coating technique was confirmed to be more efficient. The films with MFC3 top layer (basis weight of 1 g m^{-2}) gave a significant improvement of the surface water repellency and showed the highest CA of 68.5°.

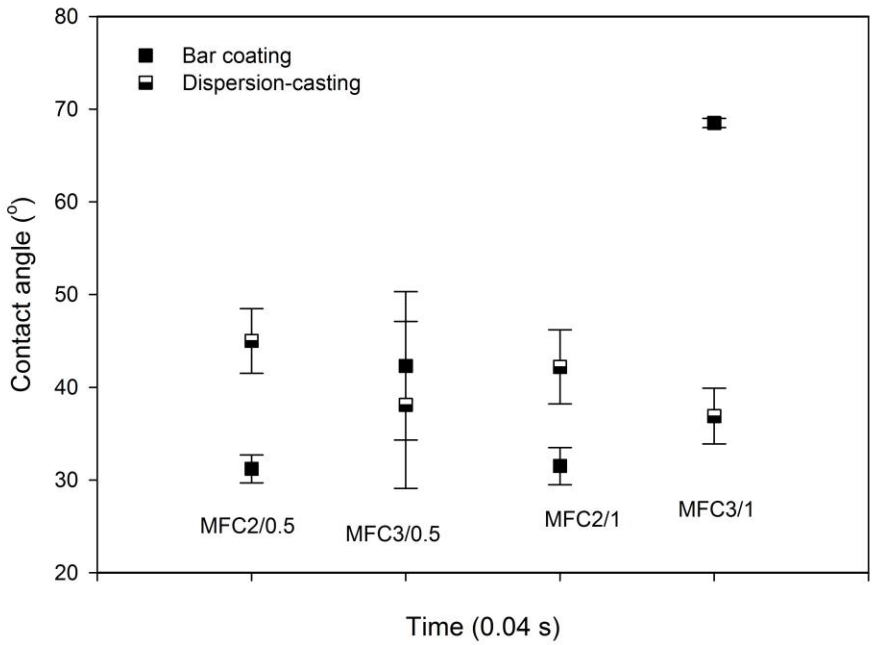

Fig. 4. Contact angles of the layered films made with MFC2/MFC3 top layers of 0.5 and 1 g m^{-2}

The mechanical properties of the layered films prepared by the bar coating with MFC2 and MFC3 layers of 0.5 and 1 g m^{-2} were investigated. The fracture stress (Fmax) is mainly determined by the properties of the base films. Thus, it was not affected by the increase in basis weight due to coating or the composition of the coating. It has been reported in the literature that the hybrid polymer based on POSS may provide an improvement of the mechanical properties (Cordes *et al.* 2010). On the other hand, the elongation at rupture of the films increased distinctly with the application of top layers (Fig. 5). Application of the coating layer requires additional drying, which leads to shrinkage of the whole film as compared to uncoated sample. This means that the coated films have an increased potential for elongation compared to the once-dried uncoated

films (Niskanen 2008). The elongation enhancement appeared to be larger when the top layer of MFC2 was applied. This might be related to the fact that the TEMPO-oxidized microfibrillated cellulose by itself exhibits a large aspect ratio of the fibrils (Isogai *et al.* 2011) and tensile strengths of 200-300 MPa (Isogai *et al.* 2011).

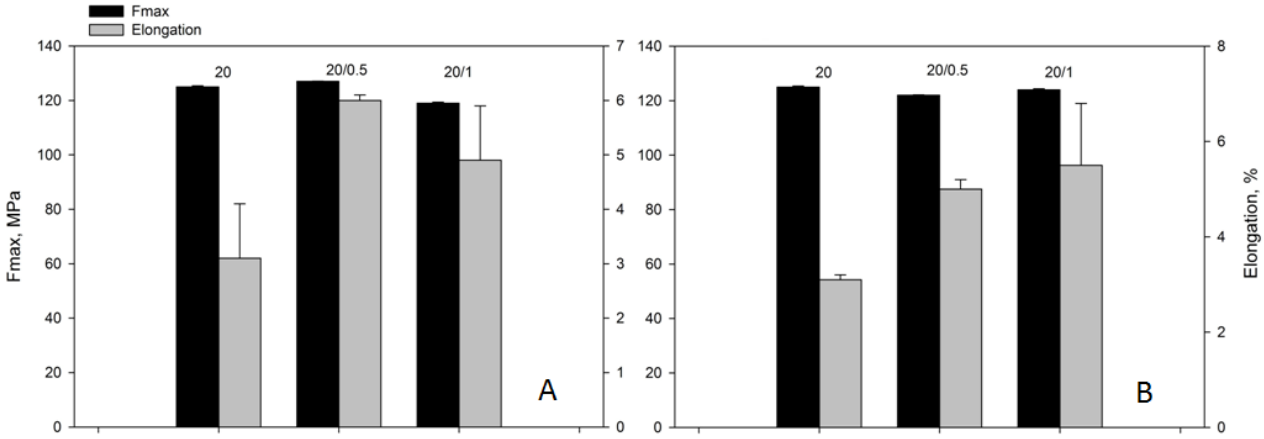

Fig. 5. Elongation and Fmax of the films coated with MFC2 (A) and MFC3 (B) layers of 0.5/1 g m^{-2} in comparison with the 20 g m^{-2} MFC1 monolayer films

CONCLUSIONS

Layered MFC films were produced using different techniques and coating formulations consisting of TEMPO-pretreated MFC2 or MFC1 mixed with the hybrid polymer, MFC3. An increase in basis weights led to better barrier properties. The drying strategies showed a clear influence on the hornification. It was concluded from the WVTR results that morphological changes caused by the hornification had an effect of the barrier properties of the films. This phenomenon should be explored in the future, as it has practical importance for the application areas of MFC. The elongation and the OTR were significantly improved by the introduction of the top MFC layers. The OTR of some films was low enough to fulfill the modified atmosphere packaging requirements of below 10 to 20 mL m^{-2} day^{-1}.

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