

Alma Mater Studiorum Università di Bologna
Archivio istituzionale della ricerca

Atmospheric plasma assisted PLA/microfibrillated cellulose (MFC) multilayer biocomposite for sustainable barrier application

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Atmospheric plasma assisted PLA/microfibrillated cellulose (MFC) multilayer biocomposite for sustainable barrier application / Meriçer, Çağlar; Minelli, Matteo; De Angelis, Maria G.; Giacinti Baschetti, Marco; Stancampiano, Augusto; Laurita, Romolo; Gherardi, Matteo; Colombo, Vittorio; Trifol, Jon; Szabo, Peter; Lindström, Tom. - In: INDUSTRIAL CROPS AND PRODUCTS. - ISSN 0926-6690. - ELETTRONICO. - 93:(2016), pp. 235-243. [10.1016/j.indcrop.2016.03.020]

Availability:

This version is available at: <https://hdl.handle.net/11585/567619> since: 2016-11-15

Published:

DOI: <http://doi.org/10.1016/j.indcrop.2016.03.020>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>).
When citing, please refer to the published version.

(Article begins on next page)

This is the final peer-reviewed accepted manuscript of:

Çağlar Meriçer, Matteo Minelli, Maria G. De Angelis, Marco Giacinti Baschetti, Augusto Stancampiano, Romolo Laurita, Matteo Gherardi, Vittorio Colombo, Jon Trifol, Peter Szabo, Tom Lindström

Atmospheric plasma assisted PLA/microfibrillated cellulose (MFC) multilayer biocomposite for sustainable barrier application

In "Industrial Crops and Products" Volume 93, 2016, p. 235-243

The final published version is available online at:

<https://doi.org/10.1016/j.indcrop.2016.03.020>

Rights / License:

The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

**Atmospheric plasma assisted PLA/Microfibrillated cellulose (MFC) multilayer
biocomposite for sustainable barrier application**

*Çağlar Meriçer,¹ Matteo Minelli,^{1,2} Maria G. De Angelis,^{1,2} Marco Giacinti Baschetti,^{*1,2}
Augusto Stancampiano², Romolo Laurita,^{2,3} Matteo Gherardi,^{2,3} Vittorio Colombo,^{2,3} Jon Trifol,⁴
Peter Szabo,⁴ Tom Lindström⁵*

¹ DICAM – Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Alma Mater
Studiorum –University of Bologna, Italy

² CIRI-MAM – Centro Interdipartimentale per la Ricerca Industriale, Meccanica Avanzata e
Materiali, Alma Mater Studiorum –University of Bologna, Italy

³ DIN – Dipartimento di Ingegneria Industriale, Alma Mater Studiorum –University of Bologna

⁴ Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Technical
University of Denmark, Denmark

⁵ Innventia AB, Stockholm, Sweden

Corresponding author

Marco Giacinti Baschetti

Tel. +39 51 2090408

Fax. +39 51 6347788

e-mail: marco.giacinti@unibo.it

Highlights:

- MFC/PLA bilayer films are fabricated as biorenewable barrier solution for packaging.
- Atmospheric plasma activation guarantees the effectiveness of coating process.
- MFC coatings improve significantly the mechanical and barrier performances of PLA.

ABSTRACT

Fully bio-based and biodegradable materials, such as polylactic acid (PLA) and microfibrillated cellulose (MFC), are considered in order to produce a completely renewable packaging solution for oxygen barrier applications, even at medium-high relative humidity (R.H.). Thin layers of MFC were coated on different PLA substrates by activating film surface with an atmospheric plasma treatment, leading to the fabrication of robust and transparent multilayer composite films, which were then characterized by different experimental techniques. UV transmission measurements confirmed the transparency of multilayer films (60% of UV transmission rate), while SEM micrographs showed the presence of a continuous, dense and defect free layer of MFC on PLA surface. Concerning the mechanical behavior of the samples, tensile tests revealed that the multilayer films significantly improved the stress at break value of neat PLA. Moreover, the oxygen barrier properties of the multilayer films were improved more than one order of magnitude compared to neat PLA film at 35°C and 0% R.H. and the permeability values are maintained up to 60% R.H.. The obtained materials therefore showed interesting properties for their possible use in barrier packaging applications as fully biodegradable solution, coupling two primarily incompatible matrices in a multilayer film with no need of any solvent or chemical.

Keywords:

Nanocellulose, polylactic acid, atmospheric plasma, multilayer film, barrier properties

1. INTRODUCTION

Plastics derived from fossil fuels have been the commodity materials in the packaging industry during last few decades and this trend has been increasing steadily mainly due to their feasibility in terms of cost and manufacturing processes.(Plastics Europe, 2015) On the other hand, limited recycling rates and waste-disposal problems associated with traditional plastic materials led to serious environmental issues. (Mohanty et al., 2002). The latest data show that the packaging industry accounts for nearly 40% of plastics usage in the world (Plastics Europe, 2015). Hence, due to increasing environmental concerns and end-of-life cycles of commodity packaging materials, over the last decade the research in developing eco-friendly and biodegradable polymer solutions has reached its peak in packaging and other sectors. (Petersen et al., 1999; van Tuil et al., 2000; Siracusa et al., 2008)

Bio-based materials can be divided into three main groups, according to the classification based on their source: polymers derived directly from natural materials (starch, cellulose, chitosan), synthesized from bio-derived monomers (polylactide - PLA, bio-polyethylene - PE etc.) and produced by living organisms such as microorganisms or bacteria (poly hydroxyl alkanoates - PHAs, bacterial cellulose) (Tharanathan, 2003; Klemm et al., 2006; Siró and Plackett, 2010; Vieira et al., 2011; Johansson et al., 2012).

Among the different biomaterials, polylactide or polylactic acid (PLA) is a biodegradable bioplastic produced by the polymerization reaction of a naturally derived monomer (lactic acid), obtained from dextrose. Being renewable and biodegradable, it decomposes in the environment into carbon dioxide and water in the appropriate conditions, PLA is a suitable candidate for the replacement of petroleum based products (Jamshidian et al., 2010), and currently offers a strong alternative in the packaging industry, also due to its easy processability through conventional

methods such as melt processing (Drumright et al., 2000; Nakagaito et al., 2009). For these reasons, PLA has been already applied in the industry for certain food products or goods, and is currently widely investigated aiming at the improvement of some key properties such as physical, mechanical and gas barrier properties in order to better compete with oil derived plastics (Auras et al., 2003, 2006; de Azeredo, 2009; Drieskens et al., 2009; Svagan et al., 2012; Guinault et al., 2012; Delpouve et al., 2012; Bai et al., 2014). In particular, the gas barrier ability still needs to be enhanced in order to use PLA in barrier packaging applications, e.g. for sensitive foods (Auras et al., 2006; de Azeredo, 2009; Drieskens et al., 2009). In this concern, several studies investigated the gas permeability of PLA-based materials, with particular attention to nanocomposites, prepared following different approaches such as melt extrusion, in situ polymerization, and solvent casting, to mix the polymer with impermeable layered silicate clays (Chang et al., 2003; Chowdhury, 2008; Picard et al., 2011; Svagan et al., 2012). However, due to difficult exfoliation and orientation of nanoclays, the reduction in oxygen permeability is somewhat limited around 60% (Chang et al., 2003; Chowdhury, 2008).

Recently, the development of nanometric sized cellulosic materials, known as microfibrillated cellulose (MFC or NFC) (Herrick et al., 1983; Turbak et al., 1983; Klemm et al., 2006; Siró and Plackett, 2010) and nanowhiskers or nanocrystals, (Samir et al., 2005; Eichhorn, 2011) produced respectively by delamination of the fibers in a high pressure homogenization process, and by acid hydrolysis to eliminate the amorphous regions of the fibrils, opened up new possibilities for barrier packaging applications primarily due to the remarkable mechanical and barrier properties of these new materials (Berglund, 2005; Samir et al., 2005; Fukuzumi et al., 2009; Henriksson et al., 2008; Syverud and Stenius, 2009; Sanchez-Garcia and Lagaron, 2010; Lavoine et al., 2012; Belbekhouche et al., 2011).

Strong and stiff films of nanocellulose can be produced from highly diluted dispersion in water by different methods (Yano, and Nakahara, 2004; Syverud and Stenius, 2009; Minelli et al., 2010; Österberg et al., 2013), and MFC can also be used as reinforcement for nanocomposites to improve the mechanical properties due to high aspect ratio of the microfibrils (Zimmermann et al., 2004; Leitner et al., 2007; Svagan et al., 2007; Iwatake et al., 2008). Moreover, cellulosic materials can be easily functionalized thanks to the high number of hydroxyl groups on the surface of microfibrils which create sites for chemical modifications suitable to various applications (Andresen et al. 2007; Lu et al., 2008; Stenstad et al., 2008; Siquera et al., 2009, Lavoine et al., 2014, Habibi, 2014).

MFC is a strong candidate for the fabrication of nanocomposites and coating formulations for barrier packaging applications in view of its high crystalline content and the ability to form dense interfibrillar network with hydrogen bonds, which eventually lead to excellent gas barrier properties (Lavoine et al., 2012; Martínez-Sanz et al., 2013; Bardet et al., 2015, Rodionova et al., 2012). The oxygen permeability of 21 μm thick MFC films produced from bleached spruce sulfite pulp at 23 °C and 0% RH was reported as $1.9 \cdot 10^{-18} \text{ mol m/m}^2 \text{ s Pa}$ (Syverud and Stenius, 2009), comparable with well-known ultra-barrier polymers, e.g. polyvinyl alcohol, PVOH or polyvinylidene chloride, PVdC (Lange and Wyser, 2003). The effect of pretreatments of the cellulose fiber on the final MFC barrier performances has been also investigated, revealing that O_2 permeability in enzymatically pretreated MFC is comparable if not slightly smaller than that in carboxymethylated MFC, being the values measured at 35°C as low as $2.6 \cdot 10^{-19}$ and $6.3 \cdot 10^{-19} \text{ mol m/m}^2 \text{ s Pa}$, for the two materials respectively (Minelli et al. 2010).

PLA and MFC are very likely the two most promising bio-based materials for industrial application in the near future, and for this reason they were often combined to form new

generation of nanocomposites for different purposes (Iwatake et al., 2008; Suryanegara et al., 2009; Mathew et al., 2005, 2006; Oksman et al., 2006; Iwatake et al. 2008). Interestingly, highly loaded nanocomposite films (up to 90 wt.% of MFC) have been obtained from an aqueous suspension of MFC and PLA followed by hot pressing of the dried sheets, leading to a tensile modulus that increases linearly with the MFC content, followed by strength and strain at fracture (Nakagaito et al. 2009). Alternatively, Fukuzumi et al. (2009, 2013) used a different approach and prepared TEMPO oxidized MFC thin coating (0.4 μm) on plasma-treated PLA film, leading to a dramatic reduction of the oxygen transfer rate. Plasma treatment can indeed modify the surface properties of PLA films, such as wettability, surface energy and chemical structure (Vergne et al., 2011; Jordá-Vilaplana et al., 2014; Cools et al., 2015), enabling and the deposition of thin coatings on the polymer surface and the consequent production of multilayer films (Benetto et al., 2015).

Although significant efforts have been devoted to the fabrication of PLA/nanocellulose composite systems by dispersion of fibrils or crystals into the polymer matrix, very few works have focused on their assembly in layered structures, which in turn are clearly more industrially attractive, especially for packaging applications. The main limitation is indeed in the large incompatibility of the two phases, which can be overcome by chemical modification, surface treatments (Fukuzumi et al. 2009), or by means of specific deposition techniques (Aulin et al. 2013).

In the present study, a bilayer system is fabricated by coating a thin layer of MFC onto a plasma activated PLA substrate, obtaining a strong adhesion between two primarily incompatible layers. Mechanical, optical and transport properties of the multilayer films were analyzed with

particular attention to the oxygen barrier, which was investigated in both dry and humid conditions, and compared with data for neat PLA and other current polymer commodities..

2. Experimental

2.1. Materials

Microfibrillated cellulose (MFC)

The neat MFC films and the coatings prepared in this work are obtained from aqueous dispersions at about 2% by weight of solid contents, produced at Innventia AB (Stockholm, Sweden). Two different MFC dispersions were used, often labeled as MFC generation 1 (MFC G1) and MFC generation 2 (MFC G2), produced from cellulose pulp after identical mechanical crushing in the high pressure homogenization step following different pretreatment procedures to obtain an easier and energy efficient fibrillation process. In particular, MFC G1 is obtained by an enzymatic pretreatment of the cellulose pulp, as described by Pääkkö et al. (2007), a carboxymethylation process is used to fabricate MFC-G2, according to Wågberg et al. (2008). A brief description of the preparation techniques of the MFC productions is here proposed, while more detailed illustration of the method and the results of their physical and morphological characterization are in the cited publications (Henriksson et al., 2007; Siró et al., 2011); .

MFC G1 is produced from 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%, whereas commercial sulfite softwood dissolving pulp (Domsjö Dissolving Plus, Domsjö Fabriker AB, Sweden), with 4.5% of hemicellulose and 0.6% of lignin content, has been used to obtain the final MFC G2 dispersion.

The fabrication of the pure MFC films is carried out by further diluting the dispersions with deionized water in order to prepare a suspension that could be easily poured (1% of solid content for MFC G1, and 0.67 for MFC G2), which is then vigorously stirred for about 3 h and finally cast in glass Petri dishes placed under a clean hood at room temperature, until complete solvent evaporation is attained.

Poly(lactic acid) (PLA)

Two different types of PLA are used as substrate, in order to explore any possible difference in the plasma activation process and in the final barrier properties; to this aim amorphous (PLA-Am) and semi-crystalline PLA are accounted for.

Amorphous PLA films were produced by solvent casting, dissolving Natureworks (4060D) pellets in dichloromethane 5% wt., vigorously stirring the solution for about 3 h, and finally pouring it into glass Petri dish which was then placed in a clean hood at ambient conditions for 24 h, until the solvent was completely evaporated. The films obtained were then treated under vacuum at 50°C to ensure the complete solvent evaporation.

Semi-crystalline PLA (Polybio 212) was a commercially available product obtained by extrusion, and kindly provided by Coopbox S.p.A; the film has a thickness of 40 µm, a crystalline fraction of about 18%, as obtained by DSC measurements.

2.2. Atmospheric Plasma treatment

PLA films were plasma treated by means of two different Dielectric Barrier Discharge (DBD) sources, named planar-DBD and DBD-roller; during the treatment, PLA films were positioned in the interelectrode gap on the grounded electrode of the DBD plasma sources.

The DBD-roller, whose details have been previously illustrated, (Boselli et al. 2012), was specifically designed to enable a roll-to-roll continuous treatment of films. The plasma source was operated in air driven by a high voltage generator (FID GmbH – FPG 20–1NMK), and the treatment was performed using peak voltage (PV) of 20 kV and pulse repetition frequency (PRF) of 330 Hz and was operated for 20 s. A planar-DBD source, also described in a previous work (Boselli et al. 2013), was operated in air as well, driven by a high voltage generator (Trek model 30/20-H-CE), connected to a function generator (Stanford Research model DS335). The operating parameter of the high voltage generator were set as follows: bipolar square-wave having a PV of 12.7 kV and a PRF of 100 Hz. PLA films were treated for 5 minutes. No bulky effect is expected to be produced by the plasma process, which is ultimately an almost purely superficial treatment: its penetration is indeed in the order of few hundreds of nanometers, not able to produce significant changes in the overall properties of the PLA film. In this respect, the gas transport properties of PLA films have been demonstrated to be practically unchanged by the plasma treatment (Boselli et al., 2013).

2.3 multilayer film preparation

PLA/MFC films are prepared by solvent casting of the MFC dispersion on top of a plasma treated PLA film conveniently located in a glassy Petri dish; alternatively adjustable casting knife technique was used on rectangular glass support (BYK-Gardner). Multilayer films are then obtained after the evaporation of water in a clean hood at ambient conditions for 2-3 days. The thicknesses of the films used in the different tests span from 10 to 60 microns (Table 1). They were obtained by controlling the exact amount of solution poured in the petri dish during casting procedure. The resulting thicknesses were then measured with a Mitutoyo micrometer (Mitutoyo

Scandinavia AB, Väsby, Sweden) in 10 different spots, resulting deviation, on the single sample, not exceeding 5 %.

It is noteworthy that the bilayer systems are obtained only after the plasma treatment of the PLA film surface. In absence of any activation, indeed, no adhesion at all could be achieved between coating and substrate.

Table 1. Bilayer films characterized in this study with their thicknesses and analyzing methods.

Film	Thickness range (μm)
PLA	40
PLA-Am	40-50
MFC G1	9-32
MFC G2	10-27
PLA/MFC G1	40 + 10-17
PLA/MFC G2	40 + 7-17

2.4. Material characterization

Scanning electron microscope (SEM)

The materials were characterized by SEM on an FEI Quanta 200 ESEM FEG at 5 kV. SEM images were obtained in order to investigate the arrangement of the different layers in the bilayer structure. Indeed, MFC G1 and MFC G2 coatings on top of PLA substrates were expected to show a dense and continuous layer, as typically observed for self-standing nanocellulose films (Minelli et al. 2010).

Tensile tests

Tensile tests were carried out by means of an INSTRON 4301 apparatus (Instron Engineering Corporation, Canton, MA, USA) at a strain rate of 1 mm min^{-1} for PLA-Am, MFC

G2 and PLA/MFC G2 films, in order to inspect the stability of the coating application and to ensure that the adhesion between two layers is retained as well as the mechanical properties are preserved. Wide rectangular shaped specimens with a dimension of 50x10 mm were prepared for testing. The Young modulus was determined from the slope of the linear region of the stress-strain range (approximately between 1% and 6% of strain).

Optical properties

UV light transmissions of PLA-Am, MFC G1, MFC G2, PLA/MFC G1 and PLA/MFC G2 films were measured using a UV-Vis spectrometer (Polar Star Omega) in the range of 220 nm – 1000 nm by triplicate.

Gas permeation apparatus

Gas permeation experiments were carried out in two different apparatuses, namely dry and humid permeation systems, already described in previous studies (Minelli et al. 2008, 2010). Both pieces of equipment exploit a standard barometric technique for the evaluation of the permeate flux from the measure of a pressure increase in a closed downstream compartment, whose volume has been previously calibrated (ASTM Standard D 1434). Humid gas tests were carried out conveniently pre-equilibrating the sample at the desired humidity by exposing both sides of the film to pure water vapor at controlled pressure (corresponding to the target activity). Therefore, when one side of the sample is fed by a humidified O₂ stream at the same RH of the preequilibration step, the water has the same chemical potential in both upstream and downstream compartment and only oxygen permeates through (Minelli et al., 2008; Ansaloni et al., 2014). Thus, at steady state conditions Eq. 1 provides the required expression for permeability:

$$P = O.T.R. \cdot \delta = \left(\frac{dp}{dt} \right)_{t \rightarrow \infty} \cdot \frac{V}{R \cdot T \cdot A} \cdot \frac{\delta}{\Delta p} \quad (1)$$

being V the downstream volume (23 cm³), A the permeation area (9.6 cm²), δ the sample thickness, and Δp the pressure difference across the film (about 1 bar), whereas O.T.R. is the oxygen transmission rate. The uncertainty in the permeation measurement can be estimated within $\pm 10\%$ of the reported values.

3. Results and discussion

PLA/MFC multilayer films obtained after plasma treatment are robust, stable and resistant even after the successive cycles of permeability tests at various relative humidity conditions. Indeed a remarkable adhesion is achieved between the two layers, and the coating cannot be peeled off even after bending or stretching the multilayer samples in atmospheric air; the sample is also able to resist to exposure to saturated water environment before each permeation test in the conditioning step. Interestingly, no aging effect has been observed; the two layers of the MFC/PLA samples, stored in standard room conditions of temperature and relative humidity, are still well attached after in almost one year after their preparation.

The effective adhesion is obtained for MFC types produced both with enzymatic pretreatment (G1) and carboxymethylation pretreatment (G2), and on top of all PLA substrates investigated (semicrystalline or amorphous polylactide). The multilayer films were then tested in order to investigate the structural stability and their performances, and the results are presented in the following sections.

3.1. SEM images

SEM micrographs of the cross section of PLA/MFC G1 and PLA/MFC G2 multilayer films are shown in Fig. 1a-d below, with two different magnifications for each sample. A dense and continuous layer of MFC coating is clearly visible in all figures, similarly to the SEM micrographs already reported for self-standing MFC films (Minelli et al. 2010); the apparent thickness obtained from the images is in the range of 3-10 and 4-13 μm for MFC G1 and G2, respectively, thus only slightly lower than the values measured by the digital micrometer. Small defects around the edges of the samples can be attributed to the cutting procedure, performed after freezing the sample in liquid nitrogen, which was required for cross section SEM analysis.

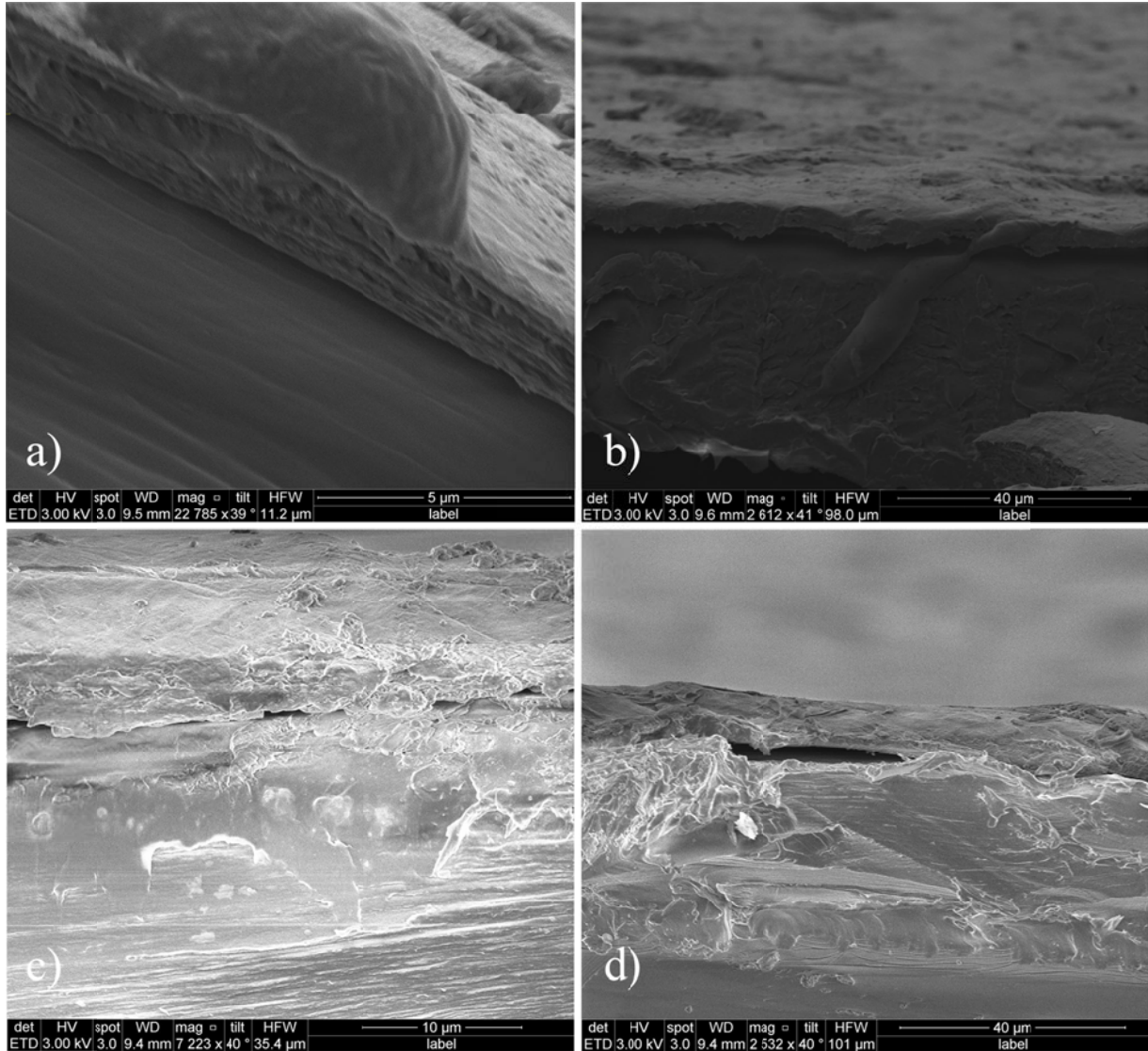


Fig. 1. SEM micrographs of PLA/MFC G1 (a, b) and PLA/MFC G2 films (c, d)

3.2. Mechanical properties

The tensile tests carried out on PLA-Am, MFC G2 and PLA/MFC G2 multilayer films provided the values of strain at break, stress at break and Young modulus, which are reported in Table 2, while the stress-strain curves are illustrated in Fig. 2. Interestingly, the results show that the MFC coating improved appreciably the Young modulus and stress at break values of neat

PLA, reaching the characteristic values of neat MFC, with no failure of the bilayer system. The values of stress at break and Young's modulus obtained for pure PLA are lower than the usual literature values, likely in view of some experimental error produced by the absence of an extensometer, although the observed behavior is the same reported from other authors(see e.g. Renouf-Glauser et al., 2005).

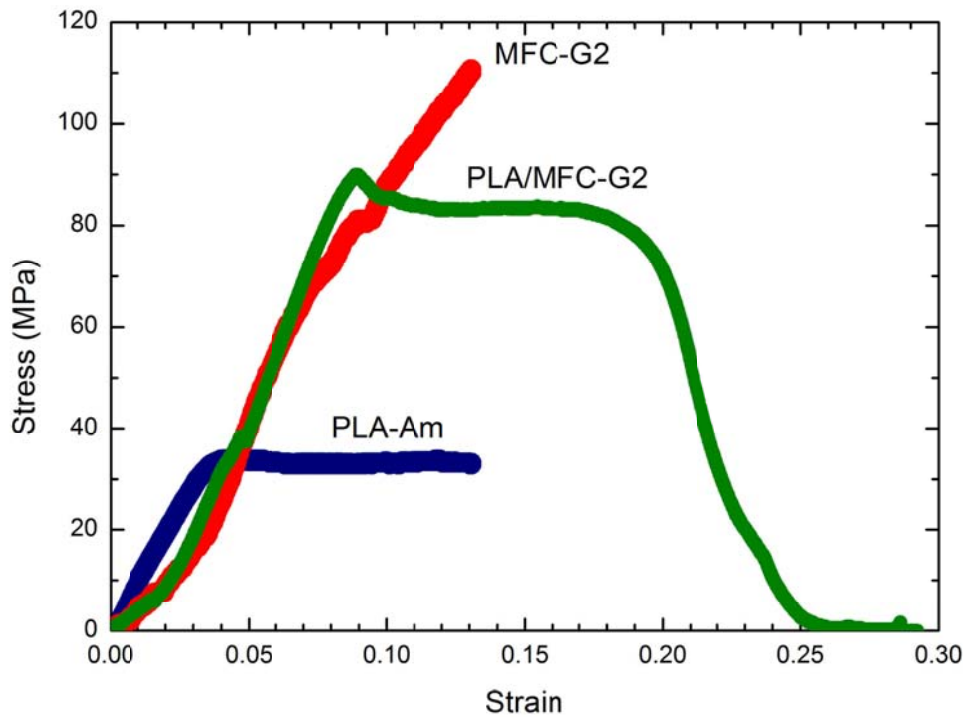


Fig. 2. Stress-strain curves for amorphous PLA-Am, self-standing MFC-G2 film, and PLA/MFC G2 bilayer film

Table 2. Mechanical properties of the films investigated in this study.

Film	Stress at break (MPa)	Strain at break (%)	Young's modulus (GPa)
PLA-Am	36 ± 4	19 ± 7	0.7 ± 0.2

MFC G2	94 ± 16	10 ± 3	1.0 ± 0.1
PLA/MFC G2	86 ± 1	-	1.12 ± 0.01

The results from mechanical tests confirmed the strong adhesion between PLA substrate and the dense MFC layer, which was able to prevent any delamination before the ultimate stress of the single MFC layer is reached. The mechanical properties of MFC G2 are comparable with those reported in a previous study (Plackett et al. 2010) for the same material except Young's modulus, which is lower in this study likely due to different casting procedures, which produced different packing of nanofiber networks. The testing procedure and setup, as well as the preparation protocol of MFC films are indeed the main causes of the literature data variability, which affect MFC mechanical properties (Svagan et al., 2007; Henriksson and Berglund, 2007; Henriksson et al., 2008).

3.3. Optical properties

Fig. 3 illustrates the UV transmittance spectra of PLA, MFC G1, MFC G2, PLA/MFC G1 and PLA/MFC G2 films, revealing that the transmittance at 600 nm (center of visible light spectrum) is about 87, 34, 27, 64 and 34%, respectively. PLA is practically transparent (almost 90% of transmittance), while MFC is typically opaque, and its effect on the overall behavior is clearly apparent. As one can see, the difference in the opacity of the two types of MFC (in the self standing films) is definitely not significant, as also reported in a previous work (Plackett et al., 2010). It is noteworthy, however, that PLA/MFC G1 sample showed satisfying transparency of 64% compared to PLA/MFC G2, even though its MFC layer was slightly thicker (about 17 μm for MFC G1 coating, and about 10 μm for the MFC G2 one).

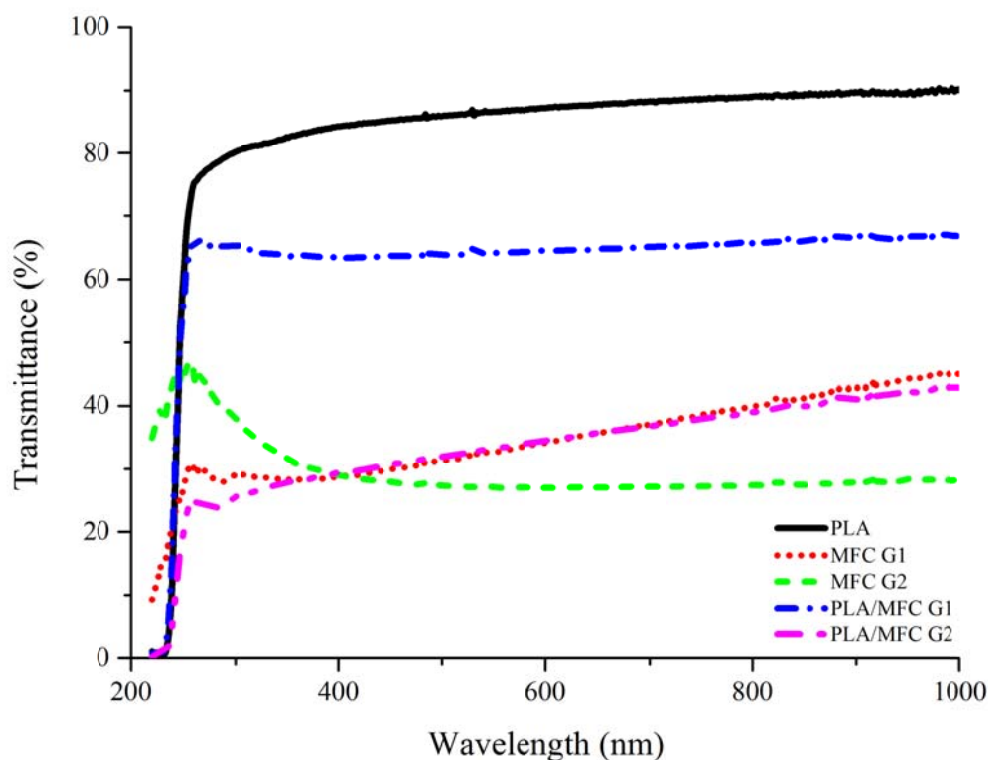


Fig. 3. UV light transmission of the films investigated in this study

3.4. Barrier properties

The dry oxygen permeability of PLA, PLA-Am, MFC G2 and PLA/MFC G2 films was measured in the dry permeation apparatus in temperature range of 25-45 °C, and the results are illustrated in Fig. 4. Results confirm that the increased crystallinity improves the barrier properties of PLA as the amorphous PLA has higher oxygen permeability compared to semi-crystalline PLA used in this study (18% crystallinity). Same measurements were carried out for neat MFC G2 and PLA/MFC G2 films in the same temperature range, and the improvement in oxygen barrier with the addition of an MFC G2 coating is more than one order of magnitude compared to what has been found for neat PLA. Moreover, the adhesion between two layers was

still stable as the bilayer film performed well within the temperature range investigated under dry oxygen permeation measurements.

Interestingly, the O₂ permeability in MFC films increases significantly at increasing temperature, appreciably more than in pure PLA films, following an Arrhenius relationship:

$$P = P_0 \cdot \exp\left(-\frac{E_p}{RT}\right) \quad (2)$$

This indicates a larger activation energy of the gas transport process for MFC films, and consequently for PLA/MFC multilayer systems. The calculated values of activation energy of permeation are 19.6 and 15.7 kJ/mol for amorphous and semicrystalline PLA, respectively, while the value of 41.8 kJ/mol is obtained for MFC self-standing films.

The barrier performances of the bilayer film were also evaluated in humid conditions, relevant in the packaging sector, and in view of the very hydrophilic nature of cellulosic materials. As already mentioned, the MFC coatings are firmly attached to the PLA substrates and no delamination is observed even in highly humid environments. Oxygen permeability at various humidity contents was then measured in PLA/MFC G1 and PLA/MFC G2 films, and successive experiments at increasing and decreasing trends of R.H. were carried out in order to investigate if any structural changes are induced in the multilayer materials, which might reduce the barrier ability. Fig. 5 shows the oxygen permeability obtained behavior at 35 °C in PLA/MFC G1 and PLA/MFC G2 films with respect to water activity (R.H.).

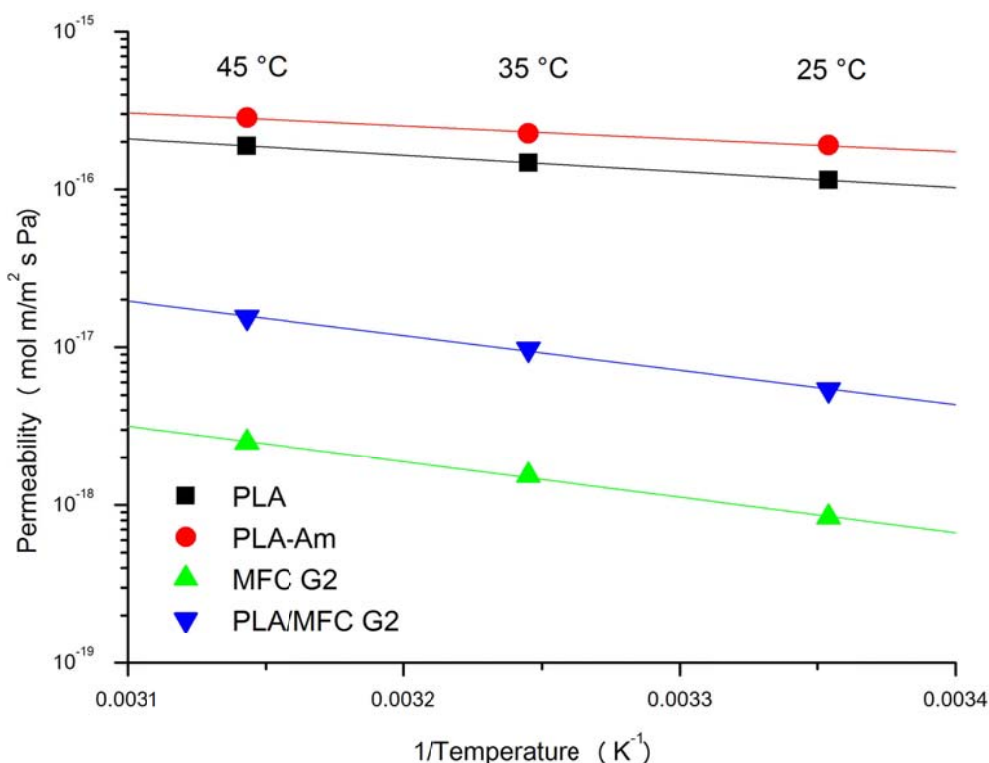


Fig. 4. Oxygen permeability of PLA films (semi-crystalline or amorphous) as well as self-standing MFC or PLA/MFC G2 multilayer films at different temperatures (25-45 °C), in dry conditions (R.H. = 0).

The values reported in the figure represent effective values of permeability of the bilayer materials, as they are obtained dividing the OTR for the total coating thickness. As one can see, the addition of a thin MFC layer produced remarkable enhancement of the barrier effect, which is preserved up to 60% of R.H.. The sharp raise of permeability at higher water activities (for both MFC G1 and MFC G2) is mainly due to the large water sorption in the MFC layer and the consequent swelling, which loosened of the original barrier properties. The ultimate oxygen permeability at 90% R.H. reached the value of pure PLA, indicating that, in such conditions, there is no more barrier effect provided by the MFC coating.

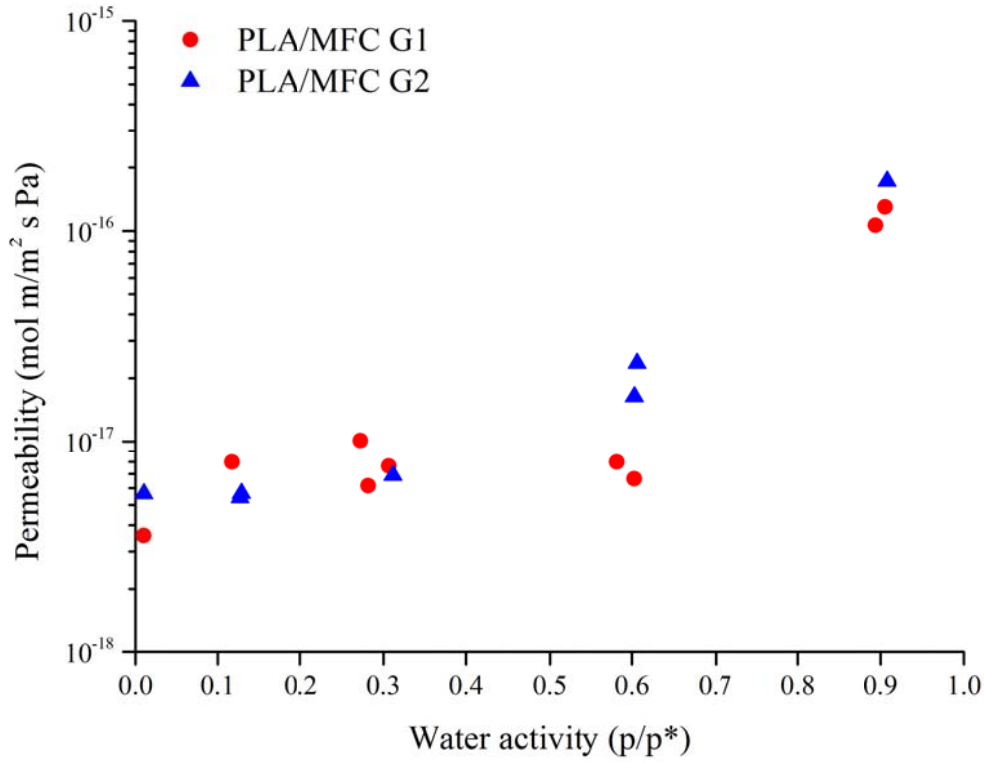


Fig. 5. Humid oxygen permeation for PLA/MFC G1 and PLA/MFC G2 films at 35 °C

It is noteworthy that data in Figure 4 has been retrieved in many successive cycles of R.H. increasing and decreasing ramps, and the bilayer films demonstrated to withstand different humidity conditions without showing any aging in terms of barrier properties or loss of adhesion. Based on the OTR data of the bilayer system, and the knowledge of PLA permeability the sole performance of the coating layer of MFC can be evaluated by means of series resistance formula:

$$\frac{1}{(OTR)_{ML}} = \frac{1}{(OTR)_{PLA}} + \frac{1}{(OTR)_{MFC}} = \frac{\delta_{PLA}}{P_{PLA}} + \frac{\delta_{MFC}}{P_{MFC}} \quad (3)$$

$$P_{MFC} = \delta_{MFC} \left[\frac{1}{(OTR)_{ML}} - \frac{\delta_{PLA}}{P_{PLA}} \right]^{-1} \quad (4)$$

Fig. 6 compares the oxygen permeability of self-standing MFC films measured at 35 °C to those of the coating layer in the bilayer film, as determined by Eq. 3, in order to analyze the coating performances. As one can see, the behavior of MFC coatings is quite similar to that in the self-standing films and only small differences are visible, indicating that a dense and homogeneous coating layer has been obtained with no apparent defect, in agreement with what already suggested by mechanical tests and SEM images.

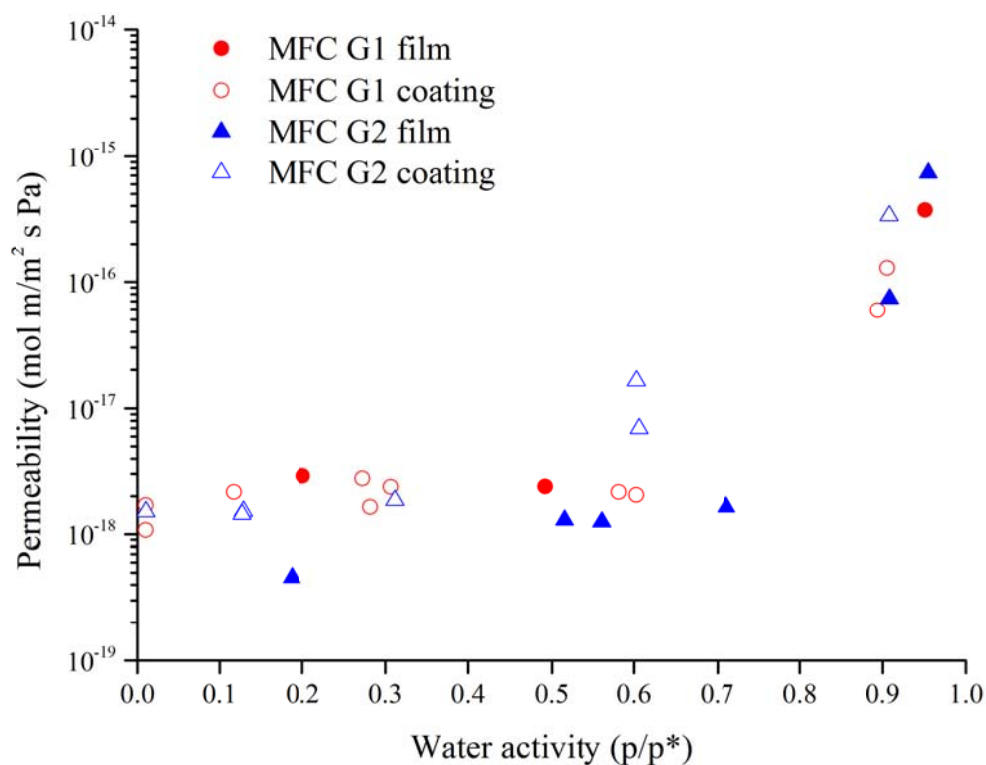


Fig. 6. Comparison of oxygen permeability for neat MFC film and MFC coating layer

Finally, the experimental permeability data at 35 °C at 50% R.H. of the samples analyzed in this work are summarized in Fig. 7, which compares their barrier performance with those of conventional oil-based polymers and other bio-renewable materials, all relevant in the packaging sector, as well as with some PLA/nanocellulose composite systems. Data from the literature are

obtained at 23 °C and 50% R.H. (Butler et al., 1996; van Tuil et al. 2000; Lange and Wyser, 2003; Aulin et al., 2013; Fortunati et al., 2012; Fukuzumi et al., 2013); however as one can see, PLA/MFC bilayer films are able to provide, even at higher temperature and in a humid environment (50% R.H.), a remarkable barrier effect toward oxygen, comparable or better to most of the conventional and renewable polymer materials.

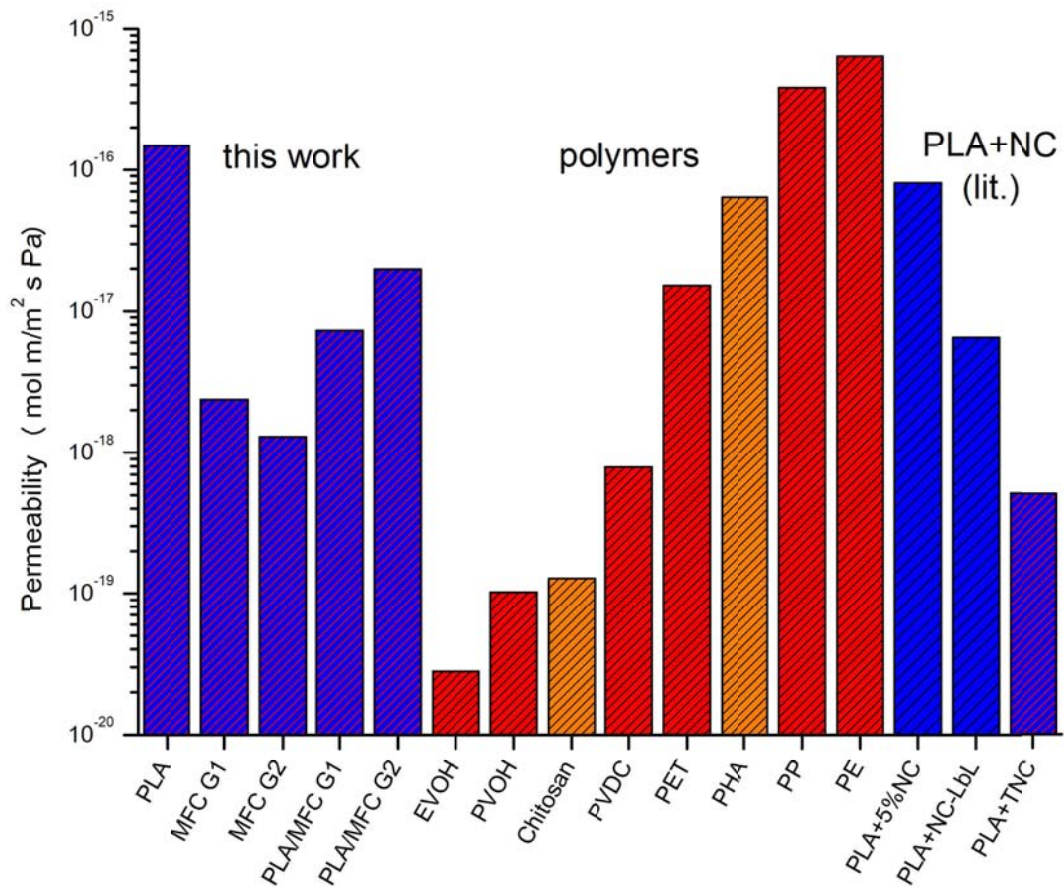


Fig. 7. Comparison of the oxygen permeabilities at (50% RH) obtained on the samples prepared in this work, with those of common polymers. (Butler et al., 1996; van Tuil et al. 2000; Lange and Wyser, 2003; Aulin et al., 2013; Fortunati et al., 2012; Fukuzumi et al., 2013)

4. Conclusions

In the present study, a fully biodegradable and biorenewable multilayer film has been developed coupling, by means of an environmental friendly method needing no additional chemicals, two primarily incompatible polymeric materials. A MFC coating was indeed deposited onto a plasma activated PLA substrate, aiming at the fabrication of an oxygen barrier and water resistant solution for barrier packaging applications. The atmospheric plasma surface activation of the PLA substrate promoted a strong adhesion between two layers, as observed by SEM micrographs and by mechanical analysis, which revealed an improved behavior of the PLA film in presence of the MFC coating.

The plasma assisted methodology, indeed, offers a sustainable tool for the fabrication of effective and stable barrier coatings on biopolymer substrates, and the presented DBD-roller plasma source has the potential for the scale up and the integration in “in-line” procedures for industrial production of multilayer films.

The oxygen permeability of bilayer films in dry conditions showed a remarkable barrier effect produced by the addition of the MFC coating on PLA substrate. As a decrease of the O.T.R. of about one order of magnitude was indeed observed that interestingly was preserved also in humid environments (up to about 60% RH at least), as revealed by the investigation of the gas permeability at various water activities. The oxygen permeability of present materials then resulted to be much lower than most of the conventional oil-based and novel bio-based barrier solutions at 50% R.H.

The calculation of the coating permeability (from series resistance expression) and its comparison with pure MFC permeability data revealed very similar results for MFC coating or self-standing films, confirming the a dense and stable thin top layer is achieved without any cracks or detachment from PLA substrate.

420

421 **ACKNOWLEDGMENTS**

422 The authors gratefully acknowledge financial support provided through the EU Seventh
423 Framework NEWGENPAK project and COST Action FP 1003 BioMatPack for the research
424 reported in this paper.

425

REFERENCES

- Andresen, M., Stenstad, P., Møretør, T., Langsrud, S., Syverud, K., Johansson, L. S., & Stenius, P. (2007). Nonleaching antimicrobial films prepared from surface-modified microfibrillated cellulose. *Biomacromolecules*, 8, 2149–2155.
- Ansaloni, L., Minelli, M., Giacinti Baschetti, M. Sarti, G. C. (2014) Effect of relative humidity and temperature on gas transport in Matrimid: Experimental study and modeling, *J. Membr. Sci.* 47, 1392–401
- ASTM Standard D 1434, 1982 (2009), "Test method for determining gas permeability characteristics of plastic film and sheeting" ASTM International, West Conshohocken, PA, **2009**, DOI: 10.1520/D1434-82R09E01, www.astm.org.
- Aulin, C., Karabulut, E., Tran, A., Wågberg, L., Lindström, T. (2013) Transparent nanocellulosic multilayer thin films on polylactic acid with tunable gas barrier properties, *ACS Appl. Mater. Interfaces* 5, 7352–7359.
- Auras, R. A., Harte, B., Selke, S., Hernandez, R. J. (2003). Mechanical, physical, and barrier properties of poly (lactide) films, *J. Plastic Film Sheet.*, 19, 123–135.
- Auras, R., Kale, G., Singh, S. P. (2006). Degradation of commercial biodegradable packages under real composting and ambient exposure conditions, *J. Environ. Polym. Degr.* 14, 317–334.
- Bai, H., Huang, C., Xiu, H., Zhang, Q., Deng, H., Wang, K., Chen, F., Fu Q. (2014) Significantly improving oxygen barrier properties of polylactide via constructing parallel-aligned shish-kebab-like crystals with well-interlocked boundaries. *Biomacromolecules* 15, 1507-1514.
- Bardet, R., Reverdy, C., Belgacem, N., Leirset, I., Syverud, K., Bardet, M., Bras, J. (2015) Substitution of nanoclay in high gas barrier films of cellulose nanofibrils with cellulose nanocrystals and thermal treatment, *Cellulose* 22, 1227–1241
- Belbekhouche, S., Bras, J., Siqueira, G., Chappey, C., Lebrun, L., Khelifi, B., Marais, S., Dufresne, A. (2011). Water sorption behavior and gas barrier properties of cellulose whiskers and microfibrils films. *Carbohydr. Polym.* 83, 1740-1748.
- Benetto E., Jury C., Igos E., Carton J., Hild P., Vergne C., Di Martino J. (2015). Using atmospheric plasma to design multilayer film from polylactic acid and thermoplastic starch: a screening Life Cycle Assessment, *J. Clean Prod.* 87, 953.
- Berglund, L., (2005). Cellulose-based nanocomposites, in *Natural Fibres, Biopolymers and Biocomposites*, ed. A. K. Mohanty, M. Misra and L. T. Drzal, Taylor & Francis, Boca Raton, pp. 807–832.

- 460 – Boselli, M., Colombo, V., De Angelis, M. G., Ghedini, E., Gherardi, M., Laurita, R.,
461 Liguori, A., Minelli M., Sanibondi, P., Stancampiano, A. (2012). Comparing the effect of
462 different atmospheric pressure non-equilibrium plasma sources on PLA oxygen
463 permeability, *J. Phys. Conf. Ser.*, 406, 012038.
- 464 – Boselli, M., Colombo, V., Ghedini, E., Gherardi, M., Laurita, R., Liguori, A., Marani, F.,
465 Sanibondi, P., & Stancampiano, A. (2013). Parametric study on the effectiveness of
466 treatment of polyethylene (pe) foils for pharmaceutical packaging with a large area
467 atmospheric pressure plasma source. 2013 (August); proceedings of 21st International
468 Symposium on Plasma Chemistry", Queensland (Australia); 495 PO.
- 469 – Butler, B. L., Vergano, P. J., Testin, R. F., Bunn, J. M., Wiles, J. L., (1996) Mechanical
470 and barrier properties of edible chitosan films as affected by composition and storage. *J.*
471 *Food Sci.*, 61, 953.
- 472 – Chang, J. H., An, Y. U., Sur, G. S. J. (2003). Poly(lactic acid) nanocomposites with
473 various organoclays. I. Thermomechanical properties, morphology, and gas permeability,
474 *J. Polym. Sci.: Polym. Phys.*, 41, 94–103.
- 475 – Chowdhury, S. R. (2008). Some important aspects in designing high molecular weight
476 poly(L-lactic acid)–clay nanocomposites with desired properties, *Polym. Int.*, 57,
477 1326–1332.
- 478 – Cools P., De Geyter N., Morent R., (2015). PLA enhanced via plasma technology: a
479 review, *New Developments in Polylactic Acid Research*, Nova Science Publishers, Inc.,
480 Courtney Winthrop pp. 79-110.
- 481 – de Azeredo, H. M. C. (2009) Nanocomposites for food packaging applications, *Food Res.*
482 *Int.*, 42, 1240–1253.
- 483 – Delpouve, N., Stoclet, G., Saiter, A., Dargent, E., Marais, S. (2012) Water barrier
484 properties in biaxially drawn poly(lactic acid) films, *J. Phys. Chem. B* 116, 4615–4625.
- 485 – Drieskens, M., Peeters, R., Mullens, J., Franco, D., Lemstra, P. J., Hristova-Bogaerds, D.
486 G. (2009). Structure versus properties relationship of poly(lactic acid). I. Effect of
487 crystallinity on barrier properties, *J. Polym. Sci., Part B: Polym. Phys.*, 47, 2247–2258.
- 488 – Drumright, R. E., Gruber, P. R., Henton, D. E. (2000). Polylactic acid technology, *Adv.*
489 *Mater.* 12, 1841–1846.
- 490 – Eichhorn S.J., (2011). Cellulose nanowhiskers: promising materials for advanced
491 applications, *Soft Matter*, 7, 303-315.
- 492 – Fortunati, E., Peltzer, M., Armentano, I., Torre, L. Jiménez, A., Kenny, J. M. (2012)
493 Effects of modified cellulose nanocrystals on the barrier and migration properties of PLA
494 nano-biocomposites, *Carbohydr. Polym.* 90, 948– 956.

- 495 – Fukuzumi, H., Saito, T., Wata, T., Kumamoto, Y., Isogai, A. (2009). Transparent and
496 High Gas Barrier Films of Cellulose Nanofibers Prepared by TEMPO-Mediated
497 Oxidation Biomacromolecules, 10, 162–165.
- 498 – Fukuzumi, H., Saito, T., Kumamoto, Y., Isogai, A. (2013). Influence of TEMPO-
499 oxidized cellulose nanofibril length on film properties, Carbohydr. Polym, 93, 172– 177.
- 500 – Guinault A., Sollogoub, C., Ducruet, V., Domenek, S. (2012) Impact of crystallinity of
501 poly(lactide) on helium and oxygen barrier properties, Eur. Polym. J. 48, 779–788.
- 502 – Habibi, Y. (2014) Key advances in the chemical modification of nanocelluloses, Chem.
503 Soc. Rev. 43, 1519-1542.
- 504 – Henriksson, M., Berglund, L. A., (2007). Structure and properties of cellulose
505 nanocomposite films containing melamine formaldehyde, J. Appl. Polym. Sci., 106,
506 2817.
- 507 – Henriksson, M., Henriksson. G., Berglund, L. A., Lindstrom, T. (2007) An
508 environmentally friendly method for enzyme-assisted preparation of microfibrillated
509 cellulose (MFC) nanofibers, Eur. Polym. J. 43, 3434–3441
- 510 – Henriksson, M., Berglund, L. A., Isaksson, P., Lindström, T., Nishino, T. (2008).
511 Cellulose nanopaper structures of high toughness. Biomacromolecules, 9, 1579–1585.
- 512 – Herrick, F. W., Casebier, R. L., Hamilton, K. J., Sandberg, K. R. (1983). Microfibrillated
513 cellulose: morphology and accessibility. J. Appl. Polym. Sci.: Appl. Polym. Symp. 37,
514 797–813.
- 515 – Iwatake, A., Nogi, M., Yano, H. (2008). Cellulose nanofiber-reinforced polylactic acid,
516 Compos. Sci. Technol., 68, 2103-2106
- 517 – Jamshidian M., Tehrany E. A., Imran M., Jacquot M., Desobry S. (2010) Poly-Lactic
518 Acid: production, applications, nanocomposites, and release studies, Compr. Rev. Food
519 Sci. Food Safety, 9, 552–571
- 520 – Johansson, C., Bras, J., Mondragon, I., Nechita, P., Plackett, D., Šimon, P., Aucejo, S.
521 (2012). Renewable fibers and bio-based materials for packaging applications - A review
522 of recent developments. BioResources. 7, 2506–2552
- 523 – Jordá-Vilaplana A., Fombuena V., García-García D., Samper M.D., Sánchez-Nácher L.,
524 (2014). Surface modification of polylactic acid (PLA) by air atmospheric plasma
525 treatment Eur. Polym. J. 58, 23.
- 526 – Klemm, D., Schumann, D., Kramer, F., Heßler, N., Hornung, M., Schmauder, H.-P., et al.
527 (2006). Nanocelluloses as innovative polymers in research and application. In D. Klemm
528 (Ed.), Polysaccharides II (pp. 49–96). Berlin, Heidelberg: Springer.

- 529 – Lange, J., Wyser, Y. (2003). Recent innovations in barrier technologies for plastic
530 packaging - a review. *Pack. Tech. Sci.* 16, 149

- 531 – Lavoine, N., Desloges, I., Dufresne, A., Bras, J. (2012). Microfibrillated cellulose – Its
532 barrier properties and applications in cellulosic materials: A review. *Carbohydr. Polym.*
533 90, 735–764.

- 534 – Lavoine, N. Desloges, I., Bras, J. (2014) Microfibrillated cellulose coatings as new
535 release systems for active packaging, *Carbohydr. Polym.* 103, 528–537.

- 536 – Leitner, J., Hinterstoisser, B., Wastyn, M., Keckes, J., Gindl, W. (2007). Sugar beet
537 cellulose nanofibril-reinforced composites. *Cellulose*, 14, 419–425.

- 538 – Lu, J., Askeland, P., & Drzal, L. T. (2008). Surface modification of microfibrillated
539 cellulose for epoxy composite applications. *Polymer*, 49, 1285–1296.

- 540 – Martínez-Sanz, M., Lopez-Rubio, A., Lagaron, J. M. (2013) High-barrier coated bacterial
541 cellulose nanowhiskers films with reduced moisture sensitivity, *Carbohydr. Polym.* 98,
542 1072-1082.

- 543 – Mathew, A. P., Oksman, K., Sain, M. (2005). Mechanical properties of biodegradable
544 composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC), *J. Appl.*
545 *Polym. Sci.*, 97, 2014–2025.

- 546 – Mathew, A. P., Oksman, K., Sain, M. (2006). The effect of morphology and chemical
547 characteristics of cellulose reinforcements on the crystallinity of polylactic acid, *J. Appl.*
548 *Polym. Sci.*, 101, 300–310.

- 549 – Minelli, M., De Angelis, M. G., Doghieri, F., Marini, M., Toselli, M., Pilati, F. (2008).
550 Oxygen permeability of novel organic–inorganic coatings. I. Effects of organic–inorganic
551 ratio and molecular weight of the organic component, *Eur. Polym. J.*, 44, 2581–2588.

- 552 – Minelli, M., Giacinti Baschetti, M., Doghieri, F., Ankerfors, M., Lindström, T., Siró, I.,
553 Plackett, D. (2010). Investigation of mass transport properties of microfibrillated
554 cellulose (MFC) films. *J. Membr. Sci.* 358(1-2), 67–75.

- 555 – Mohanty, A. K., Misra, M., and Drzal, L. T. (2002). Sustainable bio-composites from
556 renewable resources: opportunities and challenges in the green materials World, *J.*
557 *Polym. Environ.* 10, 19-26.

- 558 – Nakagaito, A. N., Fujimura, A., Sakai, T., Hama, Y., Yano, H. (2009). Production of
559 microfibrillated cellulose (MFC)-reinforced polylactic acid (PLA) nanocomposites from
560 sheets obtained by a papermaking-like process. *Compos. Sci. Technol.* 69, 1293.

- 561 – Oksman, K., Mathew, A. P., Bondeson, D., Kvien, I. (2006). Manufacturing process of
562 cellulose whiskers/polylactic acid nanocomposites, *Compos. Sci. Technol.*, 66, 2776–
563 2784.

- 564 – Österberg, M., Vartiainen, J., Lucenius, J., Hippi, U., Seppälä, J., Serimaa, R., Laine, J.
565 (2013). A fast method to produce strong NFC films as a platform for barrier and
566 functional materials. *ACS Appl. Mater. Interfaces* 5, 4640–4647
- 567 – Pääkkö, M., Ankerfors, M., Kosonen, H., Nykänen, A., Ahola, S., Österberg, M.,
568 Lindström, T. (2007). Enzymatic hydrolysis combined with mechanical shearing and
569 high-pressure homogenization for nanoscale cellulose fibrils and strong gels.
570 *Biomacromolecules*, 8, 1934–1941.
- 571 – Petersen, K., Nielsen, P. V., Bertelsen, G. Lawther, M., Olsen, M. B., Nilsson, N. H.,
572 Mortensen, G. (1999). Potential of biobased materials for food packaging, *Trends Food*
573 *Sci. Technol.* 10, 52-68.
- 574 – Picard, E., Espuche, E., Fulchiron, R. (2011). Effect of an organo-modified
575 montmorillonite on PLA crystallization and gas barrier properties, *Appl. Clay Sci.* 53,
576 58–65.
- 577 – Plackett, D., Anturi, H., Hedenqvist, M., Ankerfors, M., Gällstedt, M., Lindström, T.,
578 Siró, I. (2010). Physical properties and morphology of films prepared from
579 microfibrillated cellulose and microfibrillated cellulose in combination with amylopectin.
580 *J. Appl. Polym. Sci.* 117, 3601–3609.
- 581 – Plastics – the Facts 2015, An analysis of European plastics production, demand and waste
582 data, Plastics Europe.
- 583 – Renouf-Glauser, A. C., Rose, J., Farrar, D. F., Cameron, R. E. (2005) The effect of
584 crystallinity on the deformation mechanism and bulk mechanical properties of PLLA,
585 *Biomaterials* 26, 5771–5782.
- 586 – Rodionova, G., Saito, T., Lenes, M., Eriksen, Ø., Gregersen, Ø., Fukuzumi, H., Isogai A.
587 (2012) Mechanical and oxygen barrier properties of films prepared from fibrillated
588 dispersions of TEMPO-oxidized Norway spruce and Eucalyptus pulps, *Cellulose* 19,
589 705–711.
- 590 – Samir, M.A.S.A, Alloin, F., Dufresne, A. (2005). Review of recent research into
591 cellulosic whiskers, their properties and their application in nanocomposite field.
592 *Biomacromolecules*, 6, 612–626.
- 593 – Sanchez-Garcia, M. D., Lagaron, J. M. (2010). On the use of plant cellulose
594 nanowhiskers to enhance the barrier properties of polylactic acid, *Cellulose*, 17 (5), 987–
595 1004.
- 596 – Siqueira, G., Bras, J., Dufresne, A. (2009). Cellulose whiskers versus microfibrils:
597 influence of the nature of the nanoparticle and its surface functionalization on the thermal
598 and mechanical properties of nanocomposites. *Biomacromolecules*, 10, 425–32.

- 599 – Siracusa V., Rocculi P., Romani S., Dalla Rosa M., (2008) Biodegradable polymers for
600 food packaging: a review, *Trends Food Sci. Technol.*, 19, 634–643

- 601 – Siró, I., Plackett, D. (2010). Microfibrillated cellulose and new nanocomposite materials:
602 A review. *Cellulose*, 17, 459–494.

- 603 – Siró, I., Plackett, D. Hedenqvist, M., Ankerfors, M., Lindstrom, T. (2011) Highly
604 transparent films from carboxymethylated microfibrillated cellulose: the effect of
605 multiple homogenization steps on key properties, *J. Appl. Polym. Sci.* 119, 2652–2660.

- 606 – Stenstad, P., Andresen, M., Tanem, B. S., Stenius, P. (2008). Chemical surface
607 modifications of microfibrillated cellulose. *Cellulose*, 15, 35–45.

- 608 – Suryanegara, L., Nakagaito, A. N., Yano, H. (2009). The effect of crystallization of PLA
609 on the thermal and mechanical properties of microfibrillated cellulose-reinforced PLA
610 composites. *Compos. Sci. Technol.*, 69, 1187.

- 611 – Svagan, A. J., Samir, M.A.S.A., Berglund, L. A. (2007). Biomimetic polysaccharide
612 nanocomposites of high cellulose content and high toughness. *Biomacromolecules*, 8,
613 2556–2563.

- 614 – Svagan A. J., Åkesson, A., Cárdenas, M., Bulut, S., Knudsen, J. C., Risbo, J., Plackett,
615 D., (2012). Transparent films based on PLA and montmorillonite with tunable oxygen
616 barrier properties, *Biomacromolecules*, 13, 397–405.

- 617 – Syverud, K., Stenius, P. (2009). Strength and barrier properties of MFC films. *Cellulose*,
618 16, 75–85.

- 619 – Tharanathan R. N. (2003) Biodegradable films and composite coatings: past, present and
620 future. *Trends Food Sci Technol*, 14, 71–8.

- 621 – Turbak, A. F., Snyder, F. W., Sandberg, K. R. (1983). Microfibrillated cellulose, a new
622 cellulose product: Properties, uses, and commercial potential. *Journal of Applied Polymer*
623 *Science: Applied Polymer Symposium*, 37, 815–827.

- 624 – van Tuil, R., Fowler, P., Lawther, M., Weber, C.J. (2000). Properties of biobased
625 packaging materials, In Weber, C. J., (ed.), *Biobased Packaging Material for the Food*
626 *Industry - Status and Perspectives*, Royal Veterinary and Agricultural University,
627 Copenhagen, Denmark, 13-44.

- 628 – Vergne C., Buchheit O., Eddoumy F., Sorrenti E., Di Martino J., Ruch D., (2011).
629 Modifications of the polylactic acid surface properties by dbd plasma treatment at
630 Atmospheric Pressure, *J. Eng. Mater. Technol.* 133, 030903.

- 631 – Vieira M. G. A., da Silva M. A., dos Santos L. O., Beppu M. M., (2011) Natural-based
632 plasticizers and biopolymer films: A review, *Europ. Polym. J.*, 47, Pages 254–263

- 633 – Wågberg, L., Decher, G., Norgren, M., Lindström, T., Ankerfors, M., Axnäs, K. (2008).
634 The build-up of polyelectrolyte multilayers of microfibrillated cellulose and cationic
635 polyelectrolytes. *Langmuir* 24, 784–795.
- 636 – Yano, H.; Nakahara S., (2004). Bio-composites produced from plant microfiber bundles
637 with a nanometer unit web-like network. *J. Mater. Sci.*, 39, 1635–1638.
- 638 – Zimmermann, T., Pöhler, E., Geiger, T. (2004). Cellulose fibrils for polymer
639 reinforcement. *Adv. Eng. Mater.* 6, 754–761.