LDPE-Nanoclay films for food packaging with improved barrier properties

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Abstract

This study focuses on the development of low-density polyethylene matrix nanocomposite films for food packaging industry and aims at improving low-density polyethylene oxygen barrier properties while maintaining other relevant characteristics, such as processability, easy post-processing, optical and mechanical properties. low-density polyethylene nanocomposites, with I and 2.5wt. % nanoclay (NC) and also compatibilized with 5wt. % polyethylene grafted with maleic anhydride (PE-g-MA), were prepared and used to produce blown films. The nanocomposites were characterized in terms of their morphology, thermal, rheological, mechanical, barrier and optical properties, through scanning electron microscopy (SEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), rheological measurements, tensile tests, water vapor transmission, oxygen permeability tests and spectrophotometry. The results demonstrated good NC dispersion in the polymer matrix and decreased oxygen permeability in the compatibilized nanocomposite films. All the other properties did not significantly change when compared to neat low-density polyethylene. Overall, the film properties were improved with the added nanoclay and PE-g-MA and, have potential for food packaging.

Keywords

Low-density polyethylene nanocomposites, nanoclay, compatibilizer, permeability, blown-film, food packaging

Introduction

Adding fillers in a polymer matrix is a common process, in the plastics industry, that improves properties, such as, mechanical, gas barrier, antimicrobial and, in some cases, reduce raw material costs. [1,2]

Polymeric nanocomposites consists of a continuous polymer-based phase and one or more phases dispersed at the nanoscale. [3] According to the literature, these systems exhibit better performance when compared to micro-composites and neat polymer, even at low nanoparticle concentrations. [2,4] The size difference between micro and nanoparticles results in drastic changes in the material properties. Since the surface area

to volume ratio is inversely proportional to the particle diameter, the smaller the diameter, the greater the surface area to volume ratio, increasing the interaction between the particle surface and the matrix. [5–7] To take advantage of the improved properties resulting from this increased interaction, a good nanoparticle dispersion and distribution in the polymeric matrix is mandatory. However, it is quite difficult to obtain nanocomposites with a good NC dispersion in non-polar polymers, such as polyolefins. [8–12]

Polyolefins are widely used in flexible food packaging due to their low moisture permeability, among other features. Since they have a hydrophobic nature, their interaction with the organically modified clay is weak. Therefore the desired intercalation and/ or exfoliation of the clay lamellas, despite the high shear forces applied during melt mixing process used to produce the nanocomposite, is not always achieved. [13] Adding compatibilizers improves the interface between polymer matrix and nanoparticle surface, enhancing nanoparticles dispersion. [14] PE-g-MA (polyethylene grafted with maleic anhydride) has been widely used to improve the interaction between the nanomaterial polar surface and the nonpolar matrix. [15]

Despite the good properties associated to PE in food packaging industry, such as flexibility, transparency and good sealing properties, it has poor oxygen barrier properties, [16,17] which might be overcome using NC. With the added NC, permeability is significantly affected due to the tortuous path imposed by the NC arrangement in the matrix to gas diffusion. [12]

Therefore, since NC are authorized by the European Union in Commission Regulation (EU) No. 10/2011, as safe for food applications this study aims to improve the LDPE film barrier properties for food packaging applications. For this purpose, adding NC at 1 and 2.5wt%, with and without a compatibilizer (PE-g-MA), in a LDPE matrix affected the film performance for food packaging. The NC morphology and dispersion were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD), thermal properties were characterized by differential scanning calorimetry (DSC), and processability was assessed through melt flow index (MFI). The barrier, mechanical and optical film properties were measured through oxygen permeability, tensile and turbidity tests, respectively. To assess the film performance in post-processing operations such as heat sealing and printing), sealing and contact angles tests were carried out. The characterization protocol evaluated not only the new films adequacy for food packaging, but also their viability to be produced in an industrial environment without significantly modifying the processing conditions.

Experimental

Materials

ExxonMobil LD 159 AC a low density polyethylene, extrusion blown film grade (density = 924 kg/m^3, MFI = 1.2 g/10 min and melt temperature = 110°C) was used as matrix, Dow Inc. FUSABOND E226 a PE-g-MA compatibilizer (MFI = 1.75 g/10 min, melting temperature = 120°C), was selected. Laviosa Mineral Solutions SpA Dellite 67 G, montmorillonite modified with quaternary ammonium salt and purified was the NC used.

Preparation of low-density polyethylene based nanocomposites

Before compounding, the NC was dried for 8 h at 80°C in a forced convection oven. Table 1 shows the NC additions with/without PE-g-MA. They were prepared in a Coperion ZSK 26 co-rotating twin-screw extruder. The screw configuration used five distinct mixing zones consisting of disks staggered at 30,45 and 90° separated by conveying zones. The processing conditions were: barrel temperature = 190°C, screws speed = 250 rpm and throughput = 10 kg/h.

Blown film extrusion

The nanocomposite pellets were dried at 60°C for 4 hours before the blown film extrusion process, carried out in a laboratorial Periplast single-screw extruder (D = 25 mm and L/D = 25) coupled to an extrusion head with a 50 mm diameter annular die and 1.25 mm gap. The extruder temperature profile was set at 175°C – 180°C – 180°C, and the three heating zones of the extrusion head were set at 190°C. A blow-up 2.5 ratio (BUR) and a

Table I. Sample codes and LDPE/NC/PE-g-MA nanocomposite formulations.

Sample code	LDPE (wt.%)	NC (wt.%)	PE-g-MA (wt.%)
NanoC (1.0)	99.0	1.0	0
NanoC (2.5)	97.5	2.5	0
NanoC (1.0)MA	94.0	1.0	5.0
NanoC (2.5)MA	92.5	2.5	5.0

8.5 take-up ratio (TUR) were used in the film production. These are typical ratios used in industry. The final film thickness was between 50 and 60μ m.

These processing conditions were maintained for all the nanocomposites tested.

Structural and thermo-rheological characterization

Morphology

Scanning electron microscopy. Scanning Electron Microscopy analysis was carried out on film samples fractured in liquid nitrogen coated with gold in a Nano SEM - FEI Nova 200 equipment.

X-Ray diffraction. X-Ray Diffraction measurements were carried out, on film samples, at room temperature, $23 \pm 2°C$, using a diffractometer (i.e., Bruker D8 Discover) equipped with a $CuK\alpha$ generator ($\lambda = 1.5404Å$) at 40 kV and 40 mA , in a 2θ range from 2° to 10° with a step of 0.01° with a counting time of 1 second per step. The NC interlayer distance, d, was calculated using Bragg's law. [18]

Barrier, mechanical and optical properties

Oxygen permeability. The oxygen permeability tests were carried out on a Gas Diffusion Permeameter (DP-100A) from Porous Materials, Inc, using the pressure increase method. The 4 cm diameter film samples were subjected to a 101,325kPa (1 atm) pressure, at $23 \pm 2°C$ for 3 hours. Three specimens were used for each film sample. Before the tests, samples were stored at a temperature of $23 \pm 2°C$.

Water vapor transmission. The WVT tests were performed according to the desiccant method from ASTM E96/E96M-10. The samples with 8 cm diameter were sealed to the open mouth of a test cup, containing calcium chloride pre-dried at 200°C. The samples were placed inside a desiccator at $23 \pm 2°C$ and weighed every 24 hours for a period of 25 days to determine the water vapor transmission through the sample to the desiccant. The WVT was the slope obtained by curve fitting the weight change over time via linear regression.

Tensile tests. The tensile tests were carried out in a universal mechanical testing machine, Shimadzu AG-X, with a 1 kN load cell, at $23 \pm 2°C$, at 50 mm/min. Following ISO 527-3 standard, for each sample, 5 film specimens of type 2(160 × 25 mm) taken from the transverse (TD) and the machine (MD) directions.

Optical properties. The turbidity was determined in a XL-211 Hazegard System transmittance meter, according to ASTM D1003-00. This system measures the total light transmittance, T_T, and the percentage of diffuse transmittance, D_T. Six specimens from each sample were tested.

Thermal and rheological properties

Differential scanning calorimetry. The nanocomposite granules (or part of a granule) ($4 - 5mg$) were placed in aluminium crucibles with pierced lid under nitrogen flow rate $= 50$ mL/min on a DSC Netzsch equipment, the procedure was repeated twice for each sample. As recommended in ISO 11,357-1 each sample was subjected to two heating-cooling cycles. The samples were heated at 10°C/min, from 30°C to 200°C, held at this temperature for 1 minute, then cooled to 30°C, at a cooling rate of 20°C/ min , and then re-heated to 200°C with a heating rate of 10°C/min. The melting temperature (T_m) and melting enthalpy (ΔH_m), were obtained from the second heating. The crystallinity degree (X_c) was calculated using ΔH_m^0, the 293 J/g melting enthalpy for 100% crystalline PE. [19,20]

Melt flow index. Before this test, the pellets were dried at 60°C for 4 hours. The test was carried out in a MFI Daventest, at 190°C and using 2.16 kg weight, according to ISO 1133-1.

Post-processing. Heat sealing tests and contact angle measurements were carried out to check the possibility of maintaining the usual conditions in post-processing operations, i.e., film sealing and printing (through the film surface wettability by a liquid [21]).

Heat sealing. Films were heat sealed at 351 kPa , for 1 s , using a Labthink, model PARAM HST-H3 to obtain the minimum sealing temperatures.

For the tensile test, to measure the maximum sealing force of a 15 mm long weld, the films were again sealed under the same conditions, at 130°C for all samples. For each sample, five specimens were collected from the MD an TD direction sealed, and then tested on a LF-Plus testing machine, from Lloyd Instruments, with a 50 N load cell, at 100 mm/min.

Contact angles. The contact angle measurements were carried out in a Contact Angle System OCA equipment using distilled water on the film samples at 23 ± 2°C, in accordance with ASTM D7334-08. Distilled water (3μ) was deposited on the films at 2μl/s, using a syringe. The contact angle was measured immediately after the water drop was placed on the film surface. A total of thirty contact angles per sample were measured.

Results and discussion

Film production

The SEM micrographs in Figure 1 demonstrate that the nanocomposites exhibit different NC dispersion when the PE-g-MA at 5wt% is added. Comparing NanoC(1.0) and NanoC(1.0)MA, i.e., with the same NC amount without and with PE-g-MA, it is clearly

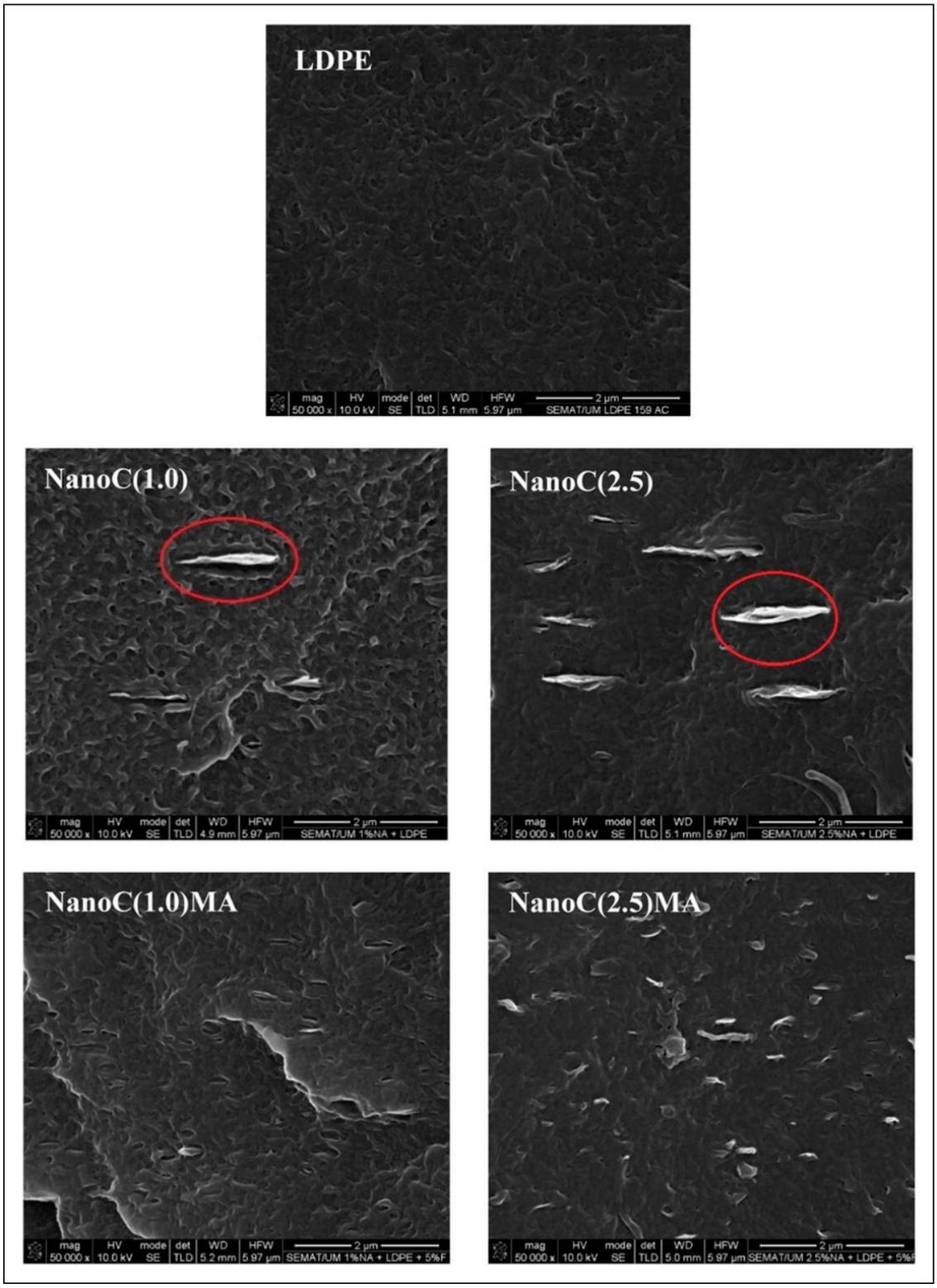

Figure I. SEM micrographs of LDPE and nanocomposite films.
visible that NanoC(1.0)MA presents a better dispersion. Similar observation can be made for NanoC(2.5) and NanoC(2.5)MA. Similar observations were made by Majeed et al. [18]

Figure 2 shows the XRD patterns for the NC, and the four LDPE/nanocomposite samples. They demonstrate that NC presents two diffraction peaks corresponding to interlayer distance d001 = 34.21Å and d002 = 18.32Å, Table 2. In samples NanoC (1.0) MA and NanoC(2.5)MA the peak at d_{001} is not observed. This can be an indication of higher intercalation or even exfoliation of NC platelets due to the added 5wt%PE-g-MA. Also the peak at d_{002} shifted to lower angles indicating an increase of the d spaces

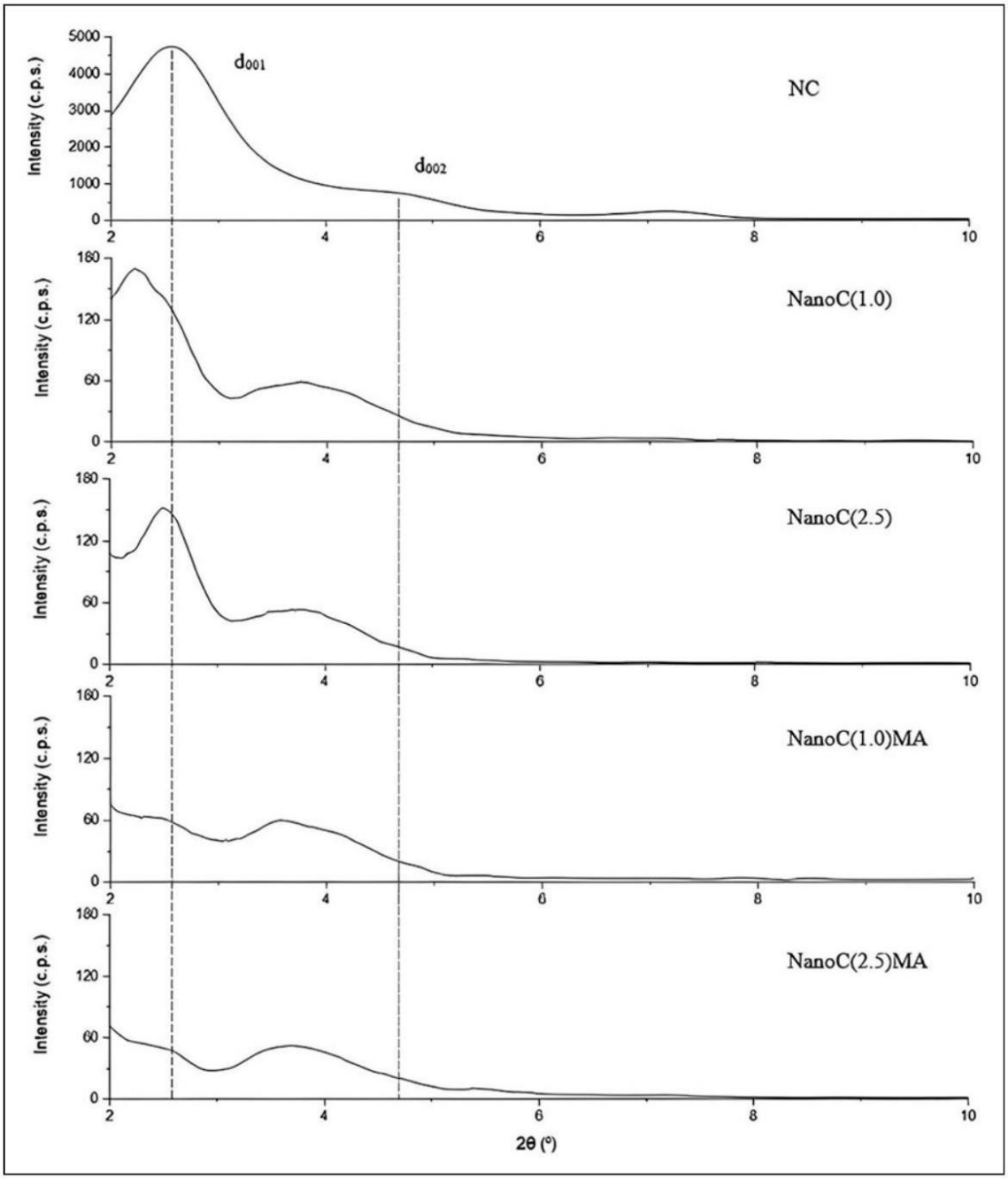

Figure 2. XRD patterns of NC and nanocomposites.
(NanoC(1.0)MA: 23.79Å Å; NanoC(2.5)MA: 23.05Å). NanoC(1.0) and NanoC(2.5) clearly

show two diffraction peaks, both d_{001} and d_{002}, that shifted to lower angles, Table and Figure 2. The shift of the peak d_{002} to lower 2θ and the low intensity of the peak at d_{001} in compatibilized nanocomposites, suggest an increase in interlayer distance promoted by the diffusion of the PE-g-MA chains into the NC galleries, this was also observed by Majeed et al. [18]

Table 2. Diffraction peaks and interlayer distance.

	d_{001}		d_{002}	
	Å	2θ	Å	2θ
NC	34.21	2.58	18.32	4.82
NanoC(1.0)	38.71	2.28	22.81	3.87
NanoC(2.5)	34.61	2.55	22.99	3.84
NanoC(1.0)MA	-	-	23.79	3.71
NanoC(2.5)MA	-	-	23.05	3.83

Film properties

Table 3 presents the film barrier properties to oxygen and water vapour. For convenience the oxygen permeability is also presented in common US units. The data shows that the added NC lowers the film oxygen permeability, particularly when compatibilizer is added. This can be due to the NC platelets in the matrix that creates a tortuous path for

Table 3. Oxygen permeability and WVT results of the films produced.

	Oxygen permeability				WVT
	$Ml \cdot cm/Pa \cdot s \cdot cm^2$		cc•mil/ 100in ^{2}.day · atm		$g/h \cdot m^2 \times 10^2$
Sample	ave	sd	ave	sd	ave, sd
LDPE	3.19×10^{-13}	9.59×10^{-15}	709	22	6.70 ± 0.63
NanoC(1.0)	2.81×10^{-13}	9.01×10^{-15}	625	20	7.87 ± 1.97
NanoC(2.5)	2.99×10^{-13}	1.26×10^{-14}	665	28	7.20 ± 1.84
NanoC(1.0)MA	1.86×10^{-13}	5.21×10^{-15}	416	12	4.91 ± 0.74

NanoC(2.5)MA	1.74×10^{-13}	1.69×10^{-14}	387	38	5.79 ± 0.87

gas permeation. [10,22] Regarding the percentage of NC used, in NanoC(1.0) the permeability decreases 11.9% with the incorporation of 1wt. % of NC, but in NanoC(2.5) the permeability only decreases 6.3% contrary to what is seen in compatibilized samples. This difference may be promoted by the poor dispersion of NC in the polymeric matrix, probably to the formation of aggregates as it was noticed by SEM. Film samples NanoC(1.0)MA and NanoC(2.5)MA, the effect of the incorporation of NC is much more effective, increasing with the rate of incorporation, and promoting a decrease in oxygen permeability of 45.5% for NanoC(2.5)MA, when compared to LDPE.

The WVT results demonstrate, in some way, a similar trend to the previous, but in this case, while the incorporation of NC without compatibilizer deteriorates the property, it improves when compatibilizer is used. The sample with the best WVT result was NanoC(1.0)MA, which has the lowest wt. % of NC, with a WVT of 4.91×10^{-2} g/(h · m^2), i.e., a reduction of around 14% relative to LDPE. The increase of WVT in NanoC(2.5)MA sample, compared to NanoC(1.0)MA, can be associated to the agglomerates, as observed by SEM, where it can be seen that although the incorporation of PE-g-MA helps to promote the dispersion of NC, it is not sufficient.

Table 4 and Figure 3 show the tensile tests results in MD and TD. The nanocomposites with PE-g-MA have the highest strength and modulus, especially NanoC(2.5)MA, which has the best results despite not being very different from NanoC(1.0)MA. Figure 3 indicates that for the same amount of PE-g-MA, the modulus increases as the NC content increases.

Table 4. Results of the films tensile tests: σ_y - yield stress; $E_{1\%}$ - Young's modulus at 1% strain; σ_m - maximum stress; ε_m - strain at maximum stress.

Sample		σ_yMPa ave, sd	$E_{1\%}$ Mpa ave, sd	σ_mMPa ave, sd	ε_m%
LDPE	MD	6.6 ± 0.3	208 ± 13.6	9.2 ± 0.6	278
	TD	6.5 ± 0.5	220 ± 15.1	$> 9.5 \pm 0.5$	>401
NanoC(1.0)	MD	6.3 ± 0.5	177 ± 18.0	8.0 ± 0.8	133
	TD	6.0 ± 0.7	209 ± 19.0	6.9 ± 0.6	89
NanoC(2.5)	MD	6.8 ± 0.6	202 ± 22.0	8.5 ± 0.8	136
	TD	6.3 ± 0.6	239 ± 26.0	7.5 ± 0.7	123
NanoC(1.0)MA	MD	8.7 ± 0.7	274 ± 31.0	11.9 ± 1.1	309
	TD	9.1 ± 0.7	279 ± 42.0	9.7 ± 1.0	222
NanoC(2.5)MA	MD	9.7 ± 0.4	333 ± 18.0	12.5 ± 0.8	263
	TD	9.2 ± 0.4	381 ± 31.0	$> 10.2 \pm 1.1$	>296

According to the data provided the reinforcing capability of the NC only increases when the compatibilizer is added, which follows the literature results that shows that two incompatible systems have poor mechanical properties due to poor interfacial adhesion between the different components. [18,23]

Table 5 presents the total light transmittance, T_T, the percentage of diffuse transmittance, D_T and turbidity. They indicate that while T_T does not vary between LDPE and nanocomposite films, D_T and turbidity increase with the added NC. The turbidity for films with and without $PE-g-MA$ at 1wt%NC is the same.

Figure 4 presents the turbidity as a bar chart. It shows that NanoC(2.5), which has 2.5wt% of NC, is the nanocomposite with the lowest transparency. This can probably be associated to the existence of NC agglomerates, resulting from the low compatibility between NC and LDPE. This result also explains the permeability results obtained for this sample.

Figure 5 shows the LDPE film and NanoC(2.5) photographed when places over some text. Although NanoC(2.5) has higher turbidity, the film transparency is not sufficiently

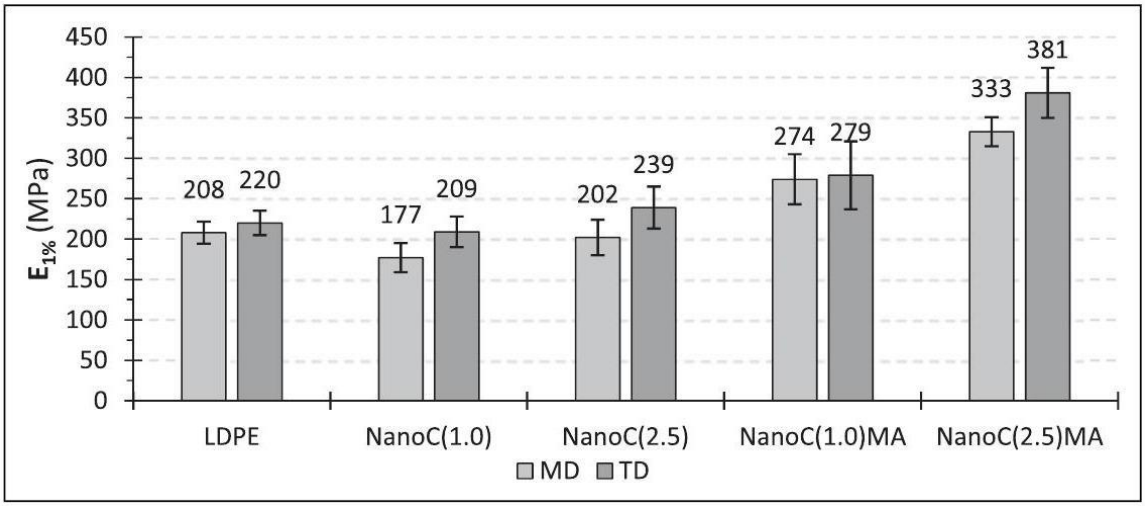

Figure 3. Young's modulus values for LDPE and nanocomposite films.

Table 5. T_T, D_T and turbidity values of LDPE and nanocomposite films.

Sample	T_T % ave, sd	D_T % ave, sd	Turbidity% ave, sd
LDPE	92.8 ± 0.1	6.2 ± 0.1	6.7 ± 0.1
NanoC(1.0)	92.3 ± 0.1	9.6 ± 0.5	10.4 ± 0.5
NanoC(2.5)	92.2 ± 0.4	14.0 ± 0.2	15.2 ± 0.2
NanoC(1.0)MA	92.5 ± 0.1	9.7 ± 0.3	10.4 ± 0.4

NanoC(2.5)MA	92.3 ± 0.4	10.3 ± 0.4	11.2 ± 0.5

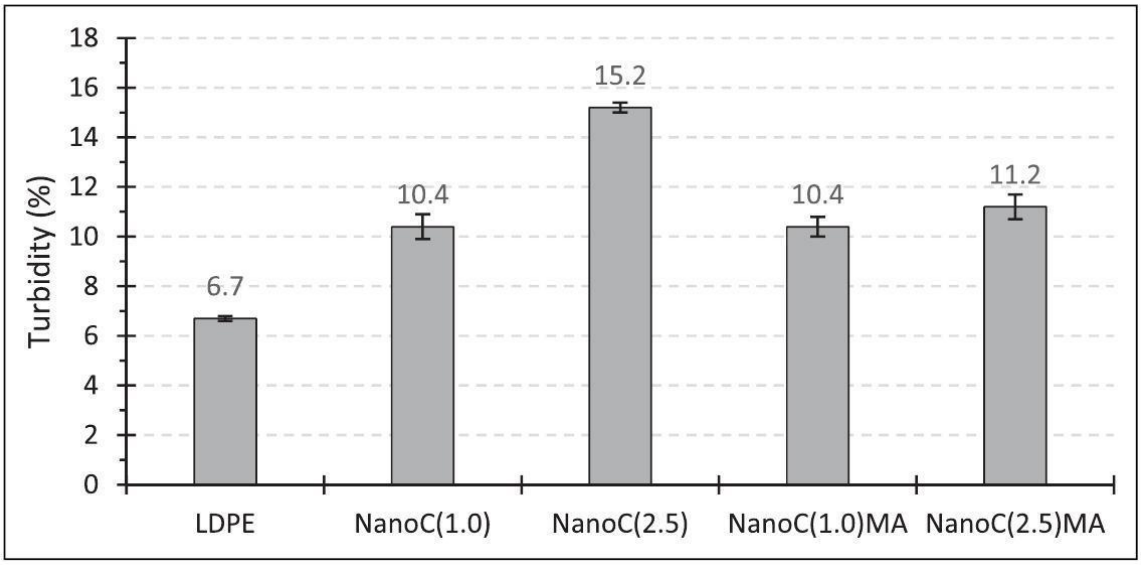

Figure 4. Turbidity of LDPE and the nanocomposite films.

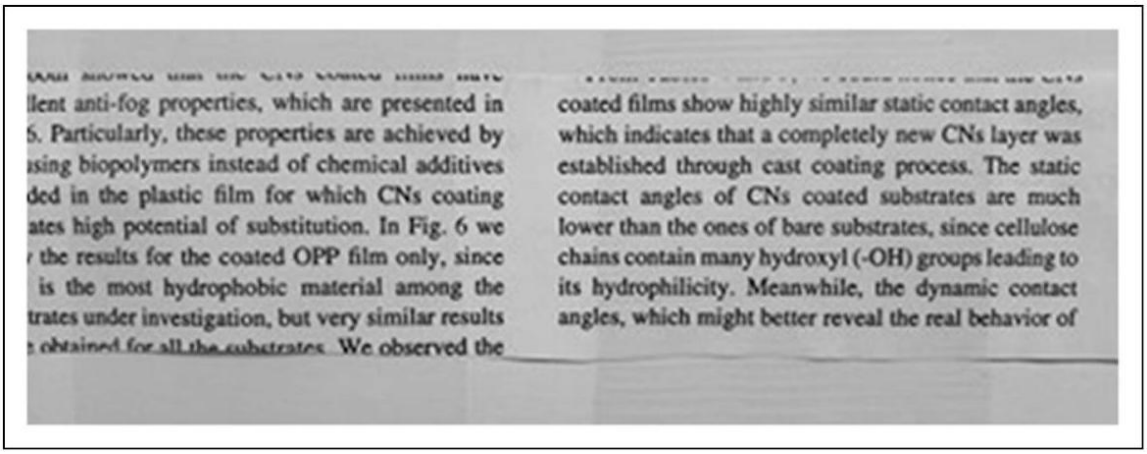

Figure 5. Transparency of the LDPE film (on the left) and NanoC(2.5) (on the right). affected to prevent reading the text positioned under the films. The colour with NC is slightly brown, the brownish colour can only be noticeable when several films overlap. The film transparency for the food packaging industry is very important to capture consumer interest and, fortunately, was kept at a reasonable level.

Film extrusion and post-processing

Taking into account the measurement error of about 10%, the average values of DSC results depicted in Table 6 show that the LDPE and nanocomposite's melting temperature T_m and the crystallinity X_c, are very similar for all the samples, revealing that the added NC does not affect the matrix melting temperature. Therefore, for processing proposes the set extrusion temperature can be maintained. This fact, together

with the similar values of
crystallinity, is also an indication that the sealing conditions of the nanocomposite films can be similar to those used for LDPE films.

MFI values (Figure 6) decrease with the added compatibilizer, i.e., these samples exhibit higher shear viscosity (at least at the low shear rate values corresponding to the MFI test), indicating that the NC are effectively reinforcing the melt. SEM results also indicate higher intercalation/exfoliation when PE-g-MA was added. The same was noticed by Pedroso and Rosa study. [24] Without compatibilizer, the added NC does not affect the MFI, revealing a low interaction (compatibility) between NC and the LDPE matrix.

The increase in apparent viscosity of the compatibilized nanocomposites had a positive impact on film extrusion, since it is also expected to impact the melt strength, increasing the bubble stability, facilitating the extrusion process.

Table 7 shows the results related with post-processing operations (heat sealing and printing), the average maximum sealing force and the contact angles. One sees that the minimum sealing temperature is not affected and it is similar to LDPE film (around

Table 6. DSC results for LDPE and nanocomposites: $\boldsymbol{T_m}$ melting temperature; $\Delta \boldsymbol{H_m}$ - melting enthalpy; $\boldsymbol{X_c}$ - crystallinity degree.

	$\boldsymbol{T_m}$	ΔH_m	$\boldsymbol{X_c}$
Sample	C°	J/g	%
LDPE	111.2	119.5	40.8
NanoC(1.0)	110.9	111.4	38.0
NanoC(2.5)	111.0	109.9	37.1
NanoC(1.0)MA	111.6	106.6	36.4
NanoC(2.5)MA	111.3	115.7	39.4

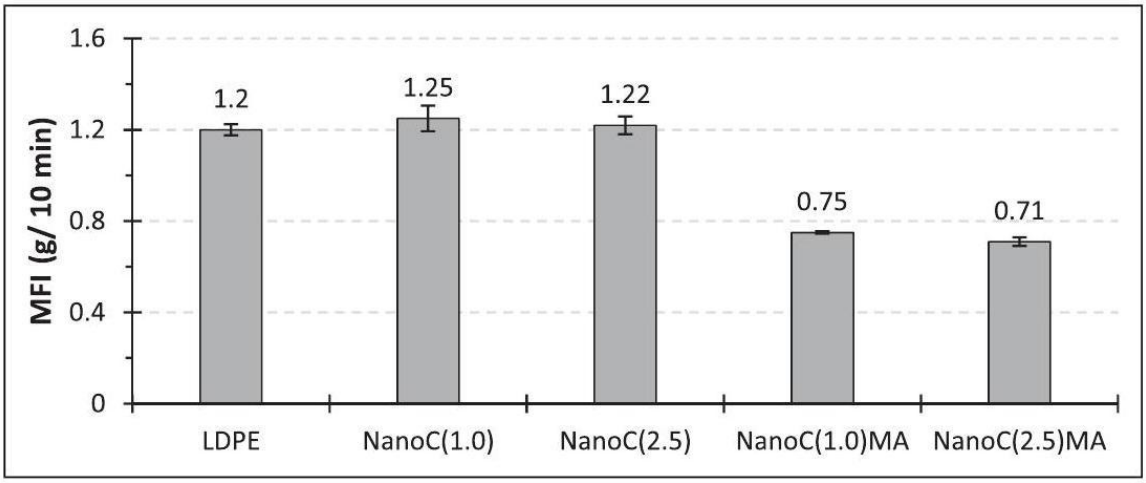

Figure 6. MFI for LDPE and nanocomposites.

Table 7. Maximum sealing force and contact angles of the films.

Sample		Maximum force	Contact angle degree
		N ave, sd	ave, sd
LDPE	MD	10.6 ± 0.6	89.08 ± 2.38
	TD	7.8 ± 0.9	
NanoC(1.0)	MD	10.5 ± 0.8	87.82 ± 3.63
	TD	8.1 ± 0.2	
NanoC(2.5)	MD	7.6 ± 1.3	85.73 ± 3.56
	TD	7.4 ± 0.7	
NanoC(1.0) MA	MD	10.7 ± 0.5	87.06 ± 2.23
	TD	9.0 ± 0.3	
NanoC(2.5) MA	MD	9.8 ± 0.6	87.24 ± 2.45
	TD	9.1 ± 0.1	

125°C) for all the samples. However, differences in the sealing mechanical resistance are noticeable, samples collected in the MD present higher maximum sealing force than the TD samples, which is in agreement with the higher MD mechanical resistance. This is due to higher MD molecular orientation promoted by a higher stretching in this direction. Moreover, it is possible to verify that when the added NC is accompanied by compatibilizer, the differences between the two main directions almost vanish, while keeping higher values.

The added NC in the LDPE matrix does not change the contact angles (Table 7). These might be associate to the low NC amount at the film surface, which leaves the film topography unchanged, keeping the same contact angle.

Conclusion

LDPE/NC nanocomposite films were produced by blown film extrusion with and without compatibilizer, PE-g-MA. Through the joint analysis of several characterization techniques, it was possible to draw conclusion about the performance of the produced nanocomposites. SEM and XRD results showed that samples with the added 5wt% PE-g-MA present better NC dispersion and higher interlayer distance compared to samples without compatibilizer. This homogeneity allows producing films with better and more balanced mechanical properties (for the monolithic films and their heat sealing strength), and slightly better barrier properties, which were the main objective of this study.

Although, the reduction in O_2 permeability did not improve the barrier performance enough to replace high barrier polymers, such as EVOH.

The nanocomposite that presented the best results for structural and physical properties was NanoC(1.0)MA, with 1wt. %NC, apart from the mechanical properties, which was NanoC(2.5)MA with 2.5wt%NC. Since good barrier properties are extremely important for food packaging production, the choice of a nanocomposite with better mechanical properties cannot be made at the expense of barrier properties. Thus, it was possible to conclude that the barrier properties as well as the other properties studied, to produce flexible films for food packaging, can be improved with by adding 1wt. %NC.

While the turbidity increased with the increased NC, the film transparency was not significantly affected. Therefore, the films produced can be used in food packaging, still enabling product visualization.

Moreover, properties such as melting temperature, heat sealing temperature and contact angles were not significantly affected by the added NC or compatibilizer, preserving the conditions for packaging production.

As for future studies, it may be relevant to study the eventual migration of NC from the film to the food packaged, as the packaging must comply with the regulations on migration of substances into food imposed by the European Commission.

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Declaration of Conflicting Interests

The author(s) declare(s) that there is no conflict of interest.

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Biographies

Carolina Barros obtained her Master's Degree in Polymer Engineering in November 2018 from the University of Minho, Portugal. In 2021, she embraced a new challenge as a PhD student in Science and Engineering of Polymers and Composites at the University of Minho. She currently works at the Institute of Polymers and Composites (IPC) as a research fellow. Carolina has been collaborating with several scientific research projects in the development, production and characterization of polymeric nanocomposite pellets and films with the aim of developing new flexible and active packaging for food. As a research fellow, she acquired knowledge in polymer processing, focusing on blown film extrusion, filament extrusion and reactive extrusion, and characterization of polymers.

Sónia Miranda has a Master's Degree in Polymer Engineering from the University of Minho. She works at Innovation in Polymer Engineering (PIEP) as a researcher, having participated in several research projects related to the production of nanocomposites. During her career she focused on the processing of polymers and composites by filament extrusion and their characterization.

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A. V. Machado is an Associate Professor at DEP, EEUM, since 2015, with a PhD in Polymer Science and Engineering. Her main areas of scientific research are polymerization, copolymerization and modification of polymers and nanocomposites. She has more than 160 scientific publications and more than 230 communications at international conferences. She has successfully supervised 13 PhD and 6 postdoctoral students and was the principal investigator of the Extrasliced45, n-STeP and ATLANTA TPV projects.

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