

Film Blowing of Biodegradable Polymer Nanocomposites for Agricultural Applications

Maria Chiara Mistretta, Luigi Botta,* Francesco Paolo La Mantia, Antonino Di Fiore, and Marco Cascone

Films for agricultural applications, such as greenhouses films or mulching films are generally made of polyolefins such as linear low-density polyethylene (LLDPE) or low-density polyethylene. However, the use of biodegradable and/or compostable polymers is increasing, which enjoy the additional advantage that they can be left on the site since a fine life would be gradually assimilated to the underlying soil. Nevertheless, biodegradable polymeric films often do not have suitable mechanical performances. In this work, biodegradable polymer-based nanocomposite films are prepared by film blowing and compared with traditional LLDPE based nanocomposites. In particular, a biodegradable polymer blend and two different inorganic nanofillers (an organo-modified clay and a calcium carbonate with a hydrophobic coating) are used for the preparation of the nanocomposites. A detailed investigation of obtained materials is performed through rheological, mechanical, and optical characterizations. Adding nanofillers led to an increase of rigidity and tear strength of blown films without negatively affecting their ductility.

1. Introduction

Films for agricultural applications, such as film for greenhouses, mulching, and other different applications, are generally produced by a film blowing process that requires the use of polymers with suitable rheological properties both in extrusion and in film blowing and therefore both in shear and in elongational flow. The materials used for these applications must possess several peculiar and specific characteristics, such as good deformability and tear resistance together with sufficient rigidity. Moreover, the transparency together with the capability to diffuse the light is an important property requested for materials used for greenhouse covering. Indeed, as reported in the literature, diffused light makes the plant growth easier and prevents damages caused by an excessive warming of the environment.^[1,2]

Films for agricultural applications are generally made with polyolefins such as low-density polyethylene (LDPE) or linear low-density polyethylene (LLDPE).^[3,4]

Often such films have a short service life and this leads to the production of huge amounts of plastic waste. Therefore, the use of biodegradable and compostable polymers to replace traditional ones is important in order to reduce the amount of post-consumer plastics so difficult and expensive to be recycled.

Among biodegradable polymers with properties suitable for produce blown films for agricultural applications, poly (butylene adipate-co-terephthalate) (PBAT) and polylactic acid (PLA) are very interesting for this application. Furthermore, these polymers are often used as a blend, attracting the interest of the scientific community and the industry.^[5–9] Nevertheless, a wide use of biopolymers is often limited by the need of increasing some functional properties such as mechanical and barrier properties. Therefore, in order to enhance the commercial potential of this class of materials, intense efforts have been made to improve their physical properties such as the incorporation of nano-sized reinforcements in the matrix.^[10–15] Indeed, it is well known that even very low amounts of a nanometric filler can lead to noticeable improvements in mechanical, rheological, and barrier properties.


Polymer nanocomposites based on biodegradable matrices could put together the sustainability of the matrix with the better performances exhibited by polymers filled with nanoparticles as reported in the scientific literature by several authors.^[16–22]

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Rasyida et al.^[16] have produced nanocomposites based on PBAT loaded with 5% by weight of organomodified or unmodified montmorillonites (MMT). In general, the thermal properties of PBAT were enhanced with the addition of clays, for a barrier effect of the nanoparticle towards the polymer ablation decomposition products. Moreover, the addition of clays led to improvements in terms of hardness.

Peng-Gang Ren et al.^[17] found an improvement of the barrier properties of PBAT films obtained by adding an extremely low quantity of graphene oxide nanosheets. The best barrier properties have been attributed to good dispersion and strong interfacial adhesion between the filler and the PBAT. Furthermore, as regards the mechanical properties, they showed an increase in Young's modulus of the nanocomposite compared to the pure matrix.

Sutinee Girdthep et al.^[18] studied biodegradable polymer nanocomposites developed as materials for use in the packaging. PLA was the main component of the nanocomposites with PBAT as a flexibility reinforcement. Tetrabutyl titanate was also added as a compatibilizer to improve the interfacial affinity between PLA and PBAT thus improving the mechanical properties of the blends. Chemically synthesized silver-loaded kaolinite has been incorporated into compatibilizer blends to improve properties. The resulting nanocomposites showed and improved thermal stability and a reduced permeability to water vapor.

S. Mohanty et al.^[19] investigated nanobiocomposites based on PBAT and organomodified layered silicates. Mechanical and thermal properties of the matrix improved in presence of the nanofillers.

Bionanocomposites may theoretically allow obtaining a material with all the characteristics requested for agricultural applications, using a reduced amount of additives and reducing environmental pollution being biodegradable.

In this work, therefore, we evaluated the suitability of bionanocomposite samples for agricultural applications from a rheological, mechanical, and optical point of view. In particular, nanocomposite films based on a biodegradable polymer blend and two different inorganic nanofillers (an organo-modified clay and a calcium carbonate with a hydrophobic coating) were prepared by film blowing and compared with traditional LLDPE based nanocomposites.

2. Experimental Section

2.1. Materials

The biodegradable polymer blend used in this work was a commercial PLA/PBAT blend supplied by BASF (Ludwigshafen, Germany) under the commercial name ECOVIO, grade F23B1, consisting of 84% PBAT, 4% of PLA, and 12% of insoluble, inert particles, having MFI (190 °C, 2.16 kg) = 5–11 g/10 min.^[5]

A LLDPE Lotrène Q1018 from Qatofin (Doha, State of Qatar) (density = 0.918 g cm⁻³, MFI (190 °C, 2.16 kg) = 1.0 g/10 min) was used as reference material.

Two different inorganic nanofillers were used for the preparation of the nanocomposites: i) an organo-modified clay, CLOISITE-20 A (hereafter coded as CL20A, particle size < 10 µm; lamellar spacing (XRD, d_{001}): 2.7 nm) supplied from BYK (Wesel, Germany); ii) a calcium carbonate with a hydrophobic coating,

Table 1. Processing conditions in the twin-screw extruder for the prepared nanocomposites.

Polymer Matrix	Temperature Profile [°C]	Screw Rotation Speed [rpm]
ECOVIO	160-170-170-180-180-190-190	200
LLDPE	180-180-190-190-200-210-220	200

Table 2. Processing conditions in the single screw extruder for the film blowing operation.

Polymer Matrix	Temperature Profile [°C]	Screw Rotation Speed [rpm]	Draw Ratio, DR	Blow-Up Ratio, BUR
ECOVIO	160-170-180-190	200	3.1	2.3
LLDPE	180-200-210-220	200	3.2	2.2

Socal 312 (hereafter coded as SOCAL, mean particle diameter of about 70 nm), supplied from Solvay (Bollate, Milano, Italy).

2.2. Nanocomposite Preparation and Film Blowing

The nanocomposites were prepared using a co-rotating twin-screw extruder with an L/D ratio of 35 (OMC, Saronno Italy). The weight ratio between matrix and filler was 95/5 for all the investigated samples. The nanocomposite was prepared under the same conditions as the corresponding pure matrix; a summary of the processing conditions is shown in **Table 1**. Prior to extrusion, both the biodegradable matrix and the nanofillers were dried in a vacuum oven: the former were treated at 70 °C for 4 h, while the CL20A and SOCAL were dried for 12 h at 120 and 90 °C, respectively.

The materials obtained after this processing step were pelletized and fed to a single-screw extruder (Brabender, D = 19 mm, L/D = 25) equipped with a film blow unit (Brabender) operating at the conditions reported in **Table 2**. The thickness of the obtained films was about 50 µm.

2.3. Characterizations

The rheological characterization at high shear rates was carried out using a capillary rheometer Rheologic 1000 (CEAST, Turin, Italy), with a capillary of length to diameter Ratio (L/D) equal to 40. Non-isothermal elongational flow characterization was performed on the same apparatus equipped with a drawing unit, located at the exit of the capillary die: melt strength (MS) and breaking stretching ratio (BSR) were then calculated, according to the procedures described elsewhere.^[23] The tests were performed at 190 °C for the ECOVIO and at 210 °C for LLDPE.

The tensile properties were measured with a Lloyd instrumental LRX dynamometer with a load cell of 100 N. The test was carried out following ISO 527-3 with a constant crosshead speed of 500 mm min⁻¹. The size of the samples is 10×1 cm.

The tear strength of all films was evaluated by means of an Elmendorf TearATS-100 pendulum (ATS Faar, Italy) according to ISO 6383 with a weight of 8 N.

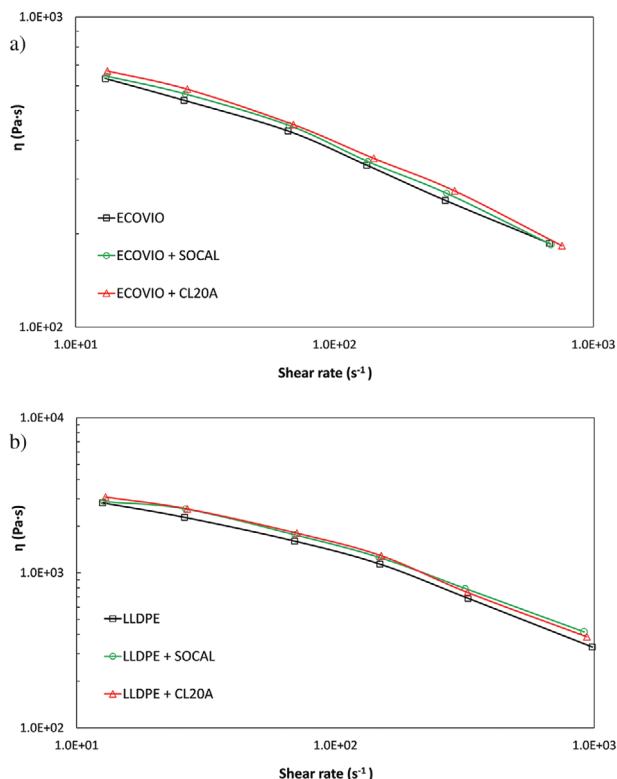


Figure 1. Viscosity as a function of shear rate for a) ECOVIO based systems and b) LLDPE based systems.

For both the characterizations the films were tested both in the machine and transverse direction.

The optical characterization of the films, that is, UV-vis spectra and haze measurements, was carried out using a Jasco V-650 spectrometer.

The morphology of nanocomposites was analyzed by scanning electron microscopy (SEM; Quanta 200 ESEM, FEI, Hillsboro, OR, USA). In particular, the samples were fractured under liquid nitrogen and then attached onto an aluminum holder. Afterwards they were sputter-coated with a thin layer of gold under argon atmosphere for 90 s (Scancoat Six Edwards, Crawley, UK) in order to avoid electrostatic charging under the electron beam.

3. Results and Discussion

3.1. Rheological Behavior

The rheological behavior of all the materials obtained by compounding in the twin-screw extruder was tested both in shear and in non-isothermal elongational flow in order to assess the filmability of the prepared nanocomposites.

Figure 1a,1b shows the viscosity as a function of the shear rate for the two examined polymer systems. From the flow curves reported in **Figure 1a**, it is possible to note that the introduction of both the fillers almost did not change the viscosity of the biodegradable matrix leading only to a very slight increase of the viscosity. Moreover, both nanoparticles give rise to about the same increment of the viscosity of their matrix. A similar rheological

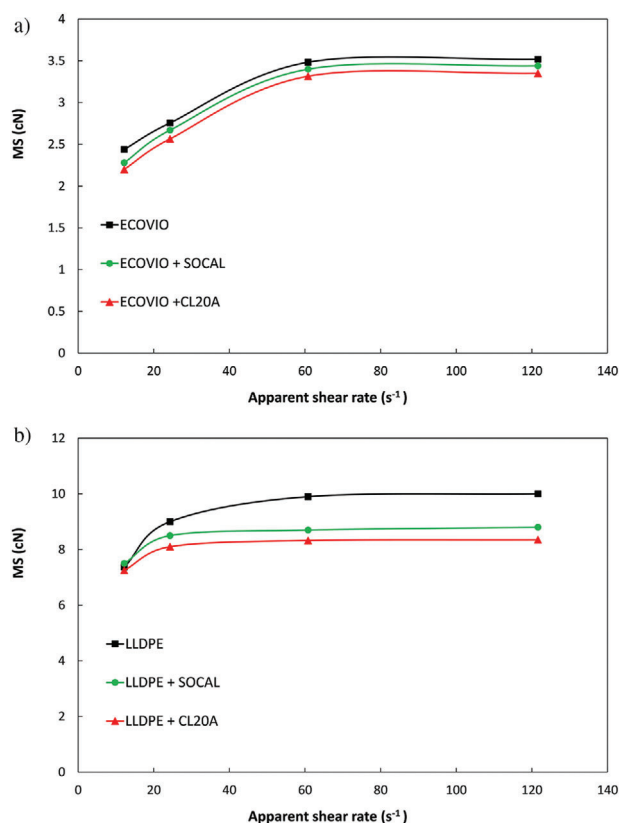


Figure 2. MS as a function of apparent shear rate for a) ECOVIO based systems and b) LLDPE based systems.

behavior can be observed for the nanocomposite systems based on LLDPE (**Figure 1b**) although, of course, the viscosity values of the two systems are different. This means, that adding the nanofiller does not significantly influence the processability of the polymer matrix in the extrusion process both for the traditional system and for the biodegradable one.

Figure 2 shows the MS of ECOVIO and LLDPE based systems. The addition of the two fillers caused a decrease of MS for LLDPE based nanocomposites in comparison with the neat matrix (**Figure 2b**). This can appear as an unexpected result since generally the introduction of an inert filler leads to an increase in the viscosity and MS values. However, this behavior can be attributed to a lower value of the melt deformability of the filament, which implies a premature breaking of the filament itself and then a lower value of the MS.^[23] Indeed, this behavior can be related to a solid-like rupture during the application of the elongational flow, involving the premature break of the material, which is not able to reach the expected stress level if compared to the typical liquid-like melt rupture.^[24] The ECOVIO based nanocomposites also showed the same behavior although the nanocomposites exhibited only a very slight decrease of the MS values in comparison with those of the neat matrix. A similar behavior has been reported for other nanocomposite systems based both on polyolefin and biopolymer matrices.^[20,21]

Figure 3 show the BSR values as a function of the apparent shear rate for the neat matrices and the respective nanocomposite systems. BSR values of neat ECOVIO and LLDPE are quite

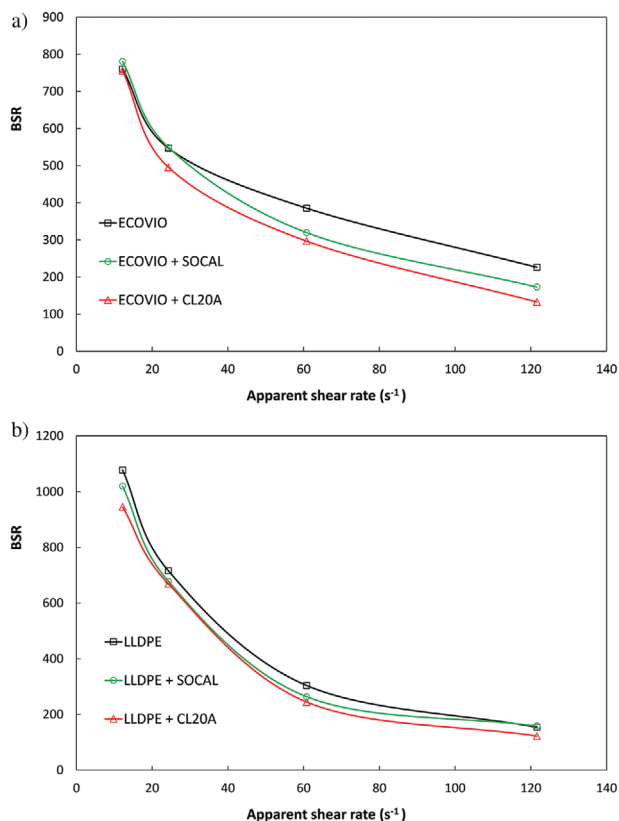


Figure 3. BSR as a function of apparent shear rate for a) ECOVIO based systems and b) LLDPE based systems.

similar, indicating the suitability of the selected biopolymeric matrix for film blowing operations. Moreover, the BSR values of ECOVIO are comparable with the values reported in the literature for other neat biopolymers or biopolymeric blends.^[8,20,21]

The incorporation of the filler, both CL20A and SOCAL, led to a slight decrease of BSR values for both the matrices. It is worth noticing, however, that this reduction of BSR did not affect the processability of the polymer in film blowing operation allowing to obtain very thin films.

3.2. Morphology

The morphology of investigated materials was evaluated through SEM observations with the aim of evaluating the degree of the nanofiller dispersion within the matrices, the level of adhesion between the two phases but also the dimensions reached by the incorporated particles through observations at high magnification.

In **Figure 4**, SEM micrographs at two different magnifications of nanocomposites containing CL20A are reported. SEM micrographs of ECOVIO based nanocomposites, **Figure 4a,4c**, reveal that the extrusion process was able to partially break up the clay particles into lamellar particles having submicrometric dimensions. In particular, the micrograph at lower magnification (**Figure 4a**) shows that a good dispersion of clay particles within the biodegradable polymer matrix was achieved. Moreover, a quite

good interfacial adhesion between the matrix and the clay is evident in the micrograph at higher magnification (**Figure 4c**), which clearly shows that clay particles incorporated in the matrix are nanosized platelets. On the contrary, SEM micrographs of the LLDPE based nanocomposites containing CL20A, **Figure 4b,4d**, reveal a poor interfacial adhesion between matrix and filler as evident in particular in the micrograph at higher magnification (**Figure 4d**) where voids around the particles are clearly visible. Moreover, although the clay is well dispersed in the LLDPE matrix, the lamellar particles have submicrometric dimensions larger than those observed for the biodegradable polymer sample.

In **Figure 5**, SEM micrographs at two different magnifications of nanocomposites containing SOCAL are reported. In SEM micrographs at lower magnification (**Figure 5a,5b**) it is possible to observe that a good level of dispersion of the globular calcium carbonate particles, having submicrometric dimensions, within both the polymeric matrices was achieved through the extrusion process. In particular, the micrographs at higher magnification (**Figure 5c,5d**) reveal that the submicrometric globular particles are actually very small aggregates of nano-sized calcium carbonate. For both the matrices it is possible to observe a good interfacial adhesion between the matrix and the filler, although the ECOVIO based nanocomposite seems to show a slightly better adhesion and aggregates with lower dimensions.

Moreover, in the micrographs of the ECOVIO based nanocomposite (**Figure 5a,5c**), it is also visible the presence of a lamellar filler within the matrix having micrometric dimensions that is part of the formulation of the biodegradable commercial blend.

3.3. Mechanical Properties

The mechanical properties of blown films were evaluated both in machine and in transverse directions since, as it is well known, the film blowing operation leads to bi-oriented films. In **Table 3** elastic modulus (E), tensile strength (TS), and the elongation at break (EB) for all the investigated samples are reported. Moreover, to better evaluate the effect of the incorporated filler on the tensile properties, the dimensionless values of the same properties, calculated by dividing the value of the nanocomposite property by that of the corresponding unfilled matrix, are reported in **Figures 6** and **7**. Both the neat polymeric films tested in machine direction exhibited a higher elastic modulus and a lower EB. This behavior can be attributed to a better orientation achieved by macromolecules in machine direction with respect to the transverse direction.

The addition of both the fillers improves the stiffness of ECOVIO based films in both directions, although the films filled with CL20A exhibit a larger increase than films filled with SOCAL, achieving an increase of 22% for the film in the machine direction (**Figure 6**). These results are in good agreement with the reported morphology and are comparable with results reported in the literature for similar bionanocomposite systems.^[20] On the contrary, the properties at breaks, TS and EB, of ECOVIO based films decrease with both the fillers and in both directions (**Figure 6**). Furthermore, the stiffer film, that is, ECOVIO + CL20A, is the one that shows the greatest reduction of the ultimate properties. Nevertheless, the materials remain

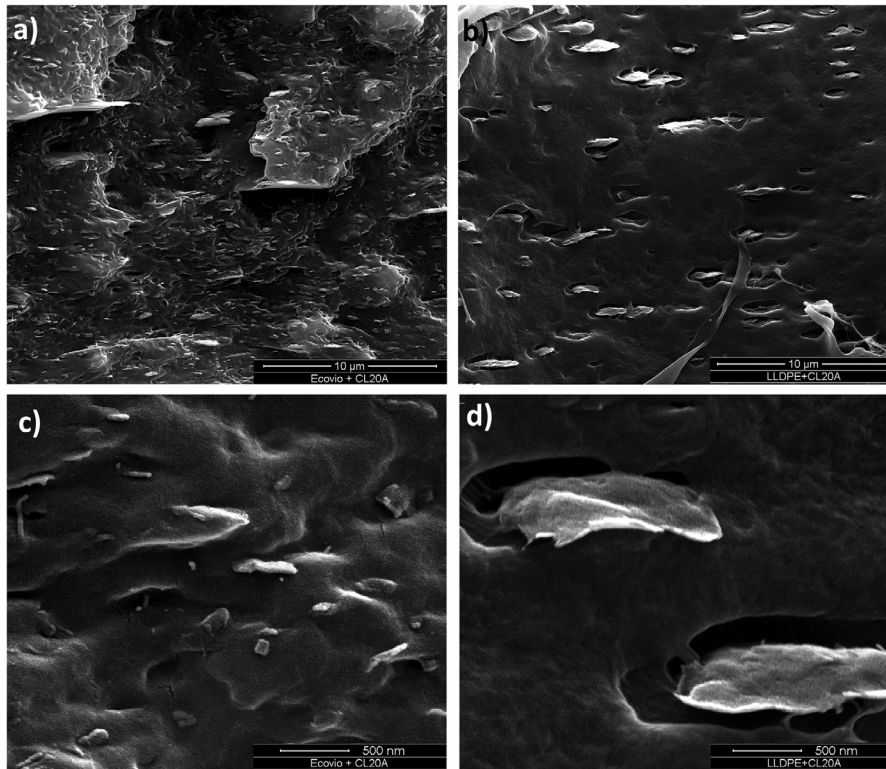


Figure 4. SEM micrographs of nanocomposites containing CL20A: ECOVIO + CL20A at a) lower magnification and c) higher magnification and LLDPE + CL20A at b) lower magnification and d) higher magnification.

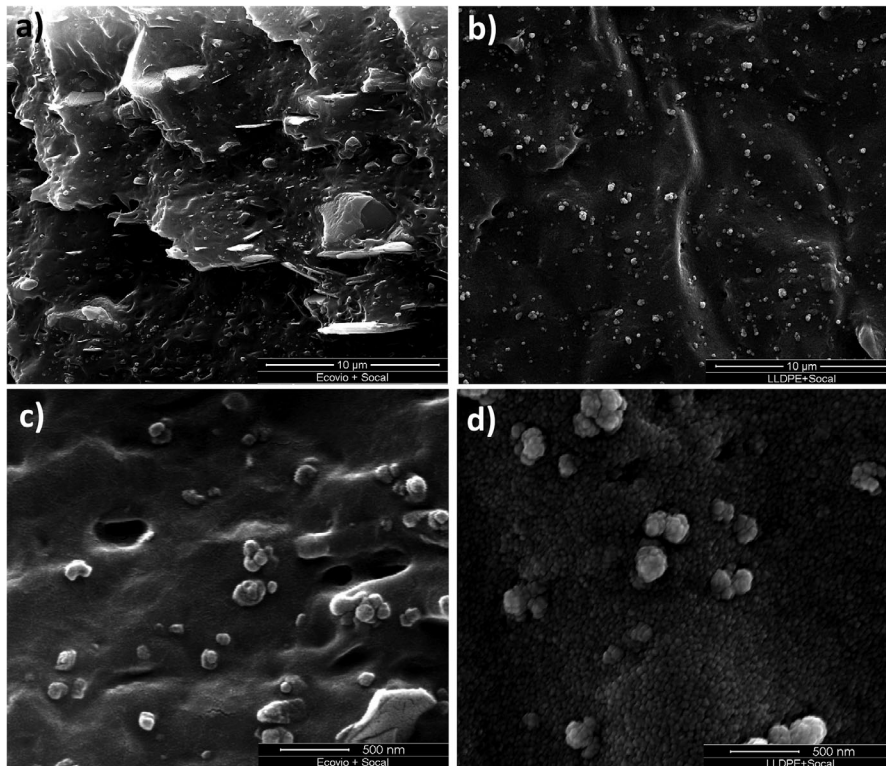


Figure 5. SEM micrographs of nanocomposites containing SOCAL: ECOVIO + SOCAL at a) lower magnification and c) higher magnification and LLDPE + SOCAL at b) lower magnification and d) higher magnification.

Table 3. Tensile properties of all blown films evaluated both in the machine and in transverse directions.

	E_{MD} [MPa]	E_{TD} [MPa]	TS_{MD} [MPa]	TS_{TD} [MPa]	EB_{MD} [%]	EB_{TD} [%]
ECOVIO	222 ± 11	187 ± 12	18 ± 0.9	19 ± 0.8	626 ± 23	690 ± 25
ECOVIO + SOCAL	247 ± 12	202 ± 13	16 ± 0.7	18 ± 0.6	558 ± 22	648 ± 22
ECOVIO + CL20A	272 ± 14	220 ± 11	14 ± 0.8	15 ± 0.6	522 ± 19	594 ± 22
LLDPE	232 ± 12	190 ± 10	34 ± 1.6	27 ± 1.2	833 ± 31	857 ± 32
LLDPE + SOCAL	261 ± 15	218 ± 13	36 ± 1.7	29 ± 1.3	831 ± 34	830 ± 33
LLDPE + CL20A	241 ± 10	226 ± 12	29 ± 1.4	23 ± 1.1	750 ± 29	770 ± 28

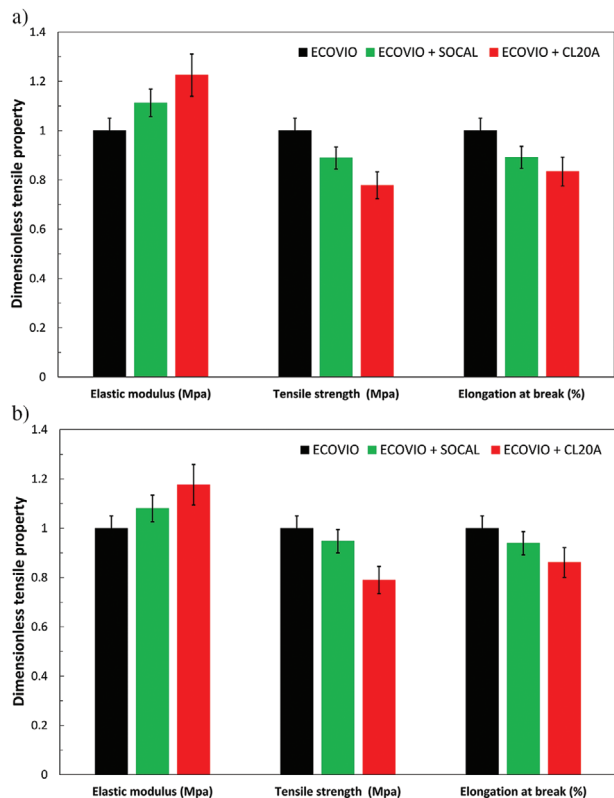


Figure 6. Dimensionless tensile properties of ECOVIO based blown films in a) machine direction and b) transverse direction.

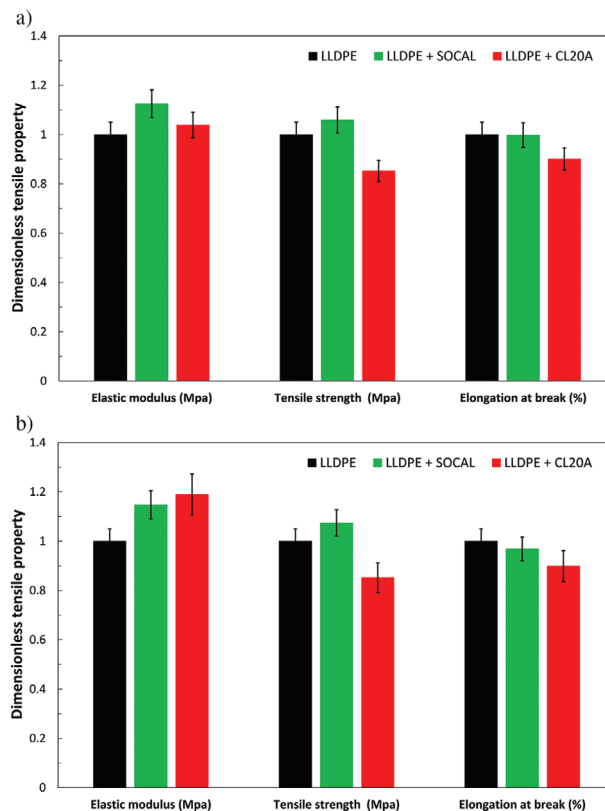


Figure 7. Dimensionless tensile properties of LLDPE based blown films in a) machine direction and b) transverse direction.

ductile and the EB remains high like the TS. The decrease of the TS can be attributed to the reduction of the EB which causes a premature breaking of the specimen.^[20,21]

LLDPE based films showed an increase of elastic modulus as a result of the addition of both the fillers, although the increase is more modest than respective ECOVIO based films. On the contrary, the ultimate properties of LLDPE filled with SOCAL are better than those of LLDPE film incorporating CL20A (Figure 7). Indeed, the film filled with neat LLDPE exhibits a decrease of both TS and EB in comparison with neat LLDPE, whereas the addition of SOCAL led to a slight increase of TS and to an unchanged value of EB. These results can be attributed to the different interfacial adhesion shown in the SEM micrographs for the two systems, that is, a good adhesion for LLDPE and SOCAL whereas a poor adhesion for LLDPE and CL20A.

Figure 8 shows the tear resistance values of the blown films in both directions, for both the nanocomposite systems. It is possible to observe that the ECOVIO and the related nanocomposites show values of tear strength higher than those of the LLDPE based systems. Moreover, the values of the tear resistance are larger in the transverse direction for all the investigated samples. These results are not unexpected and are in good agreement with the results obtained in the tensile tests that suggested a better orientation in the machine direction. The addition of the fillers caused an increase in tear resistance in both matrices and in both directions. However, a larger increase was observed for the ECOVIO based nanocomposite filled with SOCAL. In fact, this sample exhibited an increase of about 40% in the machine direction and about 15% in the transverse direction in comparison with neat ECOVIO film.

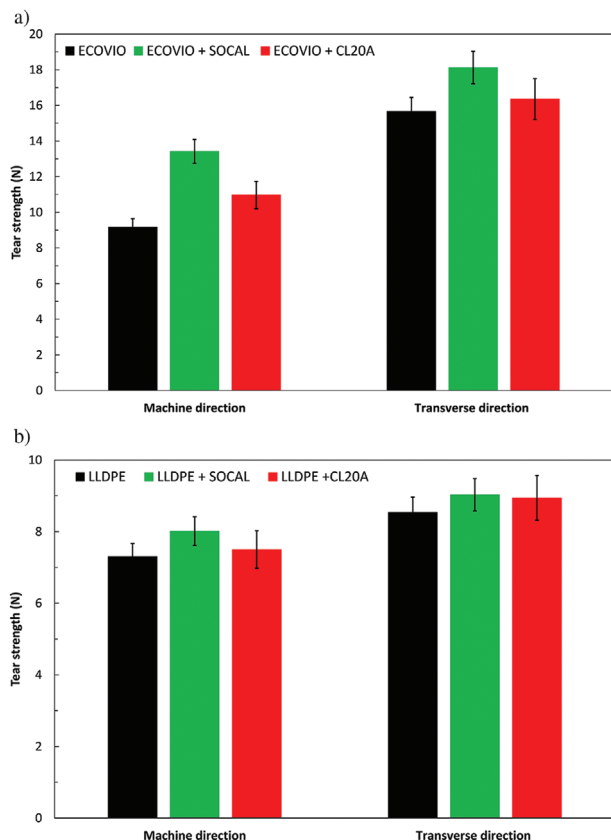


Figure 8. Tear resistance in both directions for a) ECOVIO based systems and b) LLDPE based systems.

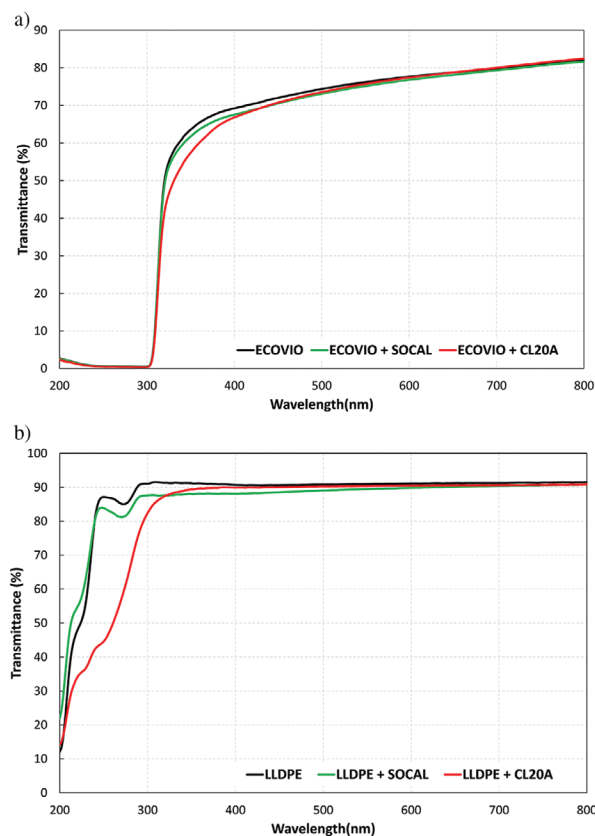


Figure 9. UV-vis spectra for a) ECOVIO based systems and b) LLDPE based systems

3.4. Optical Properties

The addition of inert fillers in a polymer matrix can negatively affect the optical properties of the films, usually reducing their transparency and this can affect the use of these materials as covers for greenhouses. Indeed, the films suitable for this use have to allow the transmission inside the greenhouse of the solar radiation fraction necessary for the rapid growth of the plants. For this reason, spectrophotometric measurements were carried out for all the films investigated in this work. In **Figure 9** UV/VIS spectra of the two systems are reported. As regards the LLDPE based systems, the addition of SOCAL does not influence the UV-vis spectrum that is almost the same if compared with that of the polymeric matrix, that is, a high transmittance for all the investigated wavelengths. On the contrary, the nanocomposite filled with CL20A absorbs in the range 200–300 nm and this is due to the presence of the clay.^[3] Whereas, the transmittance of the LLDPE based nanocomposite in the visible range of the spectrum (wavelengths 400–800 nm) remains unchanged even in presence of the nanofiller. As already reported, this is very important since solar radiations in these wavelengths are necessary for chlorophyll photosynthesis and therefore for good plant growth.

As regards the ECOVIO based films, it can be observed that the nanocomposites exhibit no variations in the spectra in the whole wavelength range when compared with the neat matrix and even in the wavelengths between 200 and 300 nm the spectra are al-

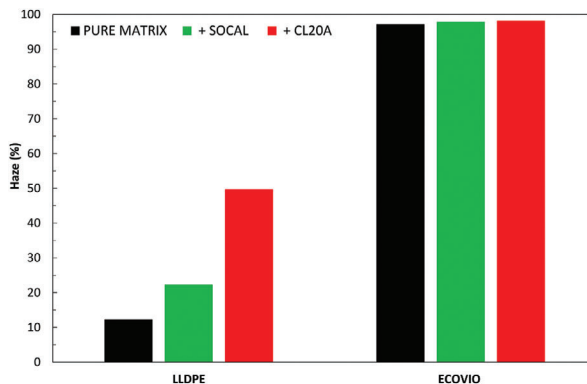


Figure 10. Haze values for ECOVIO and LLDPE based systems.

most overlapped. Indeed, even the neat matrix is able to avoid the transmission of the radiation in this wavelength range.

Finally, the Haze values of all investigated films are reported in **Figure 10**. Indeed, an important property that greenhouse films possess is the ability to diffuse the light inside the greenhouse. The haze of the LLDPE based films increases by adding both the filler. In particular, it is more intense for nanocomposites incorporating the clay rather than for the films containing the calcium carbonate. In fact, it was already reported the ability of clay to increase the haze of a polymeric film.^[3]

On the contrary, the ECOVIO based nanocomposite films did not show any significant variations in haze values in comparison

with neat ECOVIO, since even the haze of the neat matrix is very high and therefore little affected by the presence of fillers.

4. Conclusions

In this work, we demonstrated the suitability of bionanocomposite samples based on PBAT/PLA blend and two different inorganic nanofillers for the production of films for agriculture applications by comparing them with traditionally used LLDPE based films. The presence of nanoparticles does not affect the processability of the polymer in film blowing operation allowing to obtain films comparable with traditional ones. The addition of fillers improved the stiffness and tear strength of blown films without negatively affecting their ductility. Moreover, the transparency of the matrices was almost uninfluenced by the presence of the nanofillers.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

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