Recyclable-by-design mono-material flexible packaging with high barrier properties realized through graphene hybrid coatings

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Highlights

- A design-for-recycling approach has been applied to realize high performance films for packaging applications.
- Mono-material polyolefin flexible films with remarkable barrier properties to gases and UV radiation have been developed by applying coatings based on graphene derivatives.
- The applied coatings show very regular morphology, and do not alter the flexibility and the overall mechanical properties of the substrates.
- The new barrier films are easy recyclable, as demonstrated by their reprocessing by extrusion and compression moulding.
- The proposed materials represent a promising solution to realize polymer based high performance mono-material products with a sustainable end-of-life option.

Abstract

Due to the large production of plastic packaging, packaging mismanagement represents a significant problem for the environment and the related economic/social contexts. A new route towards sustainable recycling has been identified in the design of the plastic products together with their end-of-life recycling options. Following this approach, in this work, new recyclable-by-design mono-material flexible films with high barrier properties to gases and UV radiation have been developed by applying graphene oxide (GO) and graphene oxide/montmorillonite (GO/MMT) hybrid coatings on polyolefin substrates. The coatings induce a remarkable reduction of the UV transmittance (40-

60%) and of the oxygen (94-99%) and water vapour (68-73%) permeability of the films, with very good stability after prolonged water immersion. Reprocessing tests demonstrate the easy recyclability of the coated films, whose commercial analogues are currently considered as non-recyclable. By extrusion and compression moulding, recycled films are obtained in which the nanostructured phases result well embedded in the polymer matrices. The mechanical properties of the samples obtained by reprocessing coated polyethylene and polypropylene films are comparable to those of the reprocessed pristine films. Moreover, no significant release of GO by water immersion for 24h at room temperature is detected from the recycled samples. Overall, the results indicate that the application of thin GO/MMT coatings to realize mono-material barrier films for packaging applications is an effective strategy to realize high performance products able to be easily recycled. These mono-material flexible films represent a new sustainable end-of-life option with respect to current commercial multi-layer products.

1. Introduction

Protection, aimed at increasing the useful life of the products, is a fundamental objective in the packaging sector. This concept is even more important in the case of the food packaging industry, with the scope of delaying the deterioration of food and guaranteeing high quality and safety by providing chemical, physical and biological protection (Marsh & Bugusu, 2007). In this perspective, plastic food packaging should contribute to promote an increased circularity in the food supply chain, replying to the key challenge of saving food and resources (Despoudi, 2020). Thus, the development of a new generation of sustainable food packaging should be able to reduce food losses and face safety issues, by preventing food-borne diseases and contamination, being at the same time reusable/recyclable, thus contributing to an overall preservation of the environment (Guillard et al., 2018).

Oxygen and light are the main causes of most food degradation processes. Oxygen promotes the oxidation of fats, the loss of nutrients and vitamins and the growth of aerobic microorganisms (Liu et al., 2010). UV light can affect food quality generating free radicals by a number of organic photochemical reactions. Moreover, UV irradiation can induce an early decrease of the food quality, altering food flavour and colour, promoting the degradation of vitamins, proteins and food antioxidants, and generating toxic substances (Goudarzi et al., 2017).

For these reasons, the food packaging industry has always attempted to develop and exploit ever more effective materials acting as barrier to gases and light. Most of the currently available commercial barrier packaging solutions include multilayer flexible films having complex structures. These films are generally constituted by plastics and aluminium layers, by different plastic layers and/or by different plastics and metallized plastic layers. When different materials are combined in a single product by lamination or by co-extrusion, the technical advantages obtained in terms of better performances are paid for in terms of their recyclability. In fact, multi-component multi-layered packaging cannot be recycled using traditional plastic reprocessing technologies, such as mechanical recycling, due to the chemical incompatibility of the different layers (Barlow & Morgan, 2013; Ma, 2018). One of the most investigated solutions to recycle multi-component multi-layered packaging materials is based on their delamination in order to separate the different components and to recycle them separately (Anukiruthika et al., 2020). Other approaches are based on the selective dissolution of one polymer phase (Walker et al., 2020) or on the simultaneous processing of immiscible polymer phases and eventually the aluminium phase, in presence of suitable compatibilizing or process aid agents (Avella et al., 2009; Kaiser et al., 2018; Yang et al., 2018).

Nevertheless, the proposed solutions are still not technically or economically sustainable, and therefore multi-material flexible packaging films are currently landfilled or used for energy recovery (Horodytska et al., 2018; Mourad et al., 2008).

The design-for-recycling approach for flexible packaging films. An effective approach to promote higher recycling rates of plastic products, at the basis of current industrial objectives and trends, is the design-for-recycling approach,

In this context, the packaging industry has already identified high performance mono-material plastic packaging, constituted by a single polymer and without any continuous metal layer, an effective step towards the goal of recyclable-by-design products that could: i) significantly reduce the complexity of packaging products; ii) decrease the amount of non-recyclable fractions, including barrier agents and inks towards mono-materials, with preference for mono-PE and mono-PP; iii) reduce the fluctuation of the quality and quantity of recycled products delivered to consumers; iv) avoide the wrong social perception that recycled plastics could have inferior quality or even being unsafe for human health (Ahamed et al., 2021; Eriksen et al., 2019; Grace, 2019; Pettersen et al., 2020, RecyClass, Recyclability Methodology, 2020; Plastics Recyclers Europe, Challenges and Opportunities, 2021; Ceflex, Designing for a Circular Economy, An Introduction, 2020).

In particular, polyolefin mono-material flexible films have been reported as interesting products able to meet the requirements of circular economy because of their easy mechanical recyclability (Barlow & Morgan, 2013; Ragaert et al., 2020; Srebrenkoska et al., 2009). Due to the low amount of additives, polymer nanocomposites represent a typical example of mono-material. Since 1985, the year of the Toyota polyamide/montmorillonite nanocomposite (Okada & Usuki, 2006), plenty of researches aimed at realizing gas barrier nanocomposite films by effectively dispersing functional nanofillers with different aspect ratio in bulky polymer matrices (Gusev & Lusti, 2001). In these works, the tortuous path mechanism (Ellis & D'Angelo, 2003) and the interfacial effect (Avella et al., 2007; Avolio et al., 2013; Scherillo et al., 2014) have been exploited, both able to reduce the rate of gas diffusion through the material. Nevertheless, despite the high expectation, until now these types of nanocomposites with improved gas barrier properties have largely failed to reach the market for food packaging applications. More recently, approximately since 2005, a change of paradigm occurred, and the research moved towards the development of nanostructured gas barrier coatings on flexible mono-polymer films (Rovera et al., 2020). In the years, this approach has been considered ever more promising and effective for the industry because the nanostructures applied in coatings, rather than being randomly dispersed in the polymer matrix, are confined to

the external surface of the polymer films, and thus they do not modify the thermomechanical properties and the processability of the polymer substrate.

Due to their high aspect ratio and their ability to maximize the effect of the tortuous path mechanism, different 2D materials have been tested for high barrier coating applications (Yu et al., 2021). Montmorillonite and related nanocomposites (Chen et al., 2015; Findenig et al., 2012; Lim et al., 2021) have been widely investigate to realize coatings with reduced gas permeability on different flexible films. Layered double hydroxide (LDH) nanosheets dispersions were recently applied onto polyethylene terephthalate (PET) to realize high performance coatings with very low permeability towards oxygen and water vapour and described as able to replace metallized multi-layered packaging products (Ruengkajorn et al., 2021; Yu et al., 2019). Graphene derivatives were also considered as potential highly effective barrier agents on various flexible polymer substrates (Pierleoni et al., 2016; Won et al., 2018). Investigating on graphene coatings, researchers were able to understand how tailoring the self-assembled structures can enhance the gas barrier properties of the systems (Castaldo et al., 2018; Scherillo et al., 2014; Yan et al., 2015). Hybrid nanostructures constituted by graphene derivatives and phyllosilicates were also the subject of interesting researches, demonstrating their enhanced gas barrier properties when graphene sheets self-assembled with the platelets of the phyllosilicate component in well oriented nanostructures (Castaldo et al., 2019; Yoo et al., 2014). Nevertheless, only a few papers report on the recycling/reprocessing of polyethylene (Asmatulu et al., 2015), polypropylene (Triantou et al., 2017) and other polymers or polymer blends containing nanoparticles (Botta et al., 2018; Pang et al., 2021). Moreover, some papers report remarkable results on the recycling of polymer/clay nanocomposites (Chowreddy et al., 2019; Rigail-Cedeño et al., 2019).

Layout and impact of the study. In summary, the large use of multilayer films in plastic packaging represents a barrier that strongly reduces the sustainable recycling options for these materials at the end of life. The impact of this problem is well represented by the EU production of plastic packaging, that exceeded 20 million tonnes in 2020 (PlasticsEurope, Plastics – the Fact 2020 report, 2020). It is estimated that only 5% of the value of the plastic packaging material remains within the economic cycle and that 95% is lost after the first use, which usually turns out to be very short since, even today, despite the efforts of institutions and consumers, most plastics are not recycled (European Commission, Questions & Answers: A European strategy for plastics, 2018). This also happens due to how the products are designed and due to the presence of non-recyclable or multi-layered materials. The main properties required for the successful adoption of mono-material films

in the packaging sector have been identified as: suitable mechanical strength and gas/vapour barrier; low material and processing cost; efficient recyclability with conventional processing technologies at the end of life.

This work aim to address all of this points, by demonstrating the effectiveness and recyclability-by-design of mono-material films. Polyolefins were selected as the most used polymers for packaging materials, and their barrier properties were improved by the application of nanostructured GO and GO/clay hybrid coatings, deposed by a simple and scalable system. After the assessment of physical properties, the recyclability of the films was demonstrated by reprocessing them and testing the recycled materials.

2. Experimental section

2.1 Materials

Polyethylene and polypropylene cast films were supplied by Flex Packaging AL S.p.A. (Cava de' Tirreni, Italy). In particular, a 70 µm thick LDPE film (density of 0,924 g/cm^3, ASTM-D792) and a 50 µm thick PP film (density of 0,9 g/cm^3, ASTM D 1505), both corona treated, with a surface tension > 38 dyne/cm were used. These samples were coded PE and PP, respectively.

Graphene oxide (GO) water dispersion (4.5 g/L) was purchased from Nanesa S.r.l. (Arezzo, Italy), cloisite Na^+ (MMT) was purchased from BYK Additives & Instruments (Wesel, Germany). All the other solvents and reagents were obtained from Merck KGaA (Darmstadt, Germany) and used without further purification.

2.2 Application of GO and GO-MMT coatings onto flexible films

The application of the GO coating onto PE and PP films was carried out using a rod coater "K hand coater" (Royston, United Kingdom). The GO dispersion was diluted with distilled water until a concentration of 3.1 g/L. The treatment on the PE and the PP films was performed applying an amount of water dispersion tailored to obtain coatings whose dry weight was approximately 280 mg/m^2. The corresponding thickness of the coatings was in the approximate range 140-200 nm, corresponding to volume fractions of 0.2-0.3 vol% for the PE based systems and 0.3-0.4 vol% for the PP based systems. The obtained samples were named PE-GO and PP-GO.

For the preparation of GO-MMT hybrid coatings, MMT was dispersed in distilled water at 3.1 mg/mL concentration by sonication with a Sonics Vibracell ultrasonic processor (Newton, USA) (500 W, 20 kHz), at 25% of amplitude for 30 min, with 30 s/30 s on/off cycles. Then, the dispersion was mixed

in equicomposition with GO and the resulting dispersion was sonicated at the same conditions for 10 minutes. Finally, 280 mg/m^2 GO-MMT hydrid coatings were obtained on PE and PP using a rod coater obtaining, also in this case, coatings of 140-200 nm approximate thickness. These samples were coded PE-GO-MMT and PP-GO-MMT and were characterized by the same coating volume fraction of PE-GO and PP-GO.

2.3 Recycling

Before processing, differential scanning calorimetry (DSC) and melt flow rate (MFR) analyses were performed on PE and PP pristine films.

DSC measurements were performed by means of a TA-Q2000 differential scanning calorimeter equipped with a RCS-90 cooling unit (TA Instruments). The instrument was calibrated in temperature and energy with pure indium. The samples were sealed into a Tzero aluminum pan. Measurements were performed from 25 °C to 250 °C at 10 °C/min heating rate. High-purity nitrogen gas was fluxed at 20 mL/min during the measurements.

MFR analyses were performed by means of an Instron CEAST MF20 following the ASTM D1238 test conditions, at 190 °C and using a weight of 2.16 kg.

Reprocessing tests were carried out on flexible films based on PE and PP treated with GO and GO-MMT barrier coatings (PE-GO, PP-GO, PE-GO-MMT, PP-GO-MMT). The films were extruded using a Thermo Scientific HAAKE MiniLab II Rheology Solutions twin screw micro compounder. The processing time was set at 10 minutes in order to allow a sufficient melt mixing. The PE-based films were extruded at 135 °C with screw speeds of 30 rpm. The PP-based films were extruded at 165 °C with screw speeds of 30 rpm until the films were completely inserted, subsequently the speed was increased to 60 rpm. After cooling and pelletization, films about 100 µm thick were obtained by compression moulding using a hot platen press Dr Collin K40. The plates temperature was set at 140 °C for the PE-based systems and at 180 °C for the PP-based systems. The moulding time was fixed at 6 min and the pressure at 100 bar. After this cycle, the samples were quickly cooled by rapid insertion of the cooling cassette system. The so obtained recycled samples were coded with the same codes used for the starting materials, only adding the suffix _R: PE-GO_R, PE-GO-MMT_R, PP-GO_R, PP-GO-MMT_R. The neat PE and PP films, without coatings, were processed under the same conditions for comparison, obtaining the recycled films PE_R and PP_R.

2.4 Characterization

UV-visible spectra were recorded for all the samples by means of a Jasco V570 UV spectrophotometer in the range 200-800 nm.

Scanning electron microscopy (SEM) analysis was performed on the surface of PE-GO, PP_GO, PE-GO-MMT and PP-GO-MMT and on the cryogenically fractured cross sections of the recycled samples. The analyses were performed with a FEI Quanta 200 FEG SEM using a secondary electron detector and an acceleration voltage of 10–30 kV. Before the analysis the samples were sputter coated with gold/palladium.

Transmission electron microscopy (TEM) analysis was performed on the recycled samples. Ultrathin sections (nominal thickness 100 nm) of the specimens were realized with a Leica EM FC6-UC6 cryo-ultramicrotome system operating at -100 °C for PE-GO_R and PE-GO-MMT_R and at room temperature for PP-GO_R and PP-GO-MMT_R. The sections were then placed on 400 mesh copper grids and observed in bright field mode on a FEI Tecnai G12 Spirit Twin TEM operating at 120 kV acceleration voltage.

Oxygen transmission rate measurements were performed on all samples using a Multiperm Extrasolution Permeabilimeter at 25 °C and 10 % RH.

Water vapor transmission rate was measured for all the samples using the cup method (ASTM E96) at 25 °C using a difference in RH of 50 % between the inside (RH 100 %) and the outside (RH 50 %) of the testing cup.

The stability of the coatings in water was evaluated through a test designed in order to evaluate the eventual migration of the nanostructured coating in water based lacquers, paints or inks, using distilled water as simulant. Samples with a diameter of 40 mm were placed in a sealed Petri dish containing 8 mL of distilled water and stored for 24 h at 25°C. The amount of graphene oxide migrating to water was measured by analysing the aqueous media by UV-visible spectroscopy. Further details on this procedure are reported in Supplementary Information and the GO calibration curve in water is reported in Figure S1. The same method was applied to evaluate the release of GO from the recycled films.

A FTA 1000 (First Ten Ångstroms) instrument was used to measure static contact angles (CA) of pristine PE and PP films and the coated films. The samples were attached on a double-sided tape applied on a microscope glass slide and a 7.5 µL distilled water droplet was positioned on the film surface. Each measurement was repeated on six different areas of the sample. The experiments were conducted at room temperature. CA was geometrically evaluated as the angle formed by the solid surface and the tangent to the droplet. Reported data are the average of the measured values.

The recycled films were characterized by tensile tests using an Instron 5564 with a strain rate of 10 mm/min. Dumbbell samples were used with an average thickness of 100 μm, and a gauge length of 20 mm. Young's modulus, yield stress and elongation at break were obtained by statistical analysis of the results obtained on 10 tested specimens for each sample, calculating the average and the standard deviation values. PE and PP pristine films were tested in the same conditions for comparison.

The pristine PP film and the recycled PP_R film were analyzed by Fourier transform infrared (FTIR) spectroscopy in attenuated total reflectance (ATR) mode using a PerkinElmer Spectrum One FTIR spectrometer equipped with an ATR module, using a resolution of 4 cm^{-1} and 32 scan collections. Also, PP_R was analysed by DSC using the above mentioned equipment, in order to evaluate PP and PP_R crystallinity degrees.

3. Results and discussion

3.1 Barrier coatings

The overall scheme of the work performed, with the images of the obtained samples, is reported in Figure 1. After application of the GO and GO/MMT hybrid coatings by rod coater, coated samples of PE and PP films wide about 10 cm and long about 30 cm were obtained, shown in Figure 1(a1). For both the substrates, the films remained highly flexible, as illustrated in Figure 1(a2). The coated PE and PP films exhibited a light brown colour, which for both the substrates was more intense for the GO-coated samples and slightly less intense for the GO-MMT-coated samples, as shown in Figure 1, left column (coated films).

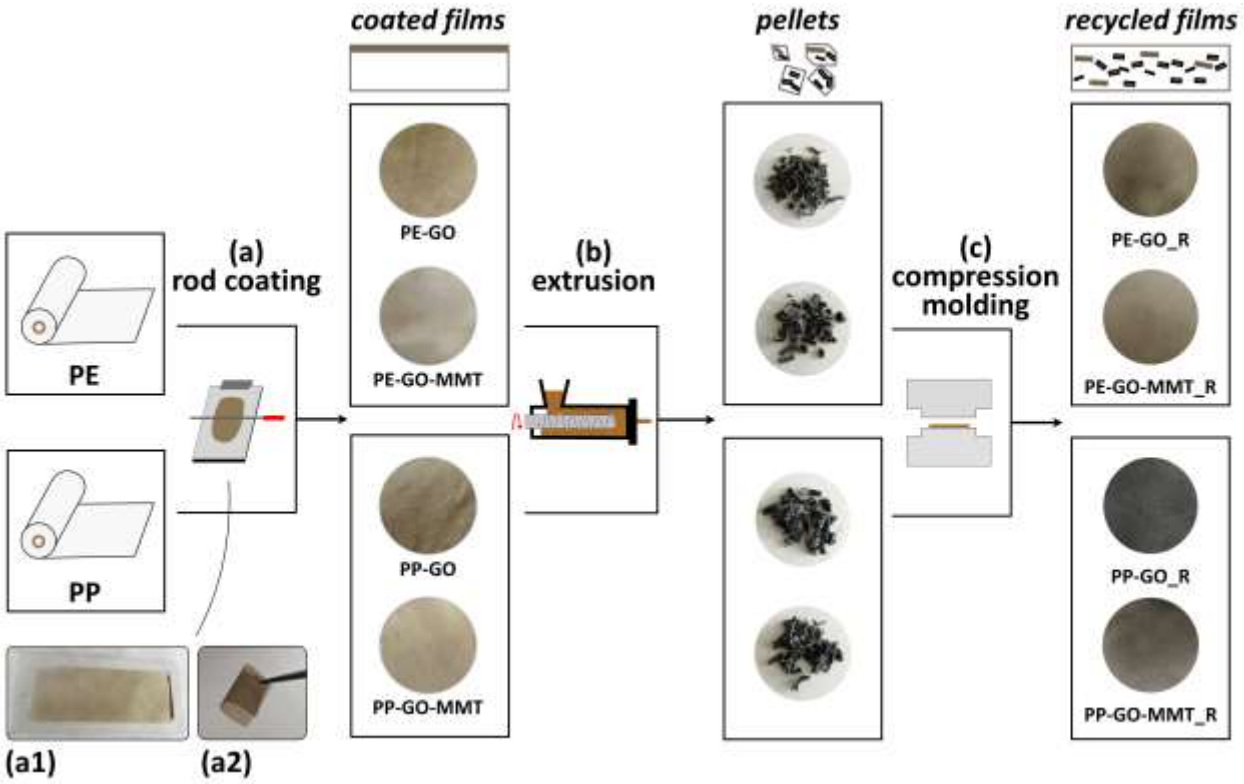

Figure 1. Overall scheme of the work, evidencing the three phases: a) coating application, with the images of the obtained samples, and with details showing the coated films realized by rod coating (a1) and the flexibility of the coated films (a2); b) reprocessing of the coated substrates by extrusion, with the images of the obtained reprocessed pellets; c) compression moulding of the reprocessed films, with the images of the obtained recycled films

UV-visible spectra (Figure S2) were collected on the pristine and coated samples in order to evaluate the reduction in transmittance caused by the coating application. All coated films show lower transmittance than the pristine PE or PP substrates in all the investigated range (200-800 nm), with a steep decrease of the transmittance at lower wavelenght. Transmittance at 400 nm and transmittance reduction with respect to the corresponding uncoated substrate are reported in Table 1. As shown, GO coatings showed a transmittance reduction at 400 nm of about 60% with respect to the pristine films. In agreement to the visual analysis, the GO-MMT coatings showed a lower transmittance reduction, ranging between 41.4% (for PE-GO-MMT) and 48.1% (for PP-GO-MMT).

Table 1. Transmittance and transmittance reduction at 400 nm, oxygen and water vapour transmission rate (OTR and WVTR) of pristine and coated PE and PP films

Sample	Transmittance (%) at 400 nm	Transmittance reduction (%) at 400 nm [a]	OTR [cm^3*mm/(24h*m^2)]	WVTR [g*mm/(24h*m^2)]
PE	75.3	-	246	0.195

PE-GO	17.1	58.2	6	0.053
PE-GO-MMT	34.0	41.4	4	0.061
PP	80.0	-	93	0.166
PP-GO	19.9	60.1	3	0.035
PP-GO-MMT	31.9	48.1	6	0.049

[a] standard deviation values < 2%

The morphology of the applied coatings was investigated by SEM analysis. SEM images of the coated films show that all the samples are highly homogeneous, with wrinkles due to the coalescence and subsequent deformation of the GO and MMT flakes during the water evaporation process, see Figure 2. GO-MMT coatings showed more pronounced wrinkles, indicating that the interactions between the graphene sheets and the phyllosilicate lamellae gave rise to hybrid morphologies. In addition, in the PE-GO-MMT and PP-GO-MMT samples sporadic particles smaller than 500 nm were evidenced on the film surface, due to the presence of poorly-dispersible clay residues in the water formulation applied on the film surface.

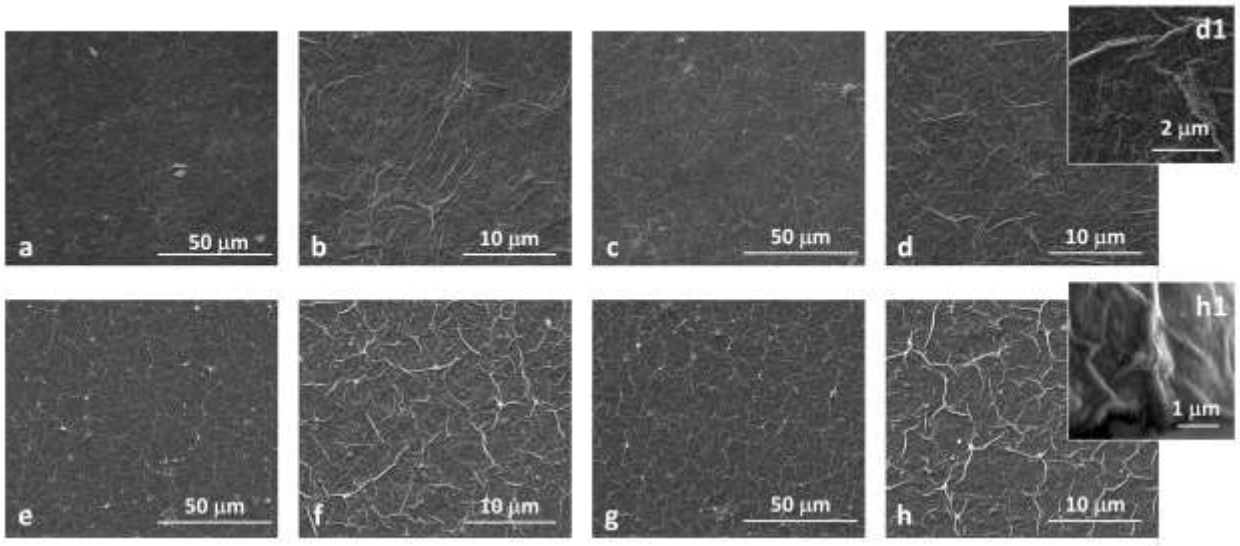

Figure 2. SEM images of PE-GO (a, b), PP-GO (c, d), PE-GO-MMT (e, f) and PP-GO-MMT (g, h)

Oxygen and water vapour permeability tests were performed on the PE and PP samples coated with either GO and GO-MMT layers. Results are summarized in Table 1. As shown, the effect of the coating on the gas barrier properties was very pronounced for both the investigated systems. For what concerns the polyethylene substrate, coatings induced a reduction of the OTR of about 97.5% for GO and about 98.5% for GO-MMT, and a WVTR reduction of about 72.5% for GO and 68.0% for the hybrid GO-MMT. Similarly, for the PP substrate, the decreases of the OTR were 96.5% and 94.0%

for GO and the GO-MMT hybrid coating, respectively, while the WVTR decreases were found respectively 78.8% and 70.4%.

The final OTR and WVTR values were comparable or even better than the values reported in literature for different classes of coatings. In particular, the developed systems showed comparable or better performances than:

- spray-assisted layer-by-layer (LbL) GO based coatings applied on polyethylene, which induced a reduction of 69 % of the OTR (Heo et al., 2019), and LbL polyvinyl alcohol (PVOH)/rGO coatings applied on PET, which induced a 92 % reduction of OTR and a 30 % reduction of WVTR of the substrate (Zhan et al., 2021);
- SiOx coatings on PE that showed a reduction of about 90% of the OTR (Li et al., n.d.), and SiOx coatings on PP, that showed a 95.5 % OTR decrease and a reduction of about 80.3 % of the WVTR (Kirchheim et al., n.d.);
- AlOx coatings on PP, that showed about 90 % decrease of the OTR (Hirvikorpi et al., 2010) and WVTR (Struller et al., 2014);
- polyvinylidene chloride (PVDC) coatings applied on PET, that showed 95 % OTR reduction with respect to the pristine polymer (Rovera et al., 2020),

Comparing the coating propose in this work with the above listed systems, it is to be taken into account that these SiOx and ALOx ceramic coatings are obtained by chemical vapour deposition techniques, such as dielectric barrier discharge (DBD) plasma or atomic layer deposition (ALD), which are far more complex and expensive than coatings applied by rod coating deposition. Moreover, concerning PVDC, one should consider that the use of chlorinated products is being gradually restricted from many packaging applications, since they are still under investigation for their difficult and possible unsafe recyclability, because during high temperature reprocessing they can leach out harmful chemicals for the environment and health.

Finally, literature reports very efficient gas barrier coatings, constituted by ethylene vinyl alcohol (EVOH) and PVOH; for example, 99.9 % reduction of OTR was achieved with EVOH coatings on PE films (Krepker et al., 2018) and 99.2 % and 93.2 % of OTR reductions were achieved with EVOH and PVOH coatings, respectively, on PET (Rovera et al., 2020). However, in the case of these polymer coatings it is to be taken into account that they are usually of micrometric thickness and they can significantly affect the recyclability of the final material.

The coating stability of the realized films in water was evaluated in order to evaluate the feasibility of further painting the coated side of the films with aqueous lacquers. Stability tests were performed

by immersing the coated films in distilled water up to 24 h, according to the procedure detailed in the experimental section. The amount of graphene oxide released from the coating by water immersion for 24h at room temperature was evaluated and results are summarized in Table 2. As shown, the stability of the coating in water is very high, since for all the developed systems the amount of GO released from the coatings after 24 h of immersion is almost negligible, i.e. 1% or less for GO coatings and less than 1.5% for GO-MMT coatings. The higher amount of GO released from the hybrids can be explained by the lower interactions established by the GO and the phyllosilicate with respect to those established amongst GO sheets.

Water contact angle measurements (Figure S3) showed a high hydrophilic behaviour of the coated surfaces in comparison to pristine PE and PP surfaces. As shown in Table 2, CA decreased from 91° and 80° for the pristine PE and PP films to values ranging between 71° and 77°, slightly lower in the case of GO or GO-MMT coatings applied onto the PP substrate. Lower values of CA for PP systems, including the pristine PP film, are ascribable to the presence of slipping agents, such as fatty amides, usually employed in the production of polypropylene films (Hahladakis et al., 2018).

Table 2. Amount of released graphene from coated flexible films by water immersion and water contact angle of coated films

Sample	**Released GO (mg/m^2)**	**Amount of released GO with respect to the amount of GO in the coating (%)**	**Water contact angle (degrees)**
PE	-	-	91
PE-GO	2.01	0.72	77
PE-GO-MMT	1.49	1.07	76
PP	-	-	80
PP-GO	2.85	1.01	74
PP-GO-MMT	2.04	1.45	71

Thus, the combined analysis of the stability tests and the water contact angle measurements indicated that the applied coatings are resistant to water despite being more affine to aqueous media than the pristine films. This demonstrate that the coatings are suitable for further surface treatments with water-based products, such as external inks and lacquers usually applied at industrial scale on flexible packaging films.

3.2 Recycling tests

As detailed in the experimental section and schematized in Figure 1, the PE and PP films with the GO and the hybrid GO-MMT coatings were subjected to reprocessing tests to evaluate their recyclability. The processing temperatures were selected taking into consideration the torque visualized during the extrusion process and the melting temperatures of the PE and PP films measured by DSC (120 °C and 160 °C for PE and PP, respectively). More in detail, the extrusion temperatures were set to maximize the viscosity of the polymer melt, in order to promote the effective dispersion of the nanostructured phase (deriving from the coating fragmentation) in the polymer melt. For PE the extrusion temperature was set 15°C above the melting temperature due to its very low MFR (0.644 g/10min) while for PP the quite high MFR (4.573 g/10min) allowed to set the extrusion temperature very close to its melting point. After a lab scale compounding test (see Figure 1b), nanocomposite pellets were obtained and further processed by compression moulding to realize recycled films (Figure 1c). No virgin PE or PP was added during the reprocessing. Therefore, the compositions of the recycled films, embedding the GO and the GO-MMT phases, correspond to the composition of the coated products. Codes and composition of the recycled materials are summarized in Table 3.

Table 3. Codes, compositions* and tensile properties (Young's modulus (E), stress at yield (σ_S) and elongation at break (ε_B)) of recycled PE and PP based samples

Sample	PE or PP content (wt%)	GO (wt%)	MMT (wt%)	E (MPa)	σ_S (MPa)	ε_B (%)
PE_R	100	-	-	114 ± 3	7.8 ± 0.4	662 ± 73
PE-GO_R	99.58	0.42	-	100 ± 5	7.3 ± 0.2	921 ± 78
PE-GO-MMT_R	99.58	0.21	0.21	113 ± 10	7.6 ± 0.1	795 ± 165
PP_R	100	-	-	750 ± 88	20.7 ± 3.1	71 ± 7
PP-GO_R	99.40	0.60	-	638 ± 28	20.2 ± 4.6	26 ± 17
PP-GO-MMT_R	99.40	0.30	0.30	740 ± 33	24.4 ± 2.8	32 ± 21

* Different compositions amongst recycled PE and PP based systems depend on the different thickness of the pristine films.

As evidenced from the Figure 1, all the samples showed a pronounced dark coloration due to the dispersion of the GO and GO-MMT phases in the polymer matrix promoted by the extrusion reprocessing. The morphology and structure of the obtained films was evaluated by SEM and TEM. Results are shown in Figure 3.

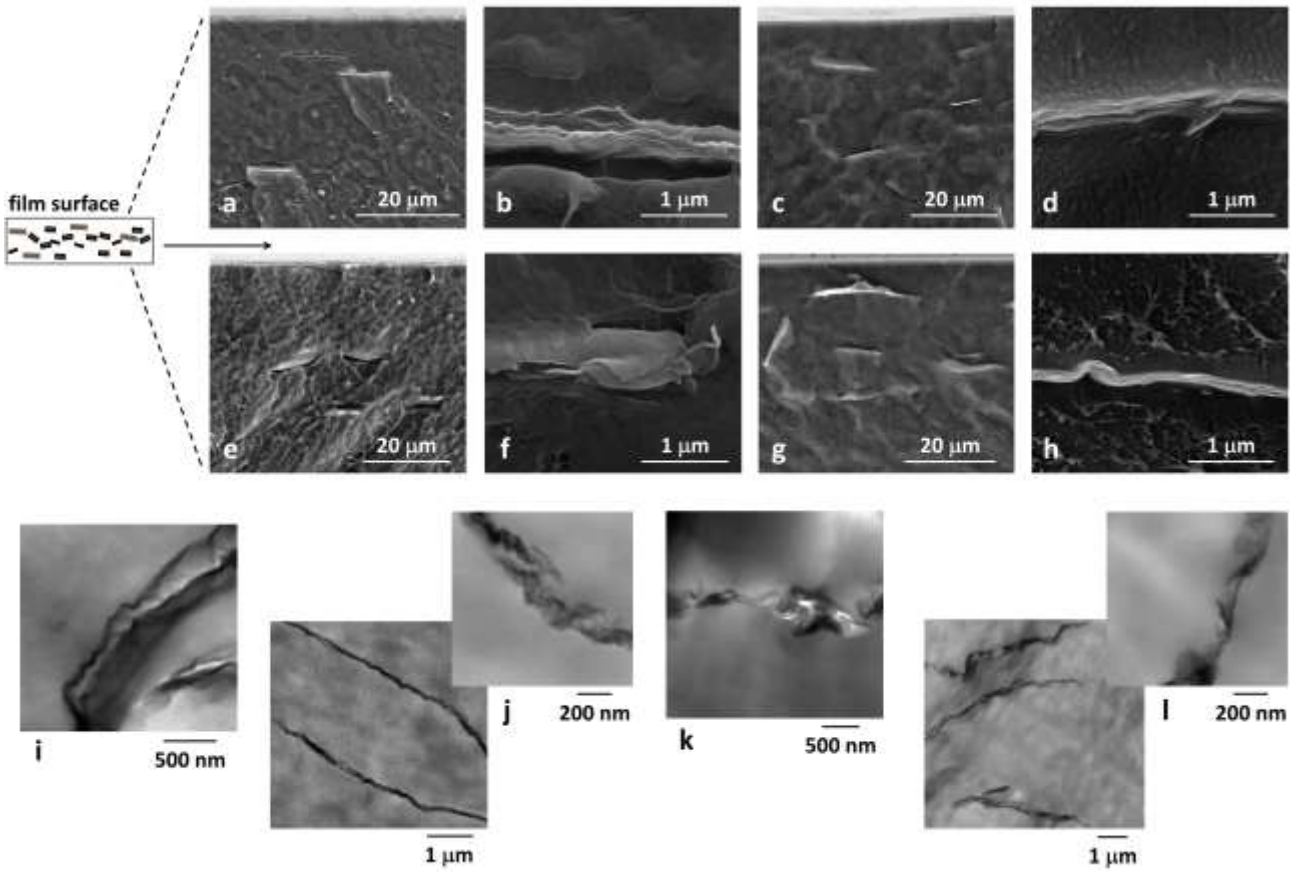

Figure 3. SEM images of the cryo-fractured cross sections of PE-GO_R (a, b), PP-GO_R (c, d), PE-GO-MMT_R (e, f) and PP-GO-MMT_R (g, h). The horizontal sides of SEM images are oriented along the film surfaces. Bright field TEM images of PE-GO_R (i), PP-GO_R (j), PE-GO-MMT_R (k) and PP-GO-MMT_R (l)

SEM images at low magnification (Figure 3a,c,e,g) revealed the cross-sectional structure of the recycled samples. After extrusion and compression moulding, 2D nanostructures with an approximate lateral size ranging between 10 and 35 µm were evidenced. These platelet-like nanostructures are oriented along the direction parallel to the surfaces of the film and their approximate thickness is slightly higher (< 1 µm) for PE-GO_R and PE-GO-MMT_R, whereas they are more compact, with thickness close to 200 nm, for PP-GO_R and PP-GO-MMT_R. The features of these platelet-like nanostructures are confirmed by TEM analysis (Figures 3i-l), that showed a more compact structure for the platelets embedded in PP-based recycled samples.

It seems evident that the platelet-like structures derive from the original GO and hybrid GO-MMT coatings applied on the PE and PP substrates, that during reprocessing are broken down in large platelets with lateral thickness < 40 µm and dispersed in the polymer matrices. For PE-based samples, TEM images show that, after reprocessing, the GO and GO-MMT platelets appear partially exfoliated with respect to their pristine stacked form. Indeed, the GO and GO-MMT phases

dispersed in the PE polymer matrix are thicker than the pristine coating, up to 350 – 400 nm, possibly because the PE phase has partially intermingled within the pristine coating structure. On the contrary, when the PP-based samples were recycled, the compact structure of the coatings resulted almost unaffected, with the thickness of the dispersed platelets comparable to the nominal thickness (140 – 200 nm) of the original coatings. This phenomenon could be explained on the basis of the very different melt behaviour of PE and PP, as revealed by their previously reported different MFR. PE is significantly more viscous than PP in the tested conditions, and these differences are certainly emphasized by the extrusion conditions employed for the recycling of the films. Therefore, while the extrusion of PE is characterized by higher shear stresses that enable the partial exfoliation of the nanostructured platelets, the extrusion of PP films is characterized by lower mixing stresses.

Despite the orientation of the lamellar nanostructures, the recycled films showed oxygen permeability values comparable to those recorded for the pristine films (see Table S1), irrespectively of the presence of the nanofillers. This can be ascribed to the very low content of nanostructured materials contained in the recycled films, lower than 0.4 vol %, that is not enough to create an effective tortuous path able to induce a permeability reduction to oxygen and water vapour in comparison to high gas barrier properties nanocomposites, usually containing 1-3 vol % of lamellar nanofillers (Wolf et al., 2018).

Finally, the recycled films were mechanically characterized by tensile tests. Results are shown in Table 3. The mechanical properties recorded for the pristine PE and PP films are reported for comparison in Table S2. To be noticed is that the thin GO and GO-MMT coating have negligible effects on tensile properties of the films.

As shown, in the case of PE based systems, the recycling only induced a slight decrease of the modulus and the stress at yield with respect to the pristine PE film, while the elongation was retained or even increased. The recycling of the coated samples resulted in materials (PE-GO_R and PE-GO-MMT_R) whose mechanical properties are essentially unchanged with respect to PE_R, confirming that the low amount of nanostructured coating, partially exfoliated during the reprocessing as shown by SEM/TEM analyses, does not affect the properties of the recycled materials.

For PP based materials, a strong effect of the recycling process is observed already for the uncoated sample: PP_R shows in fact a higher stiffness and much lower ultimate elongation with respect to pristine PP film. This finding can be explained considering that the industrial production of cast polypropylene results in an optimized film structure (in terms of crystallinity and macromolecular

arrangement) than cannot be reproduced through the lab scale compression moulding process (Lamberti et al., 2002; Sacco et al., 2020). Indeed, as shown in Figure S4, the intensity ratio between the FTIR absorption peaks centred at 841 cm^{-1}, typical of the crystalline phase, and at 973 cm^{-1}, typical of the amorphous phase (Lamberti et al., 2002), is much more intense for the recycled PP_R sample (I_{841}/I_{973} = 0.87) with respect to the pristine PP film (I_{841}/I_{973} = 0.74). Also, the crystallinity degree of PP and PP_R were evaluated by DSC analysis, which confirmed an increase of crystallinity from 34.6 % (PP) to 40.5 % (PP_R) upon recycling. This makes the mechanical response of PP_R non directly comparable to that shown by neat PP films. Thus, limiting the discussion to the recycled samples, also for the recycled polypropylene samples the presence of the filler showed negligible effects on the polymer stiffness and strength, and only slightly reduced the maximum elongation of the system, as often found in PP based nanocomposite systems, in which the filler usually acts as a defect point that promote an early rupture of the specimen during the tensile deformation in comparison to the unfilled matrix (Dittrich et al., 2013). Furthermore, in Figure S4 signals at 1645 cm^{-1}, 3190 cm^{-1} and 3390 cm^{-1} associated to carbonyl stretching and to the stretching vibrations of the NH_2 group may be indicative of the presence of fatty amides usually used in polyolefins as anti-static and slip agents, such as erucamide (Dulal et al., 2018; Gall et al., 2020).

Water stability tests were also performed on the recycled nanocomposite films, which showed no detectable graphene oxide release upon water immersion for 24h at room temperature. Indeed, in this case, the nanoparticles are well embedded in the polymer matrix of the nanocomposite films, as evidenced by SEM and TEM analyses, and therefore cannot be released to water.

Therefore, all results well demonstrate that by applying a design-for-recycling approach and exploiting the knowledge on advanced and nanostructured materials it is possible to develop novel high-performance flexible films that could replace current non-recyclable products. Despite the proposed solution is specific for a particular class of products, namely flexible packaging film, the proposed methodology has a general character and can be extended to different products of the food packaging sector.

These objectives well match the Sustainable Development Goals (SDGs) defined in the 2030 Agenda for Sustainable Development, adopted by all United Nations Member States in December 2017, that set the target of 55% recycling of plastic packaging waste by 2030 by banning landfilling and adopting stricter agreements on extended producer responsibility (EPR). By 2030, all plastic packaging will need to be designed to be recyclable or reusable to contribute effectively to food

security, sustainable industry, sustainable cities and communities, responsible consumption and production.

5. Conclusions

New recyclable-by-design mono-material flexible films with high barrier properties to gases and UV radiation have been developed by applying graphene oxide and graphene oxide/montmorillonite hybrid coatings on low density polyethylene and polypropylene substrates.

The coatings have induced remarkable UV barrier, quantified as a transmittance reduction at 400 nm wavelength of 40-60%. Moreover, by the application of the coatings, oxygen permeability has been reduced of 97.5-98.5% for polyethylene and of 94.0-96.5% for polypropylene. The water vapour transmission rate was reduced of 68.0-72.5% for polyethylene and of 70.4-78.8% for polypropylene.

To demonstrate their recyclability, reprocessing tests by lab scale extrusion have been performed on the coated films. After extrusion and compression moulding, homogeneously distributed 2D nanostructures deriving from the fragmentation of the original coatings and the dispersion of the obtained stacked platelets in the polymer matrices have been evidenced in the cross-section of the recycled samples. These platelets have been found well oriented along the film direction. In the case of polyethylene films, an intermingling of the polymer phase within the platelets has been also evidenced. What is to be remarked is that the presence of the nanofillers in the recycled samples has not significantly affected the mechanical properties of the polymers with respect to the recycled pristine films.

Both the coated films and the recycled films are stable, with low release of GO from the coatings and no appreciable release of GO from the recycled samples by water immersion for 24h at room temperature.

A scale-up phase of the proposed process will be needed to optimize the coating application and further validate at industrial scale the achieved outcomes. Nevertheless, the results obtained in this work confirm that the application of graphene based coatings to realize mono-material gas barrier films for packaging applications is a promising effective strategy to realize high performance products able to be easily recycled, thus showing a new sustainable end-of-life option with respect to current products.

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